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ICS-UNIDO INTERNATIONAL WORKSHOP

Environmentally Degradable Plastics: Industrial Development and Application

PROCEEDINGS

September 19-22, 2000
Hanyang University,
Seoul, Korea

Organized in cooperation with
Korea Biodegradable Plastics Association

Co-sponsored by

Korea Science and Engineering Foundation
US Grains Council
Hanyang University
The Polymer Society of Korea
The Korean Chemical Society

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Preface

Every country in the world suffers from MSW (municipal solid waste) problems, which include plastic wastes. The associated environmental problems are more serious in the countries where the waste is not properly treated. Industrial application of environmentally degradable plastics (EDP) is surely one of the useful solutions, but the high price of EDP hinders its extension into the real market. The second key driver of EDP promotion is the necessity to search for renewable resources for polymer production.

The International Centre for Science and High Technology (ICS), which is an Institution within the legal framework of the United Nations Industrial Development Organization (UNIDO), with headquarters in Trieste, Italy, focuses on the transfer of know-how and technology from industrialized to developing countries. ICS-UNIDO has focused on the topic of EDPs as one major branch of its activity aiming at bringing the advantages of today's direct to developing countries, and to stimulate a diffusion of harmonic decisions to be taken on the global issue of plastic waste to the benefit of these countries. Since 1996, ICS-UNIDO has organized a series of activities (Expert Group Meetings, Training Courses, Workshops, projects promotion, etc.) in this field.

The present workshop "Environmentally Degradable Plastics: Industrial Developments and Applications" was addressed to Eastern Asian countries, and Seoul, Korea, was selected as the hosting country, due to its strategic position in this region and to the high production of polymer and plastic materials. The objective of the Workshop which was organized in cooperation with Korea Biodegradable Plastics Association was to discuss all the present issues related with EDP, to demonstrate its recent developments, and to encourage the wide application of EDP. This proceeding was published from the papers presented in the workshop.

We are grateful to all those who worked tirelessly for the workshop and to the co-sponsors, Korea Science and Engineering Foundation, US Grains Council, Hanyang University, The Polymer Society of Korea, and The Korean Chemical Society. We hope that this proceeding contributes for the research, development, and application of EDPs.

December, 2000

Stanislav Miertus
Young Ha Kim
Seung Soon Im

Chapter 1:

General Aspects and Standards of EDP (Environmentally Degradable Plastics)

1. ICS-UNIDO Programmes and Activities with the Focus on the Subprogramme of Environmentally Degradable Plastics:

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The global issue of plastic waste has promoted all over the world a great deal of actions tending to provide adequate answers and suggestions for minimizing the negative impact of the increasing production and consumption of plastic materials. Many companies in industrialized countries are working on developing a wide range of innovative packaging which offer real environmental benefits.

The production and consumption of polymeric materials for commodity and specialty plastic items have to face all the constraints and regulations already operative or to be issued in the near future, dealing with the management of primary and post-consumer plastic-waste. In this respect, the production of environmentally friendly (sound degradable) polymeric materials should be a strategic option among those available for the management of plastic waste. The competition with recently adopted technologies such as burial in landfill sites, incineration with energy recovery, and mechanical or chemical recycling is expected to be strengthened although it is predicted that all of them will coexist with an appreciable decrease of land-filling practice. These new degradable plastics should replace the conventional commodity plastics in those segments in which recycling is difficult or economically not feasible.

These aspects are of particular importance for developing countries and emerging economies, where the concept of waste management and rational production of plastic items should be harmonized.

The International Centre for Science and High Technology (ICS), which is an Institution within the legal framework of the United Nations Industrial Development Organization (UNIDO), with headquarters in Trieste, Italy, focuses on the transfer of know-how and technology from industrialized to developing countries.

The following programmes are currently being developed within the area of Pure and Applied Chemistry:

Catalysis, which is an important scientific and technological area for the development of environmentally friendly chemical processes, which in turn form the basis for cleaner industrial technologies development and are also the key elements for an industrial pollution prevention approach. New, less pollutant processes together with the optimization of existing processes depend to a great extent upon the improvement of catalyst performance in the heavy and fine chemical production lines with a direct impact on the quality and quantity of by-products or waste generated.

Remediation Technologies, which are becoming an important and economical way to solve the problem of contaminated and polluted sites, especially in developing countries and economies in transition where the environmental issue has been until recently neglected. New technologies, methodologies and solutions are emerging from various applications and are becoming day by day more economically viable and feasible.

Combinatorial Chemistry and Combinatorial Technologies, which have a strong impact on the development of new chemicals (pharma-industries, agro-chemicals, new materials). Developing countries need to get acquainted with and gain expertise in combinatorial technologies to help local enterprises remain competitive and economically viable in the coming decades. Combinatorial chemistry and combinatorial technologies have a potential influence not only on industrial growth, but also on environment protection. In fact, by optimizing industrial processes and production , with the lowering of relevant costs, less amounts of waste and by-products are created.

Environmentally Degradable Plastics, where the expanding global production and consumption of polymeric materials coupled with increasing public awareness of environmental issues have created serious concern about the problems related to the disposal of plastic waste generated by various sectors of human activity. Besides recycling, re-use, incineration and composting, new technological developments of environmental degradable plastics contribute dramatically to the tackling of the environmental issue in specific sectors of plastics use.

ICS-UNIDO has focused on the topic of EDPs as one major branch of its activity aiming at bringing the advantages of today's direct to developing countries, and to stimulate a diffusion of harmonic decisions to be taken on the global issue of plastic waste to the benefit of these countries. During 1997-1999, the actions undertaken by ICS in the subprogramme of Environmentally Degradable Plastics (of the Area of Pure and Applied Chemistry) included training courses and workshops which have met a strong interest and resulted in many proposals of common projects, feasibility studies and networking coordinated by ICS-UNIDO.

The main projects in the field of EDP, which are being developed are the following:

Management of Innovation in Environmentally Degradable Plastics

The project is funded by the European Commission within the framework of the Leonardo da Vinci Programme.

The objectives of the projects are:

The creation of an information package for policy makers in the field of EDPs and of a training package

The creation of a database of EDP technologies and legislation

Plastic Waste Management and EDPs in Egypt and Turkey

The aim of the project is to produce and update an infopack and database on the situation of plastic waste and its management in countries of the Mediterranean area (Egypt and Turkey) and at disseminating the best practices in the relevant institutions. An accurate analysis of the infrastructures necessary for the production and use of EDPs and management of post-consume of plastic items will be performed.

Ecocompatible Bioplastic Packaging in China as Based on Polyesters from Renewable Resources.

This project aims at speeding up in China the production of PHAs obtained from renewable resources (sugar-sugar molasses and whey permeate) to be used as key components in the formulation of ecocompatible biodegradable packaging (films, containers and disposable utensiles). This will help China to face the problem of plastic waste "white pollution" and, at the same time, will open new ways for export markets to Chinese sugar cane farmers as a safe and environmentally sound material.

The events held in 1996-2000 in the Subprogramme on EDPs were the following:

- Scientific Planning and Coordination Meeting (SPCM) on "Polymeric Materials and Environmentally Degradable Plastics", Trieste, Italy December 1996
- Training Course on "Environmentally Degradable Plastics", Alexandria, Egypt, July 1997
- Workshop on "Environmentally Degradable Polymers", Pune, India, November 1997
- Expert Group Meeting –EGM - on "Environmentally Degradable Plastics", Trieste, Italy April 1998
- Workshop on "EDPs: Environmental and Biomedical Aspects", Antalya, Turkey September 1998
- Workshop on "Environmentally Degradable and Recyclable Polymers", Campinas, Brazil, November 1998
- Workshop on "Environmentally Degradable Polymers: Polymers and the Environment", held in Qatar, Doha, in March 1999.
- Workshop on "Environmentally Degradable Polymers: Materials Based on Natural Resources", organized in Shanghai, China, in August-September 1999, in cooperation with the Fudan University of Shanghai,
- Workshop on "Environmentally Degradable Plastics", organized in Smolenice, Slovakia, on 4-8 October 1999.

- Workshop on "Polymeric Materials and the Environment", held in Sharjah, UAE, in March 2000 held in cooperation with the University of Sharjah.

The present workshop ("Environmentally Degradable Plastics: Industrial Developments and Applications") is addressed to Eastern Asian countries and Korea has been selected as the hosting country, due to its strategic position in this region and to the high production of polymer and plastic materials.

2. Environmentally Degradable Polymers and Plastics (EDPs)-An Overview:

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Introduction

Under the general terminology of plastics we mean to include both polymeric materials and polymeric products in their multiform variety of structures, compositions, manufacturing conditions, itemization and service responses and uses.

Synthetic and semisynthetic polymeric materials and relevant products were originally developed for their durability and resistance to all forms of degradation occurring both under abiotic conditions (photophysical, mechanical and chemical degradation) and biotic conditions as mediated by enzymes and microorganisms (biodegradation). Special performance characteristics are achieved in items derived therefrom through the control and maintenance of their molecular weight and functionality during the processing and even when submitted to severe operative conditions. The polymeric materials had been and are widely accepted because of their ease of processability and amenability to provide a large variety of cost effective items that helped enhance the comfort and quality of life in modern industrial societies. In spite of the advantageous features that make these materials so convenient and useful to the human life, they have contributed towards serious plastic waste concerns, sometimes unfairly exaggerated by the media because of the visible spreading of plastic litter in the environment and the heavy contribution to landfill depletion, due to the unfavorable weight to volume ratio of plastic items with a major impact in the packaging segment. (1-2)

On the other hand the expectations for polymeric materials demand in the 21st Century are in favor of a double-triple fold increase in the production as a consequence of the increase of the plastics consumption in developing countries. Indeed a one-two order of magnitude jump in the plastics consumption with respect to the present annual level of 1-10 kg per capita can be envisaged for those countries once the living standards of industrialized countries will be reached (3).

The design, production and consumption of polymeric materials for commodity and specialty plastic items have certainly to face all the constraints requirements dictated by already in place and future regulations dealing with the management of primary and post-consumer plastic waste (3-8). In this connection the formulation of environmentally sound degradable polymeric materials and relevant plastic items, will constitute a key option among those available for the management of plastic waste. The competition with present technologies such as burial in landfill sites, incineration with or without energy recovery and mechanical or chemical recycling is expected to intensify, even though it may be predicted that all of these technologies will coexist with an appreciable decrease of landfilling practices and the introduction of the new concept of prevention to help rationalize the production and management of plastic waste. The technologies based on recovery including energetic, mechanical and chemical recycling and reuse, will be flanked by the increasing option of environmentally degradable plastics, which should replace conventional commodity plastics in those segments where recycling is difficult and heavily penalized by operative costs. Moreover the fluctuations in the price of virgin raw materials do not offer solid confidence for return on the investment necessary to start up a recycling chain which starting from curbside collection of plastic waste and going through sorting technology down to reprocessing and converting, leads generally to items with downgraded specifications.

An overview on environmentally degradable plastics cannot therefore be treated outside the framework of the global issue of waste production and its management with the vision of assessing and proposing an integrated viable solution to the plastic waste. The aspect of environmentally degradable plastics will be analyzed in terms of the development levels reached so far and future perspectives. It is perhaps worth mentioning that one major aspect that has attracted the attention of plastic manufacturers, polymer scientists, and administrations, is represented by the establishment of definitions comprising all possible categories of environmentally degradable polymers, together with suitable standards and testing protocols.

Chart 1 - Definition of Environmentally Degradable Plastics.

- Materials that retain the same formulation as conventional plastics during use
- Materials that are degraded after use into low molecular weight compounds by the combined actions of physico-chemical agents and microorganism existing in nature.
- Materials that ultimately degrade into CO_2 and H_2O

The nature and fate of the degradation products constitute another crucial point for the acceptance of environmentally sound synthetic polymeric materials undergoing degradation under specific environmental conditions.

As a conclusion of an accurate analysis, no universal standards and testing protocols can be selected to assess the environmental degradability of polymeric materials. On a case-to-case basis, specific environmental conditions and relevant test protocols have to be defined which imply a knowledge of adequate physical parameters and microbial strains eventually utilized in the evaluation tests.

The role and position taken by Environmentally Degradable Polymers and Plastics (EDPs) will be discussed and at the end of the present overview it should be possible to provide a background profile that should sound like an "identity card" for EDPs.

State of Art and Future Perspectives for EDPs

A lot of interest has been world-wide arosen on the "plastic and environment topic" and since late eighties a tremendous increase in the number of scientific publication and books have appreared on EDPs and related issues (9-13).

The annual world production of polymeric materials, including those of synthetic and semi-synthetic origin, is around 150 million tonnes, corresponding to an average annual "*per-capita*" consumption of 30 kg.

In industrialized countries the average annual consumption or polymeric materials "*per-capita*" is around 100 kg, a level that is expected to be reached by developing countries (in which the present consumption is one-two order of magnitude lower (1-10 kg), in the next 20-25 years.

Chart 2 - Production and Consumption of Plastics.

- **WORLD PRODUCTION & CONSUMPTION OF PLASTIC MATERIALS IN 1996**

  150 Mtons

- **AVERAGE CONSUMPTION PER CAPITA OF PLASTIC MATERIALS IN DEVELOPED COUNTRIES IN 1996**

  80-100 Kg

- **AVERAGE CONSUMPTION PER CAPITA OF PLASTIC MATERIALS IN EMERGING COUNTRIES IN 1996**

  1-10 Kg

In terms of consumption, polymeric materials can be put into three major classes comprising *commodity plastics*, *semi-commodity plastics* and *specialty polymers*, whose relative costs are inversely proportional to the production quantity.

From a price as low as 1-2 US$/kg and production of tens millions of tonnes in the commodity stream, the price rises to 50-5,000 US$/kg and production of hundreds of kilos in the specialty polymer stream.

Chart 3 - Average Cost of Different Polymeric Materials

- Commodity Plastics

  1-2 US$/kg

- Semicommodity Plastics

  5-50 US$/kg

- Specialty Polymers

  50-5000 US$/kg

About four fifths of the present overall production of polymeric materials is of petrochemical origin. The share of the plastics industry on the annual market output of crude oil is around 4 per cent. Given that the annual growth of wood materials is twice that of the crude oil pumped from the oil fields, it is conceivable that feedstock from renewable resources as well as semi-synthetic polymeric materials will receive ever growing attention from the plastic industry as well as from scientists involved in the fundamental development of polymer production routes.

Chart 4 - Resources for Plastic Production

- **CRUDE OIL - WORLD PRODUCTION & CONSUMPTION - YEAR 1996**

3 Gtons

Plastic Industry Share: 4%

- **ANNUAL GROWTH OF WOOD MATERIALS**

7 Gtons

- **ANNUAL AMOUNT OF CARBON DIOXIDE UTILIZED IN PHOTO SYNTHETIC BIOMASS PRODUCTION**

40 Gtons

Polymeric materials and plastics that depend upon the source of the raw material and/or the processes by which they can be converted to useful plastic items, can be grouped in three major classes:

Chart 5 - Polymeric Materials and Plastics

- **PETROCHEMICAL POLYMERS**
  - Conventional Thermoplastics
  - Conventional Thermosettings
- **NATURAL POLYMERS**
  - Bioplastics & Natural Fibers
- **MODIFIED NATURAL POLYMERS**
  - Artificial Bioplastics

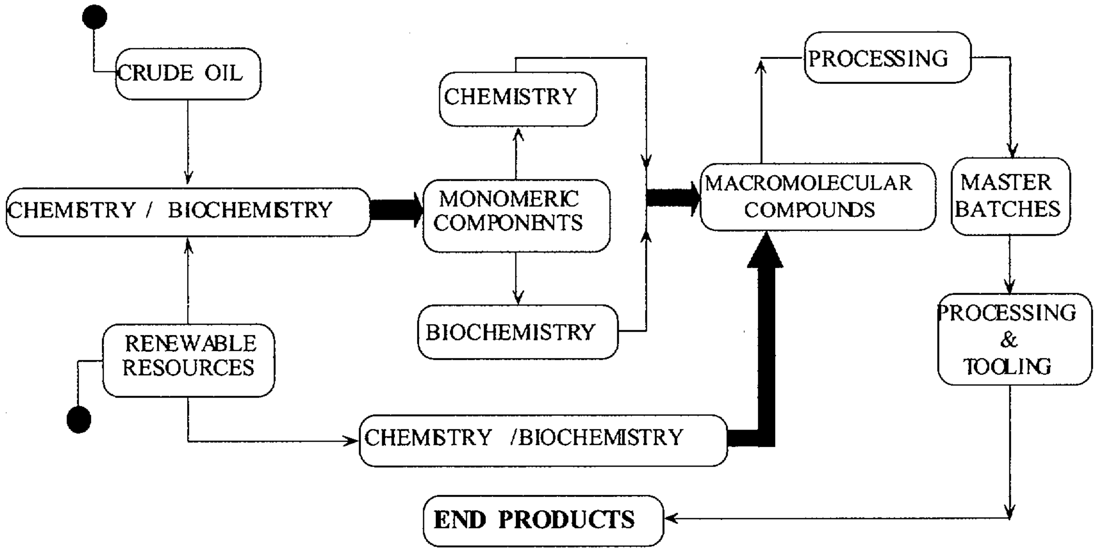
1. ***Petrochemical polymers*** (raw material crude-oil, and multistep processes for their production). They are better known as *synthetic polymers*.
2. ***Natural polymers*** of organic and inorganic origin that are used without any major chemical modification (cotton, juta, wool, silk, microbial polyesters, clays, sands, etc.). After processing they can give rise to bioplastics and natural fibres.
3. ***Modified natural polymers***. Typical examples are represented by modified cellulose (chemical cellulose, regenerated cellulose fibers) and collagen (leather).

Starting from the two different sources of raw materials, steps are required implying chemical and/or biochemical means in order to obtain the monomeric components that are converted by chemical or biochemical routes to macromolecular compounds in a first stage.

The use of renewable resources may offer the opportunity to directly obtain the macromolecular compounds, which after processing, can produce the final products.

The chemical routes are by far the most commonly used due to their versatility and minimum number of constraints which indeed play a crucial role in the case the alternative biochemical routes.

Chart 6 - Production of Plastics from Different Sources



Whatever the nature of the starting feedstock used in the formulation of the plastic master batches and further processing, the overall production layout, including the destiny of the post-consumer plastic items, comprise stages that generate waste of different value and energy content and which can be partially introduced into the productive cycle, whereas the remaining parts are disposed according to the most convenient options. In any case the ultimate fate include at the best, emission in the environment of carbon dioxide and water and damping of inert waste in controlled landfill plants.

Concerning the impact of plastic waste in the different major segments of human activity, if Western Europe, which can be considered typical of the majority of developed countries, is taken as an example, it can be seen that the major outputs of plastic waste are found in the segment of municipal solid waste (MSW) and in the distribution & industry segment, with annual shares of 10.6 million tonnes and 3.8 million tonnes respectively, over a total amount of 17.5 million tonnes.

Table 1 - Post-consumer plastic waste in different sectors - Western Europe

Sector	Agr.	Construct. & Demol.	MSW	Distribution & Industry		Cars	Electrical & Electronic
				Large Industry	Distrib.		
Amount a) (KTons)	661	956	10,580	854	2,950	927	577
% - Total waste	0.11	0.42	7.6	0.3	1.0	7.0	12.7
Total waste b) (MTons)	560	230	138	29.0		13.5	4.5
%	20.0	8.2	4.9	10.4		0.5	0.20

a) Plastic waste 0.63% of total waste; b) Total waste 2,800 MTons including agrifood, mines and sludge: 1,564 MTons (55.8%)

The major segments of the human activity that produce post-consumer waste can be identified as quoted in Chart 7.

Chart 7 - Definitions of Post-Consumer Sectors

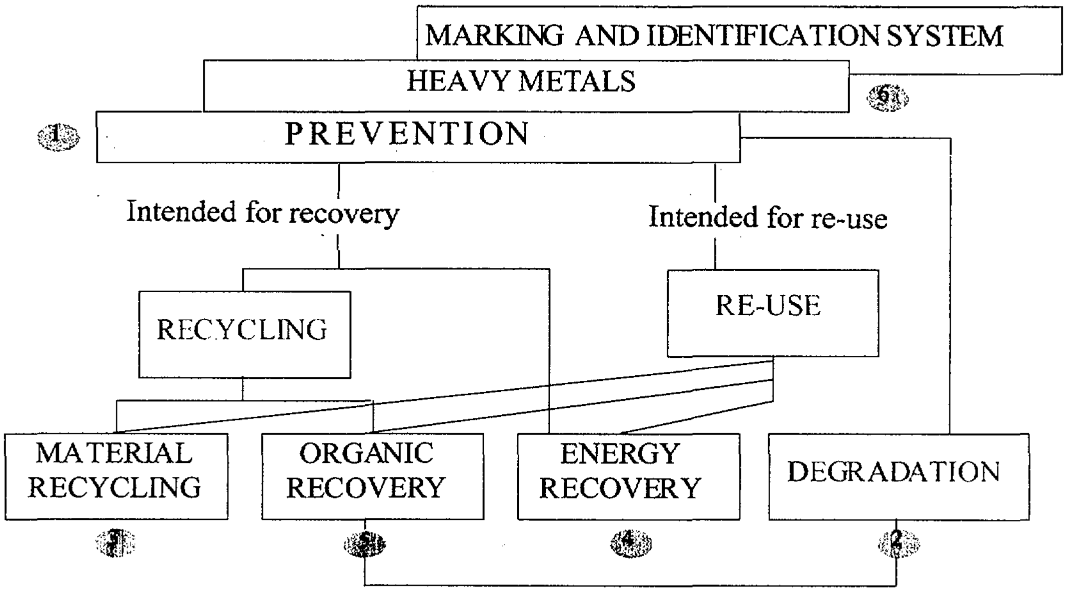
- ***Municipal solid waste***
  Waste coming from households, offices, retailers and small industries.
- ***Distribution***
  Waste generated by the distribution activity. It is mainly packaging. These waste are collected by private collectors.
- ***Large industry***
  Waste generated by large industries. These types of waste are collected like industrial waste by private collectors. They are generally never recovered and are mainly landfilled.
- ***Construction, demolition & civil works***
  Waste, mainly inorganic generated by the construction, renovation and demolition of buildings, as well as civil works.
- ***Agriculture***
  Waste, mainly organic, generated by the agricultural sector, including waste from cattle breeding.
- ***Cars and trucks***
  All used transportation vehicles which are collected and treated by metal shredding companies.
- ***Electrical & electronic***
  Data processing equipments, large and small domestic appliances, brown products and electrical industrial equipments.
- ***Other waste***
  All mineral and organic processing waste generated by the industry and by the mining sector, including also sludge with a minimum plastic content.

In the majority of these, plastic items of different nature and functional shape are involved.

An accurate analysis of the possible options that are available for a cost-effective and environmentally sustainable management of the plastic waste eventually present has to be taken in due account.

Considering that packaging constitutes the major segment of plastics utilization (35-40%), a good portion of which enters the MSW stream, countries belonging to the European Community established a Technical Committee (CEN TC261-SC4) with a mandate of issuing guidelines and standards for the management of "Packaging and Packaging Waste".

Chart 8 - Packaging and packaging waste - CEN TC249-SC4



The various options have been thoroughly examined and standards and guidelines are expected to appear by the end of 1998 (4).

In the meantime an initiative is going to be undertaken by the Technical Committee CEN-TC249 on Plastics(8) for consideration of the overall issues relevant to EDPs. The International Standards Organization (ISO) (5-6) and the American Society of Testing and Materials (ASTM) (7) are currently involved on the same topic.

The degradation of polymeric materials and plastics can occur under ***biotic condition*** as mediated by the action of macroorganisms (fragmentation) or microorganisms (biodegradation) or under ***abiotic conditions*** as mediated by chemical or physico-mechanical agents. Indeed in the majority of the cases a combination of abiotic and biotic attacks does take place.

The ***biotic degradation*** mediated by microorganisms can occur under different environmental conditions that can be discriminated and classified according to the presence (aerobic) or absence (anaerobic) of oxygen.

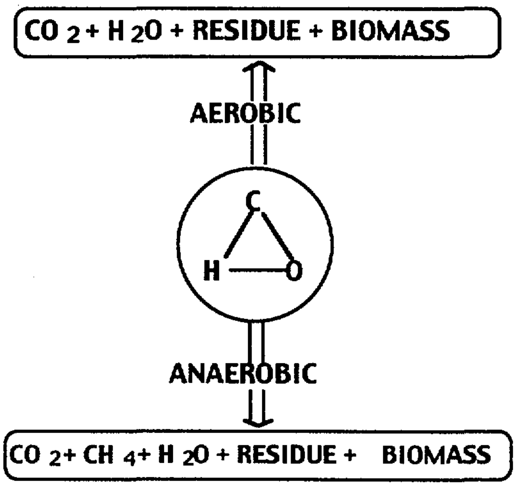
Chart 9 - Potential Factors Impacting Polymer Degradation

○ **BIOLOGICAL**	○ **CHEMICAL**	○ **PHYSICAL/MECHANICAL**
Bacteria, Fungi	Hydrolysis	Leaching
Predators	Oxidation	Sunlight
Higher Organisms		Weathering
		Mechanical Stresses
Biotic	Abiotic	

For all organic materials constituted by C, H and O, the aerobic degradation results in the production of carbon dioxide and water in addition to biomass and inert residue, whereas for an anaerobic pathway additional production of methane is detected.

In the case of organic substances containing etheroatoms N, P, S, aerobic degradation will lead to the inorganic counterparts in which the central atom may be in an high oxidation state whereas compounds with etheroatoms in a low oxidation state can be detected in the case of anaerobic conditions.

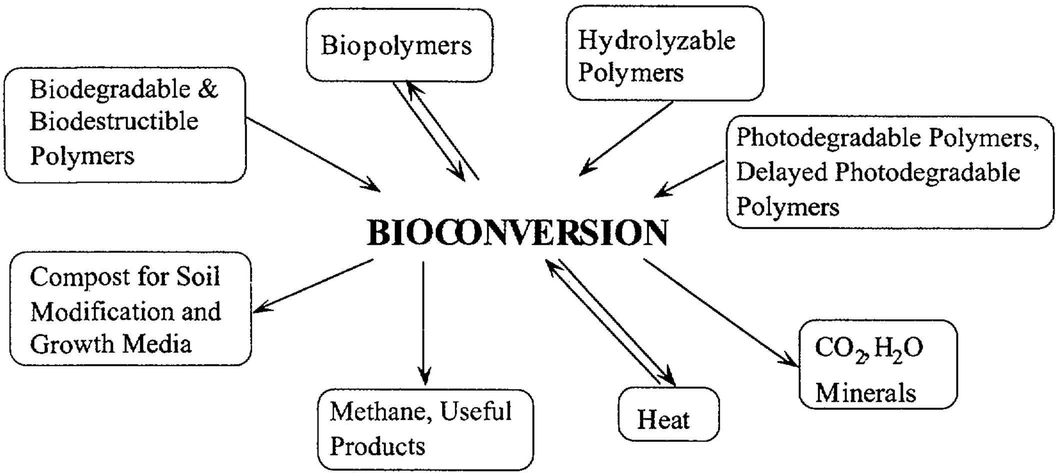
Chart 10 - Biodegradation of materials containing C, H, O



From a protocol standpoint the biodegradation can in general be included in the bioconversion processes where the feedstock is represented by polymers of synthetic or natural origin.

The output can be represented by biomass and humified organic matter with metabolites connected to the respirometric activity of the microorganisms.

Chart 11 - Biodegradable-Bioconversion



The natural polymers of animal and plant origin that can be used as raw material for a variety of industrial and consumer product formulations including biodegradable polymers and plastics.

According to the nature and typology of the repeating units, the naturally occurring polymers can be classified as polysaccharides proteins and polyester, in addition to a miscellaneous group comprising simple or more complex functional polymers.

Chart 12 - Naturally Occurring Polymers

■ **NATURALLY OCCURRING POLYMERS**

○ POLYSACCHARIDES
Starch, Cellulose, Chitin/Chitosan, Pullulan, Levan, Konjac, Elsinan, Dextran

○ PROTEINS
Collagen/Gelatin, Casein, Albumin, Fibrinogen, Silk, Elastin

○ POLYESTERS
Polyhydroxyalkanoates

○ OTHERS
Lignin, Shellac, Poly(γ-glutamic acid), Natural Rubber

Among the synthetic polymers that have been found to experience a degradation mediated by microorganisms often coupled to chemical and/or physico-mechanical degradation, one can enumerate the classes quoted as in Chart 13. Among them polyvinylalcohol and polyaspartic acid can be included in the water soluble polymers.

Chart 13 - Biodegradable Synthetic Polymers

- Poly(alkylene ester)s
- PLA, PCL, PLGA
- Poly(amide-ester)s
- Poly(vinyl ester)s
- Poly(vinyl alcohol)
- Polyanhydrides
- Polyphosphazenes
- Polyaspartic acid

Natural products do not mean that "*it is beautiful for environmental degradation*". Indeed, as for synthetic polymers, the rate of degradation and the formation of ultimate metabolites depend very much on the structural complexity of the native or artificial polymeric materials and the environmental conditions selected for the degradation trials.

As an example, Charts 14-17 represent the schematic degradation of lignin and cellulose as mediated by microorganisms. One can recognize that the processes can be rather complex as they require the involvement of different microorganism strains and some of the metabolites may be recalcitrant to a full mineralization.

Chart 14 -
Lignin degradation by *white-rot* fungi

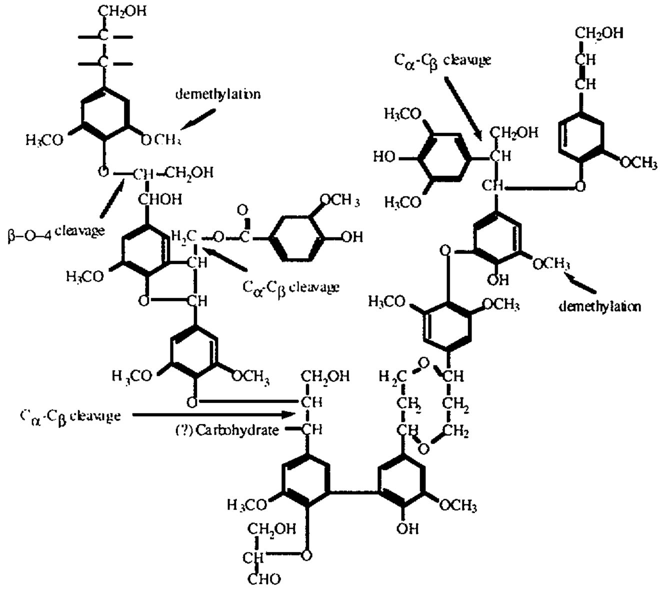


Chart 15 -
Lignin degradation by *Phanerochaete Chrysosporium*

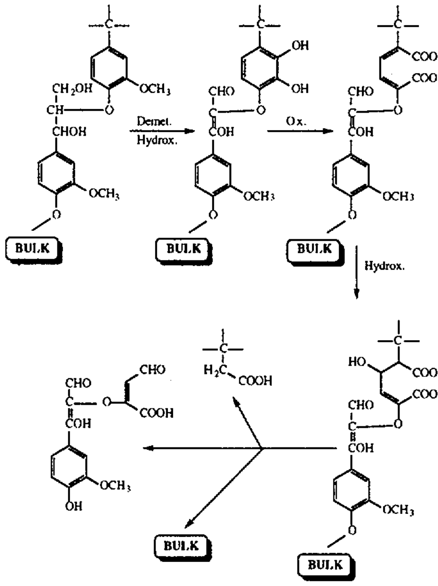


Chart 16 -
LMW fragments identified in lignin degradation by *white-rot* fungi

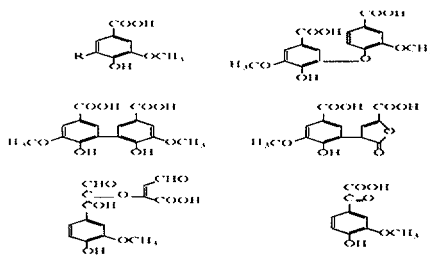
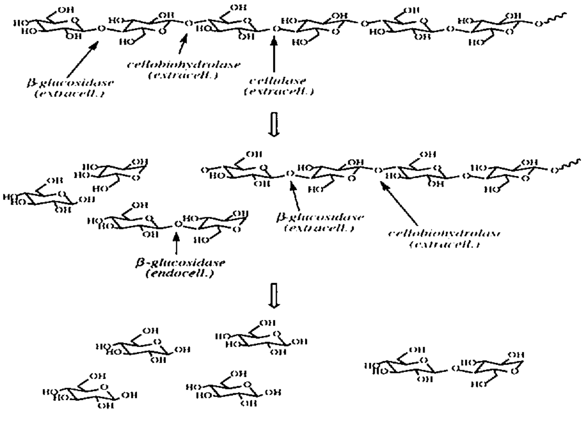


Chart 17 -
Cellulose biodegradation



It is much debated whether the connection between Environmentally Degradable Plastics and renewable resources as raw material has to be taken for "*granted*".

Indeed, by considering the balance between advantages and drawbacks (Chart 18), it is hard to come up with a very convincing statement. The secret for getting to at a firm position is closely linked to political decisions on the remedies that have to be taken into account, in order to maintain a fair ecobalance.

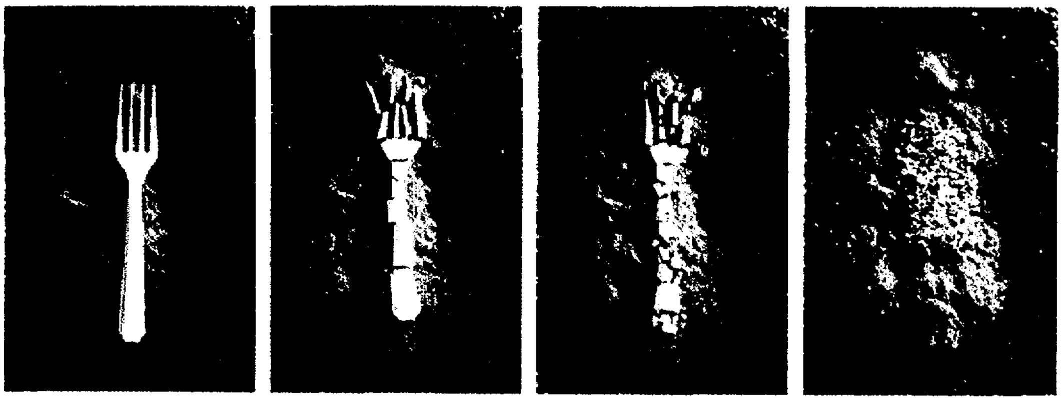
Chart 18 - Environmentally Degradable Polymeric Materials From Renewable Resources

ADVANTAGES	DRAWBACKS	REMEDIES
◆ Ample Structural Variety Combined with High Versatility	◆ Limits Imposed by Production Costs	◆ Incentives for the Development of Environmentally Friendly Polymeric Materials
◆ Limited Dependency of Raw Material Supply from Crude Oil & Coal Price Fluctuations.	◆ Limited Potential of Existing Technology in Providing a Variety of Matrix Materials at Acceptable Prices For New Applications.	◆ Political Decisions Tending to Diffuse & Appreciate the Impact of Environmentally Degradable Materials in Different Commercial & Industrial Exploitation Segments.
◆ Marginal Impact on Green-House Effect.	◆ Constraints in Processability Imposed by Inherent Structural Susceptibility to Side Reactions	
	◆ Limits of Adaptation of Existing Process Technology & Machinery	
	◆ Lack of a Global View on Definitions and Test Protocols for Environmentally Degradable Polymeric Materials	
	◆ Unsatisfactory Mechanical Properties	

Even for cellulose there is a cascade of at least five steps that require rather defined environmental conditions to permit the ultimate mineralization (Chart 17).

A visual fragmentation of an article based on PLA, kindly supplied by Cargill-Dow Co., eventually accompained by degradation mediated by chemical and biochemical agents is represented in Chart 19. It is stated that after 60 days a complete mineralization of the article occurred.

Chart 19 - ECO-PLA$_{\text{TM}}$ - The Renewable Bioplastic From Cargill-Dow



Day 0 **Day 12** **Day 33** **Day 45**

This series of photos shows major steps in a laboratory degradation process. Tests demonstrated complete degradation to carbon dioxide, water and soil nutrients after 60 days

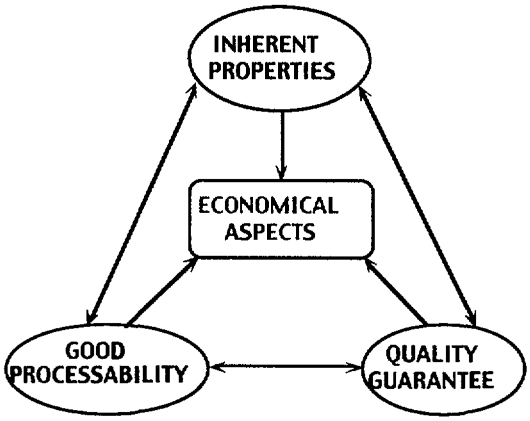
In the ecobalance, the life-cycle assessment of the plastic manufact plays indeed a key role. The main parameters to be taken into account are reported in Chart 20. A correct analysis of the impact of all them on the cost/effectiveness ratio should be taken into serious account by decision makers.

Chart 20 - Eco-Balance/LCA Assessment Steps to be Considered

Raw Material Supplying	Raw Material Pretreatment	Raw material Conversion	Production of Polymeric Materials
Processing Productions of Items	Usage of Items	Handling of End-Used Items	Transportation

The penetration onto the market of EDPs is subject to the market magic triangle centered on the economical balance derived from three fundamental properties that the materials should possess (Chart 21).

Chart 21 - Penetration of Any New Material onto the Market



In Chart 22 a collection of general advantages and bottlenecks that have to be taken into account for an acceptable development of EDPs and their penetration into the market is reported.

Chart 22 - Penetration of Bioplastics onto the Market

GENERAL ADVANTAGES OF BIOPLASTICS	BOTTLENECKS FOR BIOPLASTICS
Neutrality in Respect of CO_2-Cycle.	High Prices Tied Up with High Costs for R&D and Small Productions
Medium-Long Term Estimable Prices.	Unsatisfactory Properties in Comparison to Petrochemical Plastics
High Value Added by the Utilization of Agricultural Over Production.	Limited Number of Materials Available
Easy and Convenient Disposal by Composting.	Lack of World-Wide Accepted Regulatory Definitions and Tests
Nearly Unlimited Raw Material Resources.	Lack of Incentives for Environmentally Sound Polymeric Materials
	Unsatisfactory Disposal Systems

We have to take into consideration a general stetement that goes directly to the expectations in the development of polymeric materials expressed in the introductory remarks. This is going to reinforce the role that EDPs should play in the future (Chart 23).

Chart 23 - General Statement

- The General Substitution by Alternative Materials of all *Polymeric Materials* with their Excellent Properties is Impossible
- The Substitution of *Polymeric Materials* in the Various Branches of Packaging Segment With More Environmentally Sound Materials like *Paper, Paperboard, Glass, Metals* Leads to a Fourfold Refuse Weight and a Twofold Waste Volume.

The potential and effective utilization areas for EDPs can be found in different segments of high and low technological profile (Chart 24).

Chart 24 - Potential Utilization Areas for Degradable Polymers

PACKAGING	CONSUMPTION	TECHNICAL UTILIZATIONS	PLANT PROTECTION	AGRICULTURE & GARDENS	MEDICINE
Washing bags	One-way cutlery	Denitrification of water	Herbicide bands	Fertilizer bags	Medicine capsules
Waste bags	Napkins	Degradable carrier for chemicals	Pesticide bands with controlled lay off	Films	Serving material
Carrier bags	Sanitary towels		Dispenser	Cover films	Degradable carrier for medicines
Eggcups	"Litter products" (e.g. golftees)			Harvest bounding yarn	Fixing of fractures
Fast-food				Rentilization as animal food after sterilization	Orthopaedical surgery
Drinking packages				Bounding material	
Paddings				Sockets	
Cosmetics					
Hygienesector					
Pharmaceutics					
Washing & Cleaning					

The industrial and scientific interest on EDPs is amply demonstrated by the initiatives taken by companies (Chart 25) and academic institutions. The ICS-UNIDO action on EDPs goes in the same direction with specific attention to the diffusion of fundamental and technical concepts of EDPs in developing countries with the aim of stimulating a sustainable industrial development. Within less than a decade, specific societies, including industrial and academic operators, have been founded in Japan (JSBP) and USA (BEDPS). In Europe the foundation of an European Degradable Polymer Society (EDPS) has recently been proposed that will go to flank a world-wide Association of Industrial Manufactured of Biodegradable Products IBPMA-ORCA that is located in Belgium.

Chart 25 - List of Biodegradable Polymeric Materials Producers

EUROPE	
Avebe	Starch-based blends
BASF	Polyesters, Polyaspartic acid*
Bayer	Polyesteramides
Biopac	Extrusionable Starch Materials
Biotec	Starch-based blends
Boehringer, BPI, Ethicon	Polyesters
Deutsche Gelatin AG	Polypeptide (Proteins)*
EMS Chemie / Battelle	Extrusionable Starch Materials
EPI	Polyethylene / Additives
Fermentation Institute	Polyesters
Fluntera AG	Extrusionable Starch Materials
Idroplast	Poly(vinyl alcohol)*
Mazzucchelli	Cellulose acetate
Neste Oy	Poly(lactic acid)
Novamont	Starch-based blends
Novon Polymers AG	Extrusionable Starch Materials
Solvay	Poly(caprolactone)
Storopack	Foamable Starch Materials
Sunstarke	Foamable Starch Materials
Technicoat	Polyethylene / Additives
Tubize Plastics *(Rhône Poulenc)*	Modified Cellulose
United Paper Mills	Cellulose derivatives

USA	
Air Products	Synthetic/Products*
Amylum	Extrusionable Starch Materials
Archer Daniels	Extrusionable Starch Materials
BioPlastics	Starch/Polycaprolactone (PCL)
Cargill Dow Polymers	Poly(lactic acid)
Chronopol	Poly(lactic acid)
Dow Chemical	Polyesters
DuPont	Polyesters
Eastman Chemical Co.	Polyesters/Cellulose Derivatives
Monsanto ***(stopped activity)***	Poly(hydroxy alkanoate) (PHA)
National Starch	Starch-based derivatives
National Starch & Chemical American	
Excelsior	Foamable Starch Materials
Novon International	Starch-based Derivatives
Planet Polymer Technologies	Poly(ethyleneglycol)*
Rohm & Haas	Polypeptide (Proteins) - Poly-aspartic acid*
St. Lawrence Starch	Extrusionable Starch Materials
Union Carbide	Poly (caprolactone) (PCL)
USDA - Agritech	Extrusionable Starch Materials
Warner & Lambert	Extrusionable Starch Materials
Willow Ridge	Polyethylene / Starch Blends

---

* Materials soluble in water media

Chart 25 - List of Biodegradable Polymeric Materials Producers (*continued*)

ASIAN PACIFIC BASIN	
Aicello	Chitosan/Cellulose/Starch
Ajinomoto	Bacterial Cellulose
Chisso/Novon International	Starch / PVA or PCL Blends
Dai Nippon	Poly(aspartic acid)*
Daicel Chemical	Cellulose Derivatives/PCL Blends
Hayashibara Group	Pullulan*
Japan Corn Starch	Starch-based derivatives
Kuraray	Polyvinyl Alcohol*
Misui-Johatsu	Poly (lactic acid)
Mitsubishi	Poly (aspartic acid)*
Nippon Shokubai	Poly (ethylene succinate)
Nippon Unica	Polycaprolacone (PCL)
Nissei	Starch-based
Shimadzu	Poly (lactic acid)
Showa High Polymer	Aliphatic Polyesters

---

* Materials soluble in water media

The production costs of the EDPs presently on the market vary considerably, depending upon the nature of the materials, their use and the tonnage.

It has been recently stated that bioplastics like PLA at level of production of 120 ktons/year can reach a cost around 0,50 US$/pound, that is comparable to the retail price of major commodity plastics.

The perspectives for EDPs production and penetration into the market are rather promising as documented by the general trend of the interest for the materials that one find in the profile of publications & patents relevant to Biodegradables (Polymers, Plastics, Composites and Blends) within the time, in the 80's (Chart 26) with respect to the analogous plot found in the 90's (Chart 27).

Chart 26 - Total References & Patents on Biodegradables in the 80's

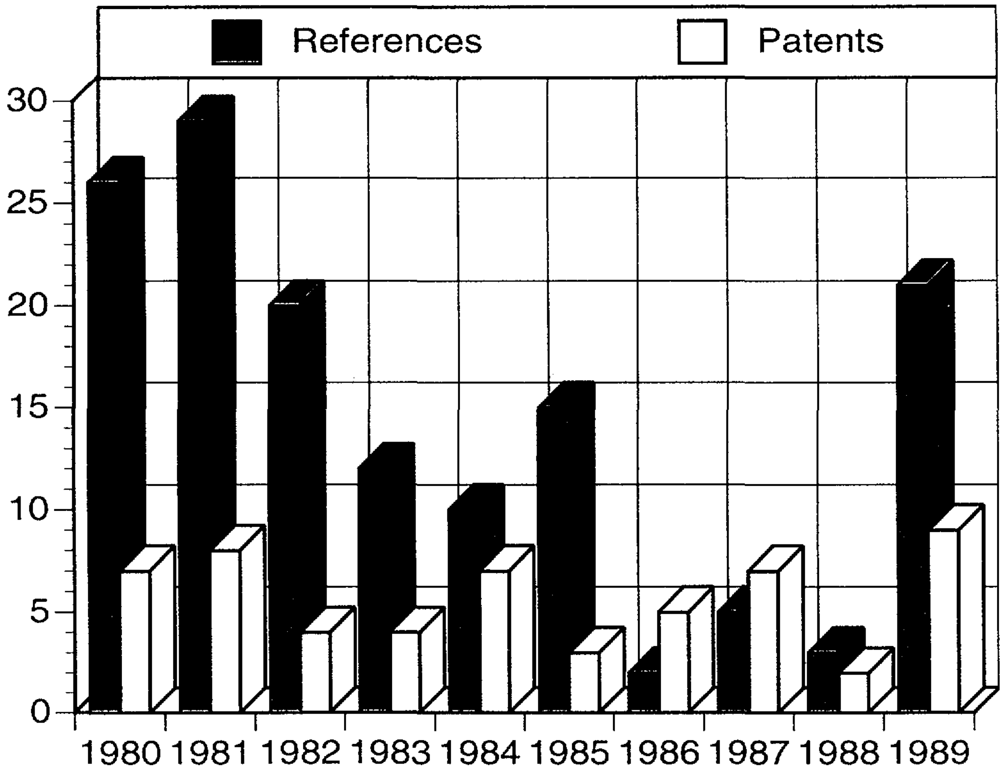
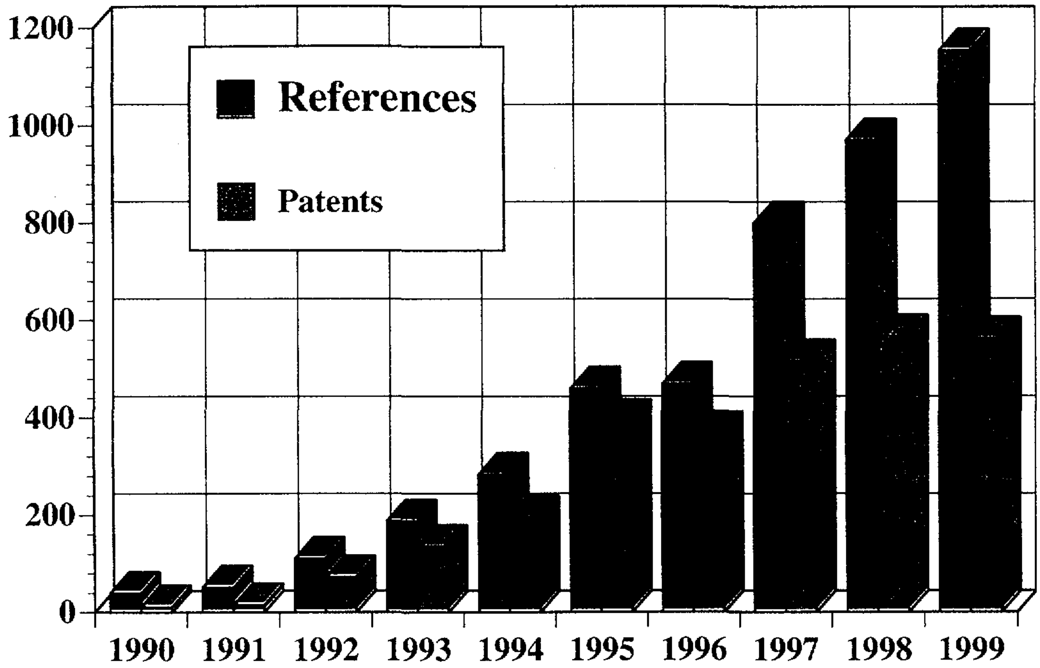


Chart 27 - Total References & Patents on Biodegradables in the 90's



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13. "Degradable Polymers" (G. Scott & D. Gilead Eds.), Chapman & Hall, London (U.K.) [1995].

3. Biodegradable Plastics For Sustainable Technology Development & Evolving World-Wide Standards

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Sustainability, Industrial ecology, Green chemistry are the new principles that are guiding the development of the next generation of products and processes. Thus, new products have to be designed and engineered from cradle to grave incorporating a holistic "life cycle thinking" approach. The impact of raw material resources used in the manufacture of a product and the ultimate fate (disposal) of the product when it enters the waste stream has to be factored into the design of the product. The use of annually renewable resources and the biodegradability or recyclability of the product is becoming an important design criterion. This has opened up new market opportunities for developing value added products from annually renewable feedstocks..

Designing products to be biodegradable and ensuring that they end up in an appropriate disposal system, that would utilize the biodegradability functionality, is environmentally and ecologically sound. For example, we can generate much-needed carbon-rich compost (humic material) by composting our biodegradable plastic and paper waste along with other *organic* compostable materials like yard, food, and agricultural wastes. Compost amended soil has beneficial effects by increasing soil organic carbon, increasing water and nutrient retention, reducing chemical inputs, and suppress plant diseases. Composting is important for sustainable agriculture practices.

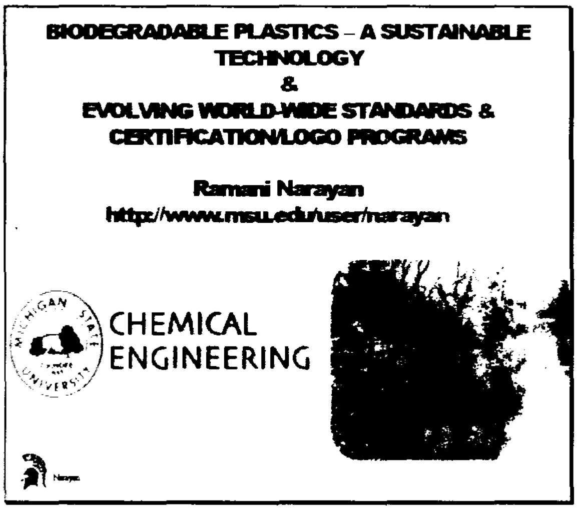
Measurement of biodegradability, and relating it to the appropriate disposal environment is an essential criterion to be met by biodegradable plastics. U.S.(ASTM), European (CEN), German (DIN) and ISO (International Standards Organization) Standards have been developed or under development to evaluate biodegradability under different environmental/disposal conditions like composting, soil, marine, wastewater treatment facility, anaerobic digestor. ASTM Standard Specification for Compostable Plastics" D6400-99 establishes criteria (specifications) for plastics and products made from plastics to be labeled compostable and subscribes to the U.S. Federal Trade Commission (FTC) Environmental Marketing Claims Guidelines for claims of compostability. This specification is comparable to what is being developed by CEN (European Committee for Standardization) in Europe today, and in harmony with the German Standard (DIN 54900), moving the industry closer to global standards.

Sustainable biodegradable plastics technologies are under development that meets the biodegradability/compostability Standards criteria.

Several technologies based on aliphatic polyesters and copolyesters have emerged spearheaded by Eastman Chemical, DuPont, BASF, Mitsui Chemicals, Showa High Polymer. Poly(lactic acid) from corn is a successful major initiative from Cargill-Dow which emphasizes sustainability and renewable resources as its major features in addition to cost and performance.

Starch based thermoplastic technologies using water or other polyhydric alcohols have been developed. One of the successful market entries is in loose-fill packaging as a substitute for polystyrene foam and has captured 20% of the U.S. market. Another innovative application for these starch foam materials is in toys, arts & crafts markets. Starch esters, and thermoplastic starch-polyester blends are also being commercialized.

Slide 1



BIODEGRADABLE PLASTICS – A SUSTAINABLE TECHNOLOGY
&
EVOLVING WORLD-WIDE STANDARDS & CERTIFICATION/LOGO PROGRAMS

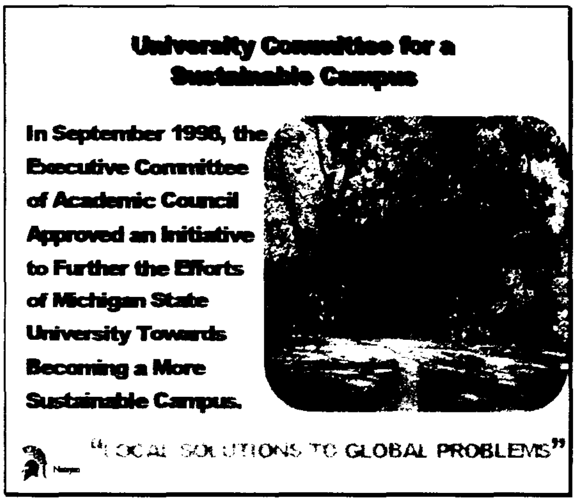
Ramani Narayan
http://www.msu.edu/user/narayan

CHEMICAL ENGINEERING

This lecture addresses two issues:

1. Role and rationale for biodegradable plastics in Sustainable Technology development.
2. Current status of Standards and certification programs for biodegradable plastics and the fundamental scientific principles behind these programs

Slide 2



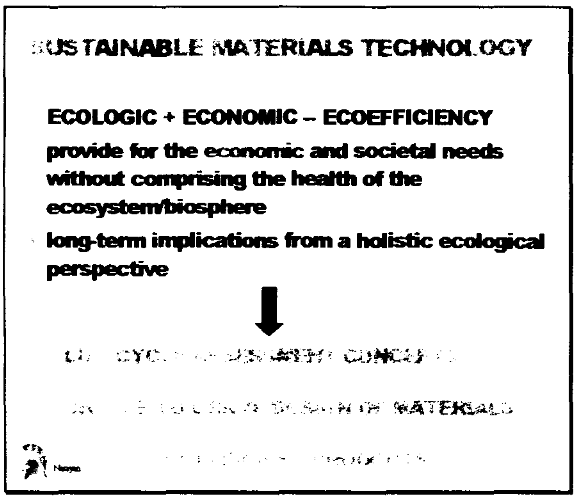
University Committee for a Sustainable Campus

In September 1998, the Executive Committee of Academic Council Approved an Initiative to Further the Efforts of Michigan State University Towards Becoming a More Sustainable Campus.

"LOCAL SOLUTIONS TO GLOBAL PROBLEMS"

The concept of "Sustainability" is becoming important and being implemented seriously at all levels – countries, towns, communities, universities. Michigan State University has made a serious commitment towards becoming a "sustainable campus" and serves as a model for others to adopt and follow. ISO 14001 Standard protocols and procedures will be followed with the goal of ultimately becoming certified

Slide 3



SUSTAINABLE MATERIALS TECHNOLOGY

ECOLOGIC + ECONOMIC – ECOEFFICIENCY

provide for the economic and societal needs without comprising the health of the ecosystem/biosphere
long-term implications from a holistic ecological perspective

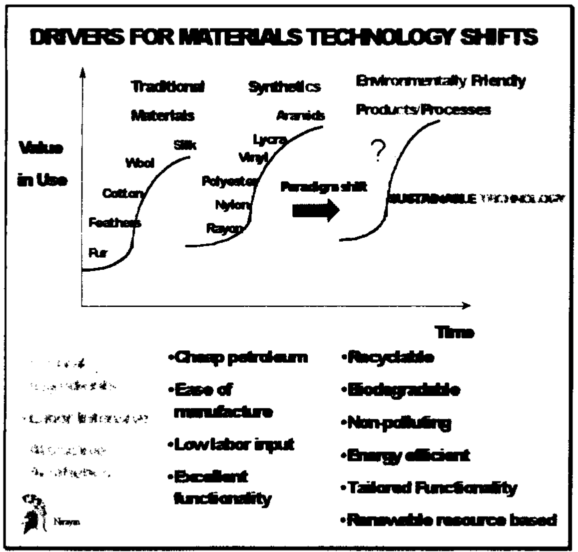
LIFE CYCLE [illegible] CONCEPTS

[illegible] DESIGN OF MATERIALS

[illegible]

This slide defines sustainable materials technology and suggests that economics is an important factor in implementing environmentally responsible materials. Therefore, ecology and economy have to be taken into consideration giving rise to the concept of "ecoefficiency" and "ecoefficient products"

Slide 4

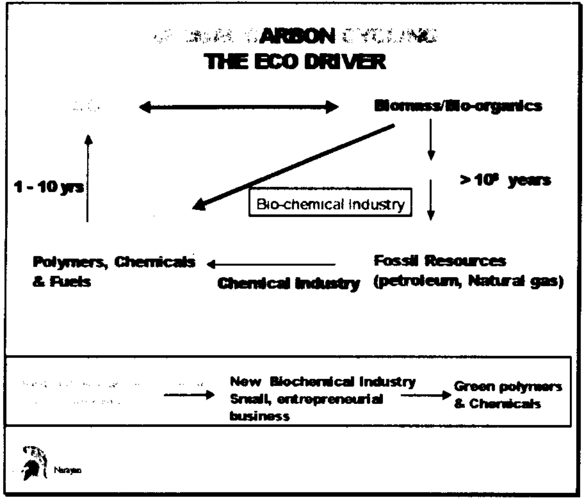

DRIVERS FOR MATERIALS TECHNOLOGY SHIFTS

- Cheap petroleum
- Ease of manufacture
- Low labor input
- Excellent functionality

- Recyclable
- Biodegradable
- Non-polluting
- Energy efficient
- Tailored Functionality
- Renewable resource based

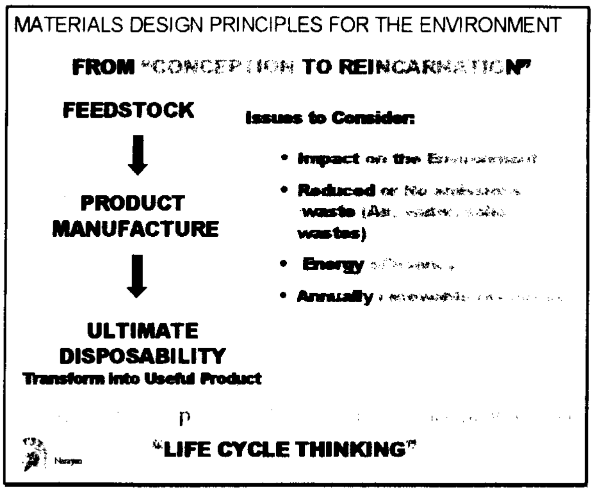
This slide explains the materials technology shifts from the traditional to the synthetics and now to the sustainable. The curves represents typical economic S-curves showing the slow acceptance of new technology by the market place, rapid expansion and growth and finally reaching the mature plateau phase. The discovery of cheap petroleum caused the paradigm shift from the traditional to the synthetics, and now we are poised for another paradigm shift focusing on sustainability, environmentally friendly and terms like biodegradable, energy efficiency etc. A new technology S-curve is beginning.

Slide 5


ARBON
THE ECO DRIVER

The importance of using biomass/ agricultural feedstocks in the context of global carbon cycles and eco drivers is explained. CO_2 is fixed by plants (photosynthesis) to produce biomass. Over geological timeframes biomass is fossilized to generate the petroleum, natural gas resources. Unfortunately, these resources are consumed with concomitant CO_2 release at a rate much faster (1-10 years) than it is fixed (>10^6 years). So the goal is to use a secondary carbon cycle and convert crops and biomass residues to polymers chemicals & fuel at a rate that fixes faster that it is utilized or at best be neutral. This begins to address the carbon cycle imbalance.

Slide 6


MATERIALS DESIGN PRINCIPLES FOR THE ENVIRONMENT

FROM "CONCEPTION TO REINCARNATION"

FEEDSTOCK

PRODUCT MANUFACTURE

ULTIMATE DISPOSABILITY
Transform Into Useful Product

Issues to Consider:

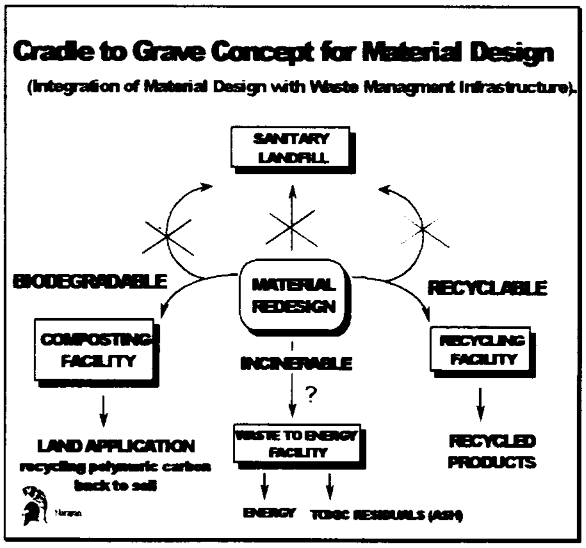
- **Impact** on the Environment
- **Reduced** or No emissions & **waste** (Air, water, solid **wastes**)
- **Energy** efficient
- **Annually** renewable resources

"LIFE CYCLE THINKING"

The need to use "life cycle thinking" for the design, use, disposal, and reuse of materials is illustrated. Design for the environment requires consideration to energy usage, environmental impact of emissions and waste for the entire life cycle from feedstock utilization to ultimate disposability when the product enters the disposal infrastructure after use by the customer

POOR QUALITY ORIGINAL

Slide 7

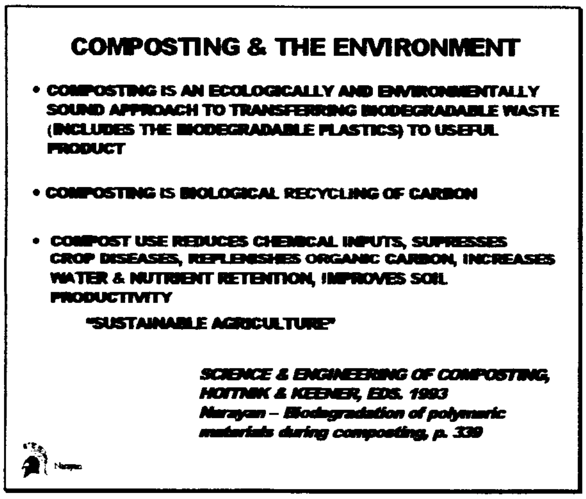


Cradle to Grave Concept for Material Design

(Integration of Material Design with Waste Managment Infrastructure).

This slide illustrates the need to integrate material design with the disposal infrastructure. Calling something biodegradable or recyclable has no meaning unless the appropriate disposal infrastructure that can utilize the functionality of biodegradability or recyclability exists. Burial of waste and persevering garbage in sanitary landfills makes no sense. Recycling makes sense if approporiate recycling infrastructures exist to recycle products in an ecological and cost-effective manner. Biodegradable materials in conjunction with composting infrastructures can transform biowastes (a resource!) into useful soil amendment (compost) that is beneficial to soil.

Slide 8



COMPOSTING & THE ENVIRONMENT

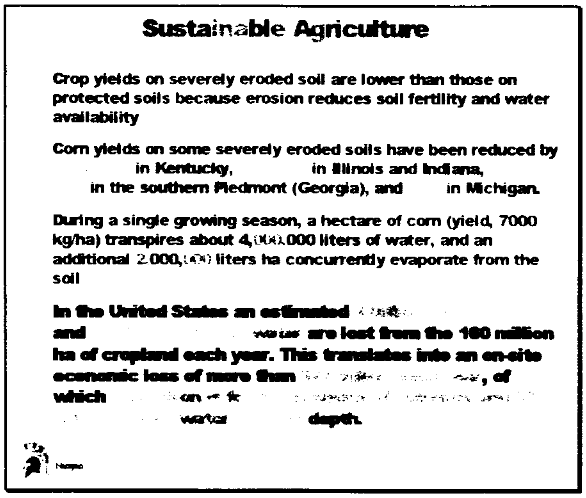
- COMPOSTING IS AN ECOLOGICALLY AND ENVIRONMENTALLY SOUND APPROACH TO TRANSFERRING BIODEGRADABLE WASTE (INCLUDES THE BIODEGRADABLE PLASTICS) TO USEFUL PRODUCT
- COMPOSTING IS BIOLOGICAL RECYCLING OF CARBON
- COMPOST USE REDUCES CHEMICAL INPUTS, SUPRESSES CROP DISEASES, REPLENISHES ORGANIC CARBON, INCREASES WATER & NUTRIENT RETENTION, IMPROVES SOIL PRODUCTIVITY

"SUSTAINABLE AGRICULTURE"

SCIENCE & ENGINEERING OF COMPOSTING, HOITNIK & KEENER, EDS. 1993
Narayan – Biodegradation of polymeric materials during composting, p. 339

This slide illustrates the importance of composting to the environment and the role it plays in "sustainable agriculture". Since composting is necessary for sustainable agricultural practices there will continue to be a growth in composting plants to handle biowastes. Therefore, biodegradable plastics can be readily assimilated in these composting infrastructures, thereby providing an ecologically and cost effective approach to transform our plastic waste into useful compost product.

Slide 9



Sustainable Agriculture

Crop yields on severely eroded soil are lower than those on protected soils because erosion reduces soil fertility and water availability

Corn yields on some severely eroded soils have been reduced by [illegible] in Kentucky, [illegible] in Illinois and Indiana, [illegible] in the southern Piedmont (Georgia), and [illegible] in Michigan.

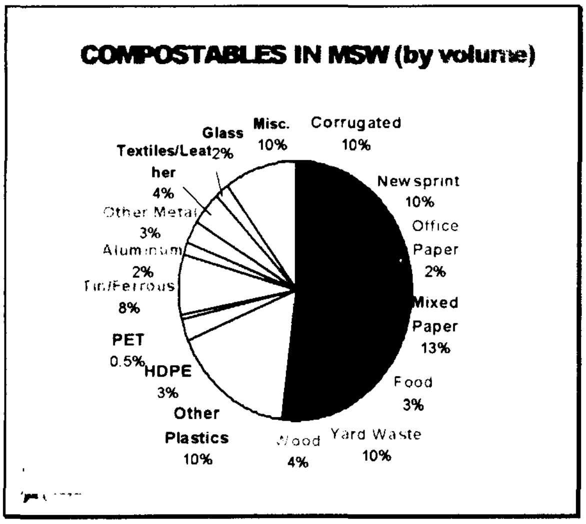
During a single growing season, a hectare of corn (yield, 7000 kg/ha) transpires about 4,000,000 liters of water, and an additional 2,000,000 liters ha concurrently evaporate from the soil

In the United States an estimated [illegible] and [illegible] water are lost from the 160 million ha of cropland each year. This translates into an on-site economic loss of more than [illegible], of which [illegible] on [illegible] water [illegible] depth.

This slide illustrates the problems faced in agriculture due to loss of nutrients and topsoil due to erosion and agricultural practices, resulting in an economic and ecological loss that is not taken into account in calculating the cost-benefit ratio. The use of compost would mitigate the problems and help ecologically and economically.

POOR QUALITY ORIGINAL

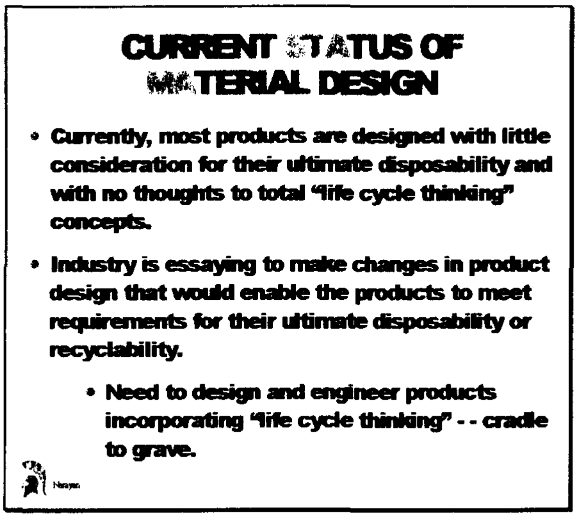
Slide 10



COMPOSTABLES IN MSW (by volume)

This slide shows that as much as 50% of our municipal solid waste (MSW) is biowastes that are fully compostable. Composting of these biowastes instead of burying them in a landfill would convert them to useful compost product that is important for sustainable agricultural practices.

Slide 11



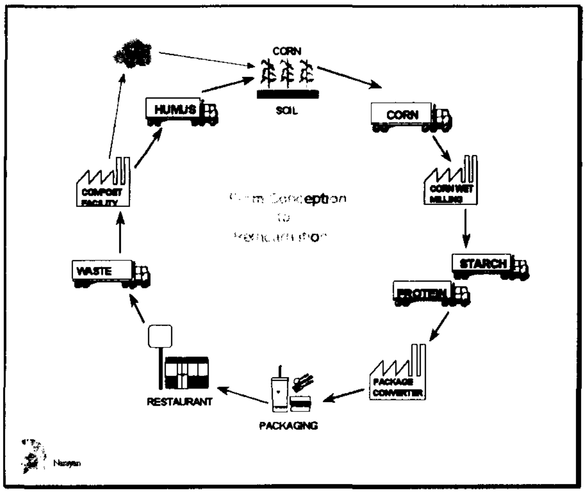
CURRENT STATUS OF MATERIAL DESIGN

- Currently, most products are designed with little consideration for their ultimate disposability and with no thoughts to total "life cycle thinking" concepts.
- Industry is essaying to make changes in product design that would enable the products to meet requirements for their ultimate disposability or recyclability.
  - Need to design and engineer products incorporating "life cycle thinking" -- cradle to grave.

Narayan

This slide documents the current status of design of materials. It introduces the need to design and engineer products incorporating "life cycle thinking"

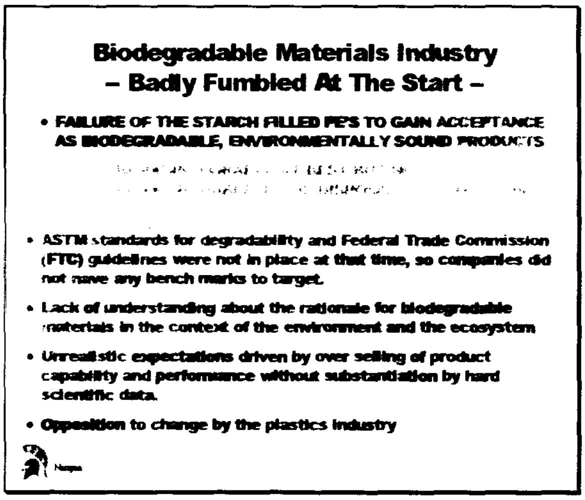
Slide 12



A conceptual scheme showing a closed loop cycling of the polymeric carbon through manufacture of industrial plastic products that after use is composted. Another important element is the use of annually renewable agricultural feedstock, corn – "sustainable feedstock"

POOR QUALITY ORIGINAL

Slide 13



Biodegradable Materials Industry
– Badly Fumbled At The Start –

- FAILURE OF THE STARCH FILLED PE'S TO GAIN ACCEPTANCE AS BIODEGRADABLE, ENVIRONMENTALLY SOUND PRODUCTS

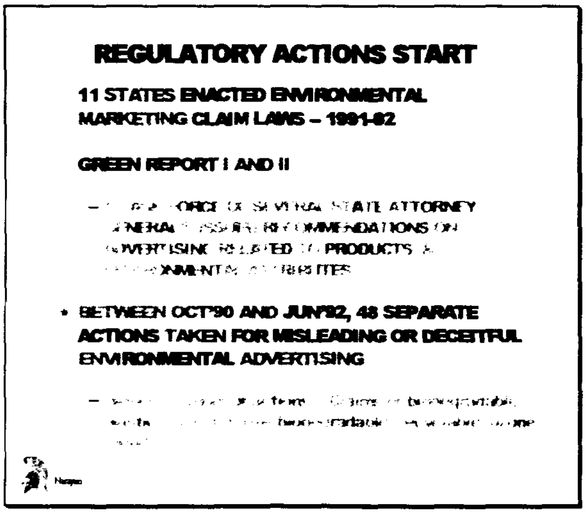
  [illegible]

- ASTM standards for degradability and Federal Trade Commission (FTC) guidelines were not in place at that time, so companies did not have any bench marks to target.
- Lack of understanding about the rationale for biodegradable materials in the context of the environment and the ecosystem
- Unrealistic expectations driven by over selling of product capability and performance without substantiation by hard scientific data.
- Opposition to change by the plastics industry

Narayan

This slide illustrates how the biodegradable plastics industry fumbled at the beginning.

Slide 14



REGULATORY ACTIONS START

11 STATES ENACTED ENVIRONMENTAL MARKETING CLAIM LAWS – 1991-92

GREEN REPORT I AND II

– [illegible] FORCE OF SEVERAL STATE ATTORNEY GENERALS ISSUED RECOMMENDATIONS ON ADVERTISING RELATED TO PRODUCTS' ENVIRONMENTAL ATTRIBUTES

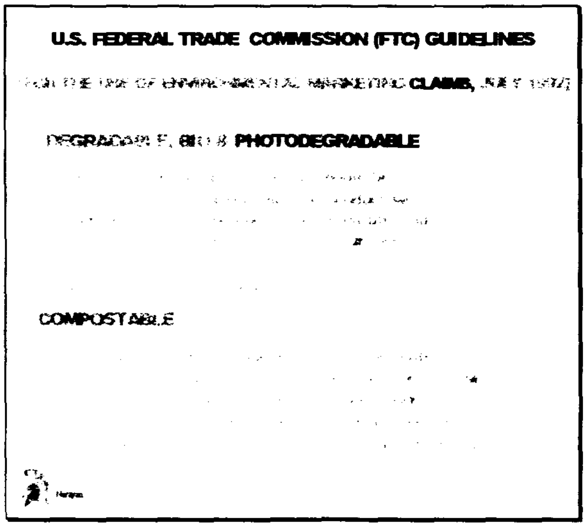
- BETWEEN OCT'90 AND JUN'92, 48 SEPARATE ACTIONS TAKEN FOR MISLEADING OR DECEITFUL ENVIRONMENTAL ADVERTISING

  – [illegible]

Narayan

This slide refers to the ensuing regulatory actions that resulted from the introduction of so-called biodegradable products with little or no evidence supporting the claim of biodegradability

Slide 15



U.S. FEDERAL TRADE COMMISSION (FTC) GUIDELINES

FOR THE USE OF ENVIRONMENTAL MARKETING CLAIMS, JULY 1992

DEGRADABLE, BIO & PHOTODEGRADABLE

[illegible]

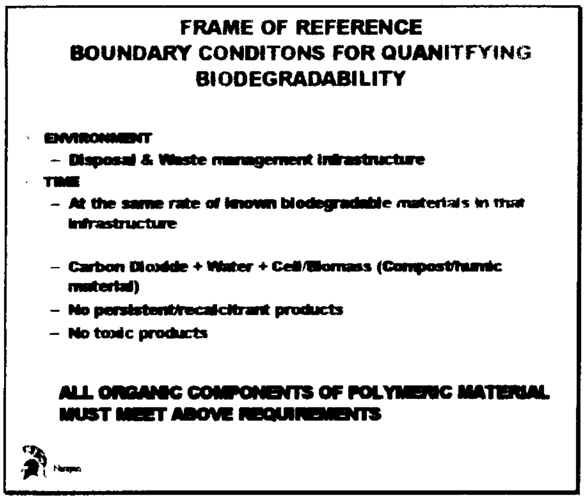
COMPOSTABLE

[illegible]

Narayan

This slide documents the FTC guidelines for making claims of biodegradability or compostability and issued because of the false and misleading claims of the starch-polyethylene products that were at best disintegrable but not biodegradable.

Slide 16



FRAME OF REFERENCE
BOUNDARY CONDITONS FOR QUANITFYING BIODEGRADABILITY

- ENVIRONMENT
  - Disposal & Waste management infrastructure
- TIME
  - At the same rate of known biodegradable materials in that infrastructure

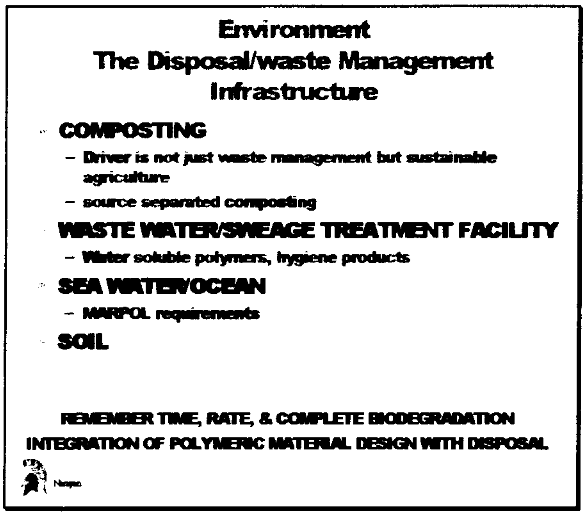
  - Carbon Dioxide + Water + Cell/Biomass (Compost/humic material)
  - No persistent/recalcitrant products
  - No toxic products

ALL ORGANIC COMPONENTS OF POLYMERIC MATERIAL MUST MEET ABOVE REQUIREMENTS

Narayan

This slide states that biodegradability cannot be quantified without specifying the boundary conditions or the frame of reference. Environment, time, and breakdown products need to be specified in talking about biodegradability.

Slide 17



Environment
The Disposal/waste Management Infrastructure

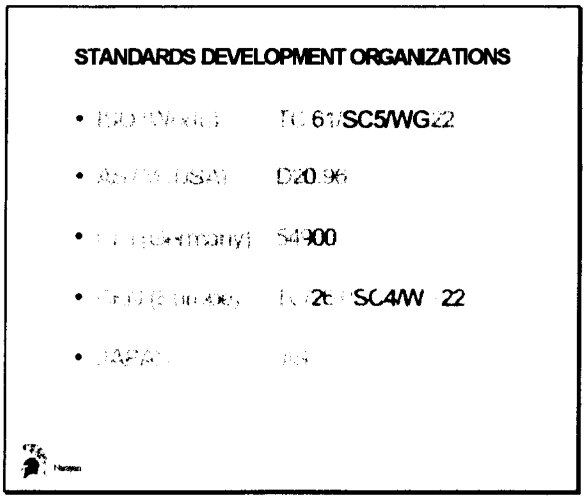
- COMPOSTING
  - Driver is not just waste management but sustainable agriculture
  - source separated composting
- WASTE WATER/SWEAGE TREATMENT FACILITY
  - Water soluble polymers, hygiene products
- SEA WATER/OCEAN
  - MARPOL requirements
- SOIL

REMEMBER TIME, RATE, & COMPLETE BIODEGRADATION
INTEGRATION OF POLYMERIC MATERIAL DESIGN WITH DISPOSAL

Narayan

This slide follows from the previous slide and defines the various disposal environments that utilizes the functionality of biodegradability in their process.

Slide 18



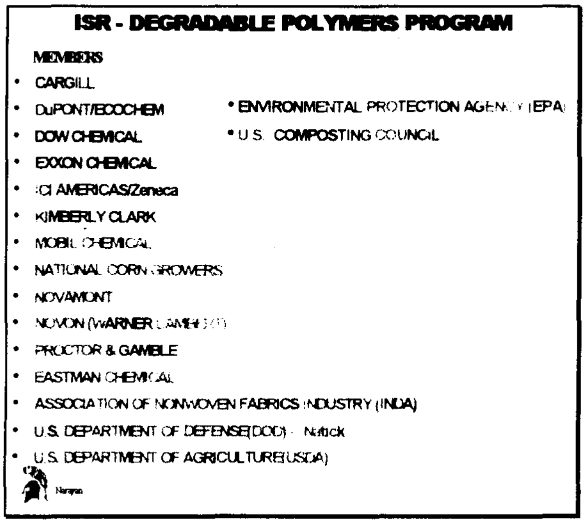
STANDARDS DEVELOPMENT ORGANIZATIONS

- ISO (World) TC 61/SC5/WG22
- ASTM (USA) D20.96
- DIN (Germany) 54900
- CEN (Europe) TC 261/SC4/WG 22
- JAPAN JIS

Narayan

This slide introduces the various National Standards Bodies that have developed and continue developing Standards for measuring and quantifying biodegradability, as well as specifications for a "compostable plastic"

Slide 19



ISR - DEGRADABLE POLYMERS PROGRAM

MEMBERS

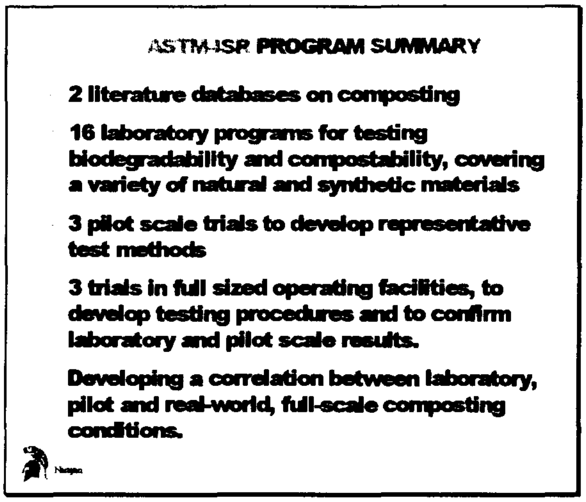
- CARGILL
- DuPONT/ECOCHEM
- DOW CHEMICAL
- EXXON CHEMICAL
- ICI AMERICAS/Zeneca
- KIMBERLY CLARK
- MOBIL CHEMICAL
- NATIONAL CORN GROWERS
- NOVAMONT
- NOVON (WARNER LAMBERT)
- PROCTOR & GAMBLE
- EASTMAN CHEMICAL
- ASSOCIATION OF NONWOVEN FABRICS INDUSTRY (INDA)
- U.S. DEPARTMENT OF DEFENSE(DOD) - Natick
- U.S. DEPARTMENT OF AGRICULTURE(USDA)

- ENVIRONMENTAL PROTECTION AGENCY (EPA)
- U.S. COMPOSTING COUNCIL

Narayan

ASTM subcommittee D20.96 created a research program at the ASTM-ISR Institute to provide for experimental validation of the developed standards for composting. Major industries, Government, and NGO's participated and funded the study, and based on the report Standards and Specifications have been developed.

Slide 20



ASTM-ISR PROGRAM SUMMARY

2 literature databases on composting

16 laboratory programs for testing biodegradability and compostability, covering a variety of natural and synthetic materials

3 pilot scale trials to develop representative test methods

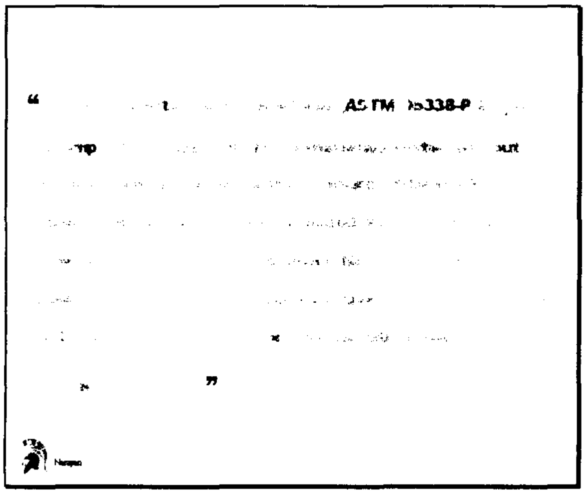
3 trials in full sized operating facilities, to develop testing procedures and to confirm laboratory and pilot scale results.

Developing a correlation between laboratory, pilot and real-world, full-scale composting conditions.

Narayan

This slide summarizes the ASTM-ISR research program studies

Slide 21

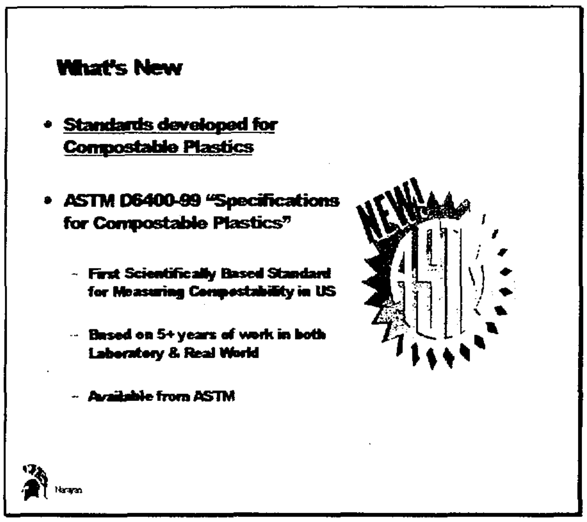


“ [illegible] **ASTM D5338-P** [illegible] ”

Narayan

This slide drives home the point that the designed laboratory scale tests were very conservative and that the pilot and or full scale test data exceeded those obtained from the laboratory scale tests.

Slide 22

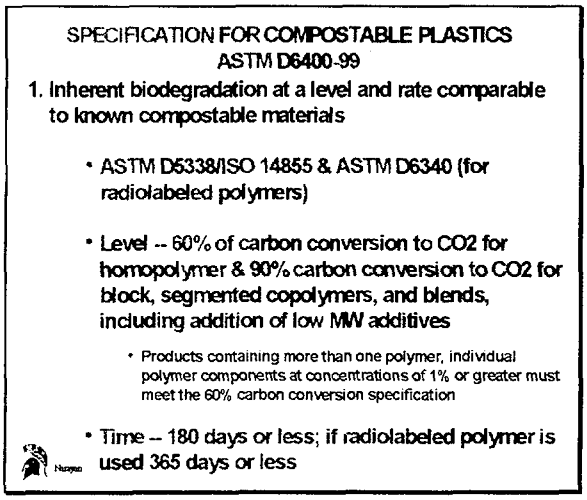


What's New

- **Standards developed for Compostable Plastics**
- **ASTM D6400-99 "Specifications for Compostable Plastics"**
  - **First Scientifically Based Standard for Measuring Compostability in US**
  - **Based on 5+ years of work in both Laboratory & Real World**
  - **Available from ASTM**

This slide focuses on the Standards developed for compostable plastics and the key one is the "Specification for Compostable Plastics"

Slide 23

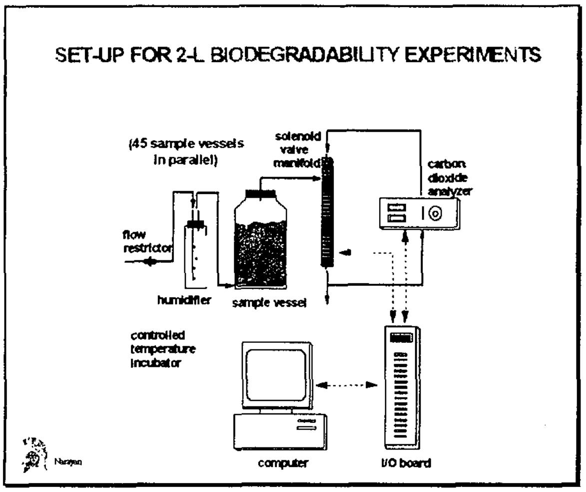


SPECIFICATION FOR COMPOSTABLE PLASTICS
ASTM D6400-99

1. Inherent biodegradation at a level and rate comparable to known compostable materials
   - ASTM D5338/ISO 14855 & ASTM D6340 (for radiolabeled polymers)
   - Level -- 60% of carbon conversion to CO2 for homopolymer & 90% carbon conversion to CO2 for block, segmented copolymers, and blends, including addition of low MW additives
     - Products containing more than one polymer, individual polymer components at concentrations of 1% or greater must meet the 60% carbon conversion specification
   - Time -- 180 days or less; if radiolabeled polymer is used 365 days or less

This slide highlights the "Specification for Compostable Plastics", and brings out the first requirement needed for compostable plastics – "inherent biodegradability"

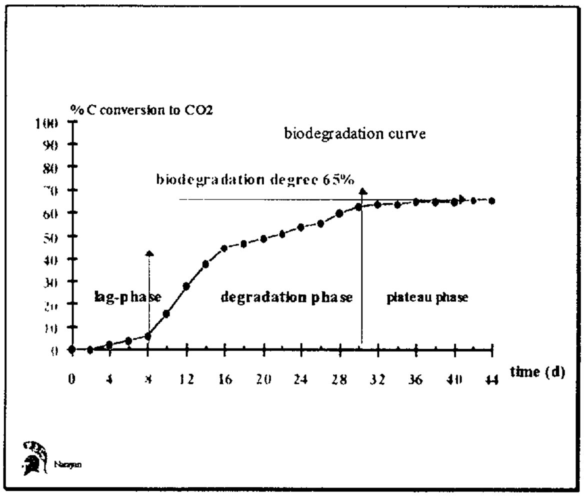
Slide 24



SET-UP FOR 2-L BIODEGRADABILITY EXPERIMENTS

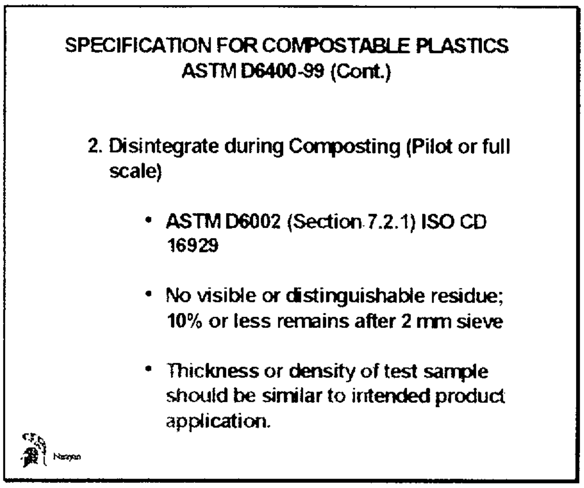
An instrumented set-up to measure biodegradability of test materials using it as the sole carbon source for the microorganisms.

Slide 25



A typical graph obtained during a biodegradability experiment

Slide 26

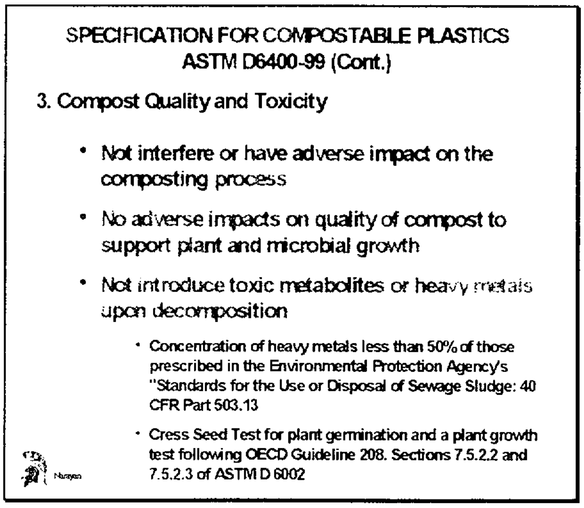


SPECIFICATION FOR COMPOSTABLE PLASTICS
ASTM D6400-99 (Cont.)

2. Disintegrate during Composting (Pilot or full scale)
   - ASTM D6002 (Section 7.2.1) ISO CD 16929
   - No visible or distinguishable residue; 10% or less remains after 2 mm sieve
   - Thickness or density of test sample should be similar to intended product application.

The second requirement for a compostable plastic -- disintegration

Slide 27

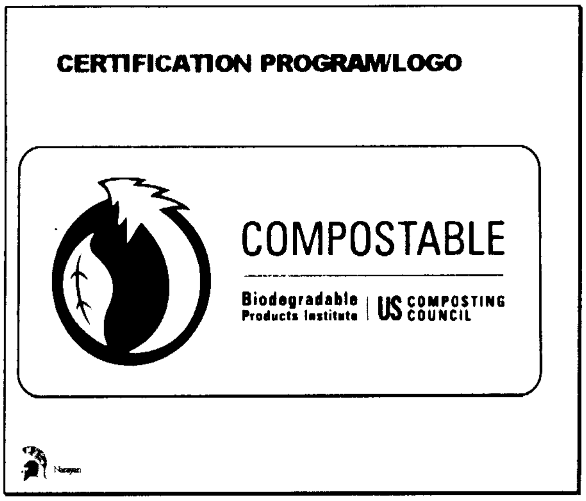


SPECIFICATION FOR COMPOSTABLE PLASTICS
ASTM D6400-99 (Cont.)

3. Compost Quality and Toxicity
   - Not interfere or have adverse impact on the composting process
   - No adverse impacts on quality of compost to support plant and microbial growth
   - Not introduce toxic metabolites or heavy metals upon decomposition
     - Concentration of heavy metals less than 50% of those prescribed in the Environmental Protection Agency's "Standards for the Use or Disposal of Sewage Sludge: 40 CFR Part 503.13
     - Cress Seed Test for plant germination and a plant growth test following OECD Guideline 208. Sections 7.5.2.2 and 7.5.2.3 of ASTM D 6002

The third requirement that needs to be met by a compostable plastic (biodegradable plastic under composting conditions) – eco and phyto toxicity

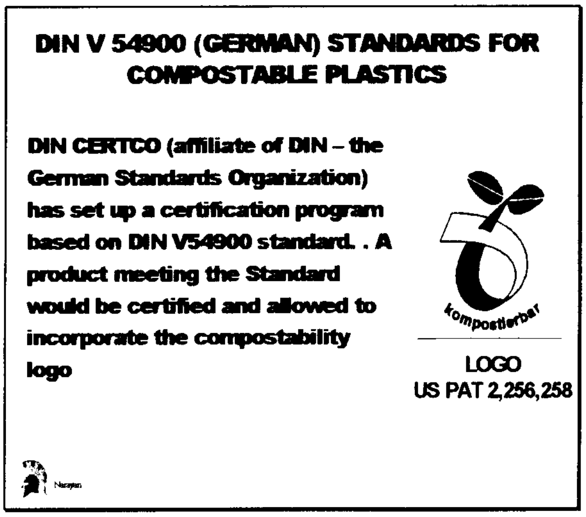
Slide 28



CERTIFICATION PROGRAM/LOGO

The International Biodegradable Products Institute (www.bpiworld.org) and the U.S. Composting Council(www.compostingcouncil.org)have developed a certification/logo program for products that passes the ASTM D6400 Specification for Compostable Plastics. BPI is a trade industry organization that represents the biodegradable products industry and the U.S. Composting Council is the voice of the composting industry. Visit the web sites for more information

Slide 29



DIN V 54900 (GERMAN) STANDARDS FOR COMPOSTABLE PLASTICS

DIN CERTCO (affiliate of DIN – the German Standards Organization) has set up a certification program based on DIN V54900 standard. . A product meeting the Standard would be certified and allowed to incorporate the compostability logo

LOGO
US PAT 2,256,258

Germany have developed a similar logo/certification scheme for compostable plastic products that is based on the DIN norm. The German norm is in harmony with the U.S. ASTM Standard except for some minor differences that is country specific. Efforts are underway to provide for mutual recognition of the respective logos.

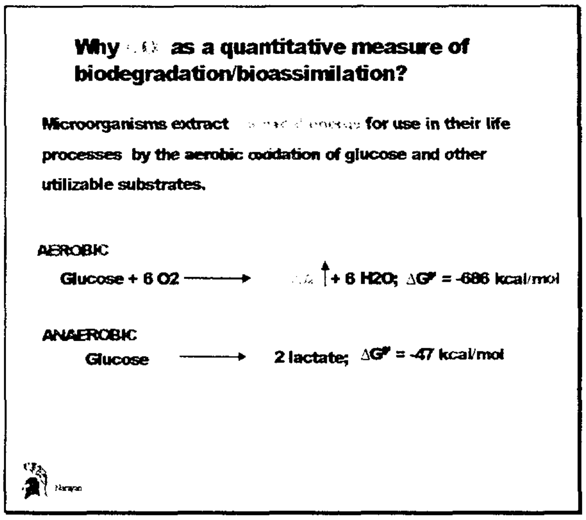
Slide 30

CERTIFICATION PROGRAM & LOGO BASED ON CEN (EUROPEAN) STANDARD (EN 13432 – Test Scheme & Criteria on Composting)

CEN TC 261/SC4/WG2 – Requirements for packaging recoverable through composting and biodegradation. Test scheme and evaluation criteria for final acceptance of packaging

This slide illustrates the CEN (European) certification/logo program. It is based on the CEN Standard. This Standard is in principle similar to the ASTM and DIN Standards with some minor differences.

Slide 31



Why [illegible] as a quantitative measure of biodegradation/bioassimilation?

Microorganisms extract [illegible] for use in their life processes by the aerobic oxidation of glucose and other utilizable substrates.

AEROBIC

Glucose + 6 O2 ⟶ [illegible] ↑ + 6 H2O; $\Delta G^{\circ\prime}$ = -686 kcal/mol

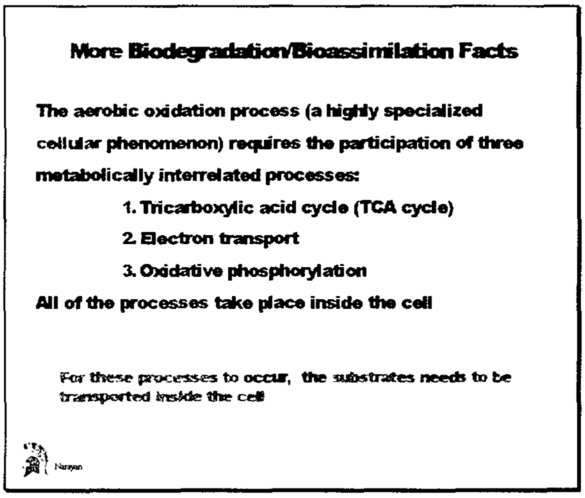
ANAEROBIC

Glucose ⟶ 2 lactate; $\Delta G^{\circ\prime}$ = -47 kcal/mol

Narayan

There have been questions raised as to the rationale for selecting the evolution of CO_2 as the quantitative measure of biodegradation. This slide and forthcoming slides illustrates that CO_2 evolution represents the microbial oxidative process to extract chemical energy for use in the cell's life process.

Slide 32



More Biodegradation/Bioassimilation Facts

The aerobic oxidation process (a highly specialized cellular phenomenon) requires the participation of three metabolically interrelated processes:

1. Tricarboxylic acid cycle (TCA cycle)
2. Electron transport
3. Oxidative phosphorylation

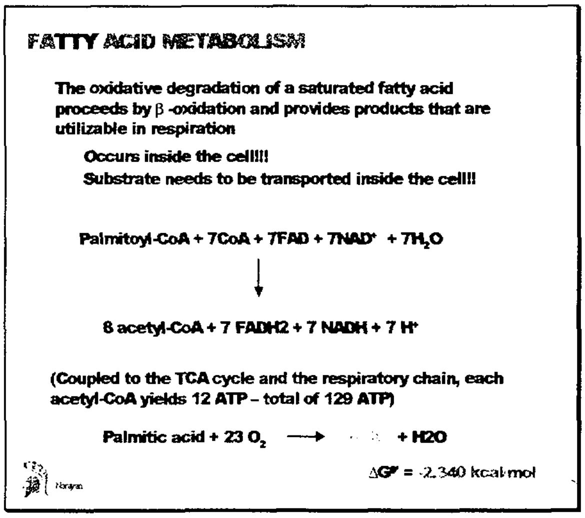
All of the processes take place inside the cell

For these processes to occur, the substrates needs to be transported inside the cell

Narayan

The key point of this slide is that the aerobic oxidation process takes place inside the cell and requires the participation of three metabolically interrelated processes.

Slide 33



FATTY ACID METABOLISM

The oxidative degradation of a saturated fatty acid proceeds by β -oxidation and provides products that are utilizable in respiration

Occurs inside the cell!!!
Substrate needs to be transported inside the cell!!

$$\text{Palmitoyl-CoA} + 7\text{CoA} + 7\text{FAD} + 7\text{NAD}^+ + 7H_2O$$
$$\downarrow$$
$$8\ \text{acetyl-CoA} + 7\ \text{FADH2} + 7\ \text{NADH} + 7\ H^+$$

(Coupled to the TCA cycle and the respiratory chain, each acetyl-CoA yields 12 ATP – total of 129 ATP)

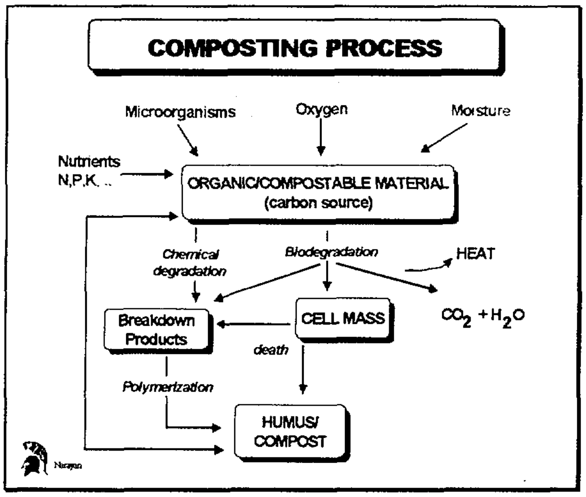
Palmitic acid + 23 O_2 ⟶ [illegible] + H2O

$\Delta G^{\circ\prime}$ = -2,340 kcal/mol

Narayan

More biodegradation process facts, establishing the evolution of CO_2 as a fundamental measure of microbial metabolism

Slide 34



COMPOSTING PROCESS

Microorganisms

Oxygen

Moisture

Nutrients N,P,K ..

ORGANIC/COMPOSTABLE MATERIAL (carbon source)

Chemical degradation

Biodegradation

HEAT

Breakdown Products

CELL MASS

$CO_2 + H_2O$

death

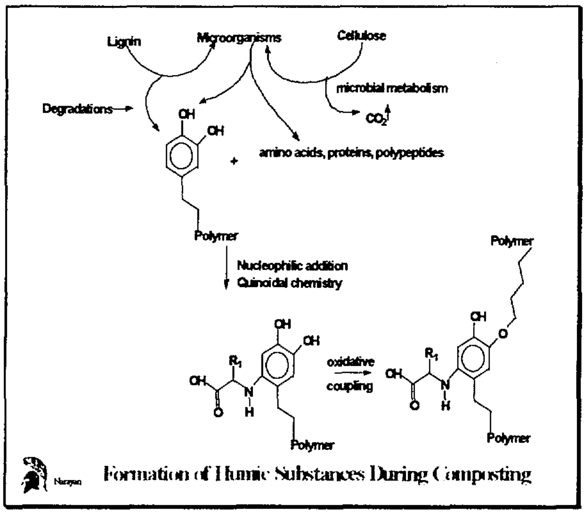
Polymerization

HUMUS/ COMPOST

Narayan

This slide illustrates the composting process. Composting is a two-step process. First there is the exothermic biodegradation step that results in cell biomass, breakdown products. These undergo a clay/soil catalyzed polymerization process to form humic/compost material that is useful as a soil amendment

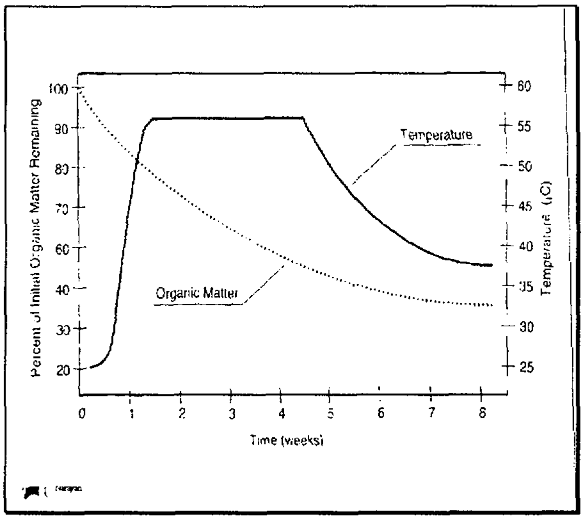
Slide 35



Formation of Humic Substances During Composting

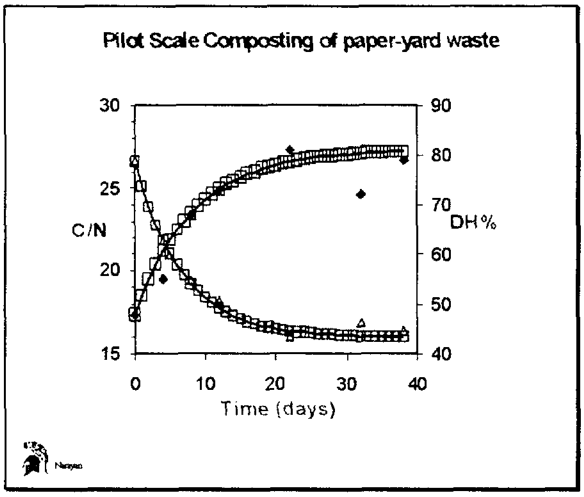
This slide illustrates the composting process chemistry. Cellulose and other utilizable substrates provide the cells with the energy and its utilization is measured by the evolution of CO_2. Lignin and the cell biomass breakdown products undergo a complex chemical reaction to form the beneficial humic substances of the soil. The process is little understood, although it has been going on in nature for centuries. Therefore, it would be a mistake to interfere in the humification process by introducing man-made products into the equation. Therefore, the rationale is to ensure that the man-made biodegradable products are readily utilizable by the microorganisms for energy production (microbial metabolism) and is completely converted to CO_2 in the process – be a food source for the microorganisms and let the natural humification process continue undistirbued.

Slide 36



This slide shows schematically the temperature profile and the carbon weight loss during composting. The key point to be noted is that during composting there is a loss in carbon mass to the extent of 70%. The maximum temperature reached is around 70 C.

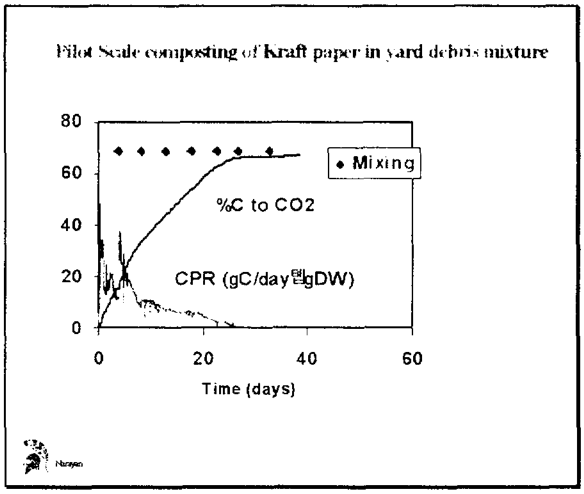
Slide 37



Pilot Scale Composting of paper-yard waste

This slide shows experimental data on what happens during the pilot scale composting of paper-yard waste. It nicely shows the reduction of the C/N ratio and an increase in the degree of humification (DH) – formation of humic and fulvulic acids.

Slide 38



Pilot Scale composting of Kraft paper in yard debris mixture

This slide documents the generous production of CO_2 during the pilot-scale composting of Kraft paper in yard debris mixture.

4. Sustainability, Green Chemistry and Biodegradable Polymers

Graham Swift
GS Polymer Consultants, USA
[grahamgswift@aol.com]

Over the last thirty years, there has been rightly much attention paid to the affects of chemicals on the environment. Although there have been some highly publicized disasters, notably oil spills, there has been spectacular, often unreported, success in the progress made by industry worldwide in curbing environmental exposure to harmful chemicals. This progress continues. The polymer industry, in particular, has aggressively and creatively attacked the issue of the production and waste-management of its products. We are obviously entering an era of increased process and raw material efficiencies as green chemistry and sustainability become entrenched in the planning of future developments.

This paper traces the development of polymers that are used beneficially in the environment or are discarded into the environment in a controlled manner after satisfying a unique requirement. These polymers were originally designated collectively as biodegradable polymers, even though abiotic degradation processes may be involved. A great deal of effort was expended in defining biodegradation and technical requirements, and testing methodology. New synthetic polymers proliferated in efforts to meet the definitions. Evaluation of these developments has given us a broad technical experience base, but, in retrospect, it has clearly led to some erroneous conclusions with respect to the behavior of polymers in the environment. These are readily apparent when one asks questions, such as:

- Why do we want polymers to disappear from the environment rapidly?
- Is biodegradation the key or is it just part of an environmental safety assessment?
- Is present test methodology excluding environmentally acceptable polymers?

Answers to these questions indicate that polymer biodegradation in the environment needs more attention, new ideas, and less restrictive thinking.

OBJECTIVE

To establish the significance of sustainability and green (polymer) chemistry **on the development of** biodegradable polymers.

SUSTAINABILITY

"To meet the needs of the present without compromising the ability of future generations to meet their own needs."

Is more than an environmental statement:

- **it is a balanced goal for industry and society.**
- **it has an economic component**
- **it includes cost / performance considerations in future developments.**
- **it is a lifestyle.**
- **it is difficult to achieve.**
- **it will not be achieved overnight.**
- **it is an evolving process requiring inventions.**
- **it must be global.**
- it demands green polymer chemistry.
  - ➢ not necessarily biodegradable polymers

GREEN (POLYMER) CHEMISTRY

(Paul Anastas)

is cradle to grave control:

- **chemistry**
- **process**
- **product isolation**
- **product formulation / compounding**
- **product use**
- **product disposal**

CHEMISTRY AND PROCESS

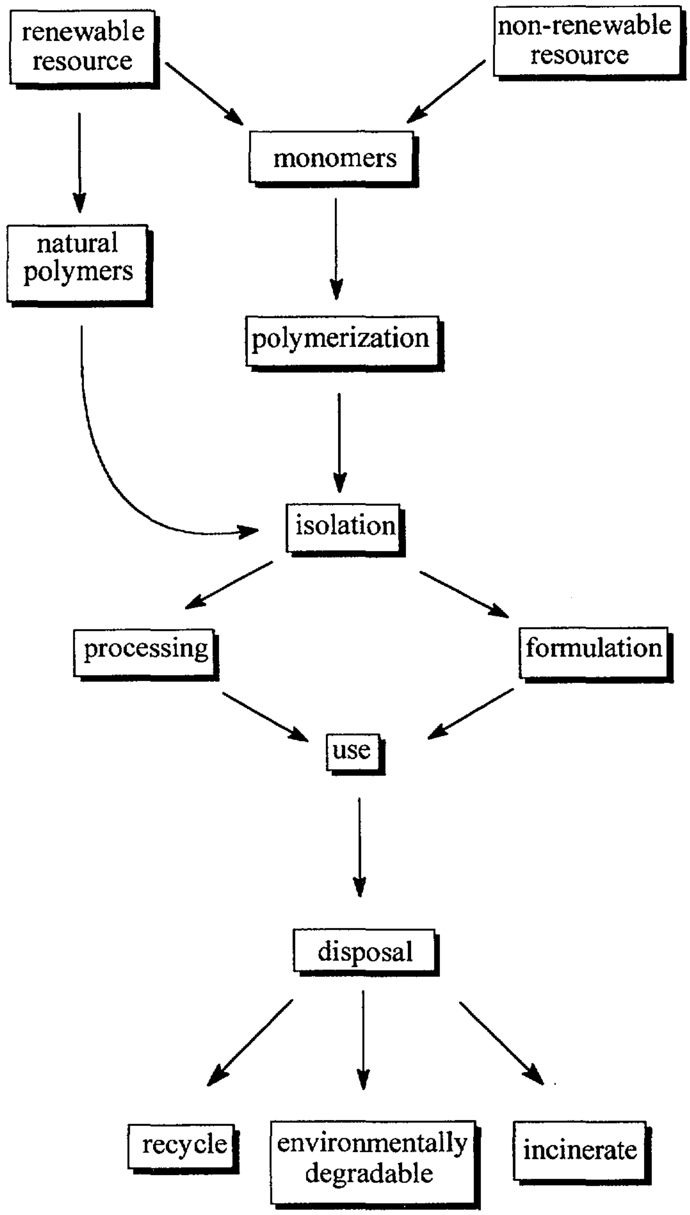
- **innocuous building blocks whenever possible**
- **renewable resources whenever possible**
  - **implies mimicking natural processes**
  - **enzymes**
  - **self-assembly**
  - **monomers**
  - **polymers**
- **benign synthesis not waste reduction is the goal**
  - **new synthetic chemistries, new catalysts, no solvents, benign solvents, etc.**

USE AND DISPOSAL OF PRODUCTS

- **formulation and use not associated with harmful environmental affects**
    - ➢ **solvents**
    - ➢ **curing byproducts**
    - ➢ **plasticizers**
    - ➢ **catalysts**
    - ➢ **etc.**

- **products should be recyclable or degrade completely at the end of useful life**
    - ➢ **no time limit or pathway for degradation**
    - ➢ **several environmental pathways known**
    - ➢ **environmentally benign degradation**

PRODUCTION OF POLYMERS

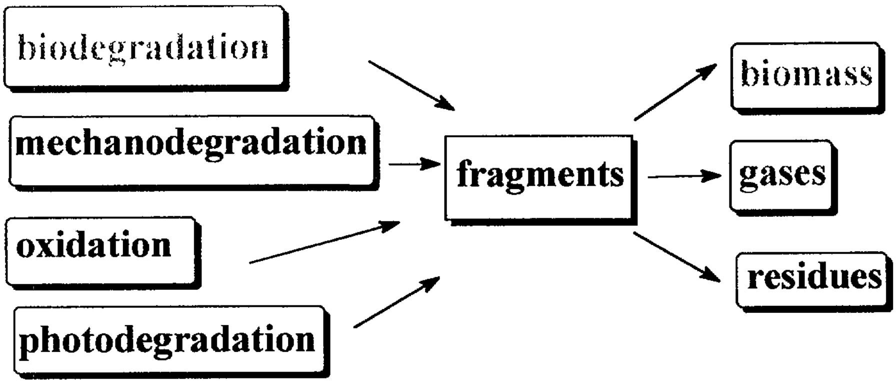


BIODEGRADATION OF POLYMERS

- **biodegradation:**
  - **promoted by living organisms**
- **mechanodegradation:**
  - **promoted by mechanical activity**
- **oxidation:**
  - **promoted by oxygen**
- **photodegradation:**
  - **promoted by sunlight**

more correctly termed environmental degradation

ENVIRONMENTAL DEGRADATION OF POLYMERS



biodegradation

mechanodegradation

oxidation

photodegradation

fragments

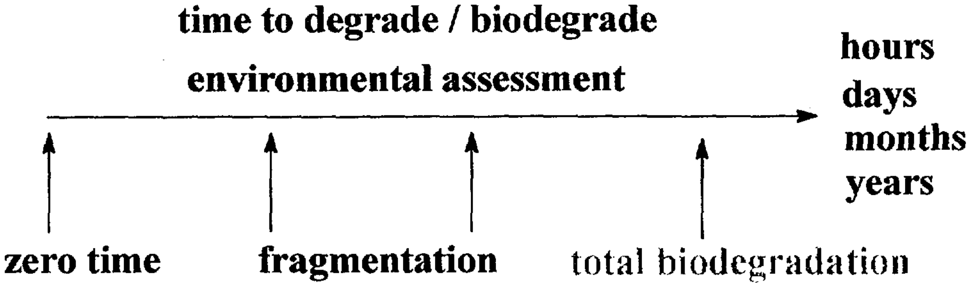
biomass

gases

residues

- ***biodegradation only pathway to complete removal***
- ***time is not significant in nature and varies widely depending on the substance***

SIGNIFICANCE OF TIME TO DEGRADE



time to degrade / biodegrade

environmental assessment

hours
days
months
years

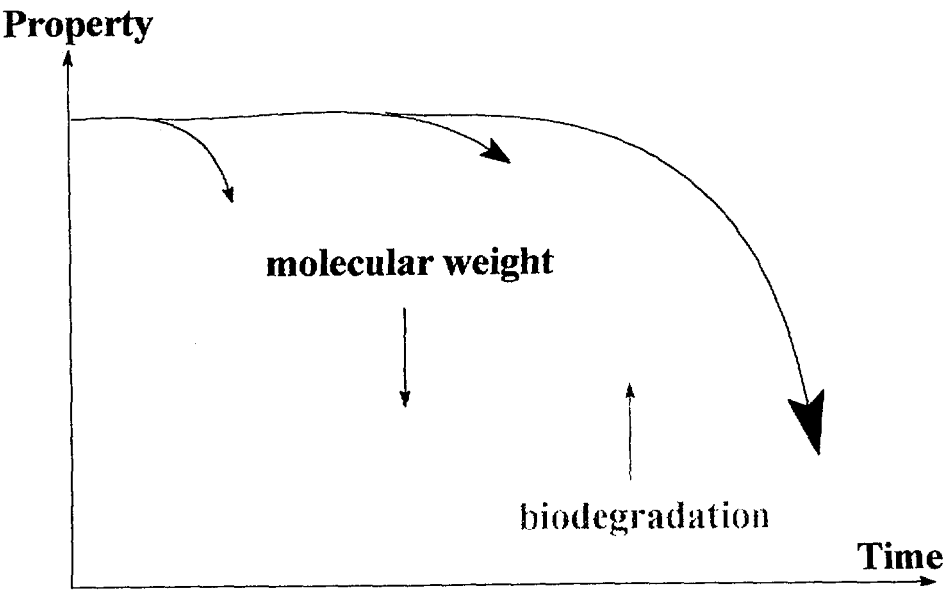
zero time

fragmentation

total biodegradation

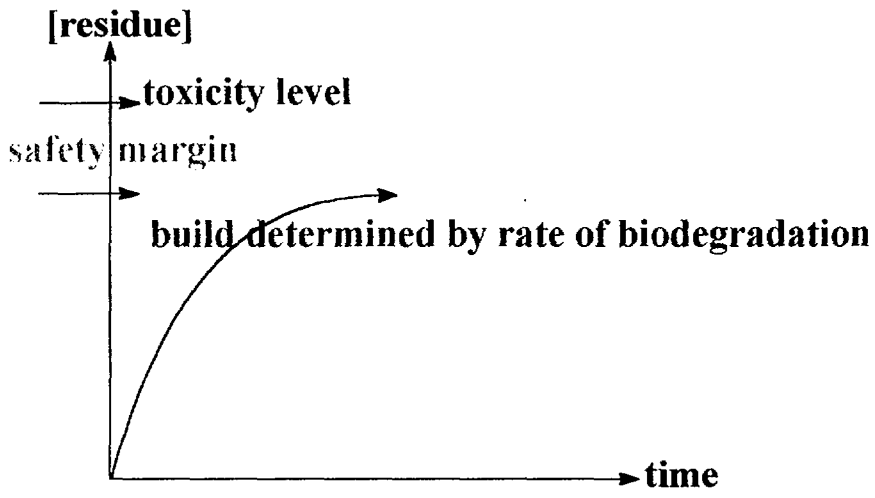
- ➢ where is acceptability?
- ➢ that is the question!!!!!
- ➢ environmental fate and effects are the drivers
  - ✓ not rate of biodegradation

CONTROLLED (BIO)DEGRADATION



SIGNIFICANCE OF BIODEGRADATION

part of an environmental fate and effects assessment:



- **degradation rates are environmentally sensitive**
- **total biodegradation may not mean freedom from harmful fate and effects (transport)**
- **incomplete / slow biodegradation not necessarily indicative of harmful fate and effects**

ENVIRONMENTAL IMPACT OF POLYMERS

- ***whatever environment***

environmental risk:

RISK = HAZARD + EXPOSURE

may be lowered by:

reducing hazard, i.e. toxicity

or

reducing exposure, i.e. loading

note:

- **much of the research on biodegradable polymers is predicated on reducing exposure (loading) rather than considering fate and effects (potential toxicity).**
- **fast biodegradation equated to best approach.**
- **ignored polymers which require stepwise envirodegradation and often slower to biodegrade.**

TEST METHODOLOGY
FOR
BIODEGRADABLE POLYMERS

- **laboratory tests for fast biodegradation in, for example, the following disposal or use environments:**
  - **compost**
  - **soil**
  - **sewage sludge**
  - **fresh water**
  - **seawater**

based on gas evolution over short time period:

aerobic:

polymer + O_2 → carbon dioxide + water + [residue]

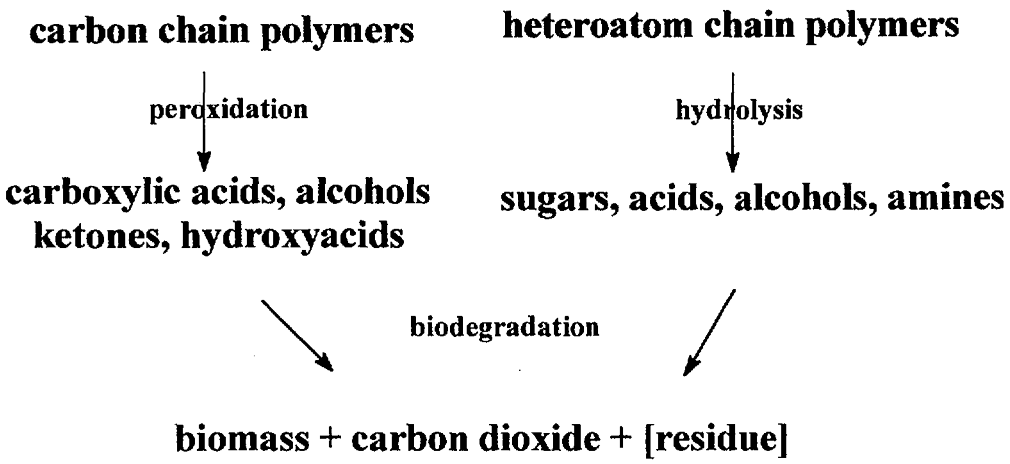
anaerobic:

polymer + (O_2) → carbon dioxide + methane + [residue]

(biomass not measured because no simple method)

POLYMER DEGRADATION BY STRUCTURE

- **research indicates that carbon-chain polymers are usually slower to biodegrade than heteroatom chain polymers:**



carbon chain polymers

peroxidation

carboxylic acids, alcohols ketones, hydroxyacids

heteroatom chain polymers

hydrolysis

sugars, acids, alcohols, amines

biodegradation

biomass + carbon dioxide + [residue]

(Gerry Scott)

- **no research or information indicates a problem in the environment for slow degraders such as polyolefins and others.**
- **test methodology unfairly penalizes slow (bio)degraders?**

CONSIDERATIONS

- **The pioneering work of Profs. A-C Albertsson, G. Scott, W. Bailey and A. Pommetto with polyethylene biodegradation**
  - **long term benign degradation products (Albertsson and Scott)**
  - **ester linkages (Bailey and Lenz)**
  - **white rot fungus (Pommetto)**

- **Biodegradation of fragments from photodegraded polyolefins by Prof. Davids**

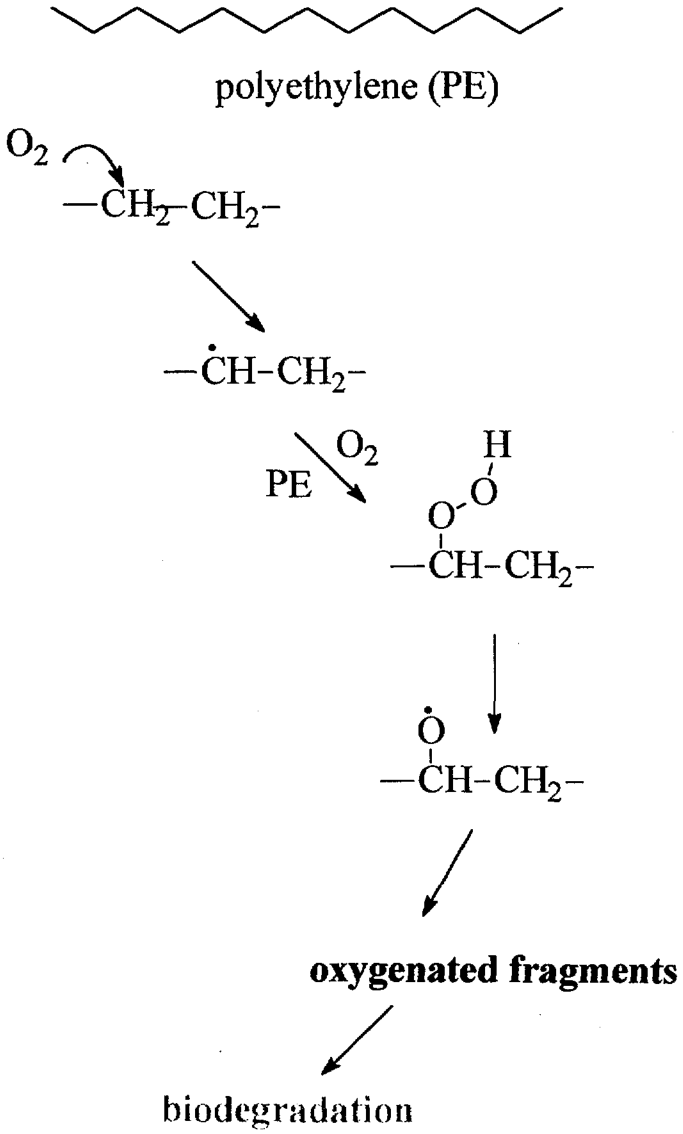
- **Poly(aspartic acid) test methodology in sewage inoculum indicates that biodegradation is in the order:**
  - **linear structure > branched-chain > highly branched-chain**

  while:

  - **in vitro enzymatic degradation indicates all are biodegradable at similar rates**

- **poly(acrylic acid) degradation by oxidation**

OXIDATIVE DEGRADATION OF POLYETHYLENE



HYDROLYTICALLY DEGRADABLE POLYETHYLENE POLYESTERS

(R. W. Lenz, S. Goodwin, and B. Wu, J. Env. Polym. Degrad., 6(1), 23, 1998)

Ethylene copolymers with keteneacetals (cf. W. Bailey)

	before		***after***	
ester	**Mw. 10^{-3}**	**Mn. 10^{-3}**	**Mw.10^{-3}**	**Mn.10^{-3}**
6.8	**15.6**	**9.6**	**1.74**	**1.11**
15.3	**17.0**	**10.8**	**1.35**	**0.92**
18.9	**9.3**	**6.4**	**3.07**	**1.16**

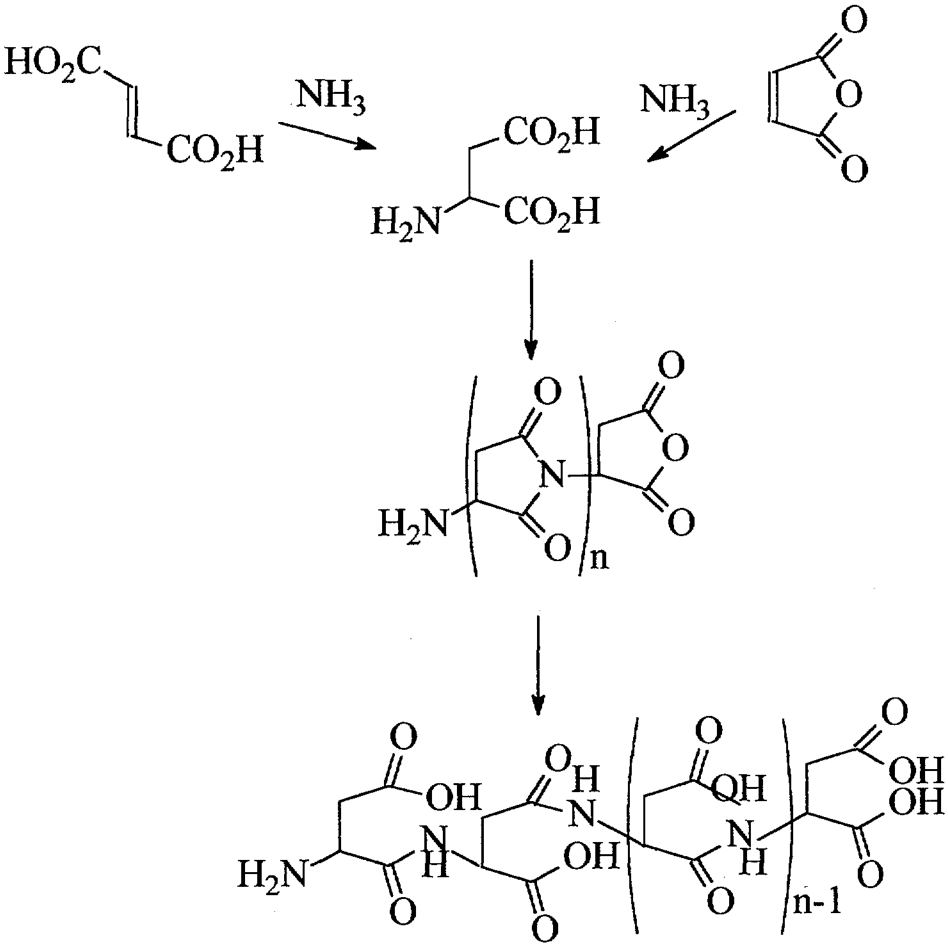
- **degradation products from samples were completely utilized in a microbial cocktail from a compost environment**

higher molecular weight olefins than Pitt looked at, and completely biodegradable

is there a molecular weight limit?

rate **of biodegradation of higher molecular weight appears to be the question** ***not whether they will or not!***

POLY(ASPARTIC ACID)S

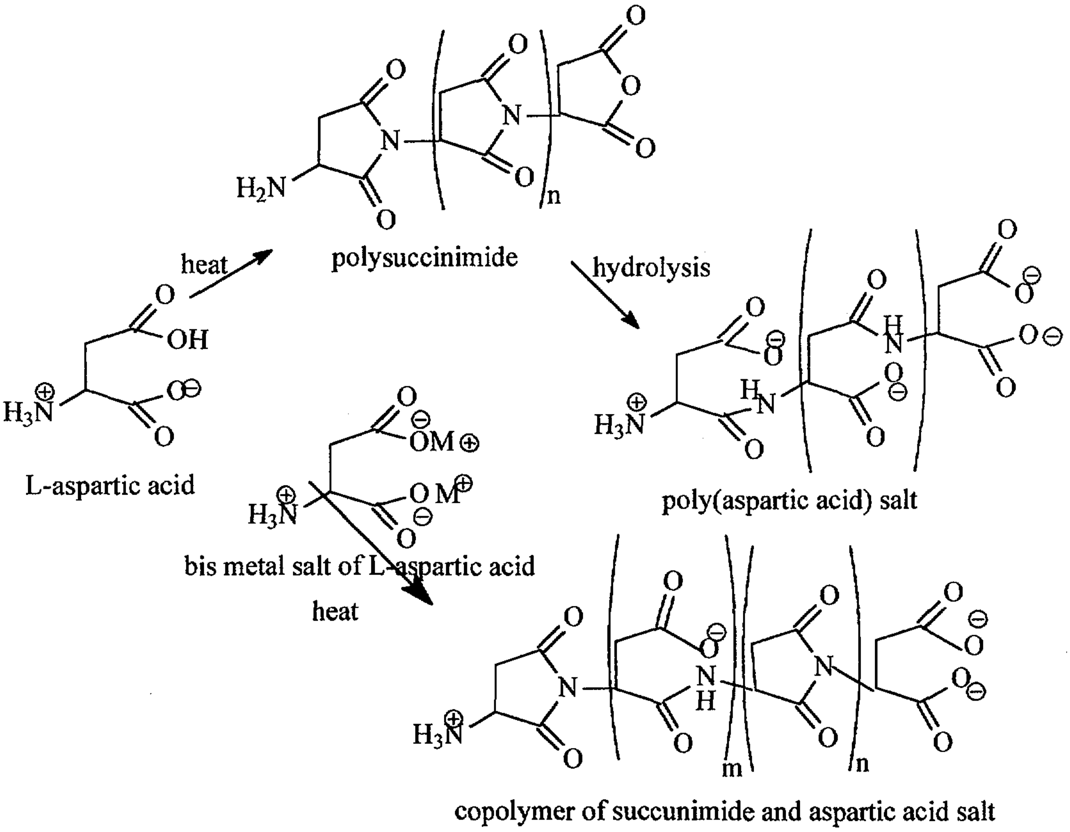


- ***process defines the polymer linearity and biodegradation in Sturm test***

BIODEGRADATION OF POLY(ASPARTIC ACIDS) WITH CHYMOTRYPSIN AT ROOM TEMPERATURE

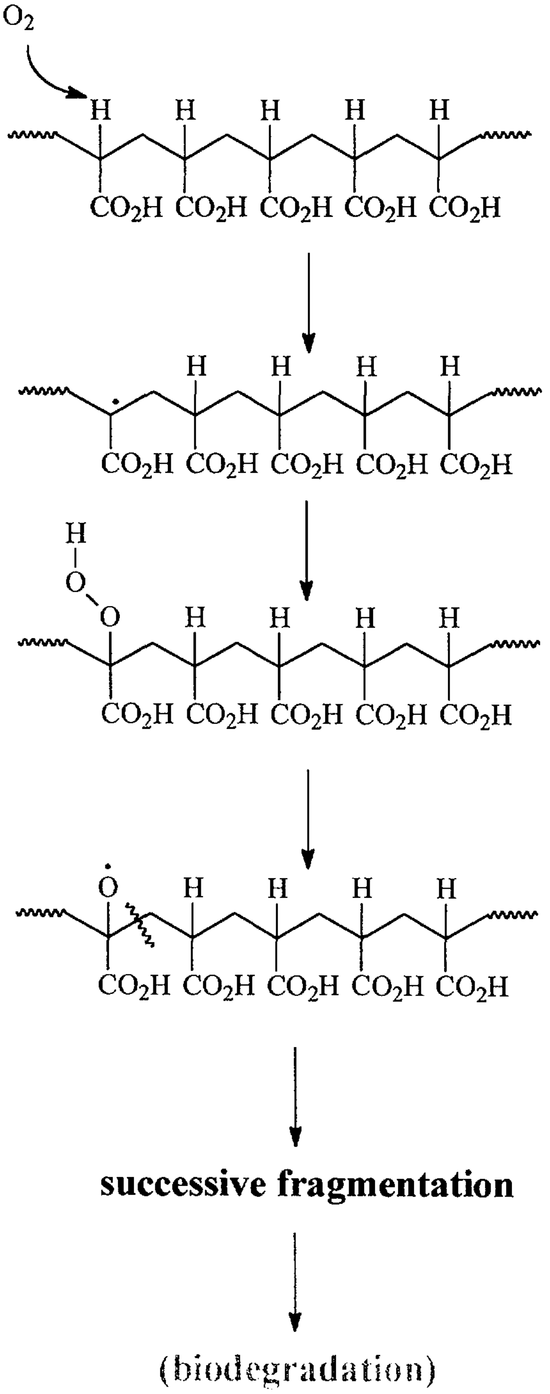
	Acid catalysis	no catalysis	maleic / ammonia
Mw	10,000	5000	3000
10 days	5000	2000	2000
20 days	3000	1800	1800
40 days	2800	1600	1600
100 days	1500	1400	1300
120 days	1300	1300	1300

POLY(ASPARTIC ACID) AND COPOLYMERS



functionalization ease and biodegradation even though not linear polymers

POLY(ACRYLIC ACID) OXIDATIVE DEGRADATION



TESTING ISSUES

- laboratory tests should correlate with full-scale testing.
- passes at laboratory scale, likely to be passes at large scale, but not necessarily.
- failure at laboratory scale does not mean failure at large scale.
- in biodegradation testing, environment is everything and laboratory tests are only simulations.
- fast biodegradation may not be the ideal solution with fast liberation of carbon dioxide.
- slow biodegradation, seen so often in nature, provides soil amendment and renewal.
- better tests are needed to embrace all classes of biodegradable polymers.

TEST METHOD CONSIDERATIONS

- chemical degradation to simulate nature
- specific enzymes
- enzyme mimics
- fate and effects testing to support biodegradation testing
- accept long-term uses where no ill effects are apparent
- chemical sense
- risk assessment nature of biodegradation

CONCLUSIONS

- **sustainability and green chemistry are the drivers for the future of the polymer industry.**
  - ➢ biodegradability is a minor but important part of these initiatives
  - ➢ biodegradable polymers will have select applications
- **the test methodology developed to date for biodegradable polymers is limited to fast degraders.**
  - ➢ **these may or may not be the best solutions**
  - ➢ **activated polyolefins are more cost effective and pass large scale testing**
- **new methodologies are needed, especially for slow degraders and should be developed.**
  - ➢ fate and effect in the environment should override rate of biodegradation
  - ➢ biodegradation in full-scale tests should obviate laboratory tests.

5. Recent Status of ISO Standard Activities in Standardization of Biodegradability of Plastics

Hideo Sawada
Convenor, ISO Committee, Biodegradable Plastics Society, Japan
[sawada@os.gulf.or.jp]

A working group (WG 22) of subcommittee (SC 5) on biodegradability was created by the International Organization for Standardization (ISO) Technical Committee on Plastics (TC61) in 1993. Test methods for biodegradability of plastics have been widely investigated by WG 22 since then.

In 1999 ISO published three aerobic test methods, namely, an aerobic aqueous test measuring O_2 consumption (ISO 14851), an aerobic aqueous test measuring CO_2 evolution (ISO 14852) and an aerobic controlled composting test measuring CO_2 evolution (ISO 14855).

The following two anaerobic biodegradation test methods have recently advanced to the FDIS (Final Draft of International Standard) stage.

1) aqueous biodegradability by measurement of biogas production under anaerobic conditions (FDIS 14853)
2) high-solids biodegradability by analysis of released biogas under anaerobic conditions (FDIS 15985)

Both aerobic soil biodegradation test (DIS 17556) and aerobic pilot-scale composting-disintegration test (DIS 16929) have recently advanced to the DIS (Draft of International Standard) stage.

Finally, WG 22 has been developing an International Standard related to a test scheme and specifications of compostable plastics for the final acceptance of the compostability.

1. What are standards?
   What is ISO?

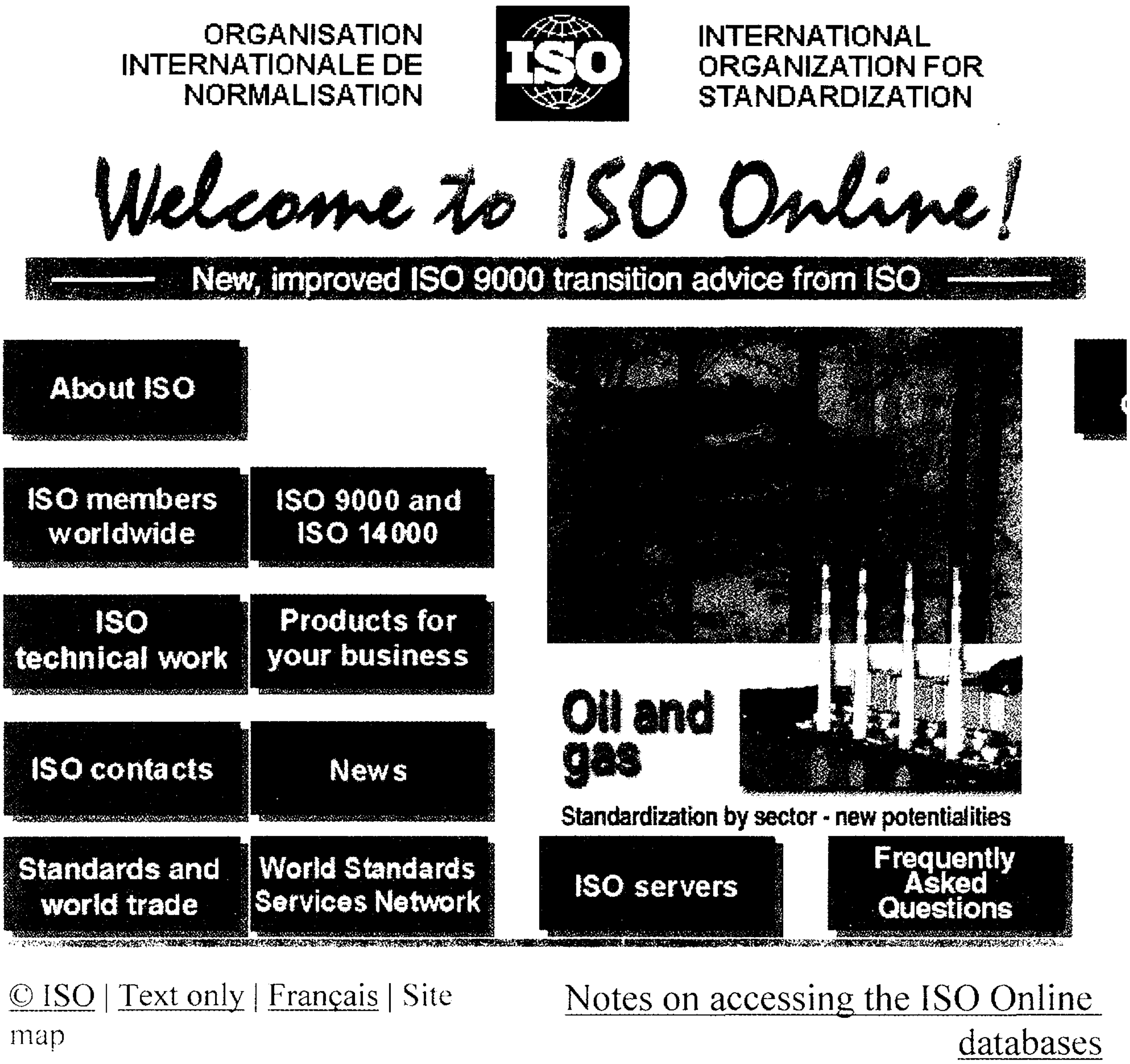
2. Background of WG on Biodegradability on Plastics
   ISO/TC61/SC5/WG22

3. Aerobic ultimate biodegradation test
   Aquatic & Compost & Soil

4. Anaerobic ultimate biodegradation test
   Aquatic & High solid

5. Test scheme & Specifications (Pass level, Criteria)

6. Summary



Welcome to ISO Online!

New, improved ISO 9000 transition advice from ISO

Standardization by sector - new potentialities

Notes on accessing the ISO Online databases

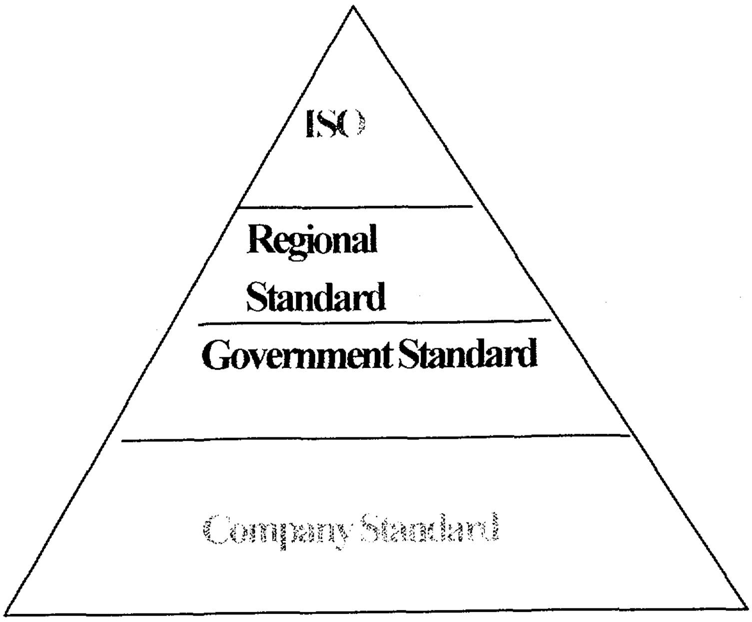
http:// www. iso. ch

THE INTERNATIONAL ORGANIZATION FOR STANDARDIZATION(ISO)

A WORLDWIDE FEDERATION OF NATIONAL STANDARD BODIES (ISO MEMBER BODIES)

THE WORK IS CARRIED OUT THROUGH ISO TECHNICAL COMMITTEES(TC).

ISO/TC61/SC5/WG22 ON BIODEGRADABILITY WAS CREATED IN 1993.



ISO PROJECT APPROACH

How an International Standard is developed

An International Standard is the result of an agreement between member bodies of ISO.

The Consensus Principles

Documents are approved if

(1) *a two-thirds majority of the votes cast by members are in favor,* and

(2) *not more than one-quarter of total number of votes cast are negative.*

Project stages and associated documents

Project stage	Associated document	
	Name	Abbreviation
1 Proposal stage	New work item proposal	NP
2 Preparatory stage	Working draft	WD
3 Committee stage	Committee draft	CD
4 Enquiry stage	Draft of International Standard	DIS
5 Approval stage	Final Draft International Standard	FDIS
6 Publication stage	International Standard	IS

Proposal stage: Stage 1
New work item
(NWI)

3 month ballot

⇩

Preparatory stage: Stage 2
Working draft
(WD)

⇩

Committee stage: Stage 3
Committee Draft
(CD)

3-6 month ballot

⇩

Enquiry stage: Stage 4
Draft International Standard
(DIS)

5 month ballot

⇩

Approval stage: Stage 5
Final Draft Intl. Standard
(FDIS)

2 month ballot

⇩

Publication stage: Stage 6
International Standard

ISO/TC61

SC1	Terminology
SC3	Mechanical Properties
SC4	Burning Behavior
SC5	Physico-Chemical Properties
SC6	Aging, Chemical and Environmental Resistance
SC9	Thermoplastics Materials
SC10	Cellular Materials
SC11	Products
SC12	Thermosetting Materials
SC13	Composites and Reinforcement Fibers

SC5 Physico-Chemical Properties

WG1	Optical Properties
WG2	Viscosity
WG8	Thermal Analysis
WG9	Melt Rheology
WG10	Gas Chromatography
WG12	Ash
WG18	Extractable Matter
WG19	Determination of melting point of semi-crystalline polymers
WG21	Application of statistical methods
WG22	Biodegradability

Background

(1) 41st ISO/TC61 "PLASTICS"
BEIJIN Meeting, Sept. 1992
(CHINA)

- o Japan proposed a new working group on biodegradation.
- o Chairman, ISO/TC61, asked Japan to provide a convenor, and to write the proposal of a New Work Item.

(2) 42nd ISO/TC61 "PLASTICS"
STRESA Meeting, Sept. 1993
(ITALY)

- o A new working group ISO/TC61/SC5/WG22 on Biodegradability had a successful meeting.
- o A new work item based on JIS K 6950 was approved.

(3) 43rd ISO/TC61 "PLASTICS"
TOKYO Meeting, Sept. 1994
(JAPAN)

- o Definition
- o Comments on Working draft
- o Discussion on New Work items (5 work items among 11 work items from ANSI)

1992	BEIJIN,	41st
1993	STRESA,	42nd
1994	TOKYO,	43rd
1995	LONDON,	44th
1996	MONTREAL,	45th
1997	DAVOS,	46th
1998	WHISTLER,	47th
1999	WILLIAMSBURG,	48th
2000	POITIERS,	49th

Test Methods of the Ultimate Aerobic Biodegradability in Aqueous Conditions

Parameter	ISO 14851	ISO 14852
Inoculum	Activated sludge Soil and/or compost suspensions	
Monitering	O_2	CO_2
Duration	max. 6 months (Plateau phase reached)	
Temperature	20～25 ± 1℃ High temperatures may be appropriate with a compost inoculum	
Test material	Powder, films, pieces, fragments or shaped articles	
Reference	Aniline Well defined biodegradable polymer (microcrystalline cellulose powder, ashless cellulose filters, polyhydroxybutyrate)	
Validity	Reference material has not been at least 60% at the end of the test.	
Negative reference	Polyethylene (optional) In the same form as the test material	

Standard test medium

Rapid biodegradation in natural environment CE, PHB/V, PCL,

- ◎ no pre-exposure with test plastics
- ◎ test material of at least 100 mg/l
- ◎ 30 mg/l suspended solids
- ◎ Carbon balance (optional)

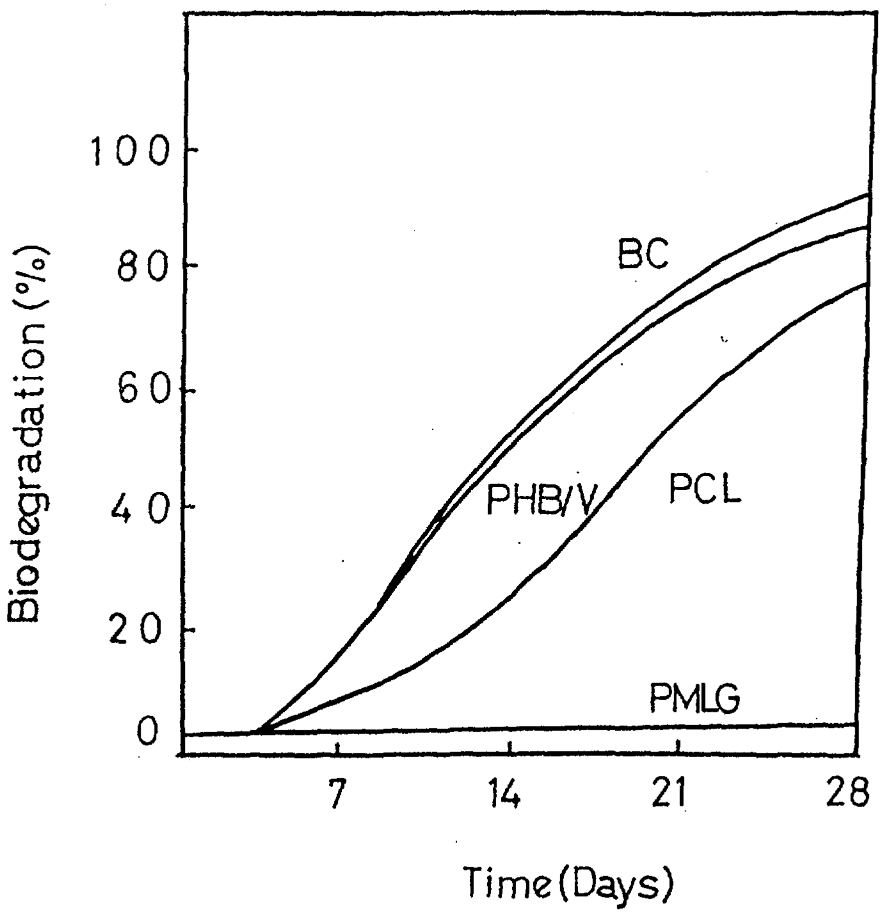
Optimized test medium

Any potential biodegradability, rapid biodegradation in natural environment may not be assumed. PLA, PVA,

- ◎ pre-exposure with test plastics
- ◎ higher buffering capacity and nutrient
- ◎ test material concentration: less than 2000 mg/l TOC
- ◎ 30 to 1000 mg/l suspended solid

● The source of the inoculum should not be prescribed, any pre-adaption should be allowed.

● Higher amount of inoculum can be used if necessary, but it may cause problems in establishing carbon balances


Biodegradation (%)
100
80
60
40
20
0
BC
PHB/V
PCL
PMLG
7
14
21
28
Time (Days)

Tests Methods of the Ultimate Aerobic Biodegradability under Controlled Composting Conditions

Parameter	ISO 14855
Inoculum	**Mature MSW compost (The age of the compost should preferably be between 2 and 4 months).**
Monitering	**CO_2**
Duration	**45 days**
Temperature	**58 ± 2℃** **In special cases, e.g. when the melting point of test material is low, another temperature may be chosen.**
Test material	**Films, formed articles like dog bones, granules or powder**
Reference	**Thin-layer chromatography grade cellulose (particle size of less than 20 μ m)**
Validity	**For a valid test, reference material is more than 70% after 45 days.**

ISO 14855 is based on ASTM D 5338 and CEN draft

ASTM test method: temperature profile-one day **35** ℃, 4 days at **58** ℃, 28 days at **50**℃ and a reduction in temp. to **35**℃ until 45 days.

CEN draft: constant temp. **58** ± **2** ℃

ASTM …**PCL** was degraded easily, **PLA** did not easily degrade.

CEN…**PLA** was degraded easily, **PCL** did not easily degrade.

ISO accepted the CEN test procedure using a constant temperature.

1. For practical reasons of test performance and test duration, it is better to use **a constant temp. 58 ± 2 ℃.**

2. In special cases, e.g., when melting point of the test material is low, **other temp. may be chosen.**

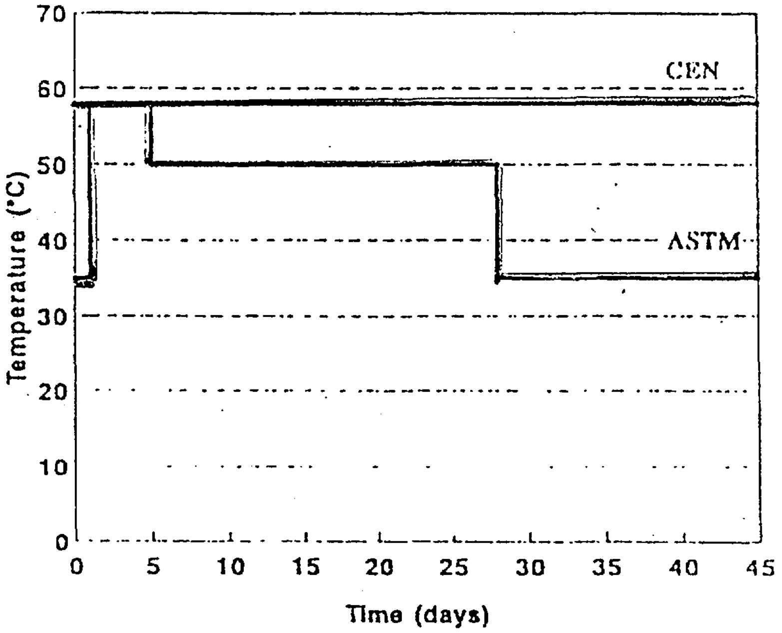


Figure 1. Temperature Profile ASTM and CEN Test Method.

Tests Methods of the Ultimate Aerobic Biodegradability under Controlled Composting Conditions

Monitoring: CO_2 , Temperature: 58 ± 2℃
Test Duration: Max.6 months, Reference: Cellulose

<table>
<tr><th>Parameter</th><th>ISO 14855</th><th>#928</th><th>#930</th></tr>
<tr><td>Inoculum</td><td>Mature MSW compost</td><td>Fresh inoculated vermiculite</td><td>Activated vermiculite</td></tr>
<tr><td>Validity</td><td colspan="2">For a valid test, reference material is more than 70% after 45 days.</td><td>80 % after 45 days</td></tr>
<tr><td>Remarks</td><td></td><td colspan="2">Carbon balance</td></tr>
</table>

COMPOSTING

ISO 14855
Mature MSW compost

- **Large blank value of CO_2**

 # 928
Fresh Inoculated Vermiculite

 # 930
Activated Vermiculite

- **Very small blank value of CO_2**
- **Determination of carbon balance**

Carbon Balance

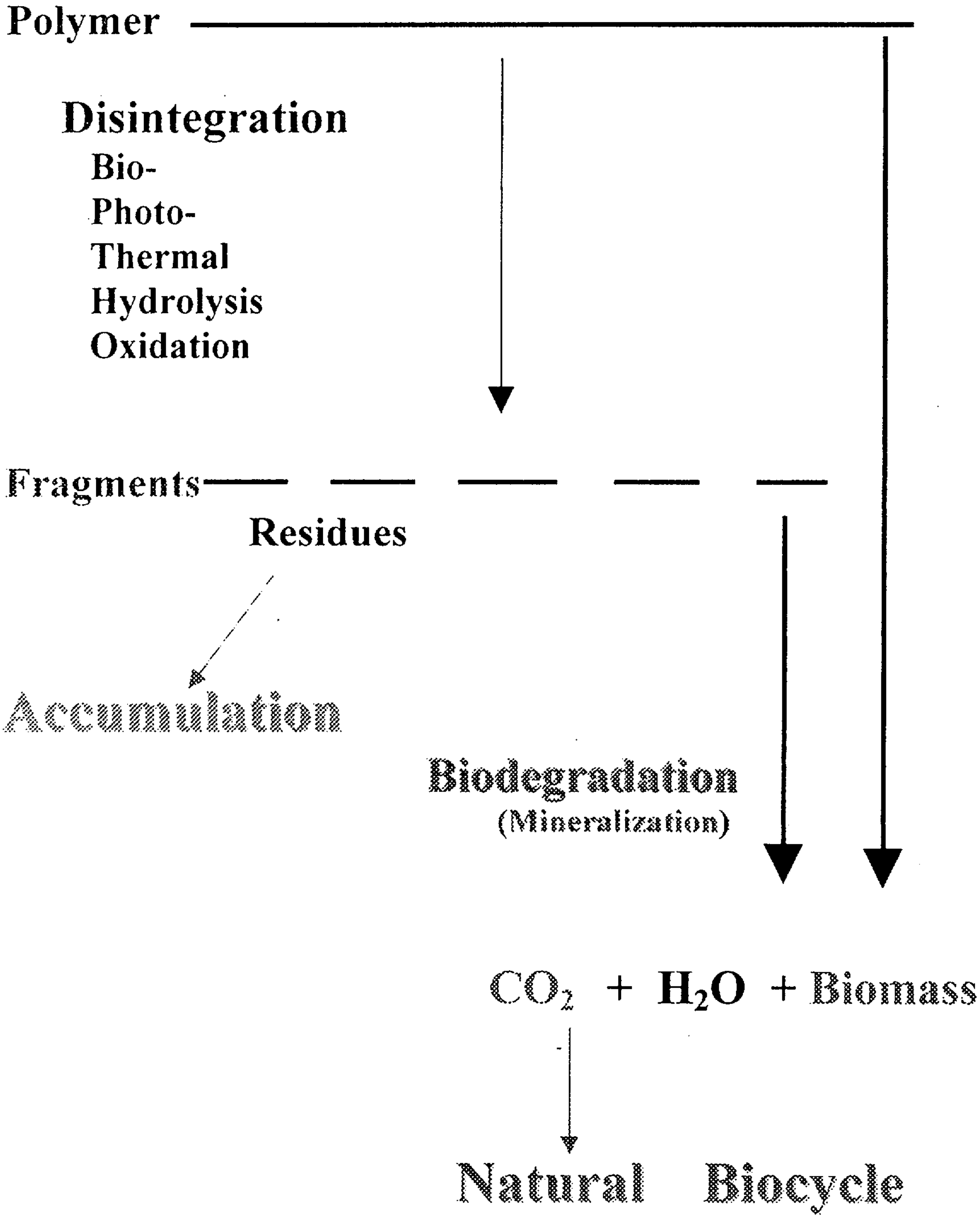
$$C_{CALC} = C_{CO2} + C_{BIO} + C_{DOC} + C_{POL}$$

C_{CO2} : CO_2 evolution
C_{BIO} : Increase in biomass carbon
C_{DOC} : Increase in DOC related to water-soluble metabolites
C_{POL} : Organic carbon in the residual polymer

Tests Methods of the Disintegration of Plastics under Defined Composting Conditions in a Pilot-Scale Test

Parameter	**ISO/DIS 16929**
Inoculum	Biowaste from the input material of a composting plant or a representative artificial self-composed biowaste
composting bin	Minimum volume **140L (pilot scale)**
Duration	12 weeks
Temperature	Maximum temperature during composting is below +75℃ during the 1st week and below +65 ℃ thereafter Above +60 ℃ for at least 1 week Above +40 ℃ for at least 4 consecutive weeks
Test material	In an identical form (e.g. shape, thickness) for the intended final use. 10 × 10 cm for films and 5 × 5 cm for other products Fine powder or granules (diameter <500 μm) for ecotoxicity use
Disintegration	**Degree of disintegration is calculated from weight of retrieved test material (sum of all fractions > 2mm)**

Biodegradation & Disintegration



Polymer

Disintegration

Bio-
Photo-
Thermal
Hydrolysis
Oxidation

Fragments

Residues

Accumulation

Biodegradation
(Mineralization)

CO_2 + H_2O + Biomass

Natural Biocycle

Tests Methods of the Disintegration of Plastics under Composting Conditions

Parameter	ISO/DIS 16929	Work item 929
Outline	Disintegration in a **pilot-scale** aerobic composting test	Disintegration in a **laboratory scale** aerobic composting test
Inoculum	**Biowaste** from the input material of a composting plant or a representative artificial self-composed biowaste	**Synthetic waste** (Sawdust, rabbit-feed, ripe compost, corn starch, saccharose, corn seed oil etc)
composting bin	Minimum volume **140L (pilot scale)**	**30 cm × 20 cm × 10 cm (l,w,h)** A box made with PP or any other material
Duration	**12 weeks**	**Maximum 90 days**
Temperature	**Max. temp. <75℃** during 1st week and <65℃ thereafter	**A constant temperature of (58 ± 2)℃** for max. 90 days If necessary, 25 ± 2℃ for max. 90 days
Test material	In an identical form (e.g. shape, thickness) for the intended final use. 10 × 10 cm for films and 5 × 5 cm for other products Fine powder or granules (diameter <500 μm) for ecotoxicity use	Thickness < 5mm, 25×25 ×original thickness Thickness>5mm, 15×15 ×thickness ≦15mm
Disintegration	Degree of disintegration is calculated from **weight of retrieved test material (sum of all fractions > 2mm)**	Degree of disintegration is calculated from **weight of retrieved test material.**

Tests Methods of the Ultimate Aerobic Biodegradability in Soil

Parameter	ISO/DIS 17556
Inoculum	Natural soil collected from the surface layer of fields and/or forests, one pre-exposed to test material if necessary. Less than 2 mm in size.
Monitering	O_2 or CO_2
Duration	Maximum 6 months
Temperature	(20 to 25) ℃ + 1℃ or at any other appropriate temperature depending on the environment.
Test material	Preferably in the form of powder, films, pieces, fragments, or shaped article
Reference	Well defined biodegradable polymer (e.g. microcrystalline cellulose powder, ashless cellulose filters or PHB)
Validity	The test is considered valid if BOD values or the carbon dioxide evolved from the duplicate blank are within 20% of the mean.

Anaerobic Biodegradation

In the absence of O_2

$$C_cH_hO_o + (c - h/4 - o/2)H_2O \rightarrow (c/2 + h/8 - o/4)\ CH_4 + (c/2 - h/8 + o/4)\ CO_2$$

Polymer → CO_2/CH_4 + Biomass + Residue

- **Aquatic**
- **High solid**

Test Methods of Ultimate Anaerobic Biodegradability

Parameter	ISO/FDIS 14853	ISO/FDIS 15985
Outline	Anaerobic digester municipal sewage sludge	High solid anaerobic digestion conditions
Inoculum	Anaerobic digester sludge at a sewage treatment Laboratory-grown anaerobic sludge Total solids content level at least 1-3g/l	Anaerobic digesters, Total solid content of at least 20 %.
Test material	Powder, films, pieces, fragments, or formed articles	Films, formed articles like dog bones, granules of powder
Duration	60 days Not exceed 90 days	15 days
Temperature	35 ± 2℃	52 ± 2℃
Monitering	CH_4 & CO_2	
Reference	Well defined anaerobically biodegradable polymers, e.g. polyhydroxybutyrate, cellulose or polyethylene glycol 400	Cellulose for thin-layer chromatography with a particle of less than 20 μm
Validity	Reference substance is more than 70%.	Reference substance is more than 70% after 15 days.

ISO/TC 207
Environmental management,
Subcommittee SC 3
Environmental Labelling

ISO 14021
Environmental labels and declarations - Self-declared environmental Claims
(Type Ⅱ environmental labelling)

ISO 14851
ISO 14852
ISO 14853
ISO 14855

Test Scheme & Specification

Test Scheme CD 15986.2

Specification # 737

CD 15986.3

Test Scheme

Characterization

Identification

↓

Biodegradability

ISO 14855

↓

Disintegration

DIS 16929

↓

Biological treatment

↓

Quality of the compost

Heavy metal
Ecotoxicity

↓

Evaluation of test results

Criteria, Pass level

Specifications

● Pass Level (Criteria)

Biodegradation

(Aerobic)

EN
ISO 14851, 14852, 14855
90% Theoretical or compared to reference
for homopolymers and
heteropolymers (polymer blends, block polymers etc.)
Max. 6 months
Exempted: Chemically Unmodified Material of
Natural Origin

ASTM
ISO 14855
60% Compared to reference for homopolymers
90% Compared to reference for heteropolymers
Max. 6 months

JP
ISO 14851, 14852, 14855
60% Theoretical for both homopolymers and
heteropolymers
Max. 6 months
Exempted: Chemically Unmodified Material of
Natural Origin

- **Reference Material (ASTM, EN, JP)**

Cellulose (Microcrystalline Cellulose e.g. Avicel)
Only for a valid test (JP)

- **Components (more than 1%)**

Biodegradability of any polymer components (ASTM)
Biodegradability of any organic components (EN, JP)
Total portion of component without testing <5% (EN, JP)

- **^{14}C**

As long as 365 days (ASTM)

- **Heavy metals (EN, ASTM, JP)**

In accordance with regional or national regulations

- **Ecotoxicity**

OECD 208	**Terrestrial Plants, Growth Test (ASTM, EN)**
OECD 201	**Algae (JP)**
OECD 202	**Daphnia (JP)**
OECD 203	**Fresh -water Fish (JP)**

- **Acute oral toxicity testing**

$LD_{50} \geqq 2{,}000$ mg/kg (JP)

- **Disintegration**

ISO/FDIS 16929
Not more than 10% of the original weight remains after sieving on a 2.0 mm sieve (EN, ASTM)

(Anaerobic)

EN
FDIS 14853, 15985
50% Theoretical Maximum 2 months

Work Items

Work item	Title	Comments
ISO 14851	Aerobic(O_2) Aquatic	JIS K 6950 & ASTM D 5271
ISO 14852	Aerobic(CO_2) Aquatic	ASTM D 5209
ISO 14855	Aerobic(CO_2) Composting	ASTM D 5338 & CEN draft
FDIS 14853	Anaerobic(CH_4) Aquatic	ASTM D 5210
FDIS 15985	Anaerobic(CH_4) high-solids	ASTM D 5511
DIS 16929	Aerobic Disintegration Composting	CEN
DIS 17556	Aerobic(CO_2/ O_2) Soil	Japan ASTMD 5988
CD 15986.3	Test Scheme & Specifications	ASTMD 6002 & 6400 prEN 13432

New Work Items

Project	Title	Remarks
#928	Aerobic composting carbon fixed bed	Germany
#929	Aerobic composting disintegration	Italy
#930	Aerobic composting solid mineral medium	Italy

Acknowledgements

Prof.R.Narayan (USA)
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Dr.F.Degli Innocenti (It)
Dr.Y.Yakabe (Jp)
Mr.K.Fukuda (Jp)

Chapter 2:

R & D and Applications of EDP

Session 1; Poly(lactic acid)

6. Nature Works^{tm} PLA-Functional and Environmental Performance

Patrick R. Gruber
Vice President, Chief Technology Officer, Cargill Dow Polymers LLC, USA
[E-mail: pat_gruber@cdpoly.com]

Poly(lactic acid) Polymers are being commercialized by Cargill Dow Polymers LLC. The use of lactic acid derived from fermentation of dextrose, coupled with a highly efficient and versatile polymerization process, provides global economics potentially competitive with conventional petroleum based polymers. The unique cost/performance property spectrum for these renewable resource based polymers is facilitating widespread acceptance across a variety of plastic markets. This presentation will discuss the functional performance of PLA and the issues around designing a polymer with the environment in mind.

Nature Works^{tm} PLA – Its Functional Performance

Nature Works^{tm} PLA polymers exhibit many of the characteristics of other more common thermoplastics and even some non-thermoplastic materials. For example, Nature Works^{tm} PLA polymers are:

- Naturally glossy and transparent, similar to polycarbonate, polyester, acrylics and general purpose polystyrene.
- Inherently stiff. Their tensile strength and tensile modulus are somewhat higher than polystyrene.
- Easily printed by all the conventional techniques. Nature Works^{tm} PLA sheet and film can also be readily metallized due to its high surface energy.
- Resistant to many greases and oils, setting it apart from many of its thermoplastic cousins.
- Barriers to the transmission of the types of flavors and odors typically found in food.
- Heat sealable at low temperatures, which makes them particularly suited for the packaging of heat sensitive foods.
- Heat resistant to temperatures well in excess of 100°C, provided a crystalline polymer backbone can be achieved in the fabricated product
- Improved wicking in sports apparel
- UV resistance useful for draperies, fabrics

Nature Works^{tm} PLA polymers also exhibit excellent dead-fold and twist retention characteristics in film form – much like Cellophane. This same characteristic is also useful in introducing crimp into fibers, which results in woven and knitted fabrics with excellent loft and softness.

The versatility of Nature Works^{tm} PLA polymers is further enhanced by their processability. It has proven to have an acceptable processing window on a wide range of conventional plastics processing equipment from extrusion and thermoforming machines to high-speed fiber spinning equipment.

Nature Works^{tm} PLA – Environmental Design

This opportunity brings with it a responsibility to manage the development of the business in a way which takes account of the interests of our “stakeholders”. Cargill Dow takes this responsibility very seriously and is embracing the "triple bottom line” approach to managing its business. This requires that the company focuses not only on the economic health of its business but also on the environmental impact and social implications of its activities. Our approaches will be presented.

As part of its commitment to manage the “triple bottom line”, Cargill Dow has completed a very thorough “cradle to factory gate” Life Cycle Inventory (LCI) for Nature Works^{tm} PLA. The results of this comprehensive study have enabled Cargill Dow to identify opportunities for improvement in the manufacturing process and to set aggressive process improvement targets. This valuable tool will be used to screen potential new application opportunities.

The LCI study is based on data projected for the integrated world-scale lactic acid/PLA manufacturing unit that will be operational by the year 2003, coupled with real life experience on Cargill Dow’s existing market development facility. The methodology used is similar to that used for the Association of Plastics Manufacturers in Europe (APME) studies, thereby facilitating comparison of Nature Works^{tm} PLA with the traditional plastic materials. The results will be presented for key topics.

The LCI for Nature Works^{tm} PLA incorporates the known energy and material inputs and outputs associated with every manufacturing operation from growing of the corn to producing the PLA granules. It is apparent from the data that the gross energy requirement for Nature Works^{tm} PLA is comparable to the gross energy requirement for many other hydrocarbon derived thermoplastics.

What is remarkable is that over a quarter of the gross energy requirement for Nature Works^{tm} PLA is attributable to the renewable resource used in its manufacture. All the carbon oxygen and hydrogen atoms which combine to form the polymer chains in Nature Works^{tm} PLA are derived from atmospheric carbon dioxide and water which are “fixed” in the growing plant as it absorbs energy from the sun during photosynthesis. This “renewable energy” is literally harvested in the corn and is converted through the Nature Works^{tm} PLA process in to the thermoplastic granules.

In addition to the performance “in use” and being made from renewable resources, Nature Works^{tm} PLA polymers are being designed to fit into any waste management system: recycling, incineration, composting, or landfill.

Nature Works^{tm} PLA can be recycled like conventional plastics, or broken down into lactic acid and converted back into PLA. It can be formulated to be fully compostable in municipal composting facilities. The polymers undergo a two-stage process of degradation. The molecular weight of the polymers is first reduced through a process of hydrolysis, and then the low molecular weight species are digested by microorganisms commonly found in terrestrial and aquatic environments. The rate at which the degradation occurs is a function of the temperature and the presence of water and suitable microorganisms. A rigid thermoformed container fabricated from Nature Works^{tm} PLA would typically degrade completely to carbon dioxide and water with a resulting increase in biomass in a well managed commercial composting facility.

Summary of Key Message

In summary, Cargill Dow believes Nature Works^{tm} PLA provides advancement in improving sustainability for products/applications currently made conventional plastic materials. It will find market based on its performance and price. It is much more than "biodegradable".

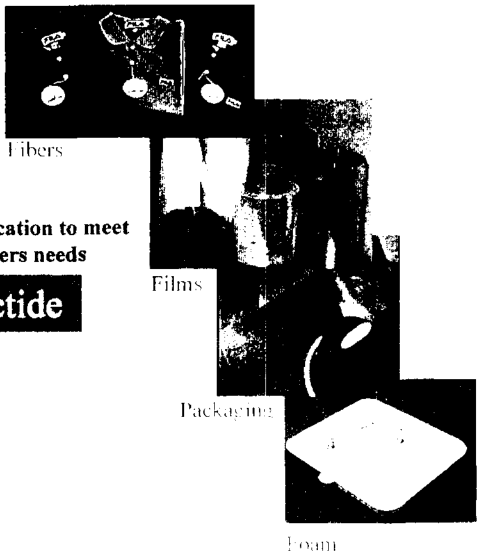
Agenda

- Business Opportunity
  - Application
  - Benefits
- Environmental Performance
  - Disposal Options
  - Energy Use
  - Carbon Dioxide

What Cargill Dow is About

- Developing and Delivering Value Added Properties
  - Create new solutions to materials issues
- Reducing "environmental footprint"
  - Drive down use of fossil resources
  - Reduce emissions of green house gases
  - Use our products to help customers and consumers to reduce their environmental footprint
- Design products with end-use disposal in mind from outset
  - Waste Options
  - Assist customers in design of their products

NatureWorks™ Process



Modification to meet customers needs

Polylactide

Chemical Processing

Lactic Acid

Fermentation

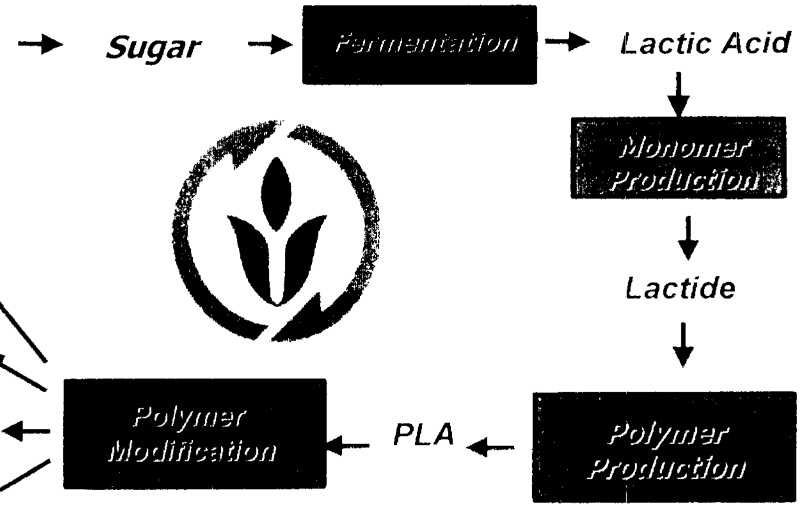
Sugar

Commodity Processing

Cargill Dow

NatureWorks

Simple Route Creates a Family of Products



→ *Sugar* → *Fermentation* → *Lactic Acid*

↓

Monomer Production

↓

Lactide

↓

Polymer Production → *PLA* → *Polymer Modification*

Polymer Grades

- Fiber
- Film
- Thermoforming
- Bottle
- Woven
- Non-woven
- Etc.

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Initial Target Markets

- Fibers
- Packaging
    - Film
    - Rigid/Thermoformed
    - Extrusion Coating (Paper)
- Emerging Markets
    - Bottle & Foams
- Chemical Intermediates

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Real Benefits Drive Commercialization

Environmental Attributes alone would be insufficient for success

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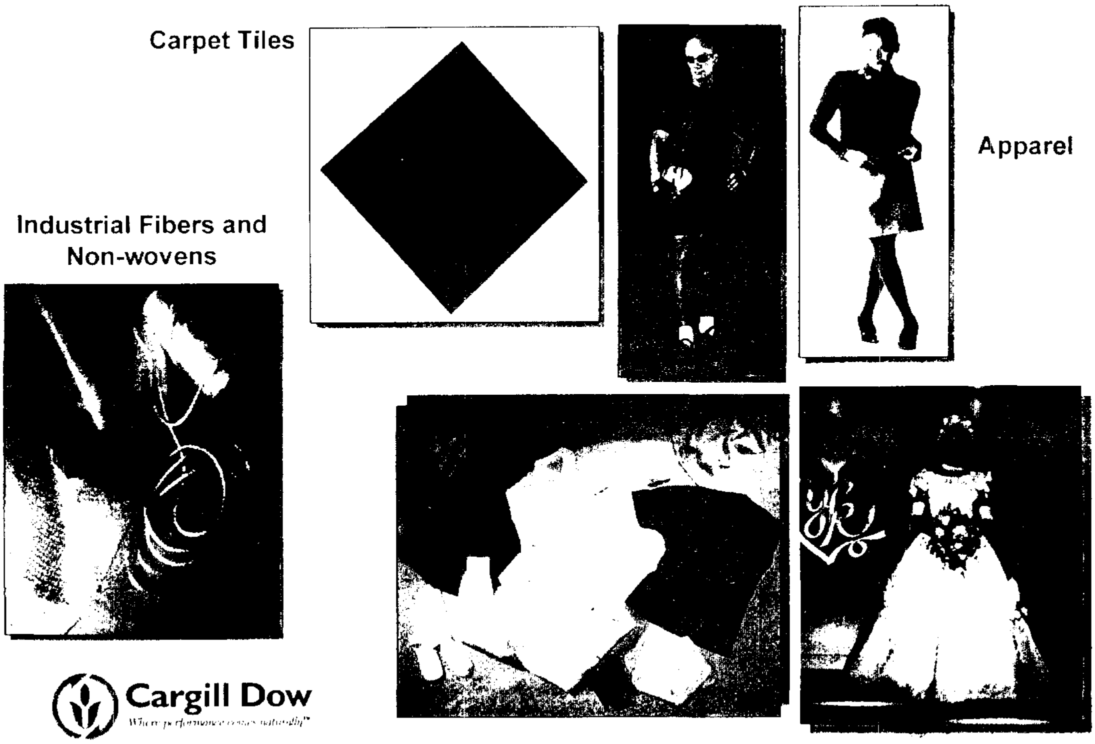
Fiber Applications



Carpet Tiles

Apparel

Industrial Fibers and Non-wovens

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Valuable Fiber Attributes of PLA

- Resilience
- Low flammability
- Processability
- Moisture management
- UV resistance
- Stain resistance
- No bacterial growth
- Natural product based fiber

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Fibers Properties

	SYNTHETHIC FIBERS			PLA	NATURAL FIBERS			
FIBER PROPERTY	NYLON 6	PET	Acrylics		RAYON	COTTON	SILK	WOOL
Specific Gravity	1.14	1.39	1.18	1.25	1.52	1.52	1.34	1.31
Tenacity (g/d)	5.5	6.0	4.0	6.0	2.5	4.0	4.0	1.6
Moisture regain %	4.1	0.2-0.4	1.0 -2.0	0.4-0.6	11	7.5	10	14-18
Elastic Recovery (5% strain)	89	65	50	93	32	52	52	69
Flammability	Medium	High smoke	Medium	Low smoke;	Burns	Burns	Burns	Burns slowly;
UV resistance	Poor	Fair	Excellent	Excellent	Poor	Fair-Poor	Fair-Poor	Fair
Wicking (L-W slope; higher slope, more wicking	-	0.7-0.8 (no finish)	-	6.3-7.5 (no finish); 19-26 (with finish)	-			

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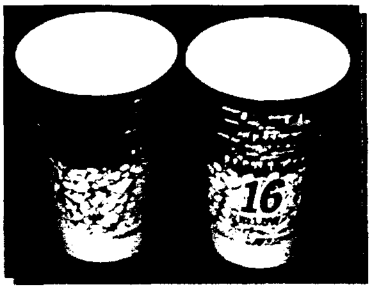
"Melt Spinnable Natural Based"

atureWorks

PLA Packaging Applications

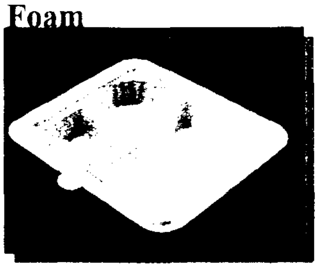
Rigid containers

Coated papers



Films

Foam



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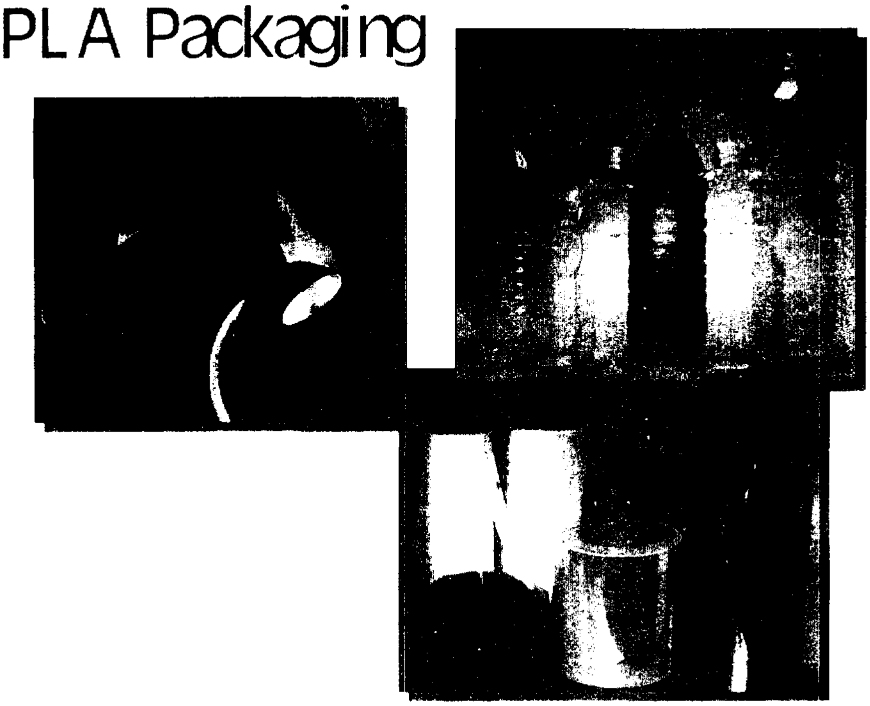
PLA Packaging



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Properties and Usefulness

Functional Property	*Packaging Improvement*
High Gloss and Clarity	Package aesthetics
High Tensile and Modulus	Wet paper strength, Ability to downguage coating
Low COF, Polarity	Printability w/o pretreatment
Deadfold, twist and crimp	Improved folding and sealing
Low Temp. Heat Seal	Stronger seals at lower temps.
Barrier Properties	Grease and oil resistance
Flavor and Aroma Prop.	Reduced taste/odor issues
GRAS Status	Food Contact Approved
Biodegradable	Compostable, Low "green" tax
Renewable Resource Based	Sustainable feedstock

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Properties of NatureWorks™ PLA Films

Film Type	MD, 1% [illegible] MPa	CD, 1% [illegible] MPa	Deadfold	Twist [illegible]	% Haze	20 Gloss	O2P	WVTR
PLA blown natural	3000	3000	--	--	0.7	110	570	340
PLA blown with COF additives	[illegible]	[illegible]	**--**	[illegible]	[illegible]	**30**	**710**	**370**
OPLA with COF additives	**3400**	**5200**	**95**	**280**	**2.8**	**60**	**570**	**320**
Cellophane	**3000**	[illegible]	**71**	**310**	**--**	**--**	**--**	**--**
OPET	4100	4100	36	190	4.1	80	50	25
BON	**1600**	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	**20**	**160**
OPP	1500	1500	12	150	--	--	1500	5
LDPE [illegible]	[illegible]	[illegible]	**--**	**--**	[illegible]	[illegible]	**6500**	**20**

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Grease Resistance of Coated Paper at 55°C

Polymer Coating	Hours to Failure
PLA	>120 hrs, no failure
LDPE	10 hrs
Fluorinated Paper	96 hrs

Tappi T507, ASTM F119

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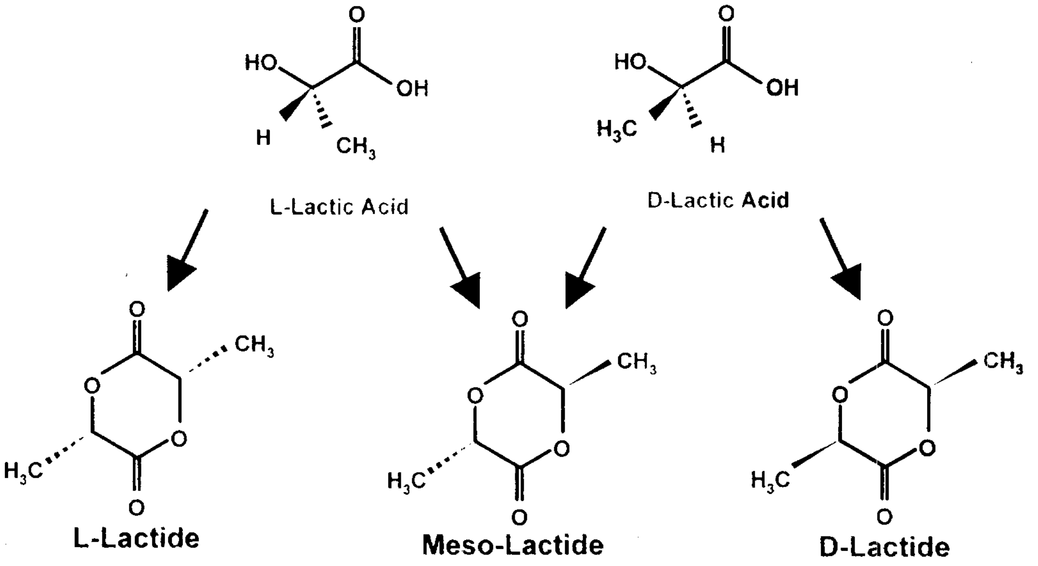
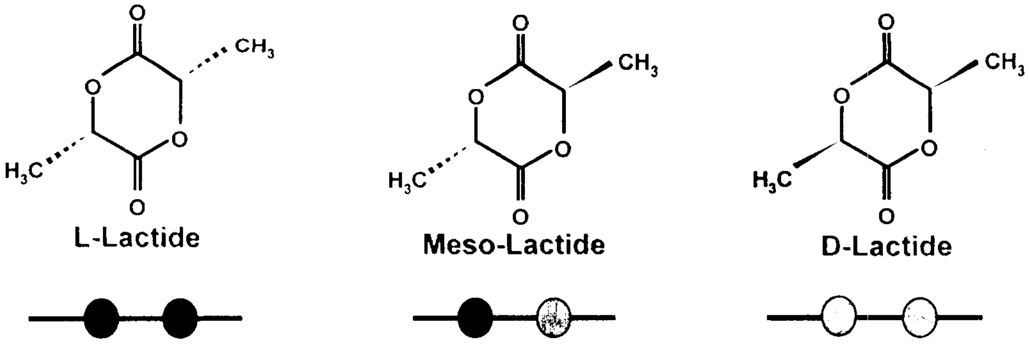
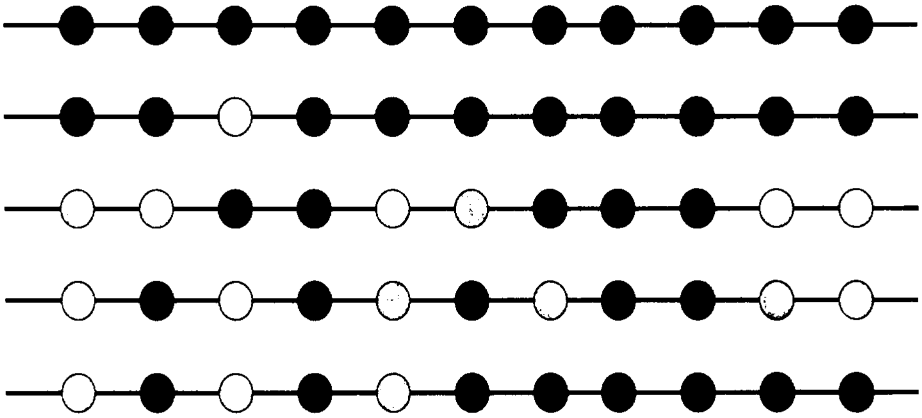
LA Makes Multiple Monomers



Lactides Give Rise to a Family of Related Materials



A Family of Polymers



○ **D-Lactic Unit** ● **L-Lactic Unit**

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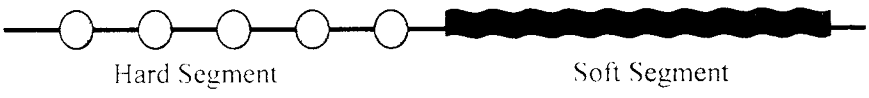
Extended Family of Materials

Interlocking PLA



○ **D-Lactic Unit** ● **L-Lactic Unit**

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Simple yet Versatile

- Control of optical composition leads to family of properties and attributes
- Modification of PLA through simple techniques extends the family further
- Production processes are relative high yield
  - Economical
  - Environmentally favorable

Properties create the business opportunity

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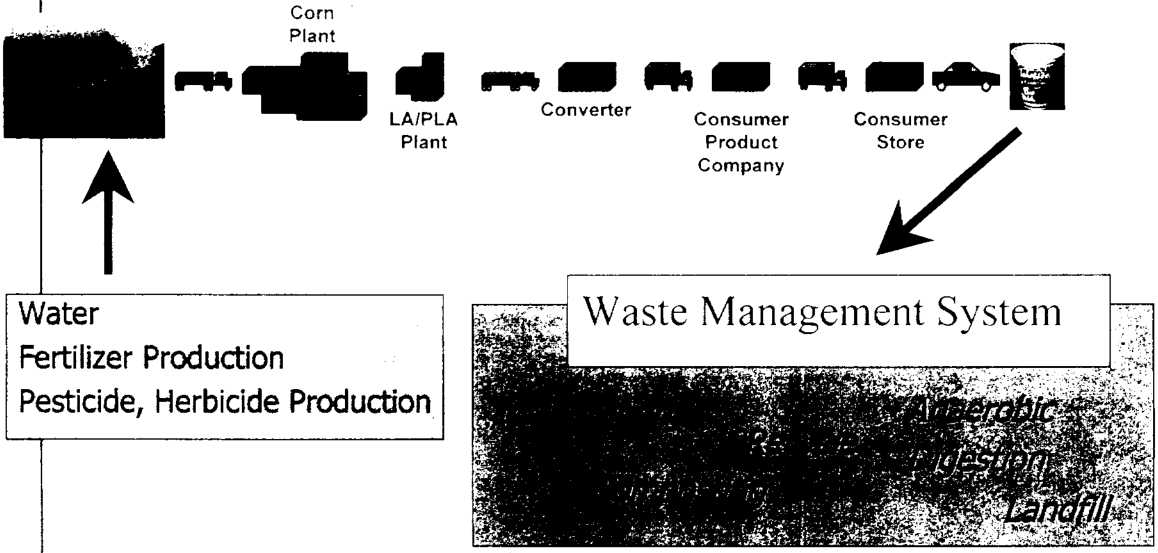
Success requires a full look at total environmental footprint



Corn Plant

LA/PLA Plant

Converter

Consumer Product Company

Consumer Store

Water
Fertilizer Production
Pesticide, Herbicide Production

Waste Management System

Anaerobic Digestion

Landfill

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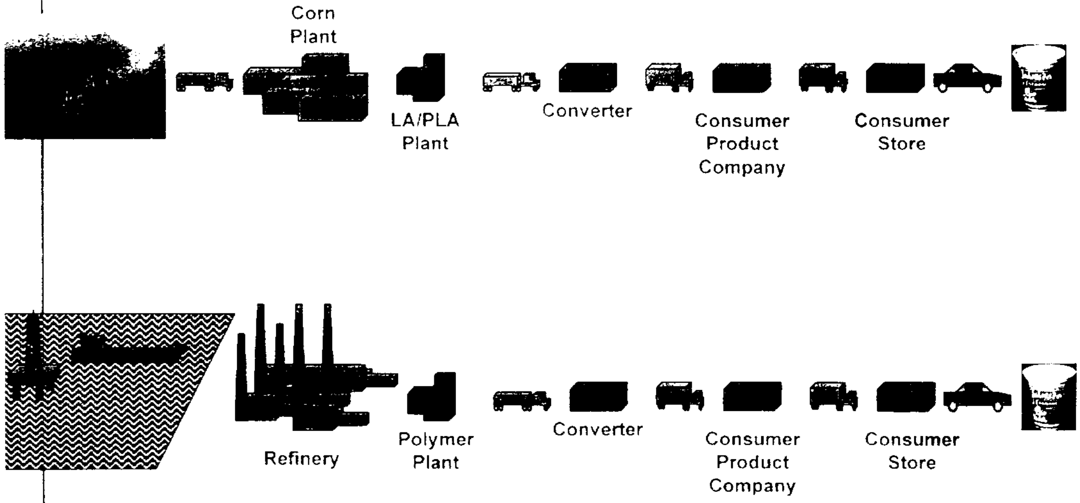
Comparisons



Corn Plant

LA/PLA Plant

Converter

Consumer Product Company

Consumer Store

Refinery

Polymer Plant

Converter

Consumer Product Company

Consumer Store

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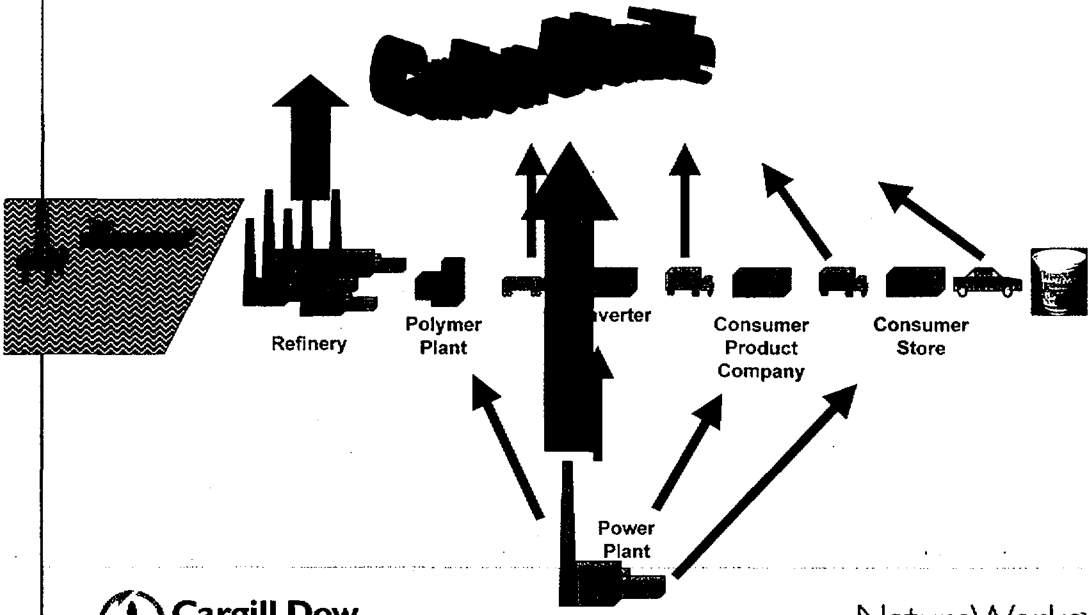
CO_2 Emissions with Typical Plastics



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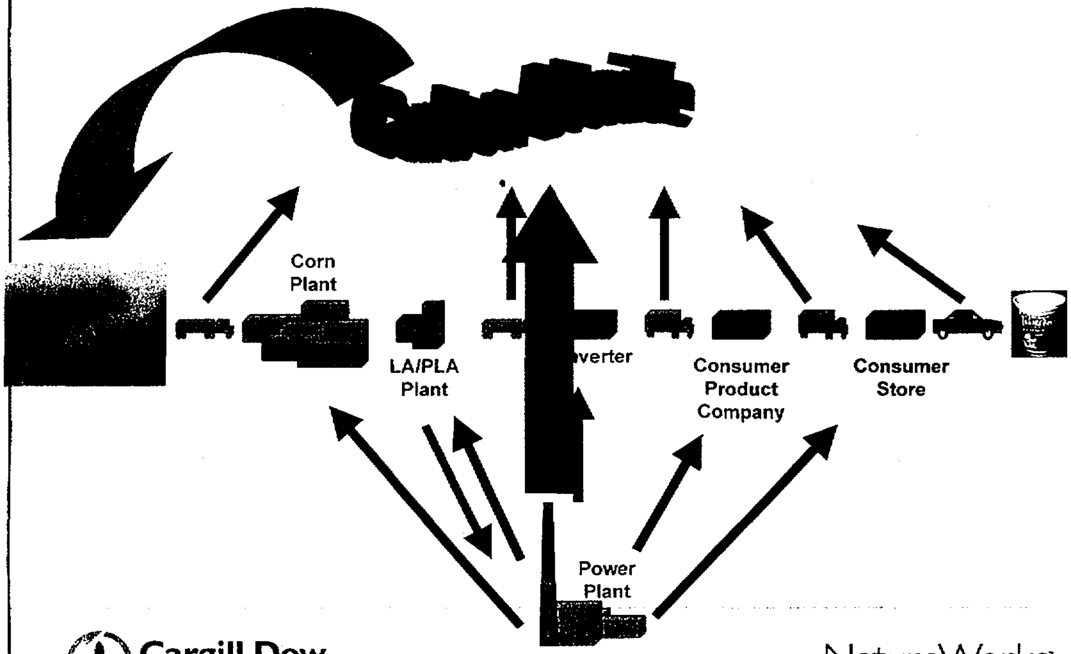
CO_2 Emissions with PLA



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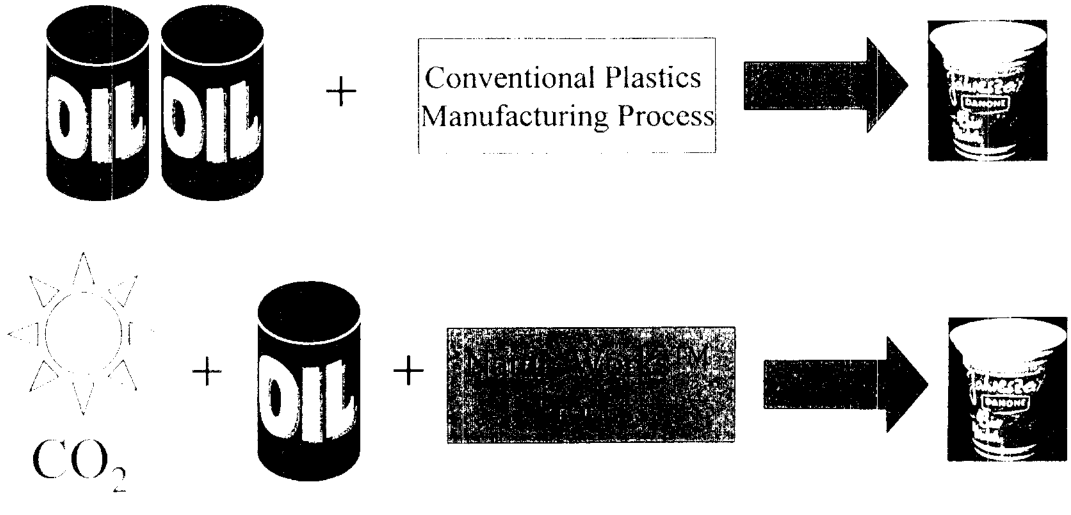
Understanding "Environmental Footprint" is crucial to making raw material, process, product choices.

Solving a problem like solid waste does no good if, for example, other unacceptable forms of environmental issues are created

Environmental Footprint

- Measure all inputs and outputs
  - Raw materials, upstream and downstream
  - All products through manufacturing and end-fate
- Energy, CO2, other impacts on environment
- Use the information to take action to improve!

Renewable Resource Benefit



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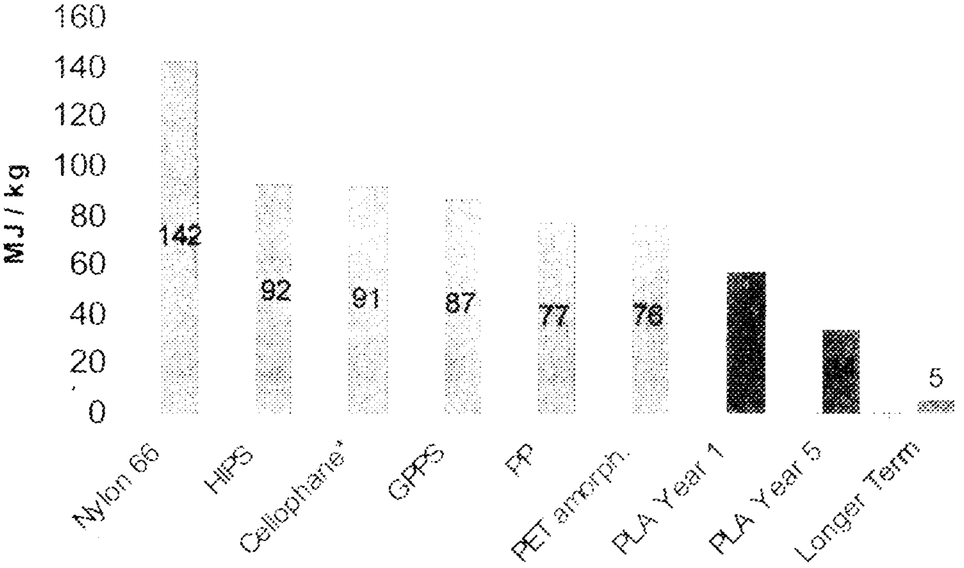
Fossil Resource use in Common Plastics Measured in Energy



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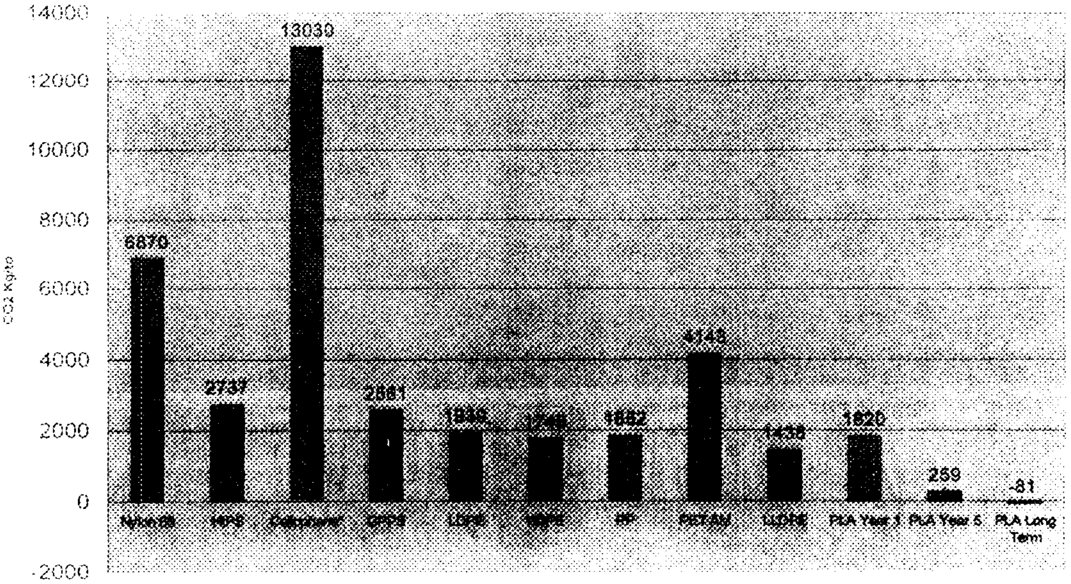
Net CO_2 Emissions to Pellets



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Designed to Fit Any Waste Management System

- Recycle
- Incineration
- Landfill
- Composting
- Anaerobic Digestion

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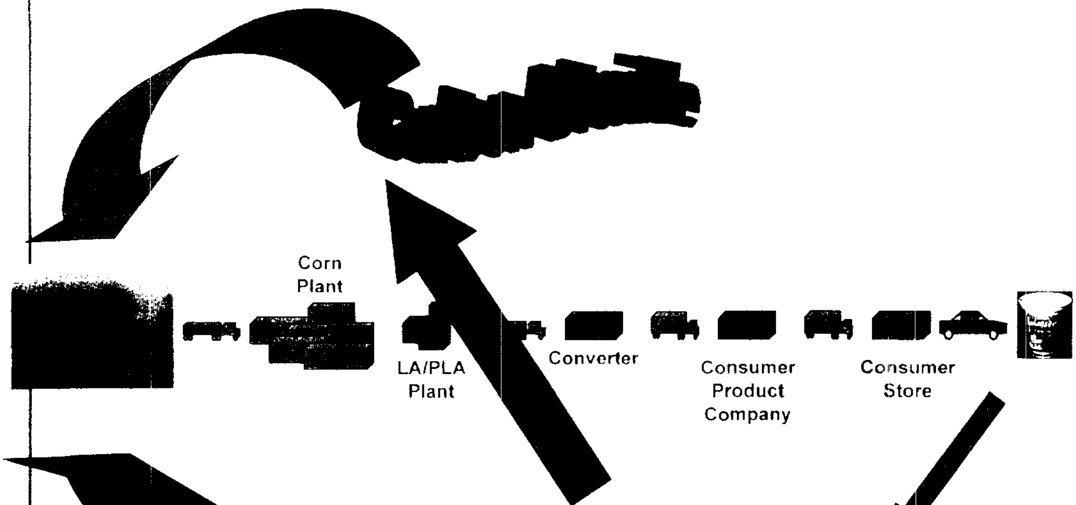
Composting of PLA



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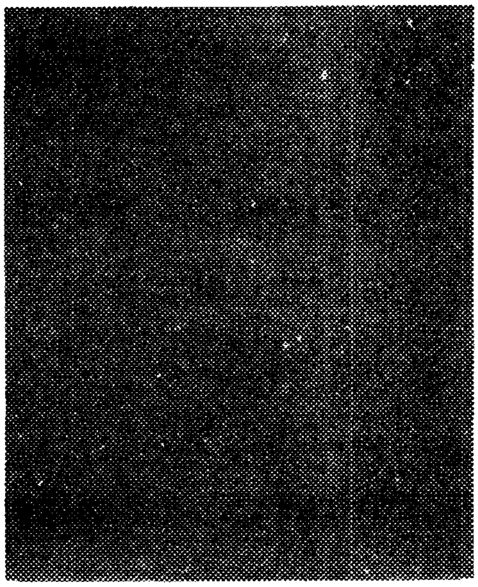
Composting

- Requires the specific conditions of high temperature and moisture found in municipal compost systems
- Specific Conditions requirement allows for products to be designed for normal use
- *Unacceptable* for a product degrade during normal use (prior to disposal)



Day 47

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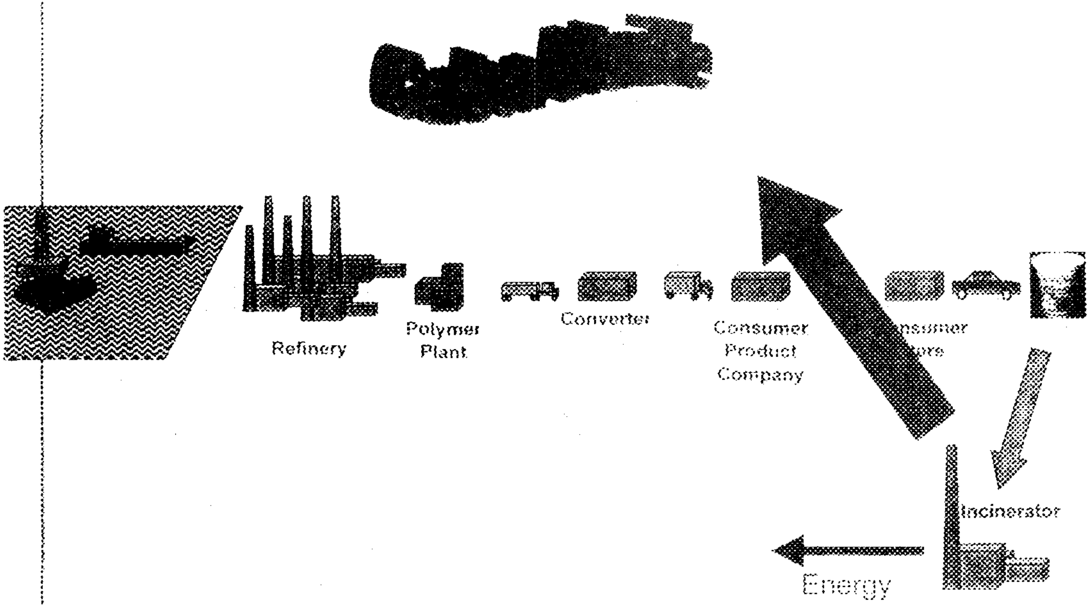
Incineration of Typical Plastics



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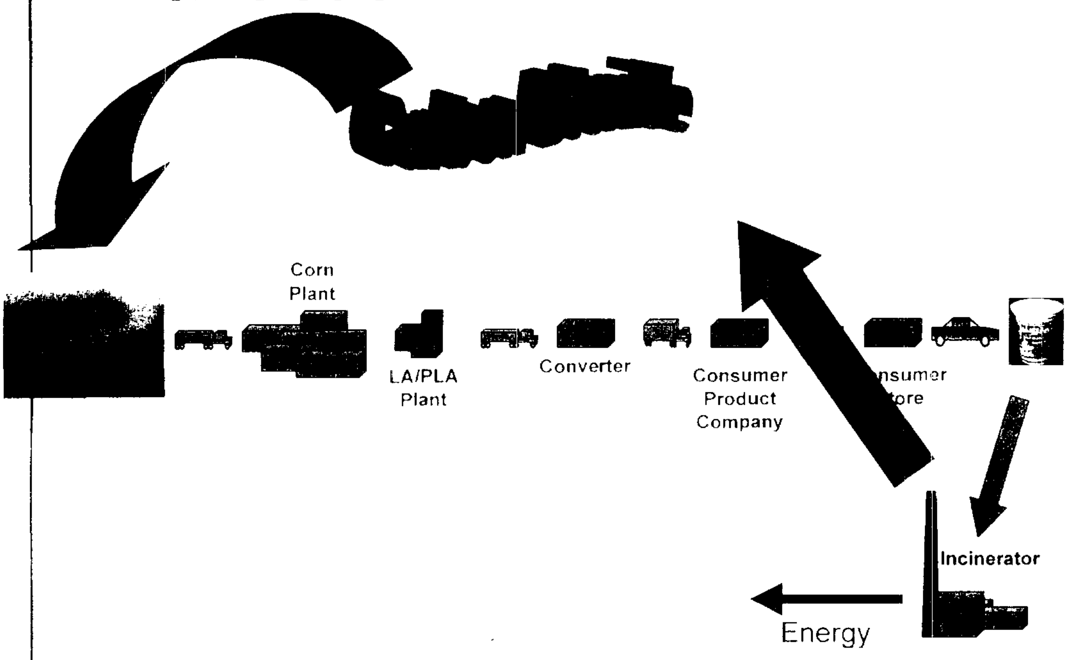
Incineration of PLA



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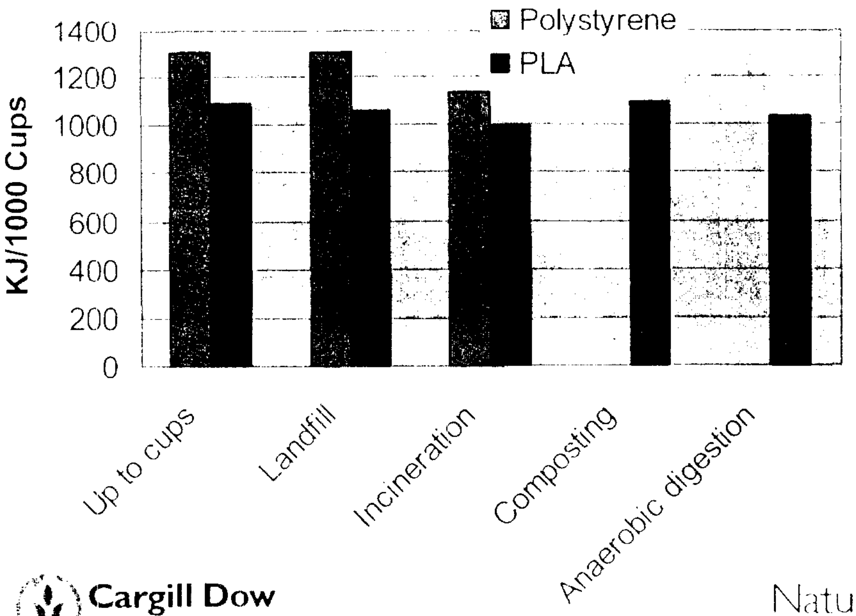
Fossil Resource Use Cradle to Grave PLA versus PS cups



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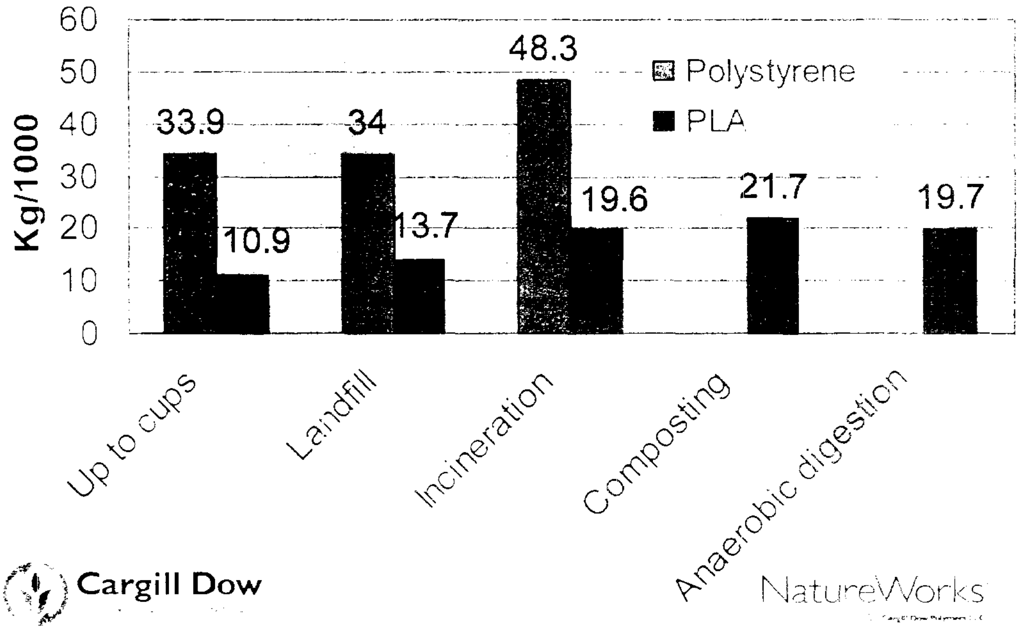
Gross Carbon Dioxide Emission Cradle to Grave PLA versus PS cups



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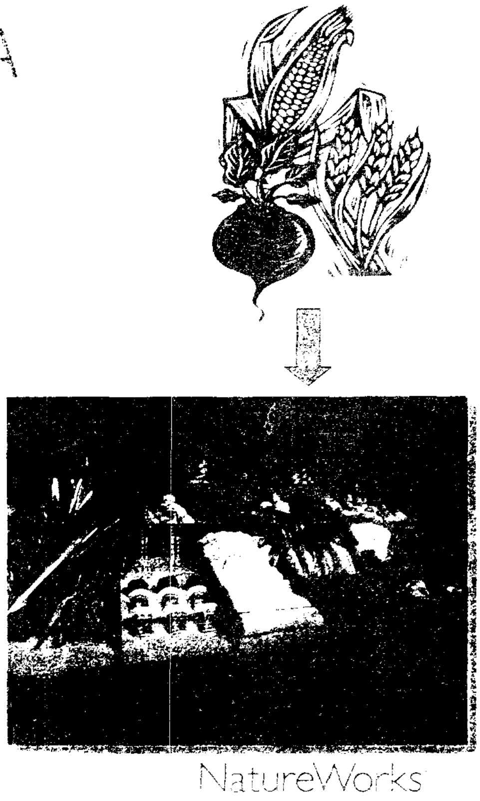
NatureWorks™ PLA

- A new thermoplastic polymer family.
- Derived from annually renewable resources like corn.
- 20 to 50% fossil resource reduction
- Provides packaging, film and fiber solutions.
- Potential market approaching 500.000 metric tons per year.



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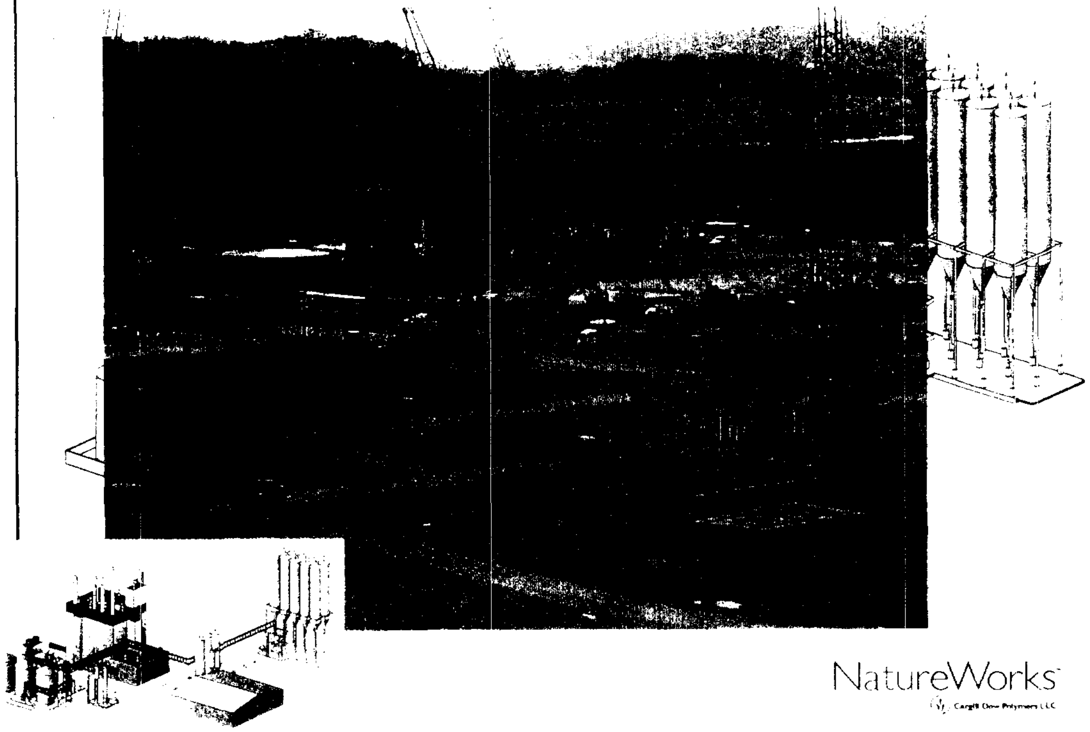
PLA Plant-Blair NE August 2000



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- Focus is on building a platform of products made from renewable resources
  - Polymers
  - Chemical Intermediates
- 200 People
- 140,000 MT PLA Capacity by end of 2001
- Offices in Europe, Japan, US
- Stand-alone organization
- "Several Hundred Million Investment"
- >110 US Patents Issued, 400 Pending Worldwide

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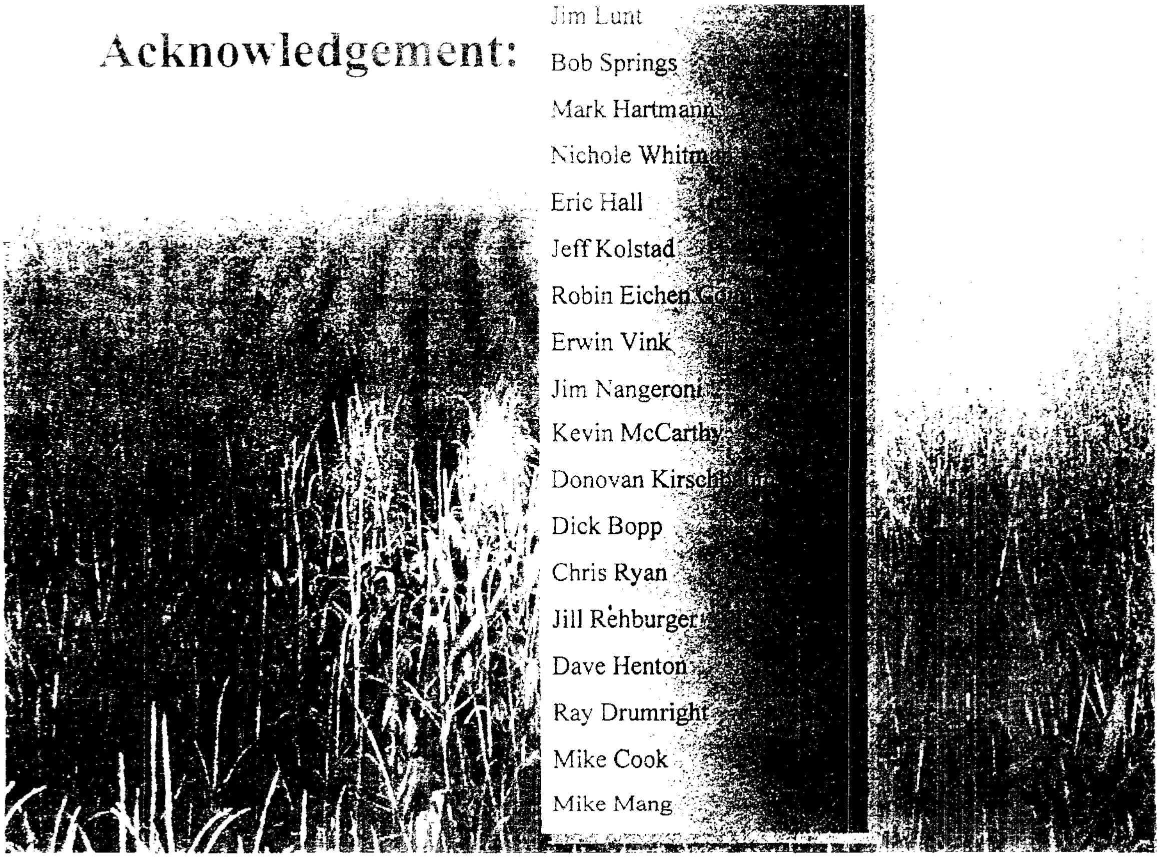

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- Kevin McCarthy
- Donovan Kirsch
- Dick Bopp
- Chris Ryan
- Jill Rehburger
- Dave Henton
- Ray Drumright
- Mike Cook
- Mike Mang

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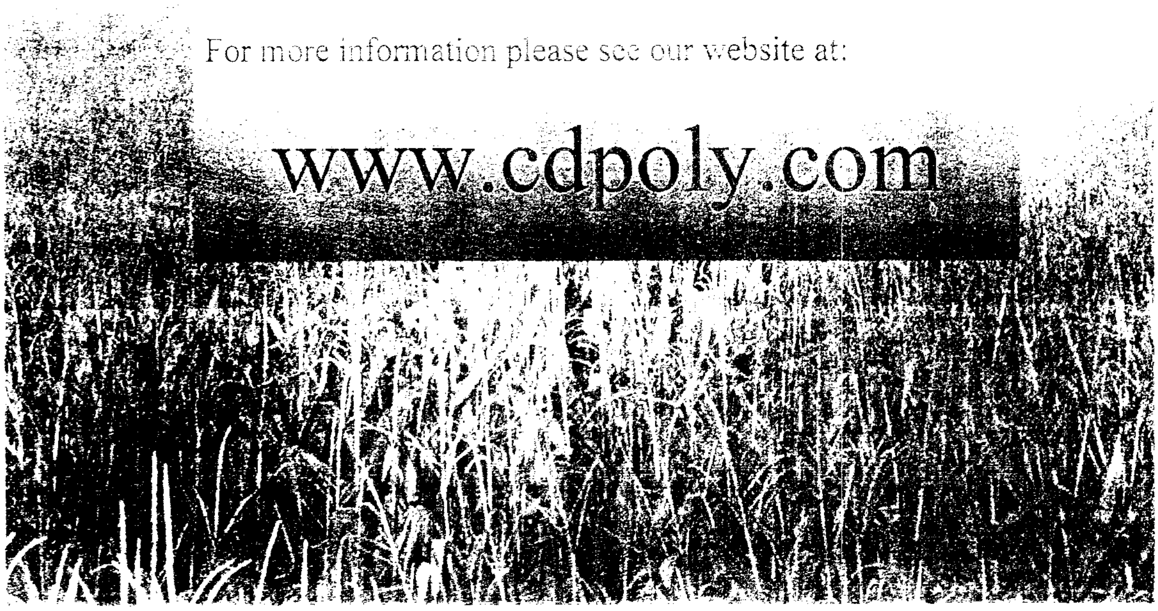

For more information please see our website at:

www.cdpoly.com

7. Biodegradability, Compostability and Toxicological Safety of Poly(lactic acid)

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Keywords: biorecyclable material, polylactic acid, compostability, toxicolgical safety, certificate

Biorecyclable materials such as polylactic acid have been developed toward a realization of "the Sustainable Society". Certificate and labeling systems have been proposed to make these materials more meaningful in an appropriate waste management system in each region in the world. In Germany and Austria, certificate for the compostability of biodegaradable materials has been introduced reflecting the increase of composting infrastructure. In Japan, the Greenpla (Greenpla is a nickname of biodegradable plastics in Japan) Guideline including the criteria of the biodegradability of the material, the safety from the view point of biological intermediates and the toxicity of additives was prepared by BPS (Biodegradable Plastics Society). And the certificate system based on its guideline started from this June. In this paper, evaluation results of the biodegradability, compostability and safety for polylactic acid (LACEA® by Mitsui Chemicals, Inc.) are reported according to the guideline proposed above.

We found that LACEA® was certified as a compostable material in the procedure according to German standard DIN V54900.

1. Chemical components in the product were harmless.
2. 60% and more of LACEA® can be degraded within the regulation period in mature compost, and within 20days in fresh compost (Fig.1).
3. The disintegration rate was 100% in the examination under the practical composting condition.
4. The plant compatibility of the compost produced from the biowaste / LACEA® mixture was proved.

We confirmed the safety of the low molecular weight polymer considered as a biological intermediate in the evaluation along the main point of the BPS Guideline.

1. Oligomer formation by hydrolysis had been known. The formed oligomer was finally degraded into monomer under the condition of pH 9 at 60℃ (Fig.2).
2. The formed oligomer showed no evidence of mutagenic activity in the reverse mutation assay.
3. Aquous extraction of compost made from the biowaste / LACEA® mixture did not also show such mutagenicity.

In conclusion, LACEA® is a compostable material, and its oligomer may exist as intermediate metabolites during the waste treatment or in the environment, which is toxicologically safe and eventually mineralized.

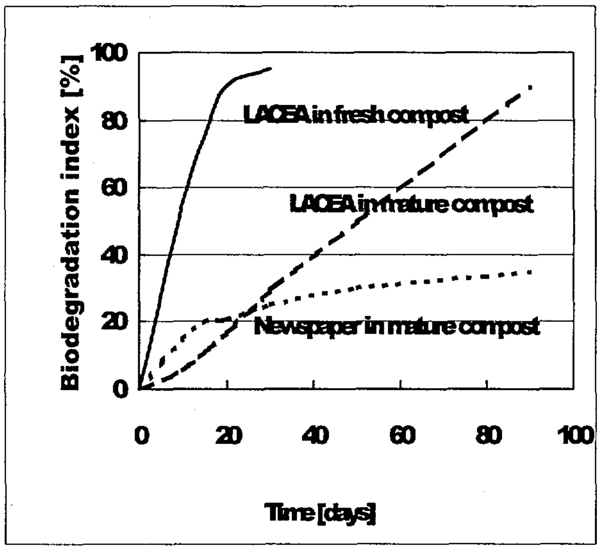


Fig.1 Biodegradability of poly(lactic acid) (ISO14855)

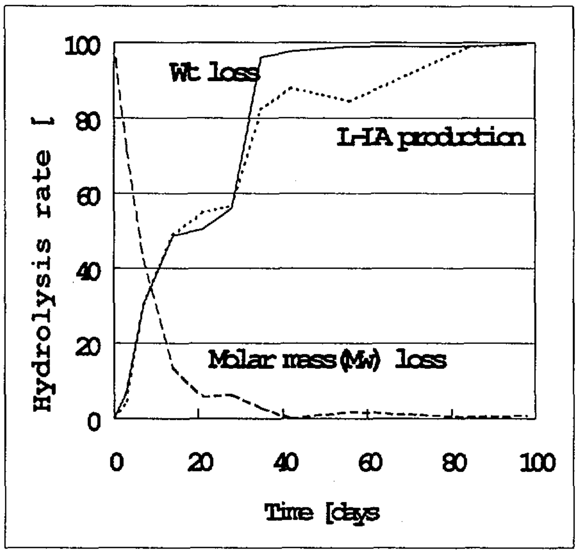


Fig.2 Hydrolysis of poly(lactic acid)(pH9, 60℃)

Outline

1) Degradation of polylactic acid

- Hydrolysis
- Biodegradation
- Degradation mechanism

2) Evaluation Results according to Guideline

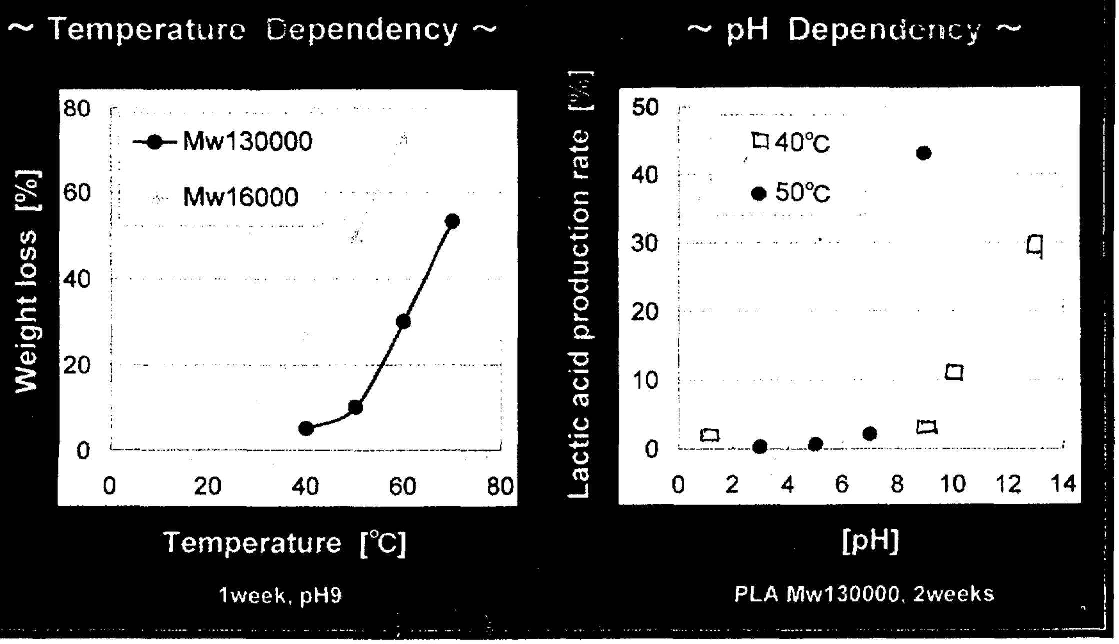
- Compostability (DIN54900)
- Ecotoxicity of biowaste/PLA (DIN54900)
- Toxicological safety of PLA oligomer as intermediate (Greenpla Guideline)
  - * : Greenpla is a nickname of biodegradable plastics in Japan.

3) Biorecyclable Material : PLA "LACEA"

- Application
- at Eco-town Kosaka

LACE

Hydrolysis of PLA

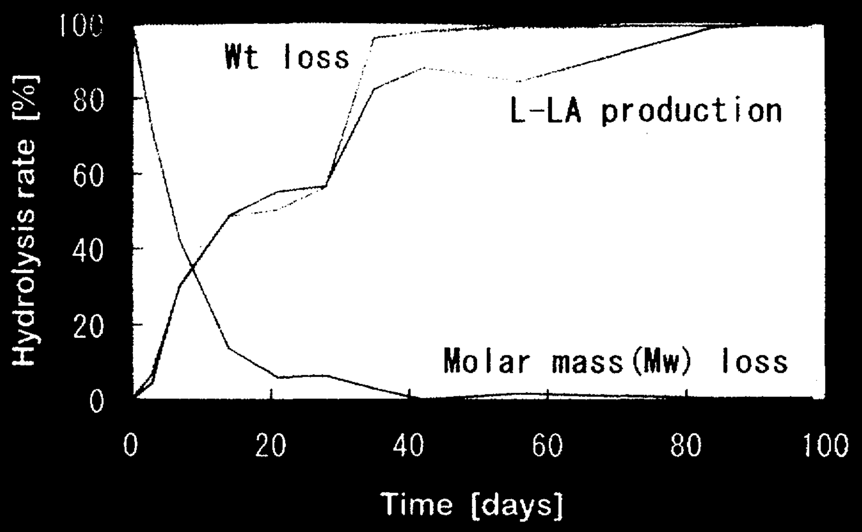


1week, pH9

PLA Mw130000, 2weeks

LACE

Hydrolysis of crystalline PLA



Test condition: pH9, 60°C

PLA-degradation microorganism

Bacteria

Pesudomonas putida <oligomer>	(M.Vert et.al., 1995)
Bacillus subtilis, *Pseudomonas* sp., *Eschericia* sp.	(Yagi et.al., 1995)
Staphylococcus hominis, *S.epidermidis*	(Tokiwa et.al, 1996)
Bacillus brevis	(Tomita et.al., 1997)
Kingella kingae, *Xanthomonas* sp.	(Nakajima et.al., 1998)

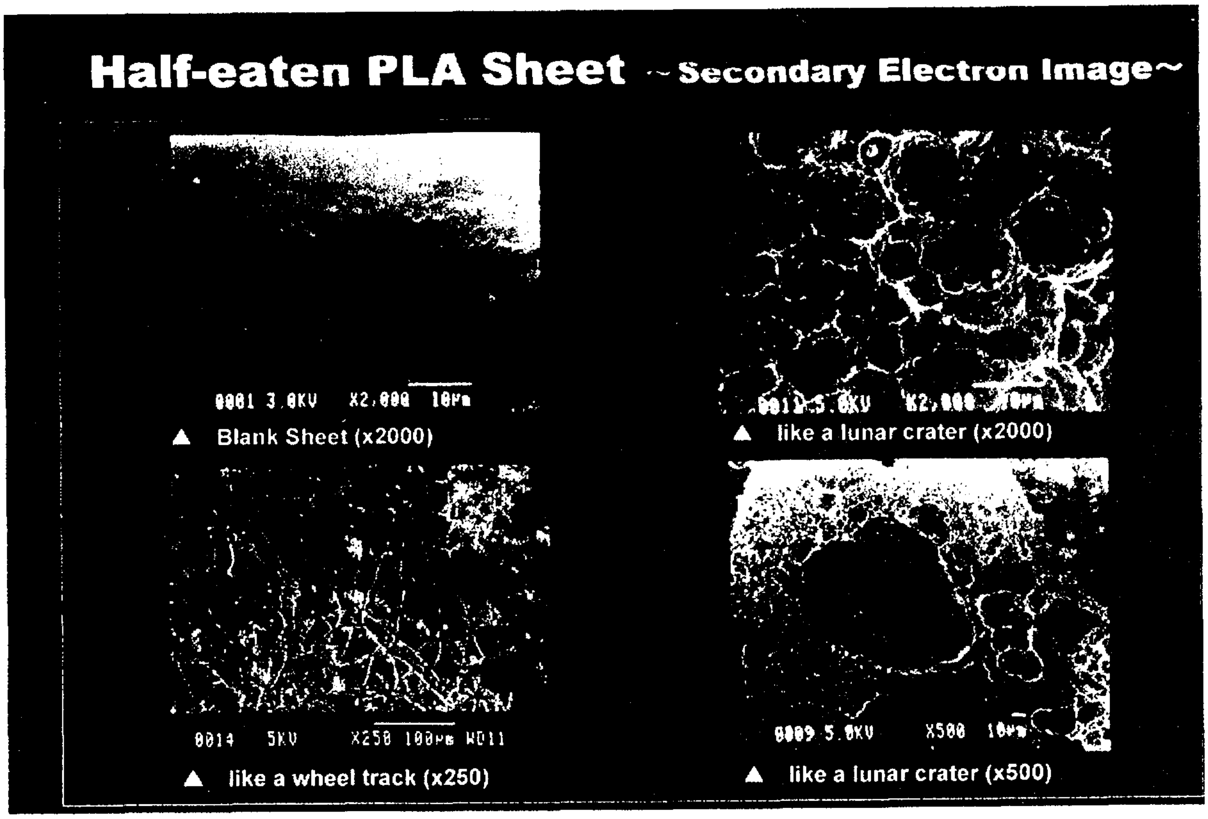
Actinomycete

Amycolatopsis mediterranei	(Tokiwa et.al, 1995)
Streptomyces violaceus, S.cyaneus	(Tokiwa et.al, 1996)
Amycolatopsis sp.	(Kudo et.al., 1998)
Amycolatopsis sp.	(Kamio et.al., 1999)

Fungi

Fusarium moniliforme <oligomer>	(M.Vert et.al., 1995)

June.1999



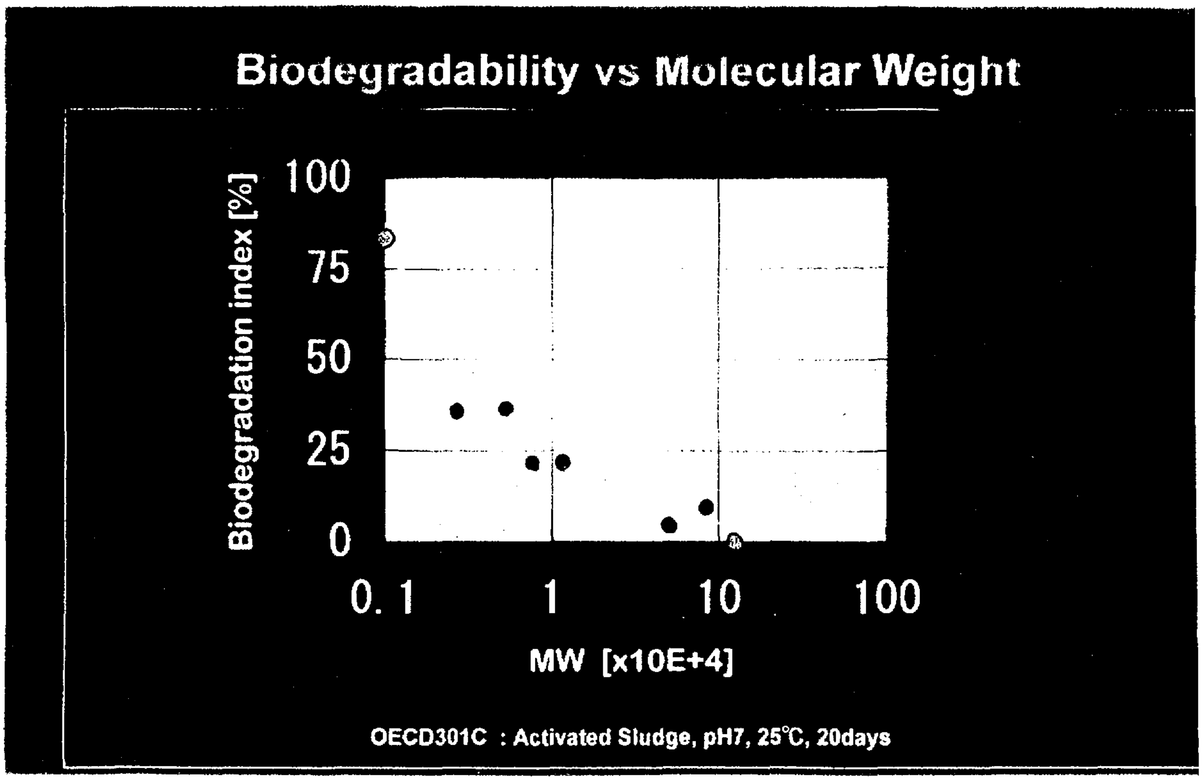
Half-eaten PLA Sheet ~Secondary Electron Image~

▲ Blank Sheet (x2000)

▲ like a lunar crater (x2000)

▲ like a wheel track (x250)

▲ like a lunar crater (x500)

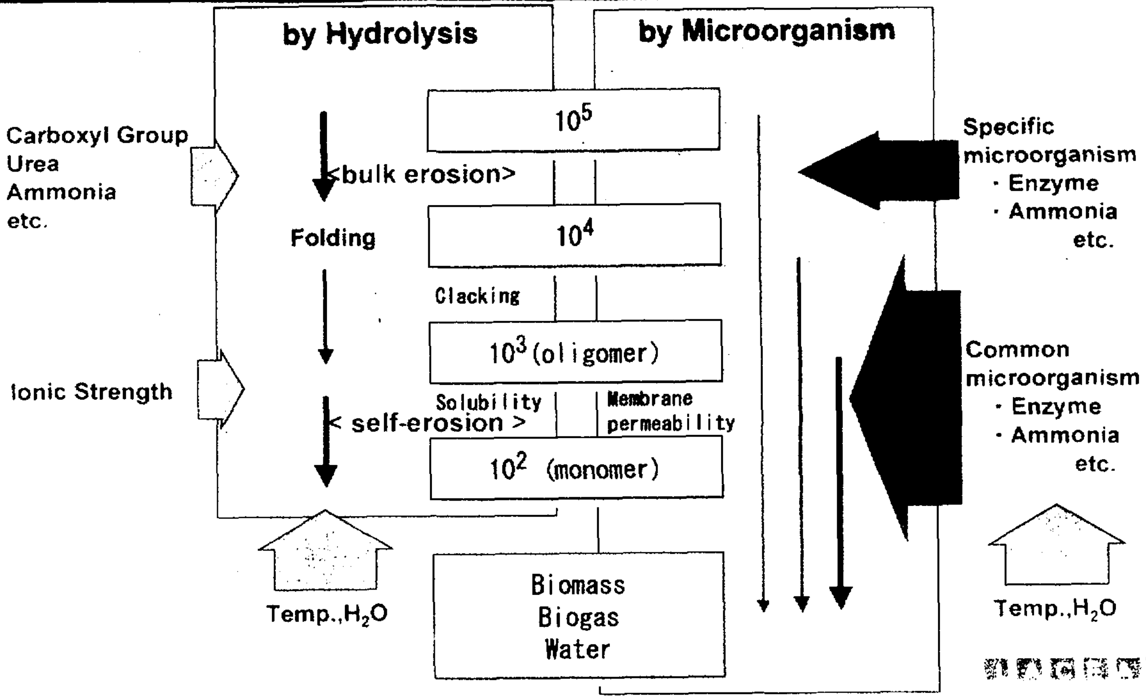


Biodegradability vs Molecular Weight

OECD301C : Activated Sludge, pH7, 25℃, 20days

Degradation Mechanism of PLA

~Logarithmic 4-step degradation~



by Hydrolysis

by Microorganism

Carboxyl Group
Urea
Ammonia
etc.

Ionic Strength

10^5

<bulk erosion>

Folding

10^4

Clacking

10^3 (oligomer)

Solubility

Membrane permeability

< self-erosion >

10^2 (monomer)

Temp., H_2O

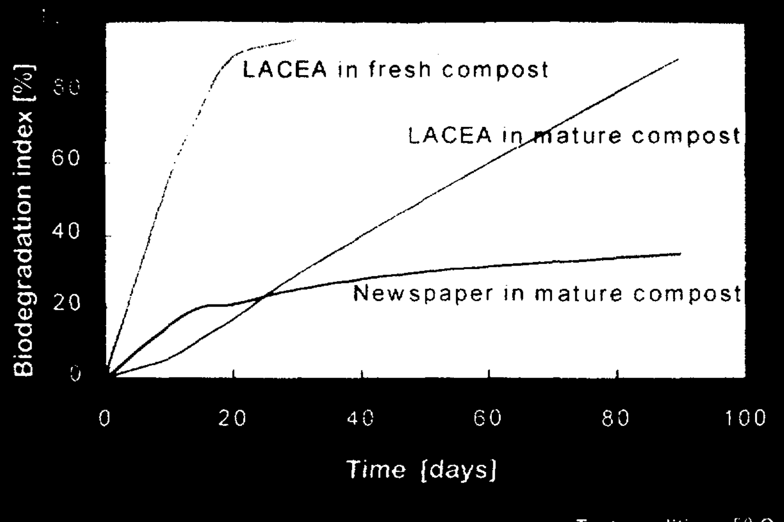
Biomass
Biogas
Water

Specific microorganism
- Enzyme
- Ammonia
etc.

Common microorganism
- Enzyme
- Ammonia
etc.

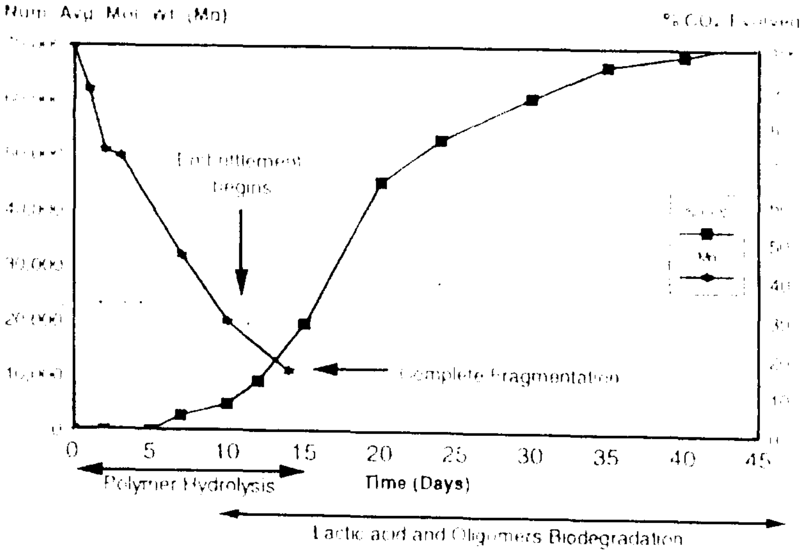
Temp., H_2O

Biodegradation of PLA



Test condition: 58 C

Degradation Mechanism of PLA



Reference J Lunt, Polymer Degradation and Stability, 59, pp.145(1998)

Degradation Period of PLA

Environment	Life Time	Characteristic	* : PLA sheet
< In Use >			
Room	> 5 [years]	Good Stability in Use	
Soil, Liver, Sea	2~5 [years]		
< after Use >			
Landfilling	2~8 [months]		
Composting	1~4 [weeks]	Appropriate Degradation Time	
Hydrolysis	1~4 [hours] (by Acid or Alkaline)		

Comparison of Biodegradable Plastics Certification

	EU	Germany Swiss	US.	Japan
Focus	Compostability	Compostability	Compostability	Biodegradability
Owner	-	IBAW	BPI	BPS
Manager	-	DIN-CERTCO	BPI	BPS
Supporter	-	-	USCC	-
	(Mandatory)	(Voluntary → Mandatory)	(Voluntary)	(Voluntary)
Norm	prEN13432 ·Material characteristic ·Biodegradability ·Disintegration ·Compost quality	DIN V54900	ASTM D6002 ASTM D6400	Greenpla PL guideline ·Material characteristic ·Acute toxicity of additives ·Biodegradability
Background	EU packaging directive EU composting directive EU landfill directive			Packaging recycling law Food-waste recycling law

Compostable Material “LACEA®”

1) Chemical components in the product was harmless.

2) 60% and more of LACEA® was degraded within the regulation period in the biodegradability test, ISO14855.

3) The disintegration rate was 100% in the examination under the practical composting condition.

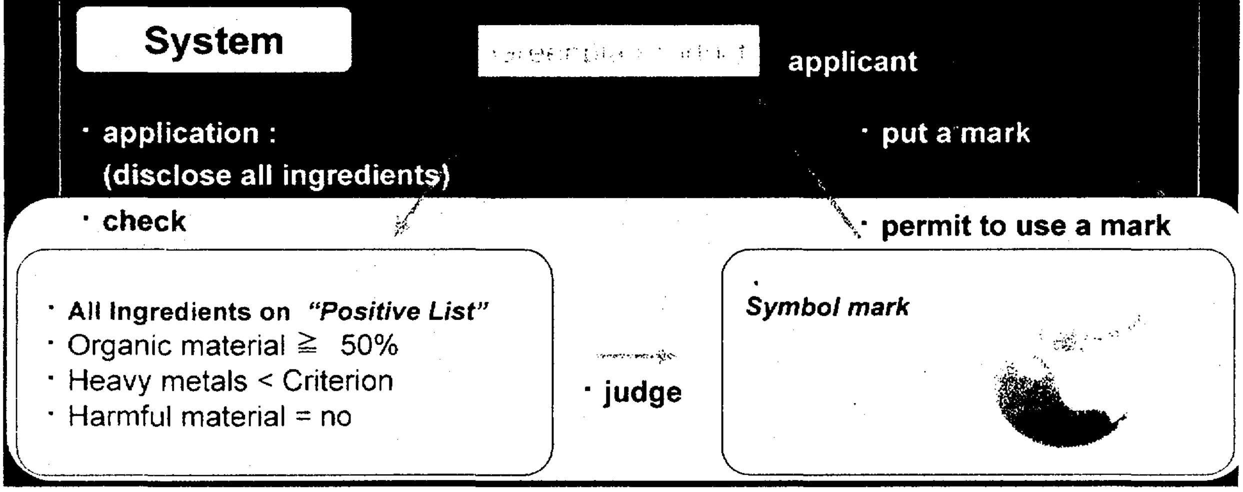
4) The plant compatibility of the compost produced from the biowate/LACEA® mixture was proved.

Identification and Labeling

Purpose

1. Identification of plastics products made of biodegradable plastics
2. Distinguish from non-degradable plastics by symbol mark

System



[illegible] applicant

- application :
  (disclose all ingredients)
- put a mark
- check
- permit to use a mark

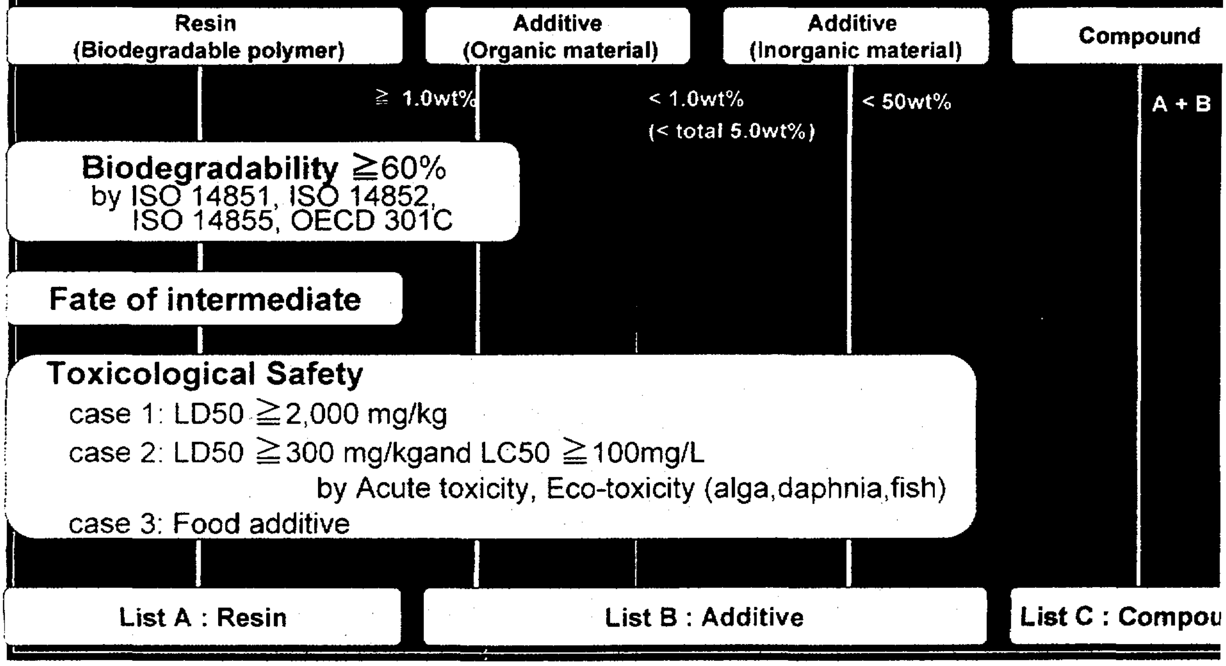
- All Ingredients on *"Positive List"*
- Organic material ≧ 50%
- Heavy metals < Criterion
- Harmful material = no

- judge

Symbol mark

Greenpla Positive List

- Guideline / Criteria -



Resin (Biodegradable polymer)

Additive (Organic material)

Additive (Inorganic material)

Compound

≧ 1.0wt%

< 1.0wt%
(< total 5.0wt%)

< 50wt%

A + B

Biodegradability ≧60%
by ISO 14851, ISO 14852,
ISO 14855, OECD 301C

Fate of intermediate

Toxicological Safety
case 1: LD50 ≧2,000 mg/kg
case 2: LD50 ≧300 mg/kgand LC50 ≧100mg/L
by Acute toxicity, Eco-toxicity (alga,daphnia,fish)
case 3: Food additive

List A : Resin

List B : Additive

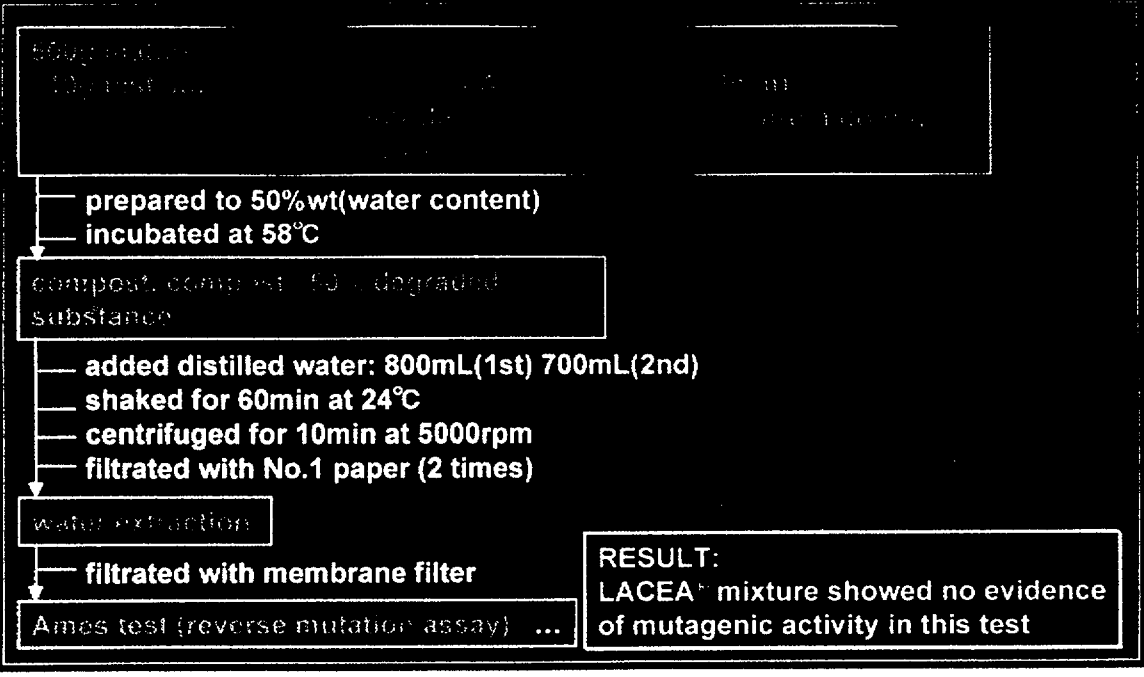
List C : Compou

Non Mutagenicity of PLA

	Ames Test
PLA polymer	-
PLA oligomer	-

-: negative

Toxicological Safety of Aqueous Extraction of Compost from Biowaste/PLA



[illegible]

- prepared to 50%wt(water content)
- incubated at 58℃

compost, compost [illegible] 50 [illegible] degraded substance

- added distilled water: 800mL(1st) 700mL(2nd)
- shaked for 60min at 24℃
- centrifuged for 10min at 5000rpm
- filtrated with No.1 paper (2 times)

water extraction

- filtrated with membrane filter

Ames test (reverse mutation assay) ...

RESULT:
LACEA® mixture showed no evidence of mutagenic activity in this test

Toxicological Safety of Polylactic Acid, LACEA®

1) PLA oligomer formation by hydrolysis had been known. The formed oligomer was finally degraded into monomer under the condition of pH9 at 60℃.

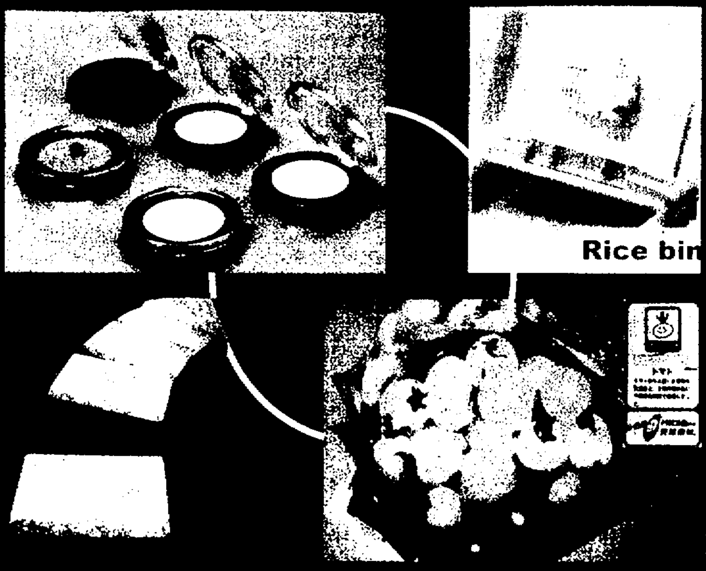
2) The formed oligomer showed no evidence of mutagenic activity in the reverse mutation assay.

3) Aqueous extraction of compost made from the biowate/LACEA® mixture did not also show such mutagenicity.

Applications

~ from nature to nature ~

from Natural Image

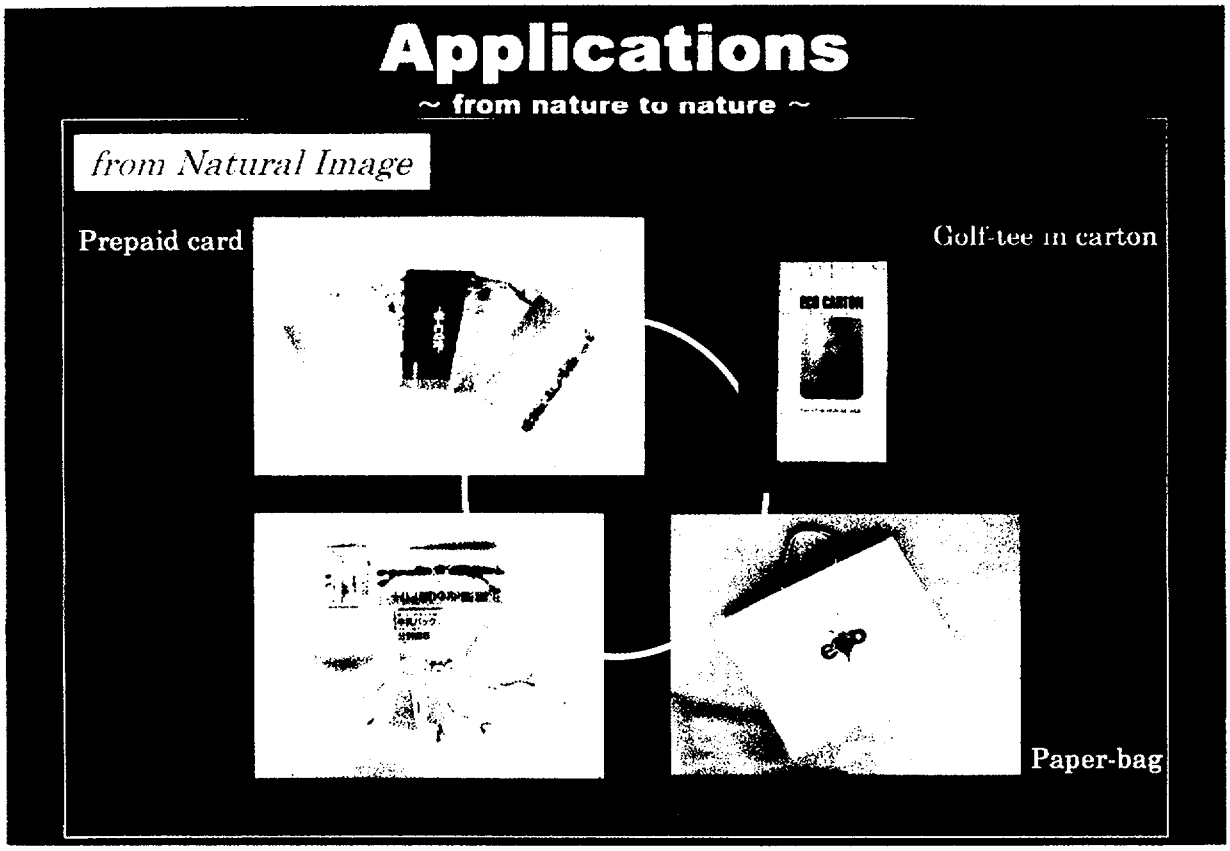


Cosmetic case

Repellent

Prepaid card

Food packaging



Applications

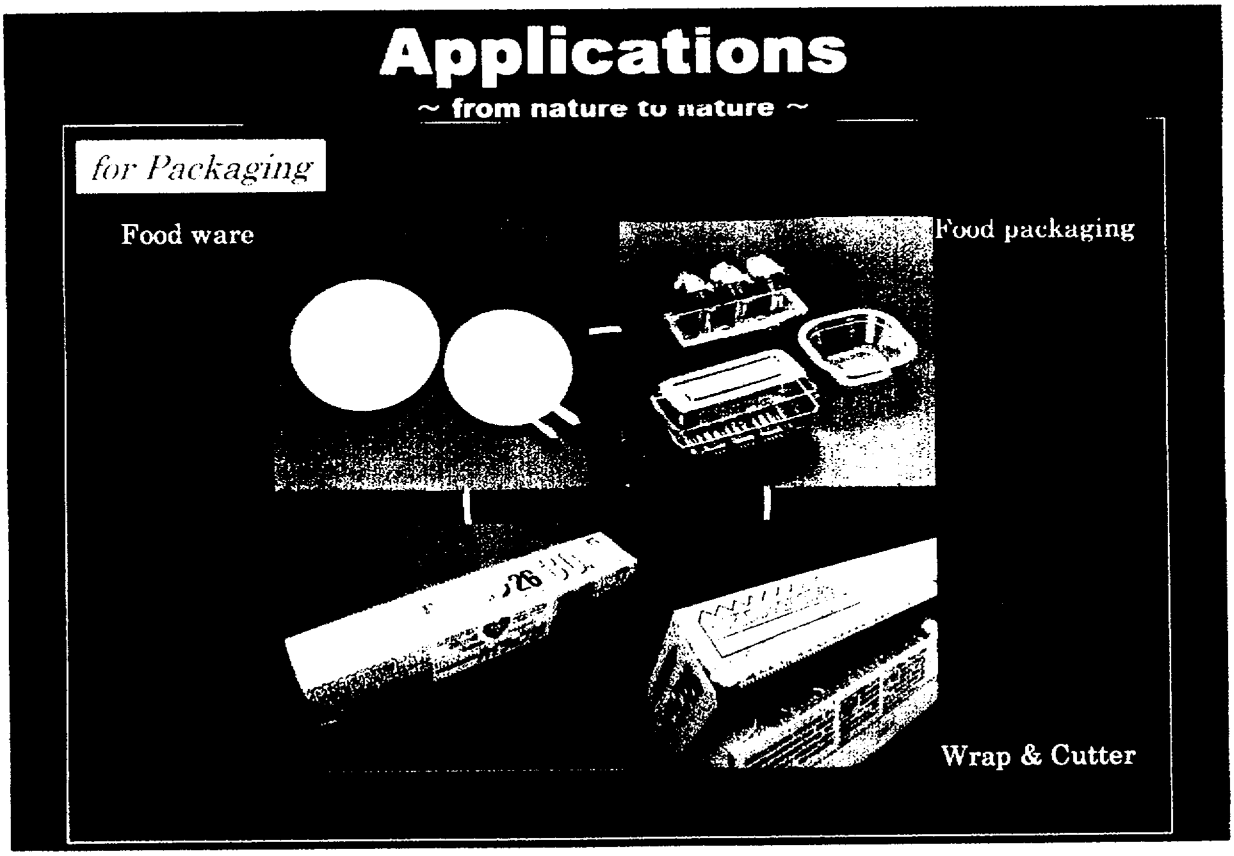
~ from nature to nature ~

from Natural Image

Prepaid card

Golf-tee in carton

Paper-bag



Applications

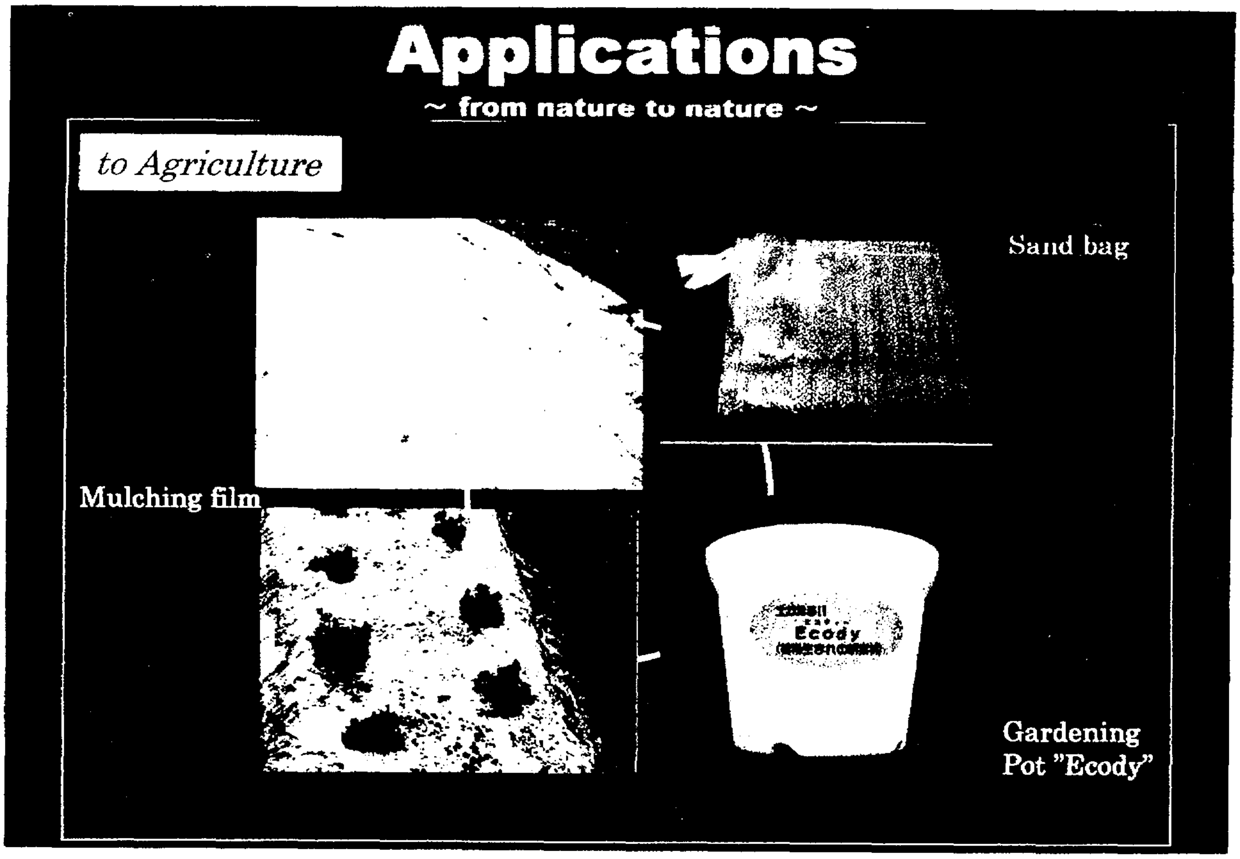
~ from nature to nature ~

for Packaging

Food ware

Food packaging

Wrap & Cutter



Applications

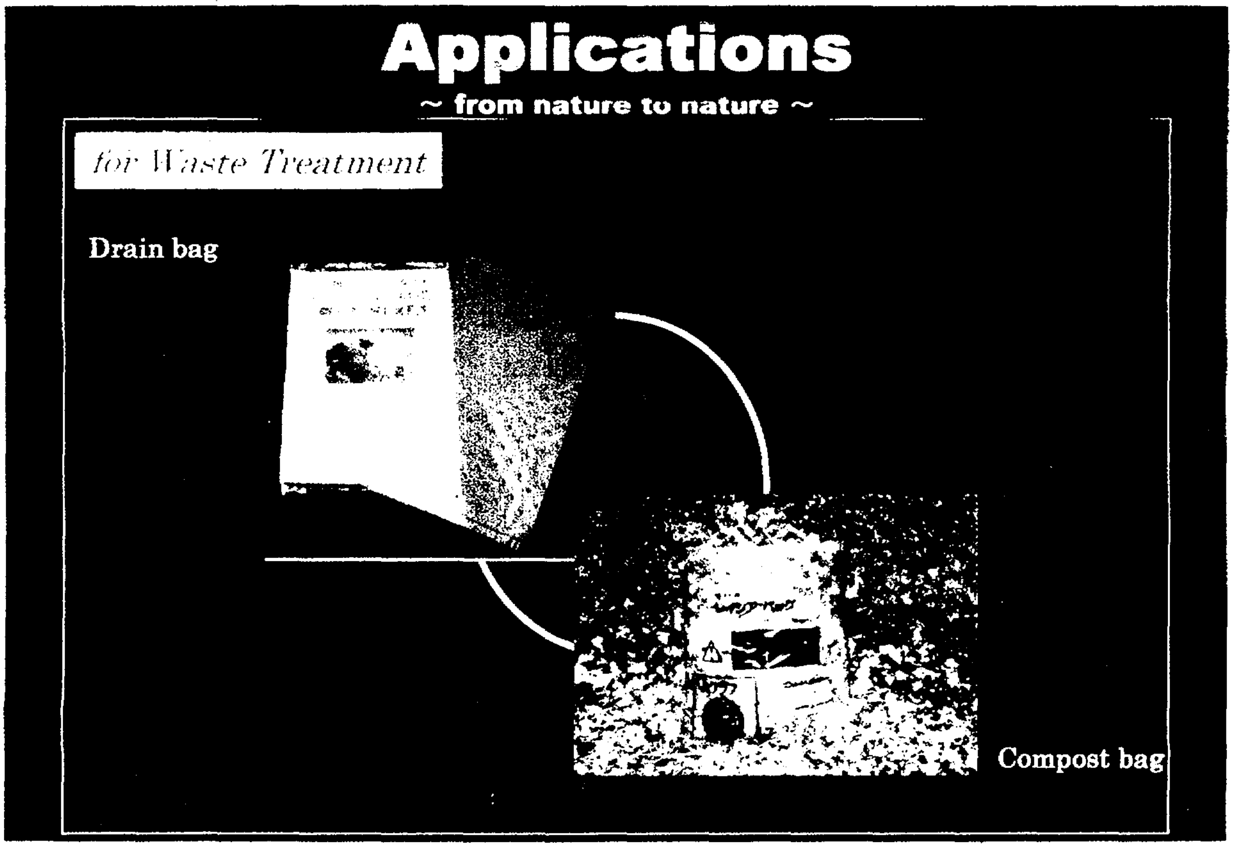
~ from nature to nature ~

to Agriculture

Sand bag

Mulching film

Gardening Pot "Ecody"



Applications

~ from nature to nature ~

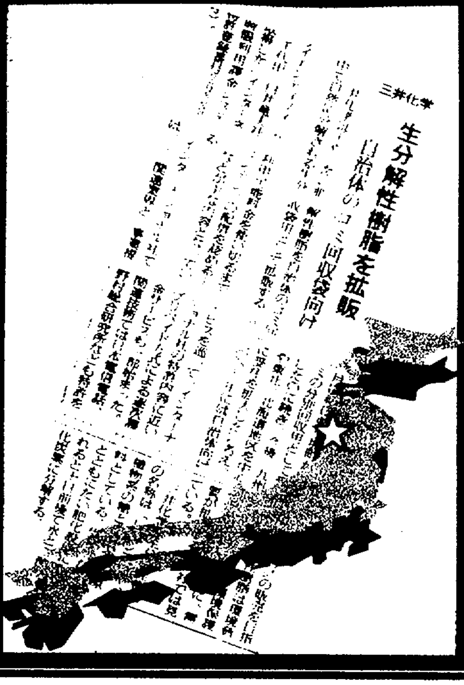
for Waste Treatment

Drain bag

Compost bag

Kosaka Town in Akita

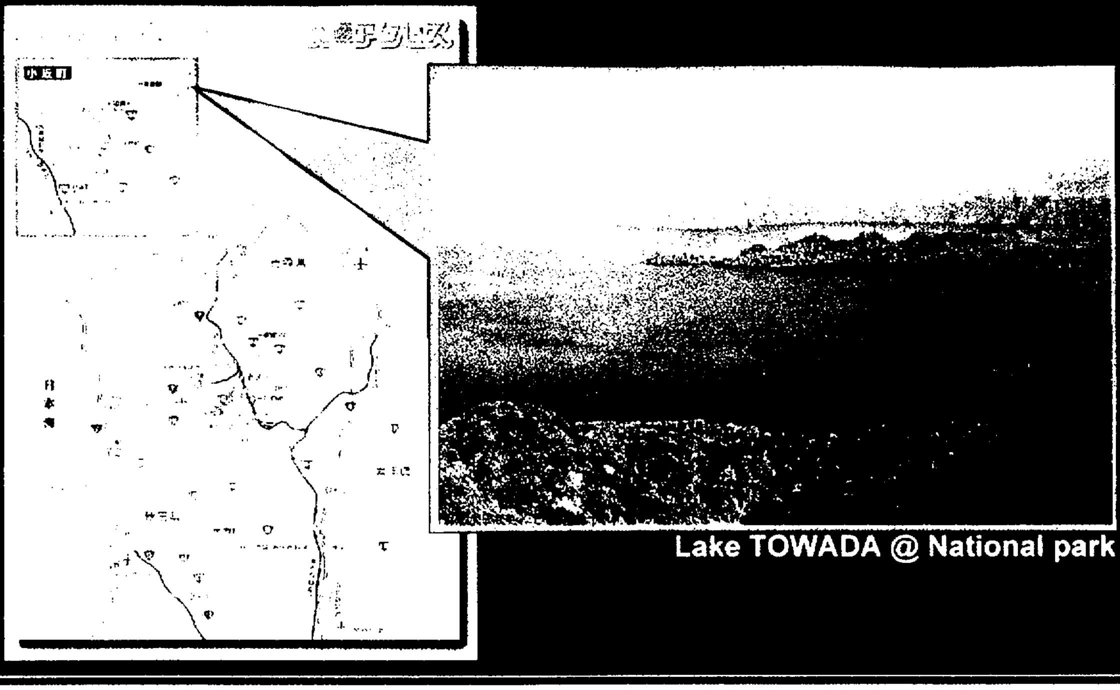
- ◆ **Data**
  Population 7,518 (Jun.1998)
  Temperature av. 9.3°C (1995)
- ◆ **Location**
  Lake Towada @ National park
- ◆ **Environmental Plan**
  Eco-town certified by MITI
  - Bio-recycling
  - Metal recycling
- ◆ **Composting**
  ... for organic farming from 1995
  ... of school meals from 1997
  ... with LACEA® bag from 1999



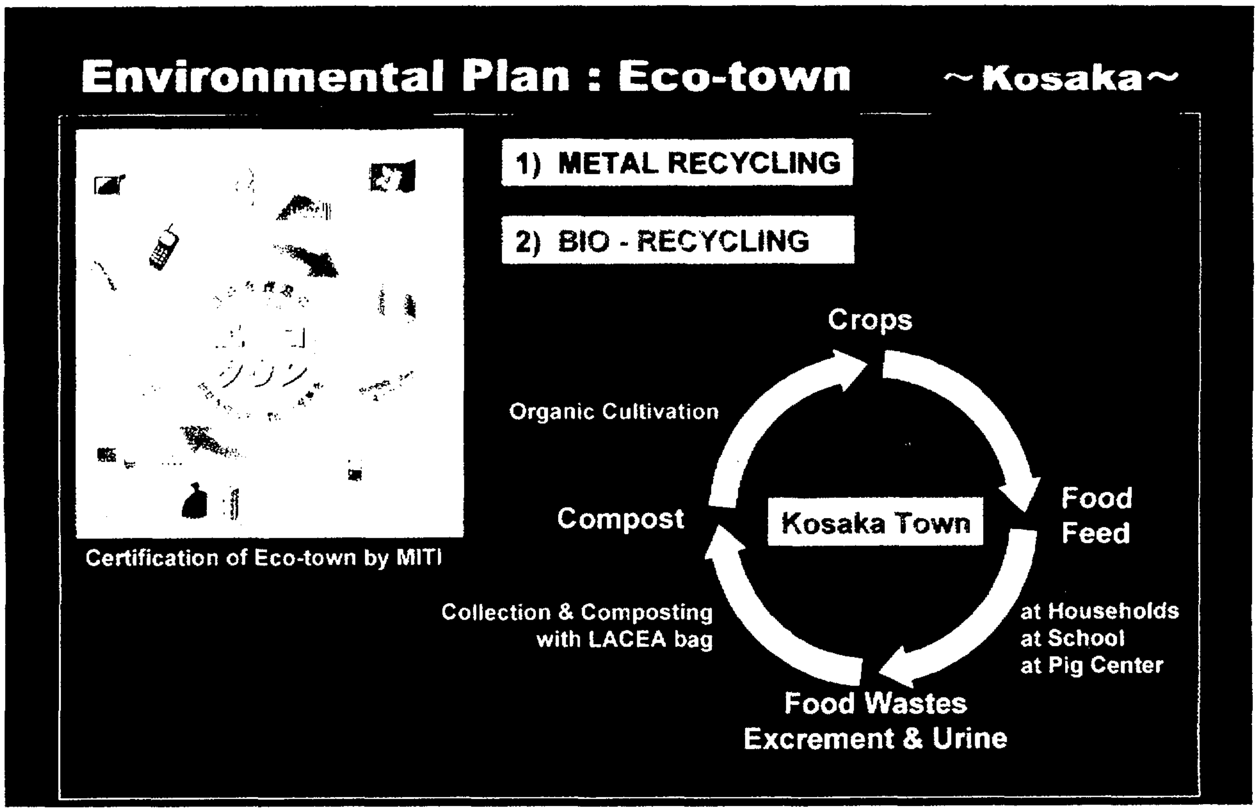
三井化学
生分解性樹脂を拡販
自治体のゴミ回収袋向け

Location

~Kosaka~



Lake TOWADA @ National park



Environmental Plan : Eco-town ~Kosaka~

Certification of Eco-town by MITI

1) METAL RECYCLING

2) BIO - RECYCLING

Crops

Food
Feed

at Households
at School
at Pig Center

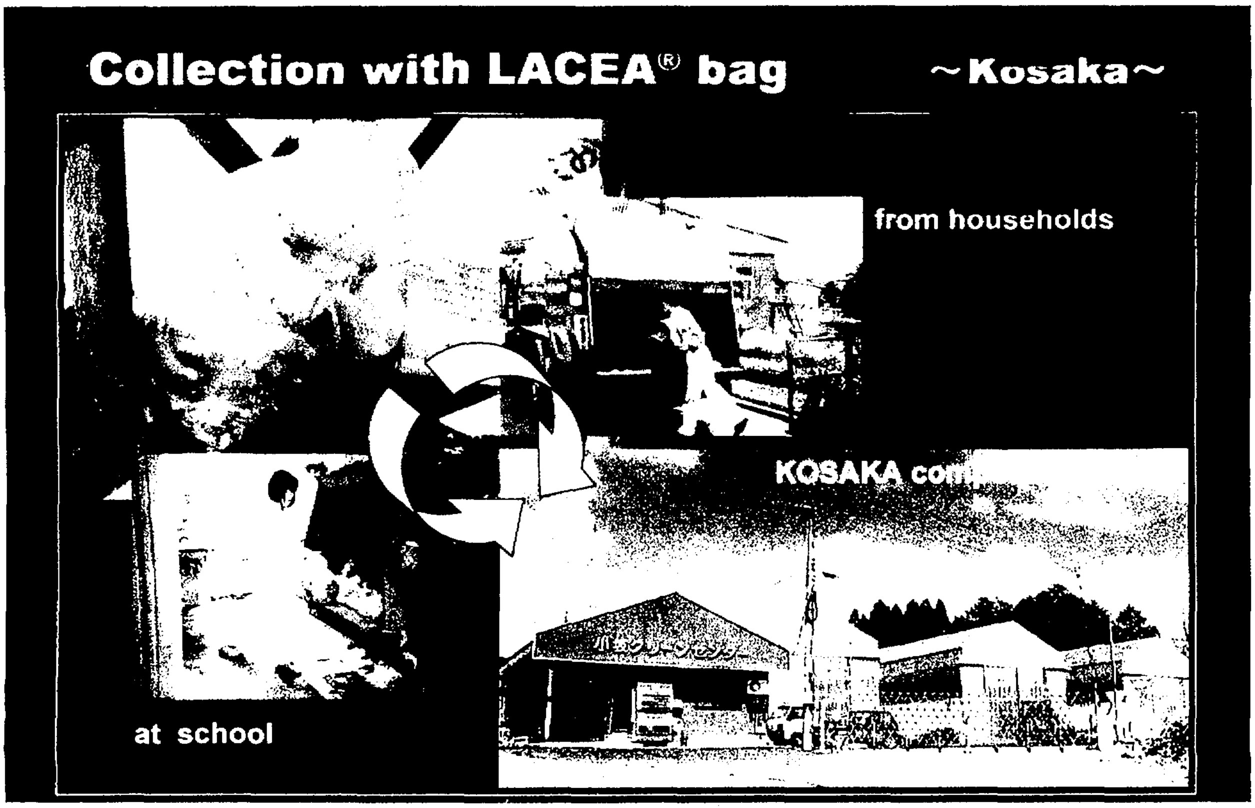
Food Wastes
Excrement & Urine

Collection & Composting
with LACEA bag

Compost

Organic Cultivation

Kosaka Town

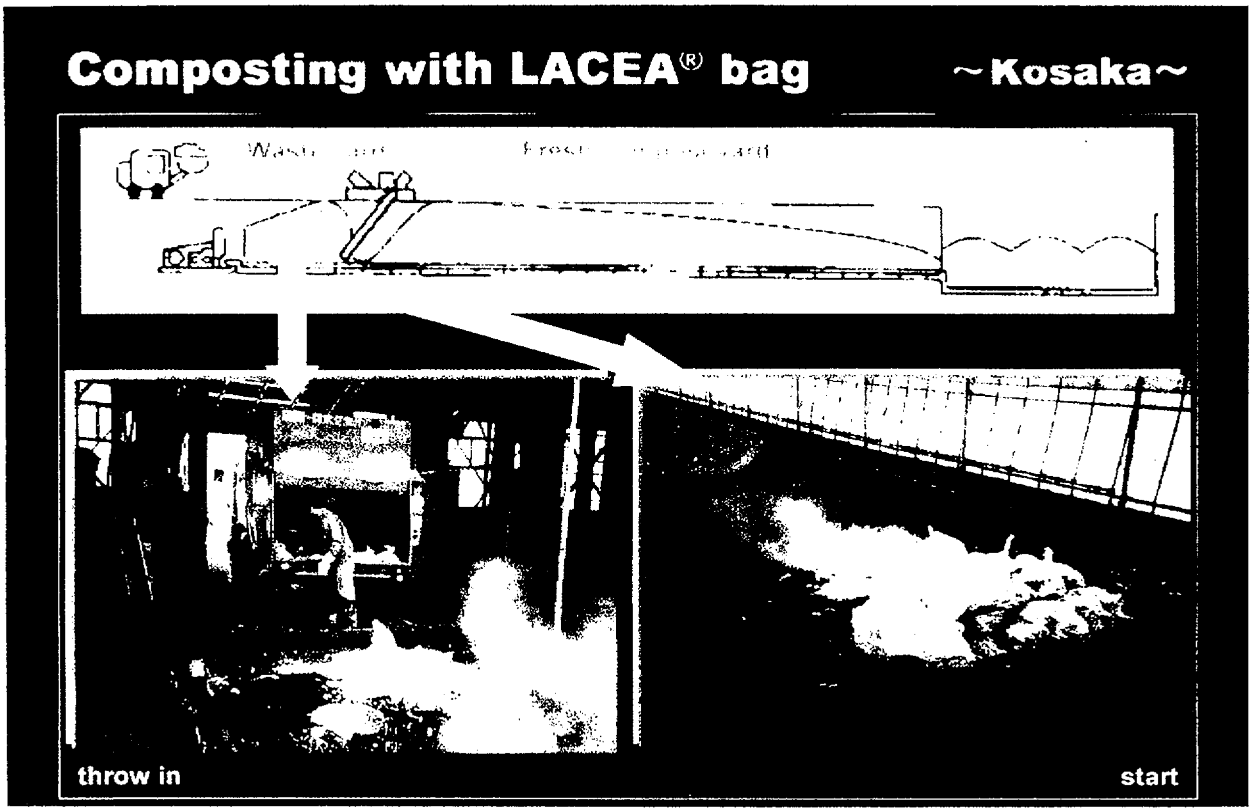


Collection with LACEA® bag ~Kosaka~

from households

KOSAKA com

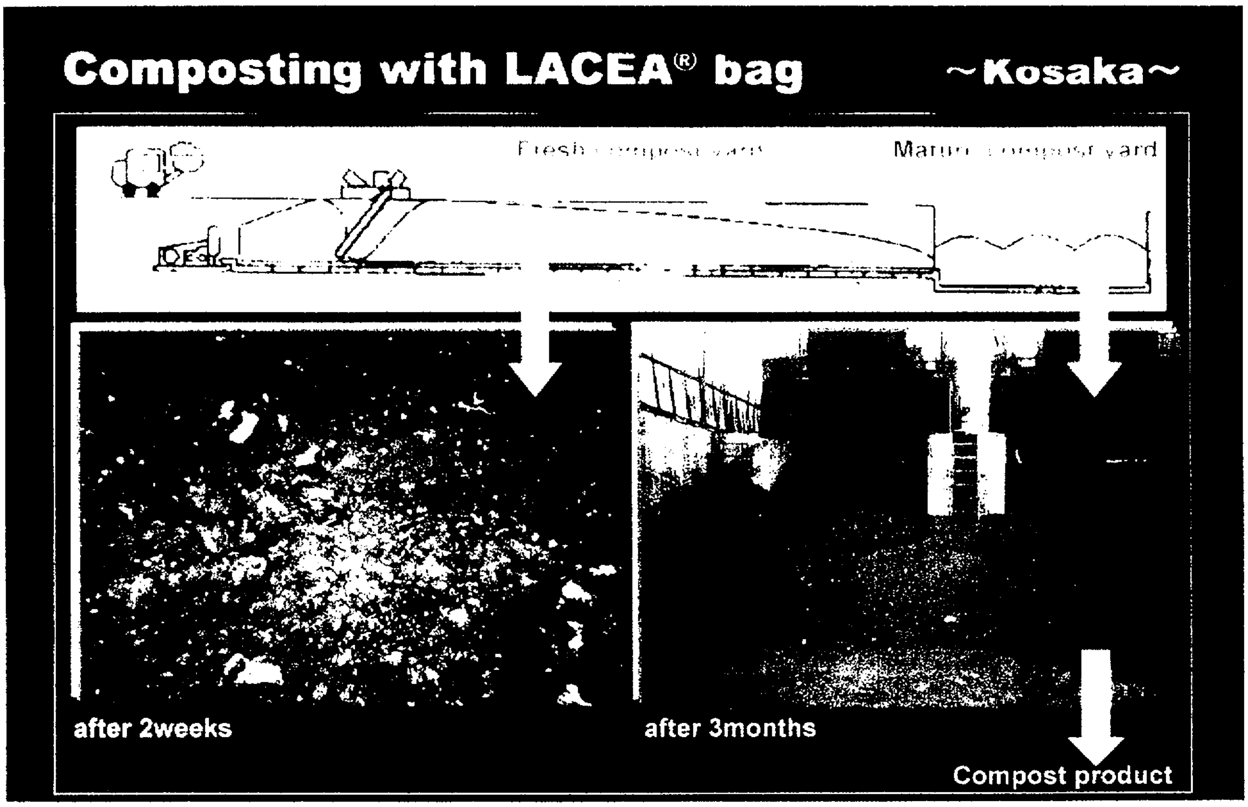
at school



Composting with LACEA® bag ~Kosaka~

throw in

start



Composting with LACEA® bag ~Kosaka~

after 2weeks

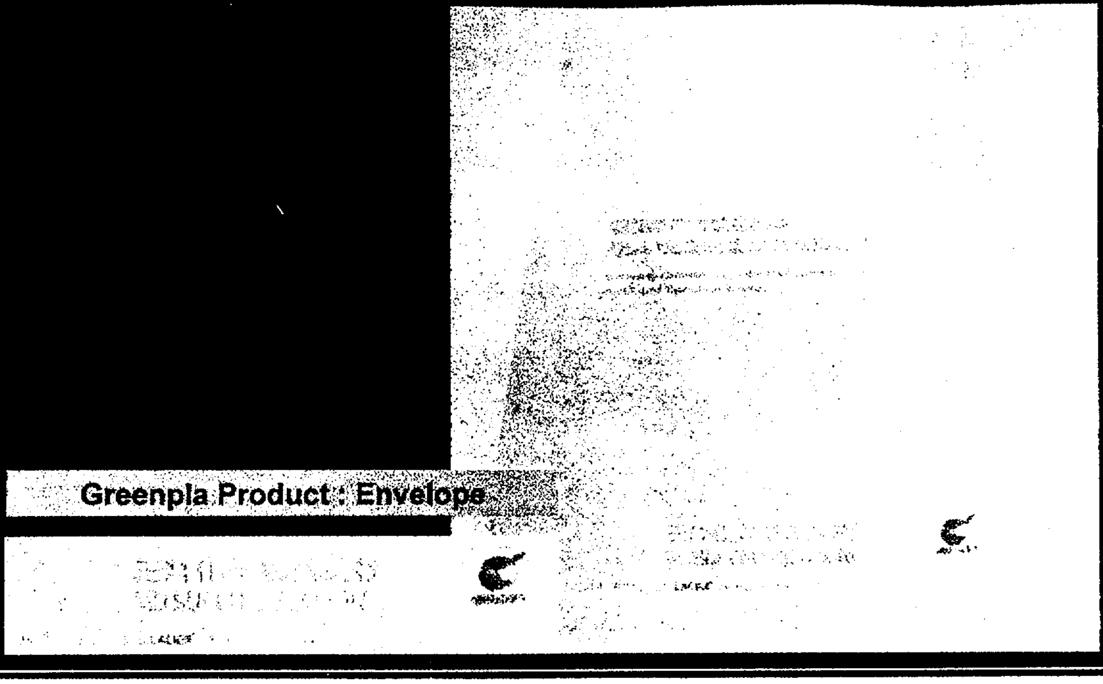
after 3months

Compost product

Organic Cultivation with Compost ~Kosaka~

Applications

~ from nature to nature ~



Greenpla Product : Envelope

Topics
～Japanese Regulations for Sustainable Society ～

- Basic Cyclic-Type Society Creation Promotion Law
  - Waste Disposal and Clean-up Law
  - Recycling Law
  - Food Waste Recycling Law
  - Construction Material Recycling Law
  - Green Purchasing Law
  - Packaging Waste Recycling Law
  - Home Appliance Recycling Law

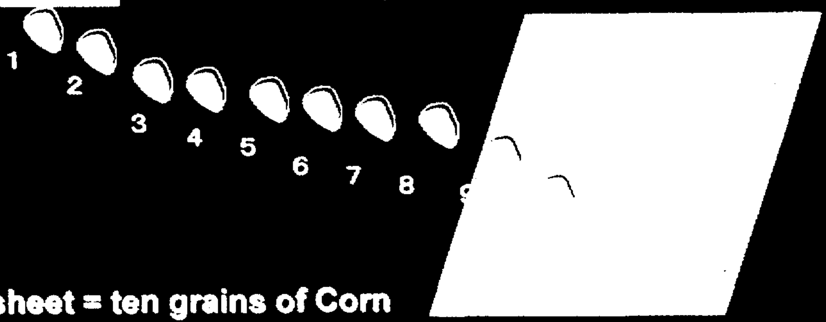
Polylactic Acid from Corn

<theoretical yield>

from Corn to Starch	**: 60%**
from Starch to Lactic acid	**: 85%**
from Lactic acid to PLA	**: 80%**

<weight>

one grain of Corn(dry)	**: ca.0.5g**
one PLA sheet(A4 size, 25 μ m)	**: ca.2g**



one PLA sheet = ten grains of Corn

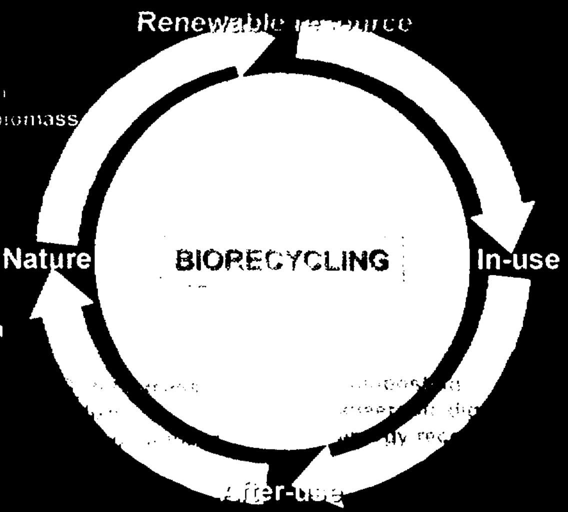
Renewable Resources and Polylactic Acid

Renewable Resources (Plant Resources)	Polylactic Acid (PLA)
10 mil MT (as sugar) worldwide plant resources production	7 mil MT worldwide plastics production

Biorecycling & Polylactic acid

Polylactic acid

- raw material
  Lactic acid derived from
  corn, beets, and other biomass



- PLA oligomer
  Plant growth promotion
- good compostability
  compost quality
  plant compatibility
  (DIN 54900)

Polylactic acid

- high transparency
- safety
  mold resistance
  (ISO FDIS846)
  non-mutagenicity
  (Ames Test)
- hydrolysis
- good biodegradability
  (ISO/CEN/DIN)

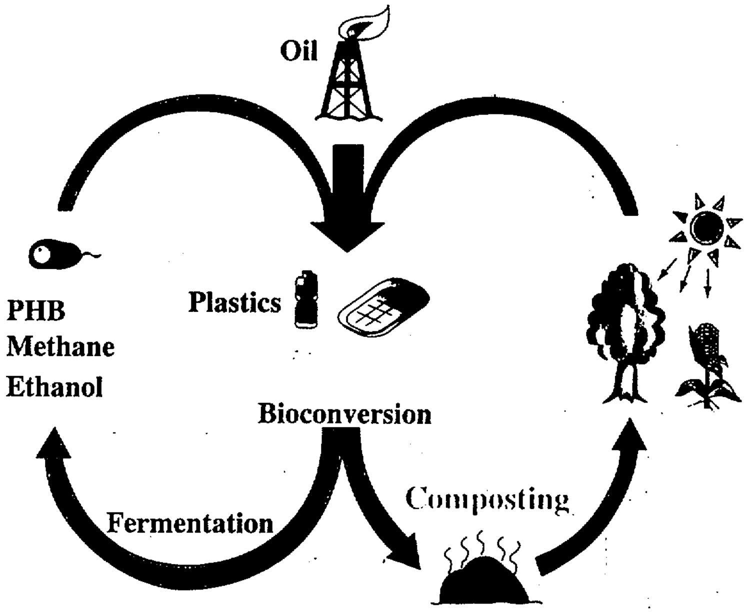
Applications
Agricultural materials
Medical supplies
Sanitary goods
Food packagings etc.

8. Diversity of Polylactide (PLA)-Degrading Microorganisms

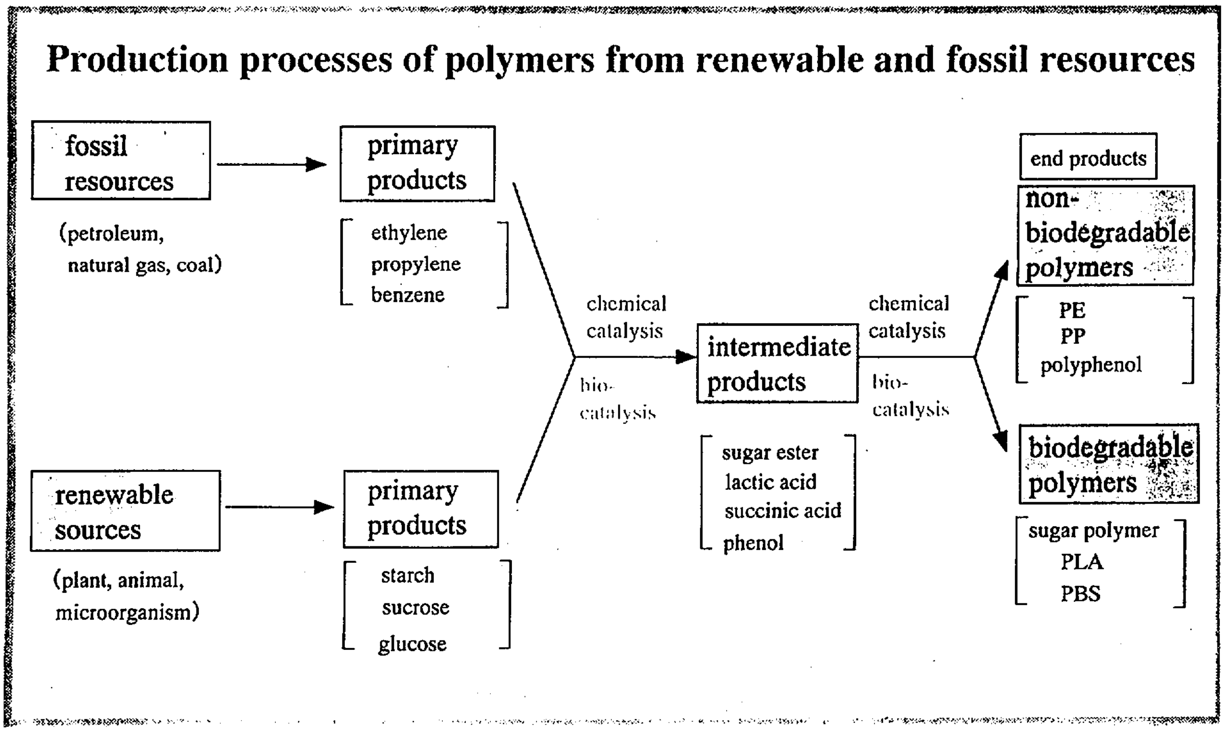
Yutaka Tokiwa, Hardaning Pranamuda, Myra L. Tansengco and Amnat Jarerat
National Institute of Bioscience and Human-Technology, Japan
[E-mail: ytokiwa@nibh.go.jp]

Recently, the price of biodegradable plastics has become rapidly low with increasing volume in their production. In January 2000, Cargill Dow LLC published a plan to build a large plant for PLA (140,000 t/y) by the end of 2001. PLA is polymerized from lactic acid, that can be produced by fermentation with renewable resources such as corn and potato starches. However it has been clear that degradability of PLA in the natural environment is very low compared to other biodegradable plastics, such as polycaprolactone (PCL), poly-3-hydroxybutyrate (PHB) and poly(butylenesuccinate) (PBS). Until now, there are few reports about microbial degradation of PLA.

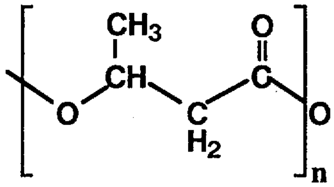
Here, we will talk about the diversity of PLA-degrading microorganisms. By using the clear-zone method on agar plates containing 0.1% emulsified polyesters at 30°C and 50°C, total microorganisms and polyester-degrading microorganisms were counted. It was found that distribution of PLA-degrading microorganisms in soil was very limited. *Amycolatopsis* sp. Strain HT-32 was isolated as a PLA-degrading microorganism. Strain HT-32 degraded about 60% of PLA film in 14 days cultivation at 30°C. Among genus *Amycolatopsis*, *A. orientalis*, *A. mediterranei*, *A. tolypophorus*, *A. alba*, *A. azurea*, *A. coloradenis* and *A. fasidiosa* showed PLA-degrading activities. Other genera of actinomycete also indicated PLA-degrading activities.



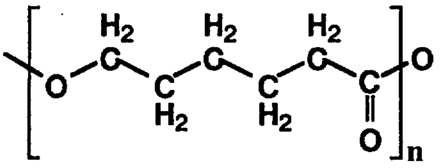
Conceptual scheme of biological recycling for biodegradable plastics


Production processes of polymers from renewable and fossil resources

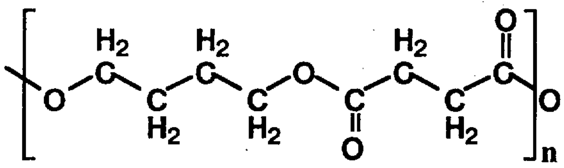
Aliphatic polyester for biodegradable plastic



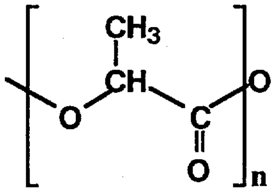
ポリ（β-ヒドロキシ酪酸）
PHB



ポリ（ε-カプロラクトン）
PCL



ポリ（ブチレンサクシネート）
PBS



ポリ乳酸
PLA

at 30°C , 45 samples

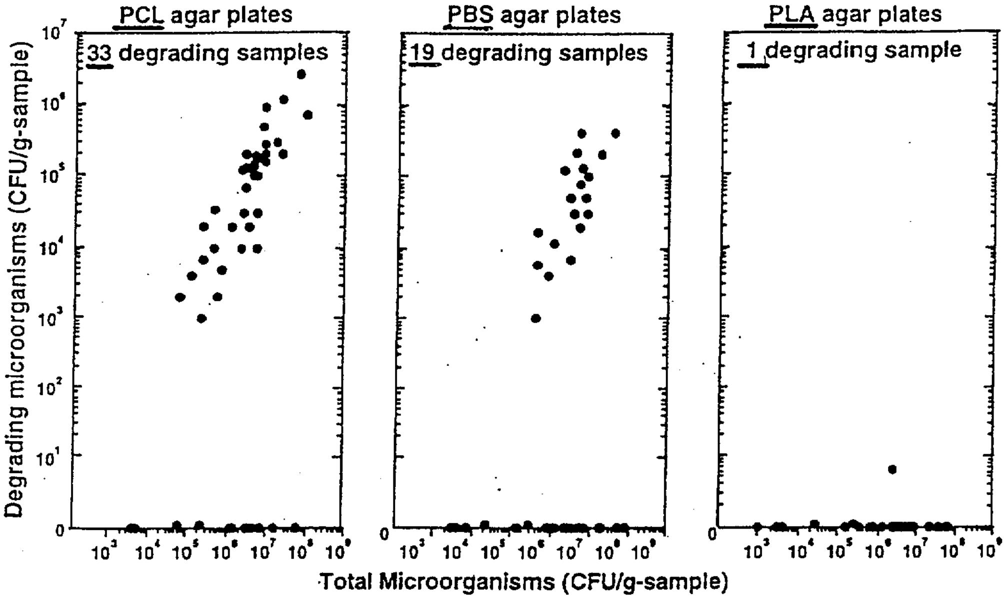
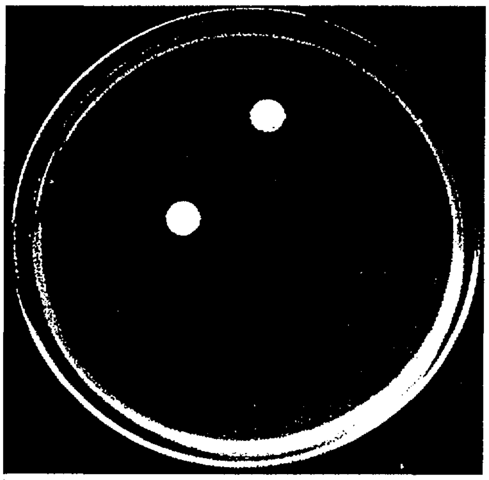


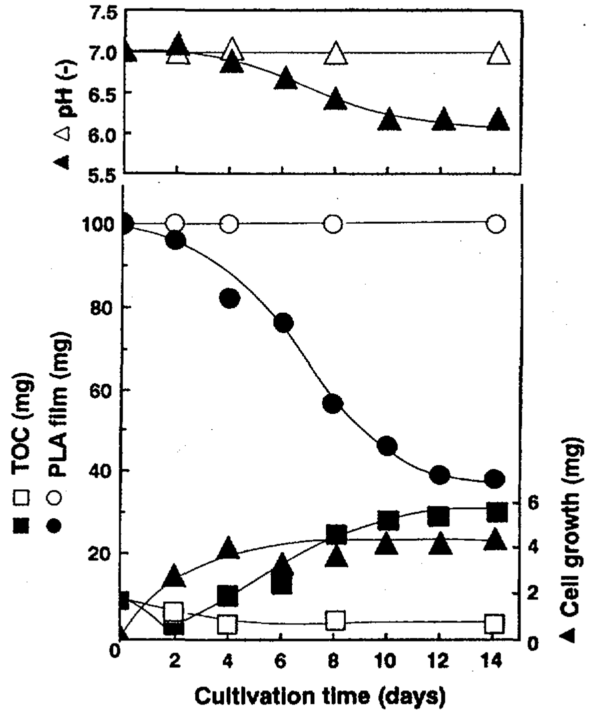
Fig. Relationship between numbers of total microorganisms and of polyester degrading microorganisms.

The state distribution of polyester-degrading microorganisms at 50 ^{o}C in natural environments.

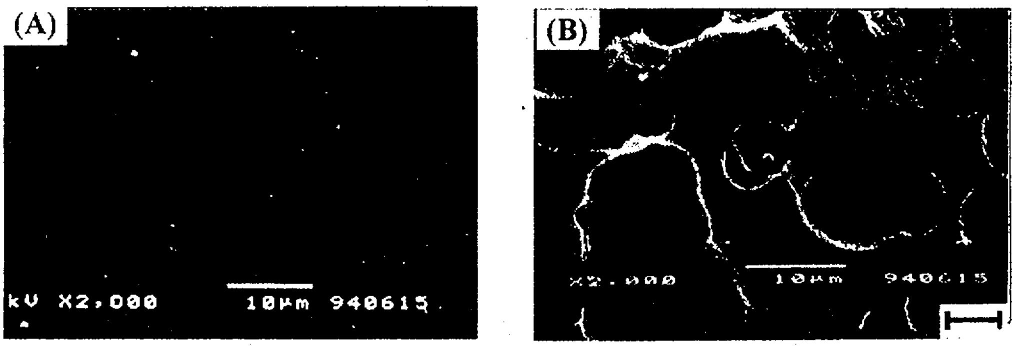
PHB = PCL > PBS > PLA



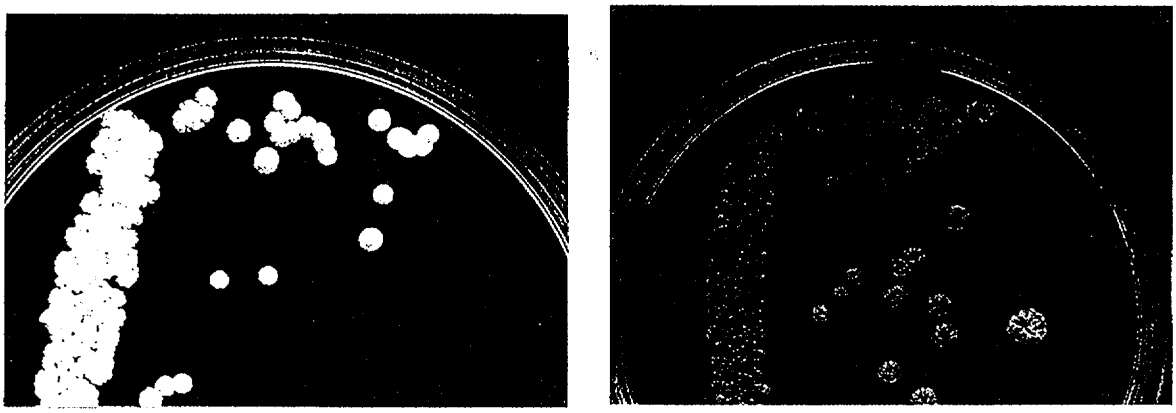
PLA degrader identified as *Amycolatopsis* HT-32



PLA film degradation by strain *Amycolatopsis* HT-32
Open symbols : Control without cell inoculation ;
Close symbols : Control with cell inoculation



Surface structures of PLA film after degradation by strain *Amycolatopsis* HT-32.
(A) : without inoculation ; (B) : with inoculation ; scale bar : 5 µm



PBS Degrader

PLA Degrader

Amycolatopsis HT-6

Amycolatopsis HT-32

Colonies of PBS and PLA degraders on ISP no.2 plates

Composition of basal medium

Polyester	1,000 mg/l
Plysurf A210 G	50 mg/l
$(NH_4)_2SO_4 \cdot 7H_2O$	1,000 mg/l
$MgSO_4 \cdot 7H_2O$	200 mg/l
NaCl	100 mg/l
$CaCl_2 \cdot 2H_2O$	20 mg/l
$FeSO_4 \cdot 7H_2O$	10 mg/l
$Na_2WO_4 \cdot 2H_2O$	0.5 mg/l
$Na_2MoO_4 \cdot 2H_2O$	0.5 mg/l
$MnSO_4$	0.5 mg/l
K_2HPO_4	1,600 mg/l
KH_2PO_4	200 mg/l
Yeast Extract	100 mg/l

***Amycolatopsis* strains**

11 strains from JCM

7 strains from IFO

7 strains from ATCC

Isolate *Amycolatopsis* HT-32 was used for comparison

(1) Clear zone forming ability on polyester-emulsified plates

(2) Liquid culture using PLA film

Clear zone forming ability of *Amycolatopsis* strains on agar plate emulsified with aliphatic polyesters

Strain	PHB	PCL	PBS	PLA
Isolate *Amycolatopsis* HT-32	◉	○○	○	○○
A. orientalis subsp. *orientalis* JCM 3128	⊙⊙⊙	○○	◉	○
A. orientalis subsp. *orientalis* JCM 4235	⊙	○	◉	○
A. orientalis subsp. *orientalis* JCM 4600	⊙	○○	○	○
A. orientalis subsp. *orientalis* IFO 12360	○⊙○	○○○	⊙	○
A. orientalis subsp. *orientalis* IFO 12362	⊙○○	○	○	○
A. orientalis subsp. *orientalis* ATCC 35165	⊙○○	○○	○	○
A. orientalis subsp. *orientalis* ATCC 39444	○	○○	○	○
A. orientalis subsp. *orientalis* ATCC 43333	○	○○	○	○
A. orientalis subsp. *orientalis* ATCC 53550	○	○	○	○
A. orientalis subsp. *lurida* JCM 3141	⊙⊙○	○○	⊙	○
A. mediterranei IFO 14843	⊙⊙⊙	○○	○	○
A. mediterranei JCM 4789	⊙⊙⊙	○	○	○
A. mediterranei ATCC 21271	⊙⊙⊙	○	○	○
A. mediterranei ATCC 27643	⊙⊙	○○	◉◉	○○
A. mediterranei ATCC 31064	⊙⊙	○	○	○
A. tolypophorus IFO 13151	◉◉◉	○○○	◉◉	○
A. tolypophorus IFO 14664	⊙	○	◉	○
A. alba IFO 15602	⊙	○	◉	○
A. azurea JCM 3275	⊙⊙	○	◉	○
A. coloradensis IFO 15804	○	○	○	○
A. fastidiosa JCM 3276	⊙⊙⊙	○○	◉	○
A. methanolica JCM 8087	○	○○○	◉◉	○
A. rugosa JCM 9736	○	○○	◉	○
A. sulphurea JCM 3142	○	○	◉	○
Amycolatopsis sp. JCM 4936	⊙	○	◉	○
	19	25	14	16
	Total strains: 26			

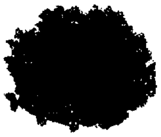
Clear zones were observed after 14 day cultivation at 30°C for 14 days.

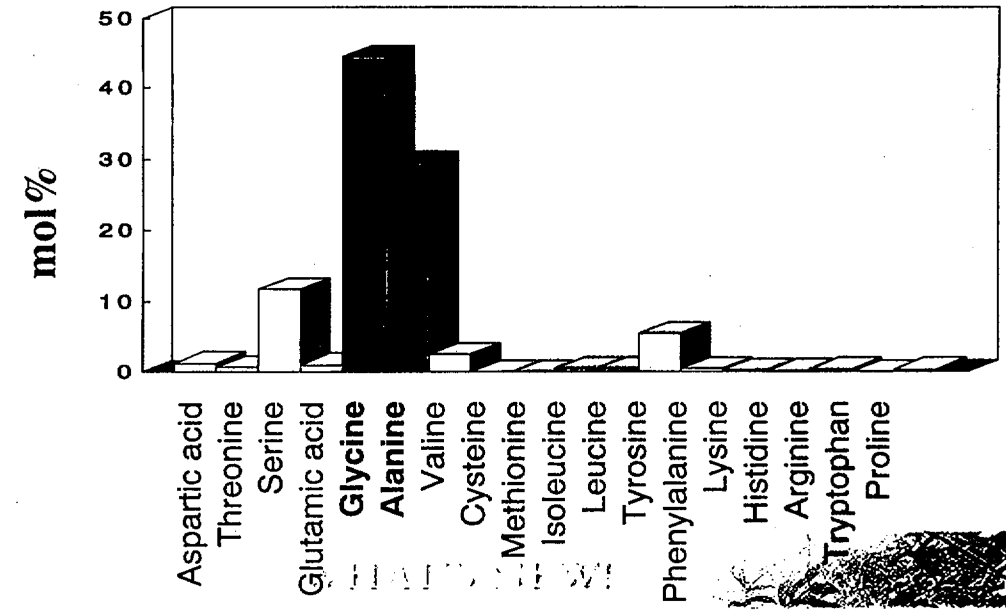
○○○>○○>○ **○ : no clear zone was formed.**

Liquid cultures of *Amycolatopsis* strains using basal medium with emulsified PLA

Strain	TOC (mg/l)	L-lactic acid (mg/l)
Control (no cell inoculation)	50	23
Isolate *Amycolatopsis* HT-32	239	121
Amycolatopsis sp. JCM 4936	83	36
A. orientalis subsp. *orientalis* JCM 3128	59	31
A. orientalis subsp. *orientalis* JCM 4235	78	35
A. orientalis subsp. *orientalis* JCM 4600	91	32
A. orientalis subsp. *orientalis* IFO 12360	88	28
A. orientalis subsp. *orientalis* IFO 12362	102	46
A. orientalis subsp. *orientalis* ATCC 43333	67	6
A. mediterranei JCM 4789	75	10
A. mediterranei ATCC 27643	36	0
A. tolypophorus IFO 14664	87	22
A. alba IFO 15602	50	21
A. azurea JCM 3275	98	28
A. coloradensis IFO 15804	67	24
A. fastidiosa JCM 3276	77	22
A. methanolica JCM 8087	75	15

Amino Acid Composition of Silk Powder





Classification of strain KT-s-9

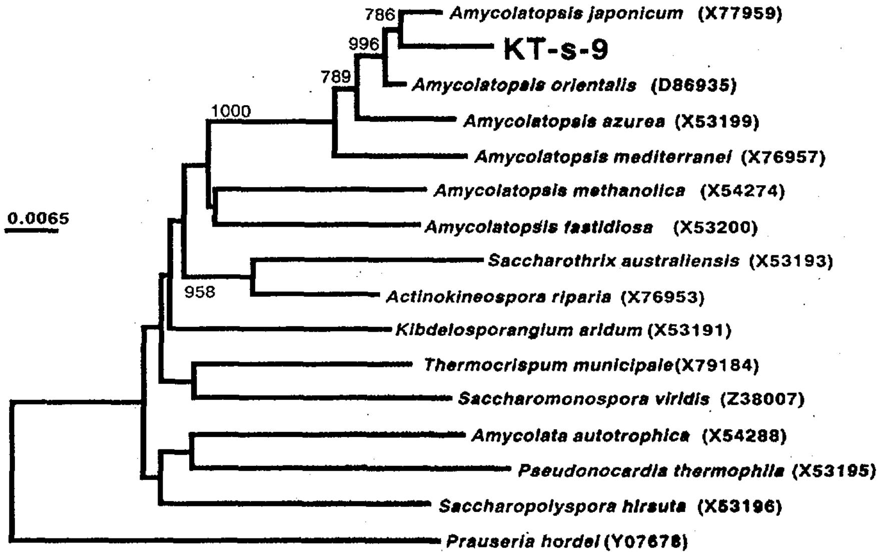
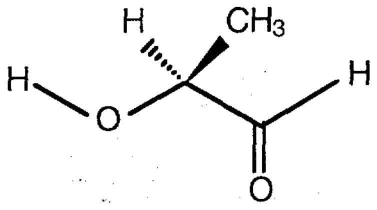


Figure Phylogenetic relationships of Amycolatopsis species and some related
16S rRNA gene sequences. The branching pattern was generated by the

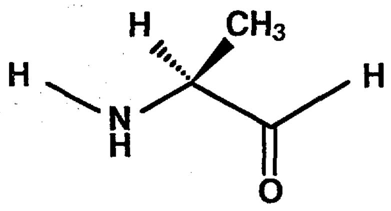
Similarity in chemical structure between L-lactic acid and L-Ala

Poly (L-lactide)
L- lactic acid

Silk Fibroin
(Gly - Ala)$_2$ - Gly - Ser - Gly - (Ala)$_2$ - Gly - [Ser - Gly -(Ala - Gly)$_n$]$_8$ - Tyr



L- lactic acid



L- Alanine

Clear zone forming ability of *Amycolatopsis* strains on PLLA and silk agar plates

Strain	PLA	Silk
Isolate *Amycolatopsis* HT-32	○○	○
A. orientalis subsp. *orientalis* JCM 3128	○	○○
A. orientalis subsp. *orientalis* JCM 4235	○	○
A. orientalis subsp. *orientalis* JCM 4600	○	○
A. orientalis subsp. *orientalis* IFO 12360	○	○○
A. orientalis subsp. *orientalis* IFO 12362	○	○
A. orientalis subsp. *orientalis* ATCC 35165	○	○
A. orientalis subsp. *orientalis* ATCC 39444	○	○
A. orientalis subsp. *orientalis* ATCC 43333	○	○
A. orientalis subsp. *orientalis* ATCC 53550	○	○
A. orientalis subsp. *lurida* JCM 3141	○	○○
A. mediterranei IFO 14843	○	○
A. mediterranei JCM 4789	○	○
A. mediterranei ATCC 21271	○	○
A. mediterranei ATCC 27643	○○	○
A. mediterranei ATCC 31064	○	○
A. tolypophorus IFO 13151	○	○
A. tolypophorus IFO 14664	○	○
A. alba IFO 15602	○	○
A. azurea JCM 3275	○	○○
A. coloradensis IFO 15804	○	○
A. fastidiosa JCM 3276	○	○
A. methanolica JCM 8087	○	○
A. rugosa JCM 9736	○	○
A. sulphurea JCM 3142	○	○
Amycolatopsis sp. JCM 4936	○	○
	16	**13**
	Total strains: 26	

9. High Strength Polylactide by Solid-State Processing

Soo Hyun Kim*, Jung Yul Lim, Soonho Lim, and Young Ha Kim
Biomaterials Research Center, Korea Institute of Science and Technology, Korea
[E-mail: soohkim@kist.re.kr]

Biodegradable polymers such as polylactide (PLLA) can be used as internal fixation devices. They have many advantages over metallic or ceramic implants such as no corrosion, progressive transfer of stresses, and no need for the second removal operation. However, biodegradable polymers have inferior mechanical properties, which make it difficult to be used for the fixation of high strength materials such as femur. In this study, high strength PLLA was produced through vacuum compression molding followed by solid-state extrusion technique [1-4].

PLLA (M_w = 220,000 by GPC) was vacuum compression molded at 200°C for 2 hours, and then cooled at 10°C/min to room temperature or to 80°C and placed at room temperature. Cylindrical and rectangular billets were machined out from molded PLLA to have various diameter and thickness. Solid-state extrusion of rod and plate was performed with a circular die (ϕ = 5 mm) and a rectangular die (4 mm × 1 mm). Extrusion was done at 130°C with drawing rate varied at 40 mm/min - 145 mm/min. Various structural estimations were performed, e. g., DSC, GPC, WAXS, birefringence, and three point flexural test.

Different cooling conditions produced PLLA having crystallinity of 10% and 30%. Dimensions of the extruded PLLA were smaller than those of the dies, which implies that further drawing occurred outside the die exit. Notwithstanding billet morphology, draw ratio, and drawing rate, all the solid-state extruded PLLA had M_v over 190,000, which indicates that the decrease in molecular weight was highly suppressed to be about 10%. With increasing draw ratio, more sharp and resolved PLLA orthorhombic crystalline peaks were obtained in WAXS patterns. DSC thermograms showed that the heat of crystal melting also increased with draw ratio. In addition, solid-state extrusion led to the increase in molecular orientation, and birefringence showed higher values at higher billet crystallinity, draw ratio, and drawing rate. Both flexural modulus and strength increased with increasing billet crystallinity, draw ratio, and drawing rate up to the maximum values of 8.3 GPa and 221 MPa, respectively. Flexural strengths increased with increasing crystallinity and birefringence of solid-state extruded PLLA. A distinct linear correlation between birefringence and flexural modulus was found.

[1] W. T. Mead and R. S. Porter, *J. Polym. Sci., Polym. Symp.*, **63**, 289 (1978).

[2] S. M. Aharoni and J. P. Sibilia, *J. Appl. Polym. Sci.*, **23**, 133 (1979).

[3] T. Shimamoto et al., US patent 5,431,652 (1995).

[4] S. Ferguson, D. Wahl, S. Gogolewski, *J. Biomed. Mater. Res.*, **30**, 543, (1996).

Biodegradable Polymers

- No need for surgical removal
- No foreign-body reaction
- Help to regenerate tissues
- Provide better healing

Main Biomedical Application

- Wound management
    - Absorbable suture
    - Surgical mesh
    - Clips
    - Staples
    - Bioadhesive
- Orthopedics repair products
    - Joint prostheses technology
    - Tendon implant materials
    - Bone trauma fixation
        - Plates, Screws, Pins, Rods
    - Cartilage material
- Polymeric drug and drug delivery systems
- Tissue engineering

Properties of Biodegradable Polymers

Specimen	Modulus (kpsi)	Strength (kpsi)	Degradation time (month)
Poly(glycolide)	483	11.2	2-4
Poly(L-lactide)	314	8.5	18-24
Poly(D,L-lactide)	313	6.6	12-16
Poly(D,L-lactide-glycolide, 85:15)	324	6.3	10
Poly(D,L-lactide-glycolide, 50:50)	349	7.7	2
Poly(D,L-lactide-caprolactone)			2

Introduction

Internal Fixation of Bone Fracture

- **Hard tissue replacements**
  - Bone repair
  - Joint replacement
  - Dental implant

- **Bone repair**
  - External fracture fixation
  - Internal fracture fixation

- Internal fracture fixation devices should meet the general requirements of biomaterials, that is, ***biocompatibility***, ***sufficient strength within dimensional constraints***, ***corrosion resistance***, and ***a suitable mechanical environment for fracture healing.***
  - → Stainless steel, CoCr alloys, and Ti alloys are suitable.
    However, these internal fixation devices causes discomfort and requires removal.
  - → ***Biodegradable polymers***, e. g., poly (L-lactic acid) (PLLA) and poly (glycolic acid) (PGA), have been used for minimally loaded fractures.

Metals and Ceramics

▣ **Metallic fixation devices**

- They prevents the periosteal callus formation and deprives the bone the normal stress pattern due to the large difference in stiffness (bone: 1-30 GPa, metal: 100-200 GPa): ***Long-term stress-protection*** → ***Mechanically inferior bone structure*** (***bone atrophy***) → *Refracture*
- ***Corrosion*** of metals releases foreign ions or particles → Short-term complication (Inflammation or infection) and unknown long-term effects
- ***Removal*** of metallic implants after healing is thus recommended.

▣ **Ceramic fixation devices**

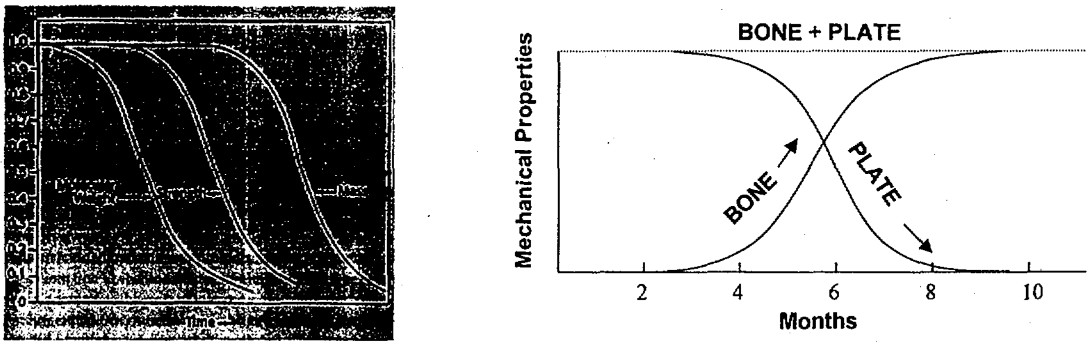
- Corrosion problems can be avoided with Al_2O_3.
- However, such ceramics are still rigid. (up to 400 GPa Young's modulus)

Biodegradable Polymeric Internal Fixation Devices

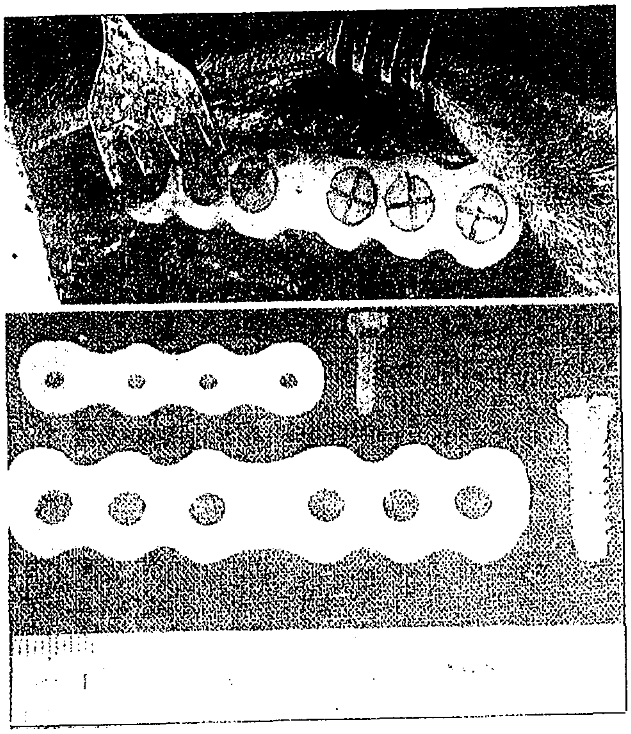
▣ **Characteristics**

- Good *biocompatibility*
- *No corrosion* problems
- Absorbable to *ensure progressive transfer of stresses to healing bone*
- Absorbable to *obviate the second removal operation*
- *Safe reduction of the fracture*

Biodegradable Polymeric Internal Fixation Devices

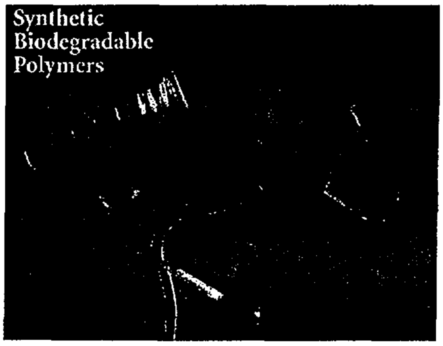


Time dependence of mechanical property
required for bioabsorbable bone plate



Biodegradable Polymeric Internal Fixation Devices

- **Currently Used Polymeric Implants**
  - PLLA, PGA, and their copolymers
  - *Insufficient stiffness* for bone plates for long bones like femur
  - *Found applications for lower strength materials*, e. g., interference screws and rods in the ankle, knee, and hand; tacks and pins for meniscal repair and ligament attachment; suture anchors; craniomaxillofacial repair



Partially Absorbable Composites

- **Partially absorbable composites = *Absorbable matrix* + (*non-absorbable*) *Reinforcements***

  e. g., Polylactide matrix + Carbon fibers (plates, rods, ligaments, tendons, and scaffolds),
  Glycolide/lactide copolymer rod + Carbon fibers,
  Poly-DL-lactide plate + Carbon and ceramic fibers.

- Reinforced polymeric composites can fulfill the high mechanical demands of safe bone fracture fixation materials.

  Disadvantages:
  - The long-term effects of biostable or slowly eroding fibers in living tissues are not known.
  - Poor adhesion between matrix and reinforcement leads to rapid strength loss.
    + Adhesion promoters (silanes and titanates) are usually highly toxic.

Totally Absorbable Composites

- **Totally absorbable composites = *Absorbable matrix* + *Absorbable Reinforcements***
  e. g., PLLA matrix + Absorbable ceramic fibers (calcium phosphate fibers),
  PLLA matrix + PGA fibers.

- Totally absorbable reinforced composites are satisfactory because of the safe bone fracture fixation and no long-term problems.
  Disadvantage:
  - It is also difficult to obtain good adhesion between matrix and reinforcement.

Self-Reinforced (SR) Absorbable Composites

- **Self-reinforced absorbable composites**
  - Reinforcing elements and the matrix have ***the same chemical element composition***.
  - Reinforcing elements: microfibrils, macrofibrils, fibers, extended chain crystals, etc.
  - Good adhesion between the matrix and reinforcement (No special adhesion promotes)
  - Excellent mechanical properties
  - Various applications including craniomaxillofacial repair (Biosorb, Bionx, Inc.)

- **Methods for self-reinforced absorbable composites**
  - ***Sintering of fibrous materials*** or the mixture of fibrous and powdered material into a solid object at elevated temperature and pressure.
  - Reinforcements and polymer melt are mixed and cooled rapidly before reinforcements lose their orientation.

Biodegradable Polymeric Internal Fixation Devices

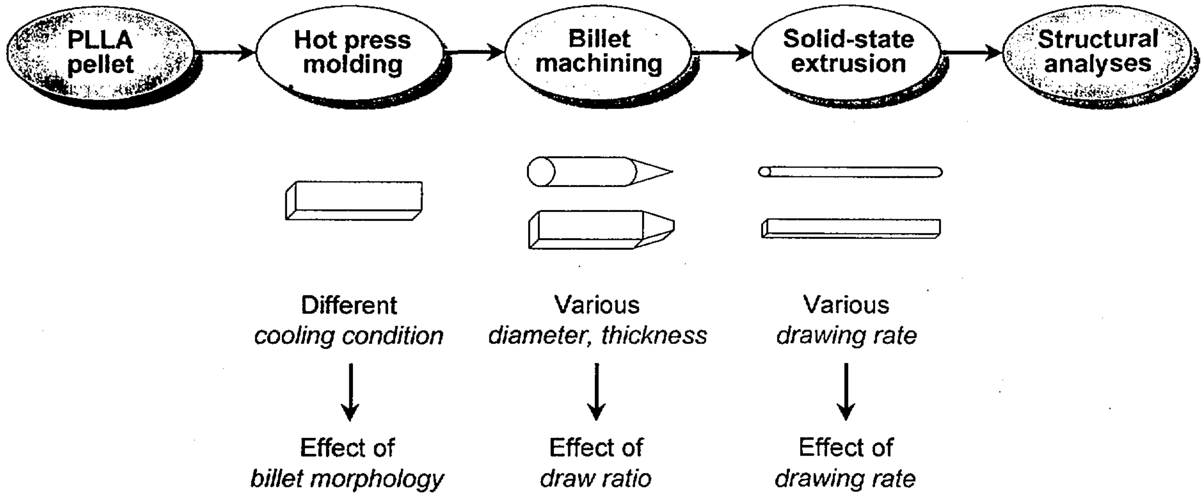
Objectives of this Study

- Production of *PLLA rods, screws, plates* by *solid-state processing*
- *Enhancement of mechanical properties* of PLLA
- *Minimization of molecular degradation* during processing
- Investigation of effects of molecular *orientation* and *crystallinity* on the flexural strength of PLLA

Solid-State Processing

- *Solid-state extrusion between T_g and T_m*
- Production of PLLA rods and plates through *circular and rectangular dies*

Procedure



PLLA pellet → Hot press molding → Billet machining → Solid-state extrusion → Structural analyses

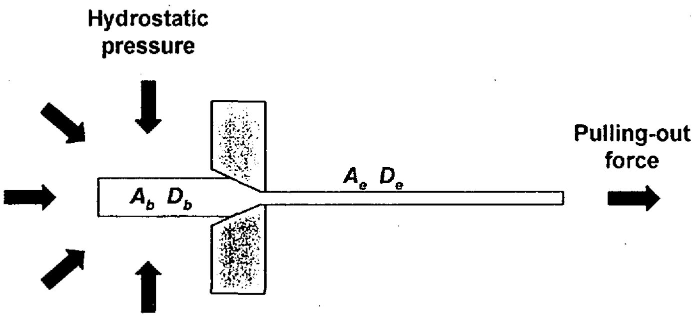
Different *cooling condition* ↓ Effect of *billet morphology*

Various *diameter, thickness* ↓ Effect of *draw ratio*

Various *drawing rate* ↓ Effect of *drawing rate*

Introduction

Solid-State Extrusion



$$\text{Draw ratio} = \frac{D_b^2}{D_e^2} \quad \text{(Circular die)} \qquad \text{Draw ratio} = \frac{A_b}{A_e} \quad \text{(Rectangular die)}$$

Where D_b: diameter of the billet
D_e: diameter of the extruded rod

Where A_b: area of the billet
A_e: area of the extruded plate

Figure 1. Schematic representation of solid-state extrusion.

Results and Discussion

Draw Ratio and Molecular Weight

Table 1. Draw ratios and molecular weights of extruded rods.

Sample	Billet diameter (mm)	Drawing rate (mm/min)	Diameter of extruded rod (mm)	Draw ratio	M_w
Control					220,000
Molded					210,000
10	11.5	40	4.84	5.6	209,000
	12.0	40	4.75	6.4	208,000
	12.5	40	4.73	7.0	206,000
	13.0	40	4.70	7.7	205,000
		75	4.55	8.2	204,000
		110	4.40	8.7	203,000
		145	4.30	9.1	201,000
	13.5	40	4.55	8.8	200,000
30	11.5	40	4.84	5.6	205,000
	12.0	40	4.75	6.4	203,000
	12.5	40	4.73	7.0	202,000
	13.0	40	4.70	7.7	200,000
	13.5	40	4.55	8.8	196,000

Wide Angle X-Ray Scattering (WAXS)

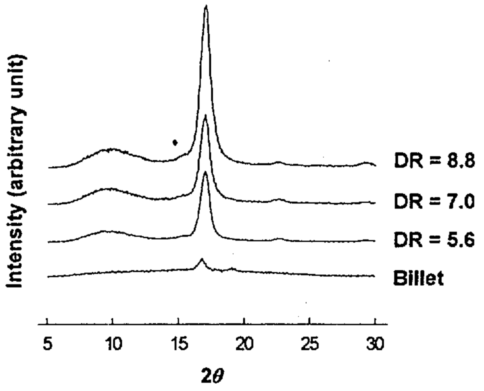


Figure 10. Equatorial WAXS diffractograms of PLLA billet (crystallinity = 30%) and solid-state extruded rods (DR = draw ratio).

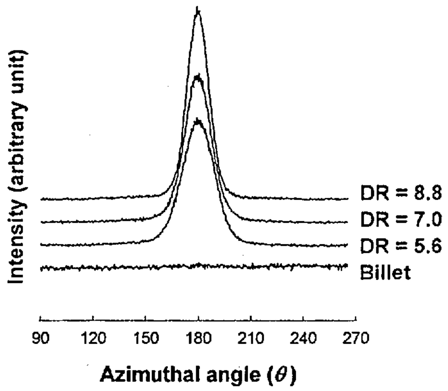


Figure 11. Azimuthal WAXS diffractograms of PLLA billet (crystallinity = 30%) and solid-state extruded rods (DR = draw ratio).

Thermal Analysis (DSC)

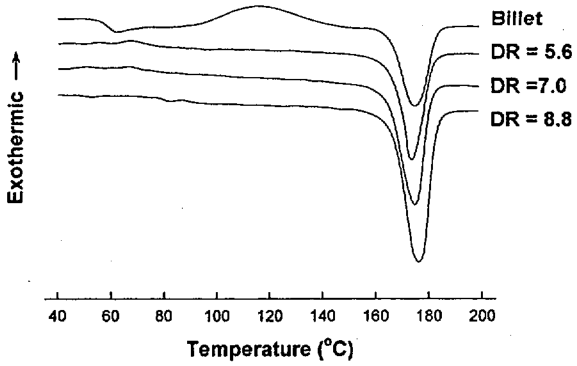


Figure 12. DSC thermograms of PLLA billet (crystallinity = 30%) and solid-state extruded rods (DR = draw ratio).

Flexural Stress-Strain Curves

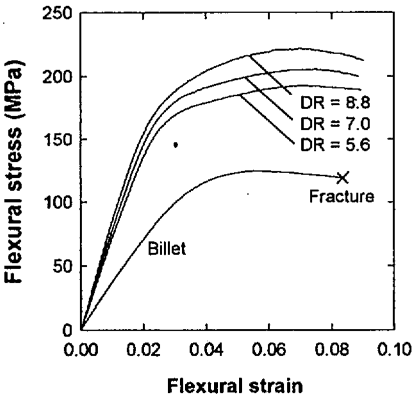


Figure 13. Flexural stress-strain curves of solid-state extruded PLLA rods (DR: draw ratio).

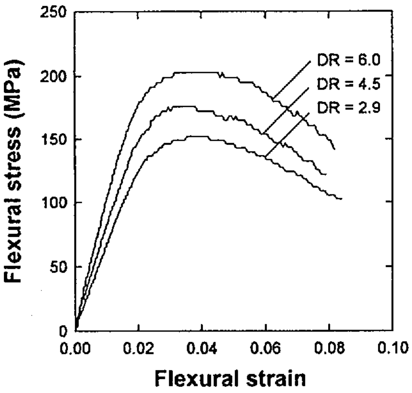


Figure 14. Flexural stress-strain curves of solid-state extruded PLLA plates (DR: draw ratio).

Enhancement of Mechanical Properties

Table 5. Mechanical properties of PLLA rods before and after solid-state extrusion

Specimen	M_w	σ (MPa)	E(GPa)
Control	220,000		
Melt extruded (vacuum)	210,000	105	2.6
Hot press molded	~ 210,000	106	3.5
Solid-state extruded	~ 200,000	221	8.4

σ: flexural strength; E:flexural modulus

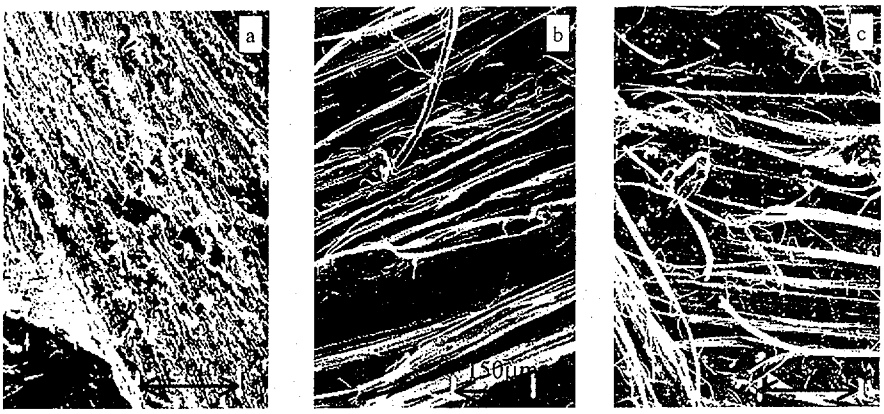


Fig. SEM of the split surface of PLLA before (a) and after (b) 1.33 cm/min, c) 3.46 cm/min) solid-state extrusion at 130 °C

Results and Discussion

Solid-State Extruded Rods and Plates

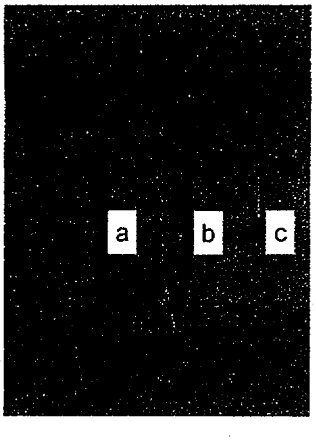


Figure 4. Cylindrical billets (a, b) and solid-state extruded PLLA rod (c).

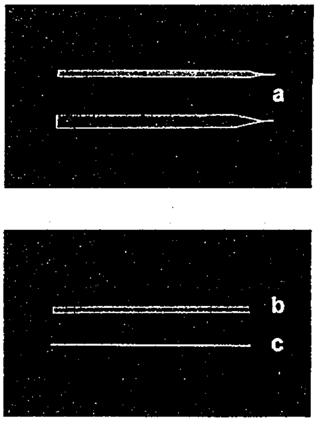


Figure 5. Rectangular billets (a) and solid-state extruded PLLA plates (b: top view; c: side view).

Products from Rods

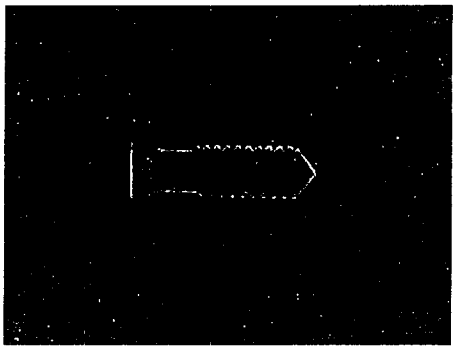


Figure 19. Screw machined out from the solid-state extruded PLLA rod.

Products from Plates

Figure 20. Simple bending motion to produce a bended plate from the solid-state extruded PLLA plate.

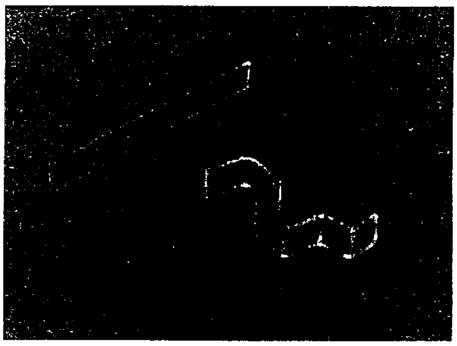


Figure 21. Solid-state extruded PLLA plate and bended plate form it.

Products from Rods and Plates

Figure 8. Stent form rounded from the solid-state extruded PLLA plate.

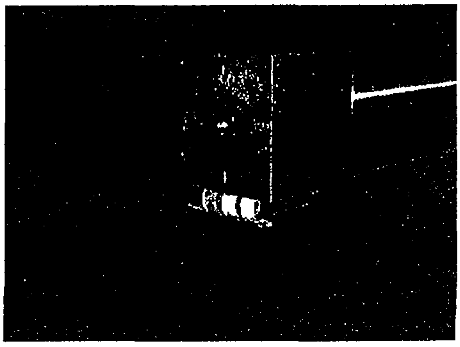


Figure 9. Stent form of solid-state extruded PLLA plate under heavy weight.

High Strength Polylactide by Solid-State Processing

☐ Solid-state Extrusion

- Maximum extrudable draw ratio: 9.1 (circular die) and 5.9 (rectangular die)
- Decrease in molecular weight < *10%*
- Circular die: max. *flexural modulus of 8.4 GPa*; *flexural strength* of *221 MPa*
- Rect. die: max. *flexural modulus of 9.7 GPa*; *flexural strength* of *202 MPa*

☐ Effects of extrusion condition

- With increasing *draw ratio*,

crystallinity, *apparent crystal size*, and *birefringence* increase.

→ *Flexural modulus* and *flexural strength* increase.

Session 2; Microbial Polyesters (PHB)

10. Structure and Enzymatic Degradation of PHA Crystals

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In the last quarter of this century, plastic products have gained universal use not only in food, clothing and shelter, but in the transportation, construction, medical and leisure industries as well. Synthetic plastics were developed as durable substitute product. Recently, there is a growing demand for biodegradable plastics as a solution to problems concerning the global environment and the solid waste management. The research on biodegradable plastics and polymers has been carried out worldwide with the aim of achieving a harmony between human activities and natural environment.

Microbial polyesters attract industrial attention for use as environmentally degradable thermoplastics in a wide range of agricultural, marine and medical application. A wide variety of microorganisms synthesize an optically active polymer of R(-)-3-hydroxyburyric acid in the form of granules with diameters in 0.3–1.0 μm range and accumulate the biopolymer amounting to 80% of their cellular dry weight. Several new types of copolyesters have been found in our laboratory to be produced by some bacteria from renewable carbon sources such as sugars, plant oils and alkanoic acids. The microbial polyesters are thermoplastics with biodegradable and biocompatible properties. Their physical properties can be regulated by varying the copolymer composition. This may make possible to get a wide variety of materials from hard crystalline plastics to elastic rubber.

Aeromonas caviae, for example, produces a random copolymer of 3-hydroxybutyric acid (3HB) and 3-hydroxyhexanoic acid (3HH) under aerobic conditions when sodium salts of alkanoic acids of even carbon numbers ranging from C12 to C18 or plant oil are fed as the sole carbon source. The weight-average molecular weights of P(3HB-*co*-3HH) were in the range (2-11)×10Da. The structure and physical properties of P(3HB-*co*-3HH) with compositions of 5-25 mol% 3HH were characterized by ^{1}H and ^{13}C NMR spectroscopy, X-ray diffraction, differential scanning calorimetry, mechanical tensile measurement, and optical microscopy. The degree of X-ray crystallinity of solvent-cast P(3HB-*co*-3HH) films decreased from 60 to 18% as the 3HH fraction was increased from 0 to 25 mol% suggesting that 3HH units are excluded from the P(3HB) crystalline phase. The rates of enzymatic erosion increased markedly with an increase in the 3HH fraction to reach a maximum value at 15mol% 3HH, followed by a decreased in the erosion rate.

A fragment of *A. caviae* PHA synthase structural gene (*phaC*$_{AC}$) was amplified by PCR with primers designed from the highly conserved regions among known PHA synthases. A cosmid library of *A. caviae* gDNA was screened by colony hybridization with the PCR-amplified fragment as a probe, and several positive clones were isolated. The *phaC*$_{AC}$ was mapped on a 11-kbp Sal1 fragment and a nucleotide sequence of 5.0-kbp EcoRV-EcoRI fragment was determined. The *phaC*$_{AC}$(1782bp) encoded a protein composed of 594 amino acids with a molecular weight of 66,334 Da.

The ability of *Alcaligenes eutrophus* was evaluated to grow and produce polyhydroxyalkanoates (PHA) on plant oils. When olive oil, corn oil, or palm oil was fed as a sole carbon source, the wild-type strain of *A. eutrophus* was well grown and accumulated poly(3-hydroxybutyrate) (PHB) during its stationary growth phase. In addition, a recombinant strain of *A. ertrophus* PHB-4 (a PHA-negative mutant) harboring a PHA synthase gene from *Aeromonas caviae* was revealed to produce a random copolyester of 3-hydroxybutyrate and 3-hydroxyhexanoate from these plant oils with a high cellular content (approximately 80wt%). The mole fraction of 3-hydroxyhexanoate unit was 4-5 mol% independently of the structure of triglycerides fed. The results demonstrate that renewable and inexpensive plant oils are excellent carbon sources for efficient production of PHA copolymers using recombinant *A. eutrophus* strains.

Ultra-high-molecular-weight PHB was produced from glucose by a recombinant *Escherichaia coli* XL-1 Blue (pSYL 105) harboring *A. eutrophus* PHB biosynthesis *phb*CAB genes. Six kinds of PHB samples with different weight-average molecular weight (*M*w) from 1.1×10^6 to 11×10^6 were respectively produced at pH values of 7.0 to 6.0 in culture media. Solvent-cast PHB films of high-molecular weights over *M*w of 3.3×10^6 were stretched easily and reproducibly at 160°C to a draw ratio of 400-650%. Mechanical properties of the stretched PHB films were markedly improved relative to those of solvent-cast film. The elongation to break, Young's modulus, and tensile strength of stretched films (Mw=11×10^6) were 58%, 1.1 GPa, and 62 MPa, respectively. X-ray diffraction patterns indicated that the stretched film was highly oriented and had a high crystallinity over 80%.

Structure and Enzymatic Degradation of PHA Crystals

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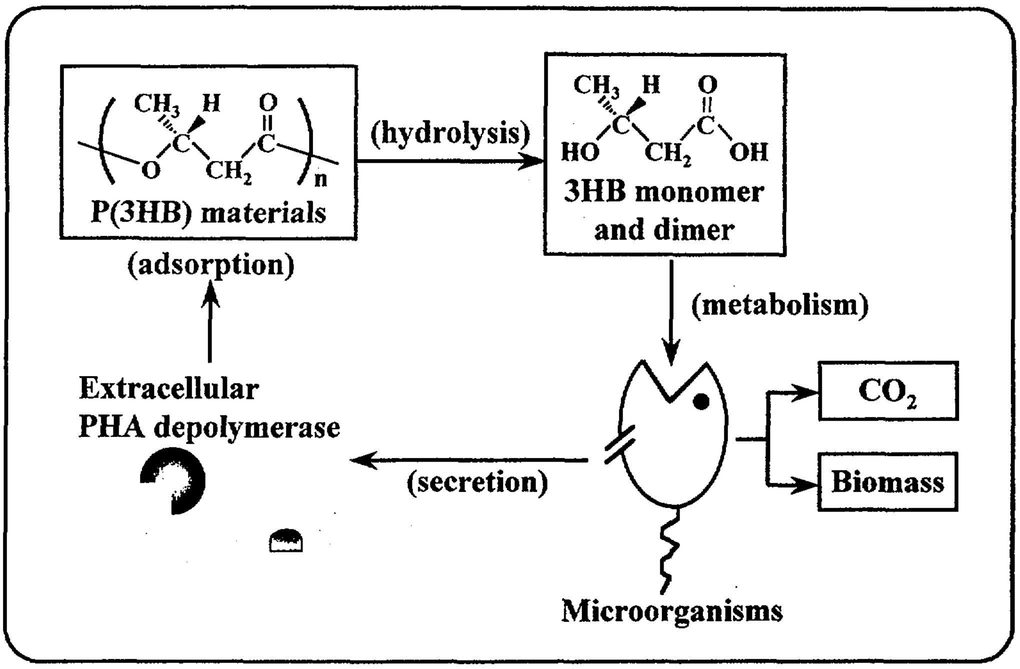
Polymer Chemistry Lab., RIKEN Institute

1. **Biodegradation of PHA Materials**
2. **Structure and Enzymatic Hydrolysis of PHA Single Crystals**
3. **Crystal Growth and Enzymatic Hydrolysis of PHA Thin Films**
4. **Material Design of PHA Materials**

RIKEN

1. Biodegradation of PHA Materials



P(3HB) materials

(hydrolysis)

3HB monomer and dimer

(adsorption)

(metabolism)

Extracellular PHA depolymerase

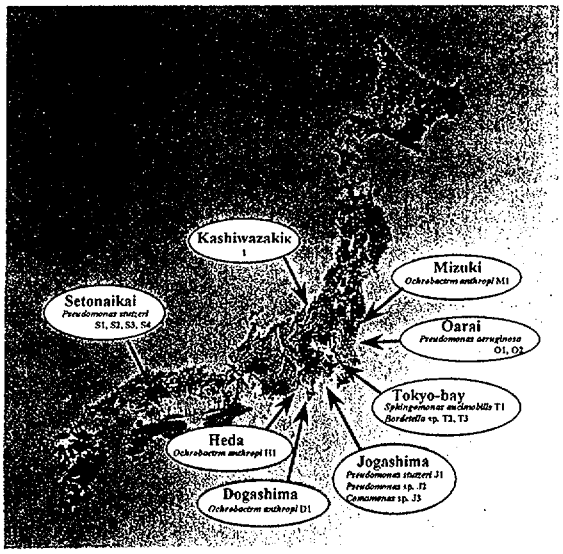
(secretion)

CO_2

Biomass

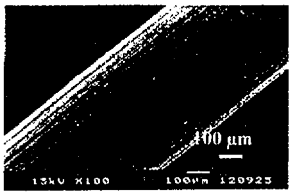
Microorganisms

P(3HB)-degrading Microorganisms Isolated from Different Seawater



Morphology of Monofilament during Biodegradation

0 day



21 days

P(3HB)-degrading Bacteria and Their Extracellular PHA Depolymerases

Bacterium	Source	Properties of PHA depolymerase			Reference
		Mol. mass	pI	Optimum pH	
Comamonas testosteroni	Seawater	50,000	8.4	10.0	Mukai *et al.*, 1993
Pseudomonas stutzeri	Seawater	60,000	7.3	7.5	Mukai *et al.*, 1993
Comamonas acidovorans	Freshwater	50,000	N.d.	9.0	Mukai *et al.*, 1994
Pseudomonas stutzeri	Freshwater	48,000	9.4	9.5	Mukai *et al.*, 1994
Comamonas testosteroni	Soil	49,000	9.2	8.5	Kasuya *et al.*, 1994
Pseudomonas pickettii	Soil	40,000	7.7	5.5	Yamada *et al.*, 1993

Molecular Characterization of PHA Depolymerases

Type A

Pseudomonas stutzeri
(Ohura, Kasuya & Doi, 1998)

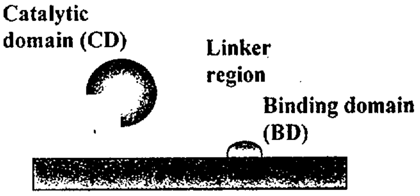
Type B

Comamonas acidovorans
(Kasuya *et al.*, 1997)

Comamonas teststeroni
(Kasuya *et al.*, 1997)

■ **Catalytic domain** □ **Linker region** ■ **Binding domain** ■ **Lipase box**
(Gly-Xaa-Ser-Xaa-Gly)

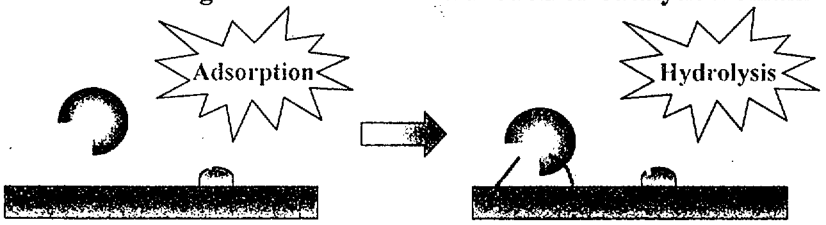
Properties of PHA Depolymerase



CD : 270-400 aa
Linker : 50-100 aa
BD : 35-55 aa
(L(BD)=3-4 nm)

Molecular Characterization of PHA Depolymerases

Function of Binding Domain **Function of Catalytic Domain**



Adsorption of PHA Depolymerase

① Adsorption is partially reversible.

② BD is specific for the adsorption to polyester.

③ BD binds to the whole surface of P(3HB) by a cross-area of 15 nm^2 per one BD molecule.

④ BD works independently of CD.

Hydrolysis Mechanism

① The hydrolysis rate of ester bonds in soluble 3HB oligomers over trimer is much faster than that of dimer.

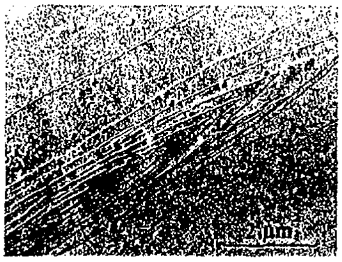
② The rate of P(3HB) hydrolysis in amorphous state is much faster than that in crystalline state.

③ Endo-exo processive hydrolysis of a P(3HB) chain takes place at the edges of P(3HB) crystals.

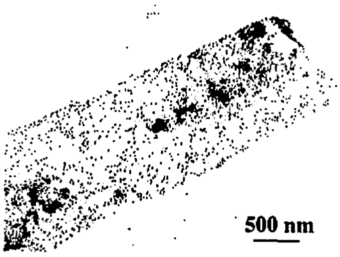
④ CD has the hydrolysis activity independently of BD.

⑤ The hydrolysis of P(3HB) by CD is often inhibited by a dense adsorption of BD on the surface of P(3HB).

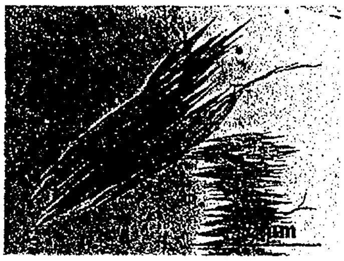
2. Structure and Enzymatic Hydrolysis of PHA Single Crystals



P(3HB) Single Crystals

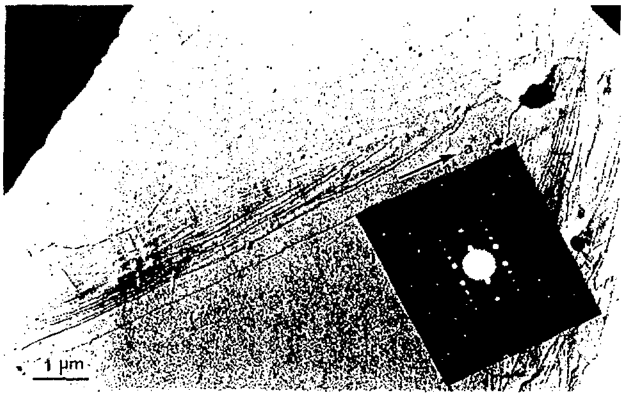


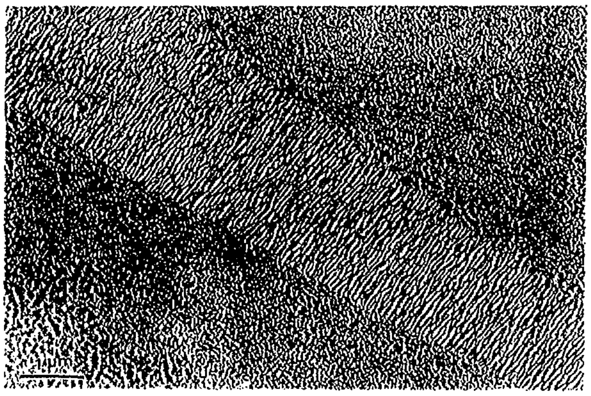
Adsorption of Enzyme
(Immuno-gold labeling)

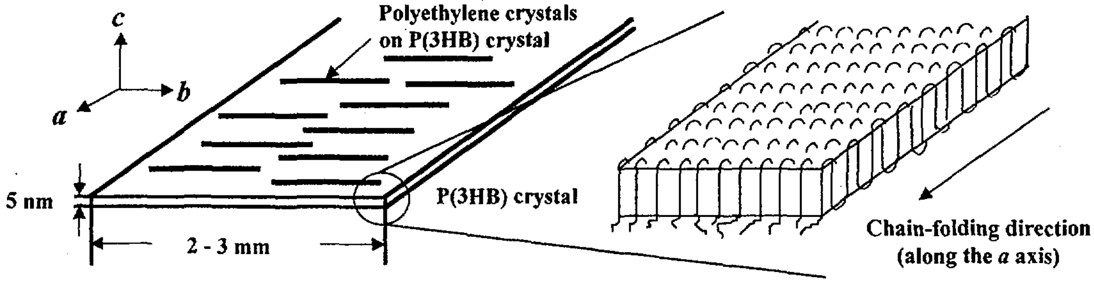


Degradation by Enzyme

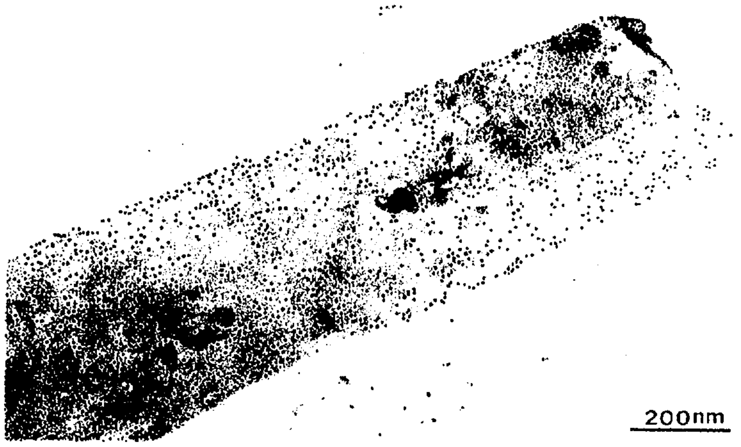
Structure of Poly([*R*]-3-hydroxybutyrate) Single Crystal

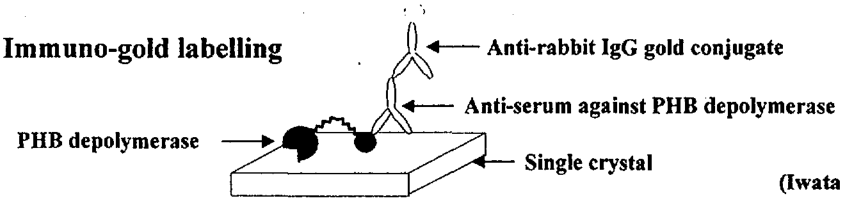






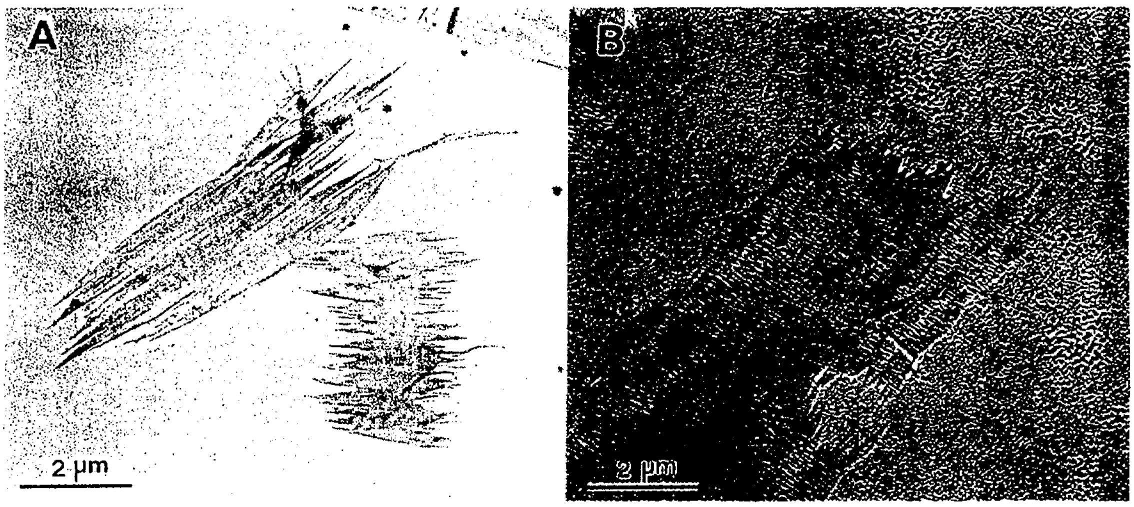
Adsorption of PHB Depolymerase on P(3HB) Single Crystal




Immuno-gold labelling

(Iwata *et al.*, 1997)

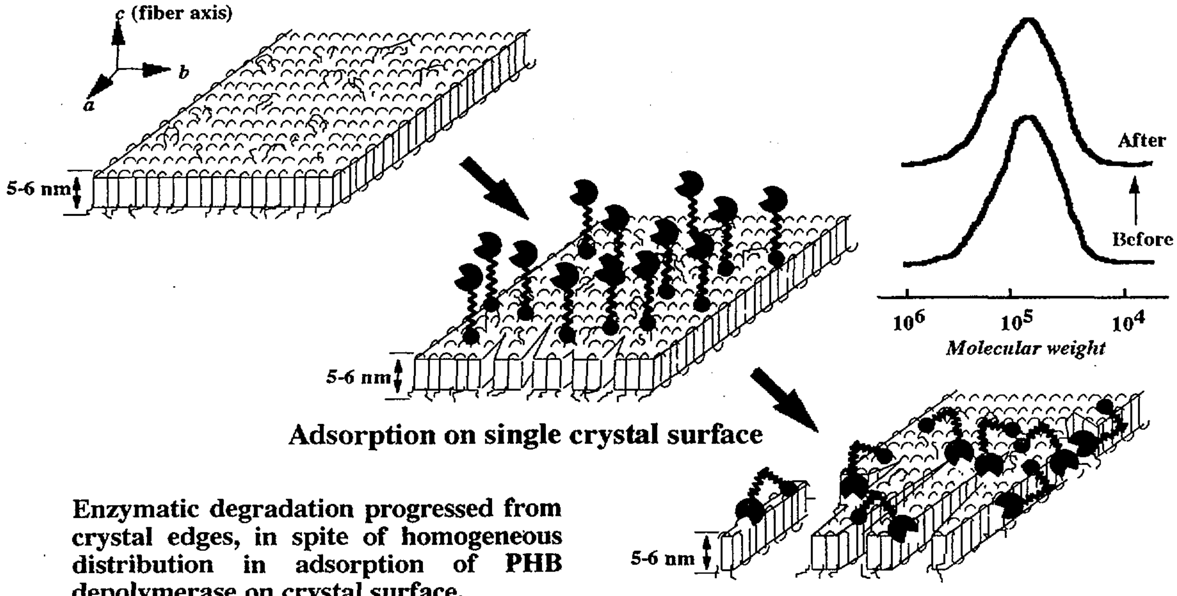
P(3HB) Single Crystals after Enzymatic Degradation



(A) shadowed with a Pt-Pd alloy and (B) decorated with polyethylene

(Iwata *et al.*, 1997, 2000)

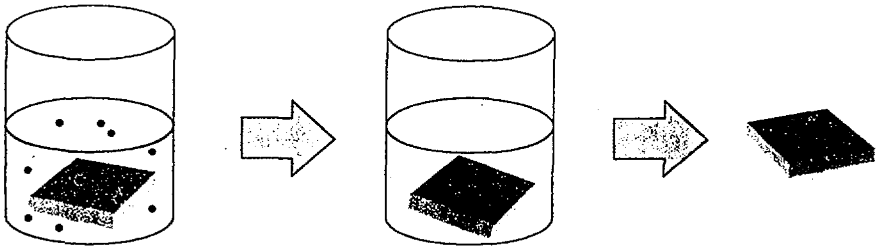
Schematic Model of Enzymatic Degradation of P(3HB) Single Crystal



Enzymatic degradation progressed from crystal edges, in spite of homogeneous distribution in adsorption of PHB depolymerase on crystal surface.

(Iwata *et al.*, 1997, 1998)

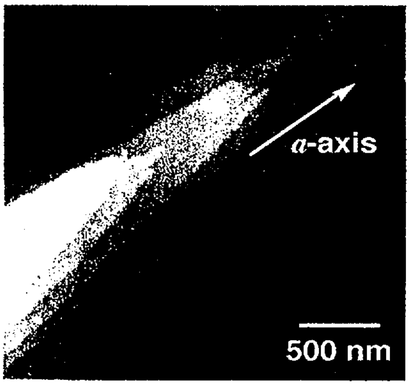
Deposition of P(3HB) Single Crystals on Substrate



	substrate				
	mica	cover glass	hydrophilic glass	silicon wafer	HOPG*
treatment before immersion	cleaved	washed	washed	washed	cleaved
adsorption of single crystals	no	no	no	no	yes

*HOPG: Highly Ordered Pyrolytic Graphite

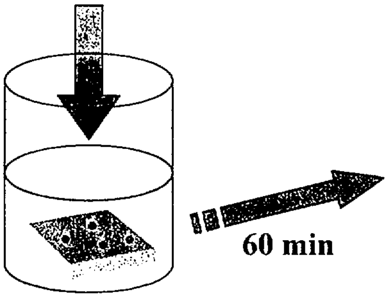
P(3HB) Single Crystals on HOPG



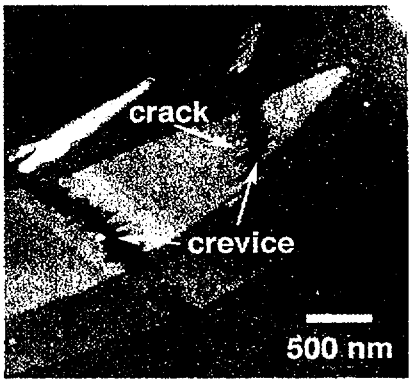
AFM Image of P(3HB) Single Crystals
Adsorbed on Highly Ordered Pyrolytic Graphite (HOPG)

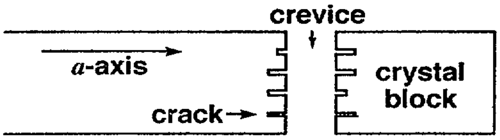
Enzymatic Degradation at 37 °C for 60 min

PHB Depolymerase from
***Alcaligenes faecalis* T1**

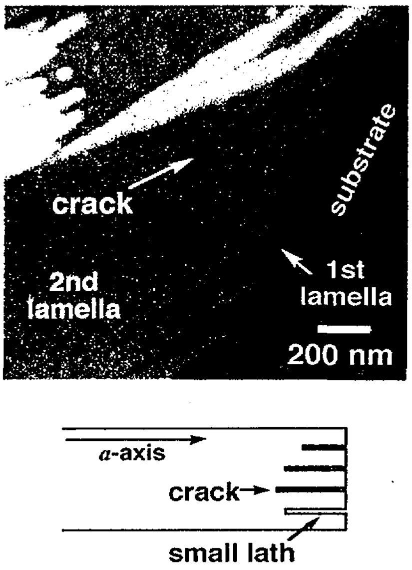


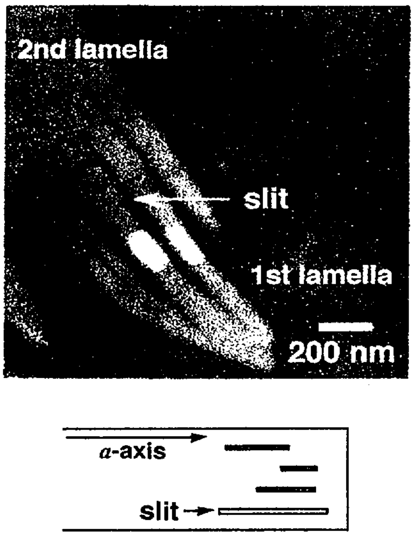
Incubated at 37 °C
in Tris Buffer Solution



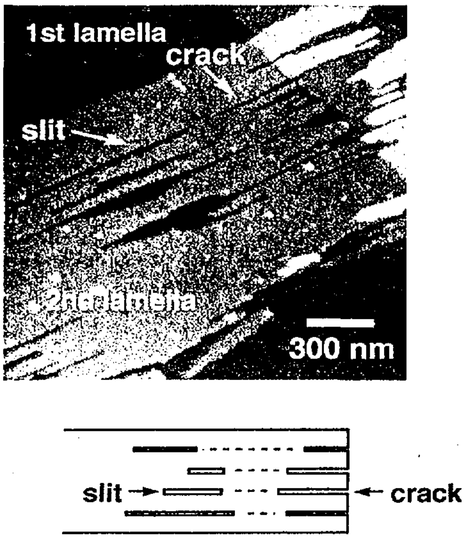


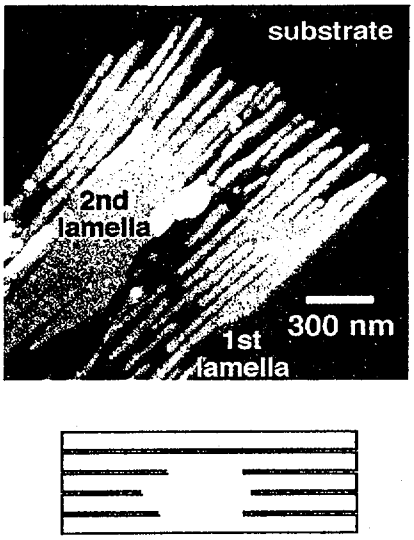
Enzymatic Degradation at 37 °C for 90 min



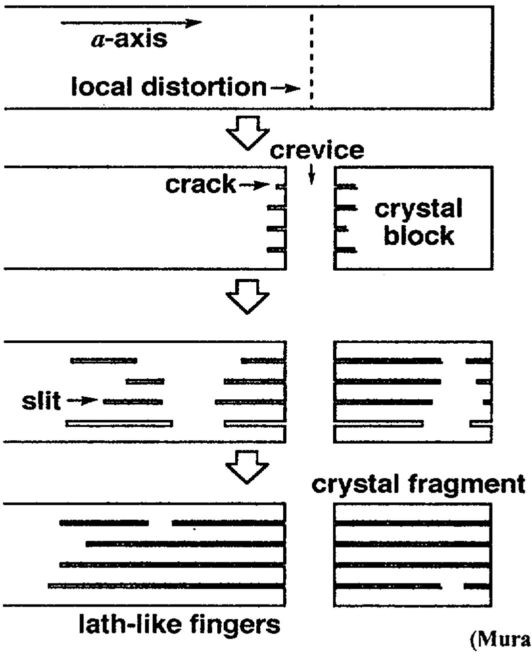


Enzymatic Degradation at 37 °C for 90 min



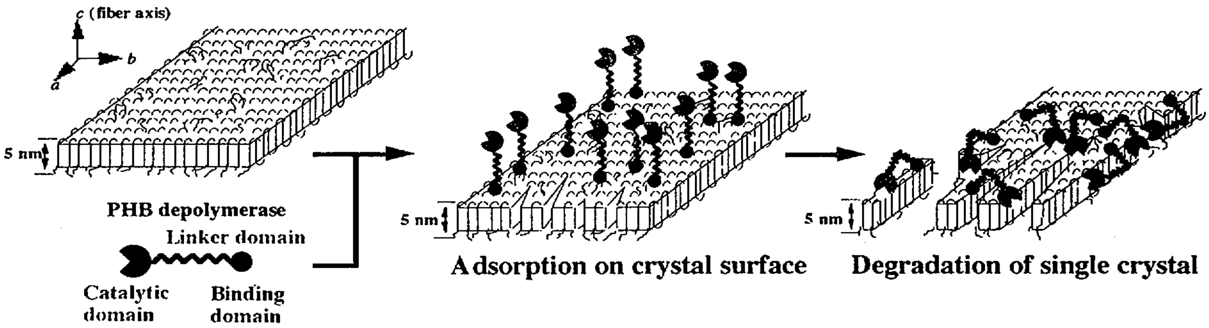


Schematic Model for the Degradation Behavior

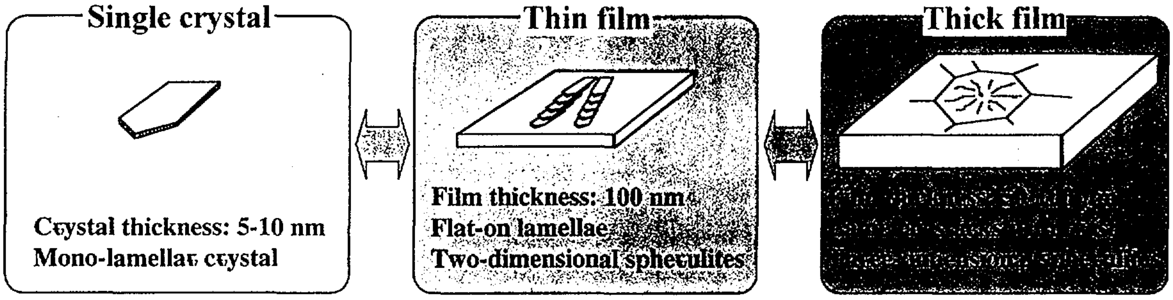


(Murase, Iwata & Doi, 2000)

Structure and Enzymatic Degradation of P(3HB) Single Crystals



3. Crystal Growth and Enzymatic Hydrolysis of PHA Thin Films



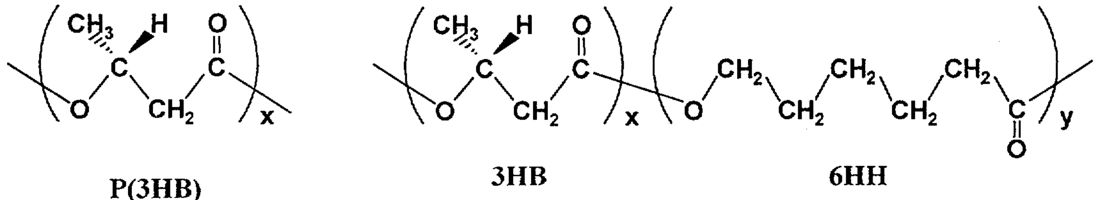
1. **Preparation of thin film and characterization of lamellar morphologies**
   (Optical microscopy, Transmission electron microscopy (TEM), Atomic force microscopy (AFM))

2. **Visualization of the lamellar growth manner in thin film**
   (Temperature-controlled atomic force microscopy (TC-AFM))

3. **Enzymatic degradation of thin film**
   (Atomic force microscopy (AFM))

Preparation of Melt-crystallized PHA Thin Films

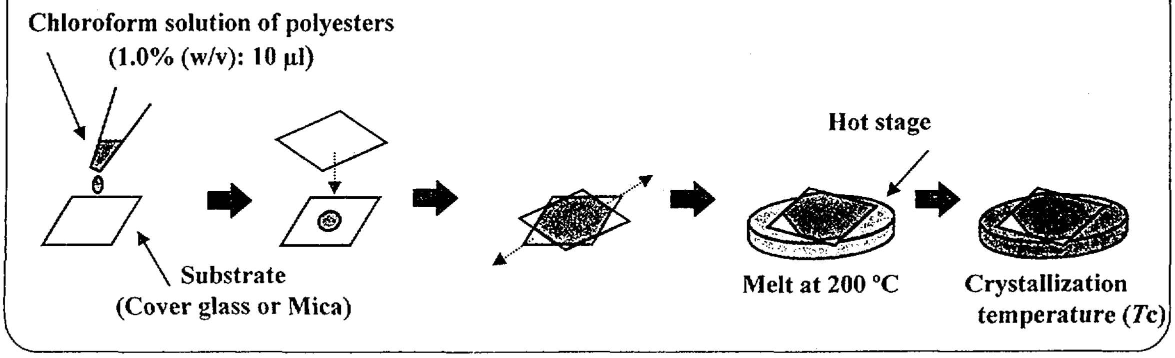
Samples



P(3HB)

3HB 6HH

P(3HB-*co*-6HHx)

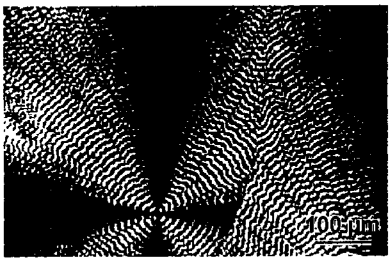


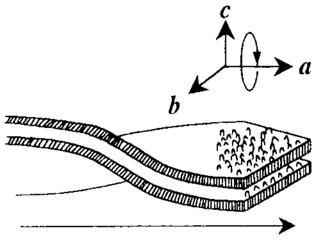
Optical Micrograghs of P(3HB-*co*-10mol%-6HHx) Spherulites

Thick film (film thickness: 100 μm)

Three-dimensional growth

Tc=85 °C





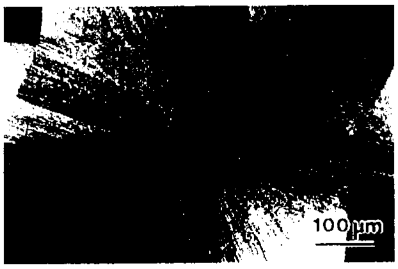
Direction of spherulitic growth

Thin film (film thickness: 100 nm)

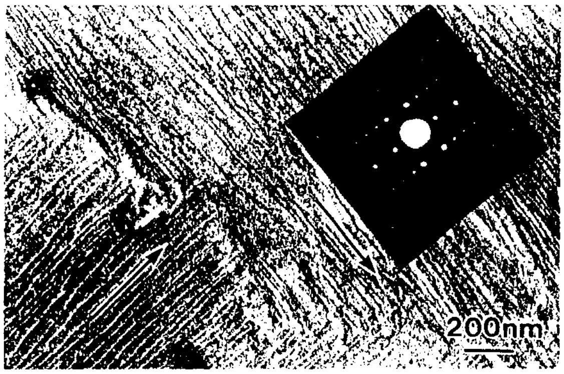
Two-dimensional growth

Tc=50 °C

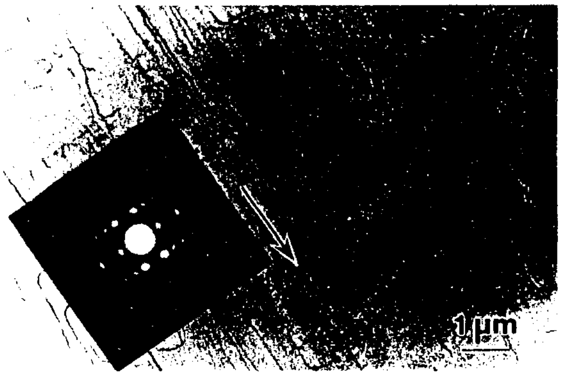
Tc=110 °C



TEM Micrograghs of Thin Films for P(3HB) (*T*c=120 °C) and P(3HB-*co*-10mol%-6HHx) (*T*c=110 °C)

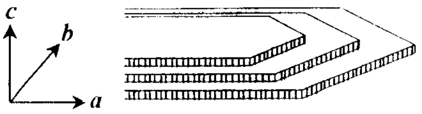


P(3HB) (*T*c=120 °C)



P(3HB-*co*-10mol%-6HHx) (*T*c=110 °C)

Flat-on lamellae



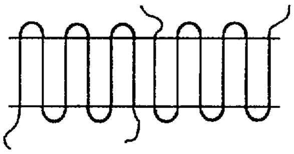
Molecular chains are parallel to the substrate

Crystal Structure of Lamellar Crystals in PHA Thin Films

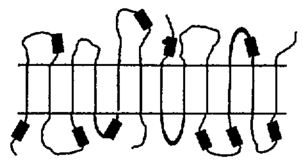
d-spacing values of PHA lamellar crystals determined from electron diffractogram

(hkl)	d-spacing (nm)	
	P(3HB)	P(3HB-*co*-10mol%-6HHx)
020	0.660	0.656
040	0.330	0.328
110	0.528	0.528
120	0.434	0.435
130	0.350	0.350
140	0.286	0.285
200	0.288	0.288
220	0.264	0.265
240	0.217	0.217
260	0.175	0.174

P(3HB) lamellar crystal

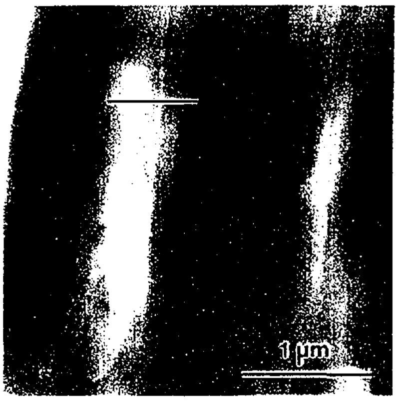


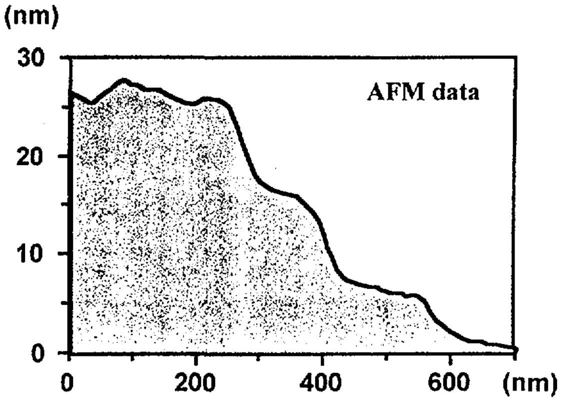
P(3HB-*co*-10mol%-6HHx) lamellar crystal



▬ 6HH unit

Lamellar Thickness of PHA Thin Films, and Line Profile Data





P(3HB)

Tc (°C)	lamellar thickness (nm)
60	5-7
90	6-9
120	8-10

P(3HB-*co*-10mol%-6HHx)

Tc (°C)	lamellar thickness (nm)
50	3-5
80	6-9
110	8-10

AFM Images of Thin Films for P(3HB) (*T*c=120 °C) and P(3HB-*co*-10mol%-6HHx) (*T*c=110 °C)

P(3HB) (*T*c=120 °C)

P(3HB-*co*-10mol%-6HHx) (*T*c=110 °C)

Microfibril crystals formed at the growth front of lamellae

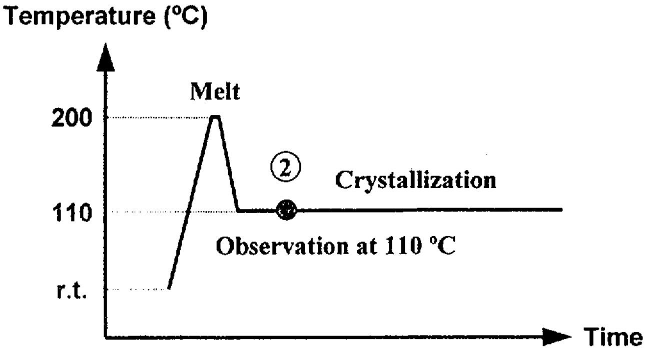
width: 30-50 nm
length: 50-400 nm
thickness: 8-10 nm

In-situ Observation by Means of Temperature-Controlled AFM

Melt and crystallization

↓

Observation at 110 °C

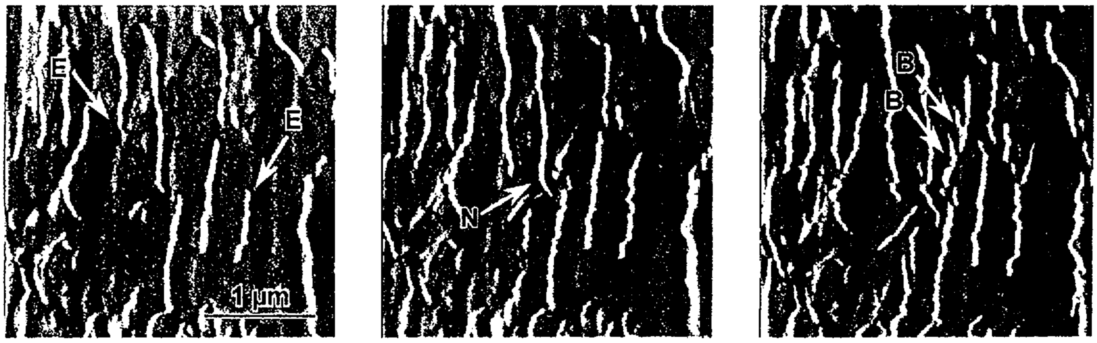


②

Hot stage equipped in AFM

Melt at 200 °C → Crystallization at 110 °C → *In-situ* observation at 110 °C

AFM Images of P(3HB-*co*-10mol%-6HHx) Thin Film during Isothermal Crystallization at 110 °C

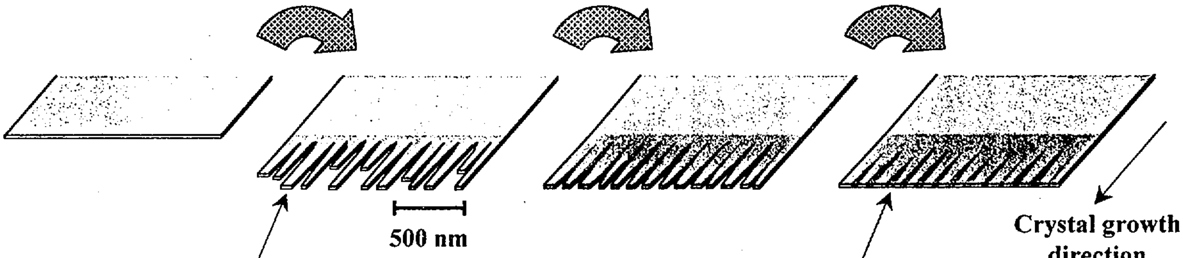


t min　　*t*+30 min　　*t*+60 min

E: typically elongating and expanding microfibril crystals
N: newly formed microfibril crystals
B: branching microfibril crystals

Schematic Model on the Growth of PHA Lamellar Crystals

Lamellar growth model



Microfibril crystals are formed at the growth front of lamellae.

Polymer chains fill up between microfibril crystals

Microfibril crystals (tightly chain packing region)

loosely chain packing region

Crystal growth direction

Enzymatic Degradation Test

PHB depolymerase from *Alcaligenes faecalis* T1

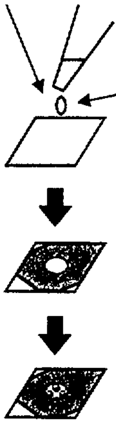
Isolated from activated sludge
Optimum pH: 7.5
Optimum temperature: 40 °C
Molecular weight: 47,000

▨ Catalytic domain ▌ Lipase box

■ Substrate binding domain

□ Linker domain

0.1M phosphate buffer (pH=7.4); 1.0 ml
PHB depolymerase from *A. faecalis* T1; 1 μg

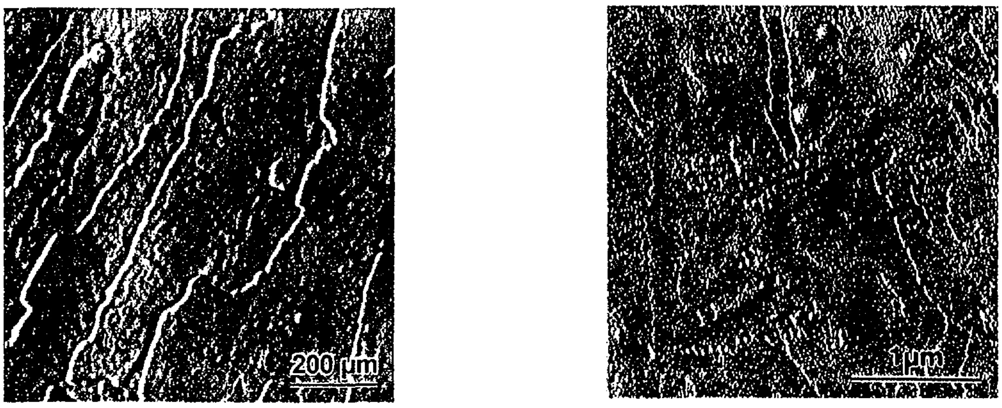


Droplet of enzyme solution (50μl)

at 25 °C, 15 min

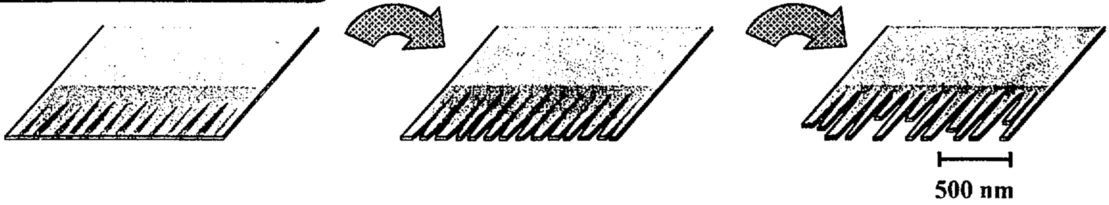
Dried after washing with distilled water

AFM Images of P(3HB) Thin Film Before and After Enzymatic Degradation



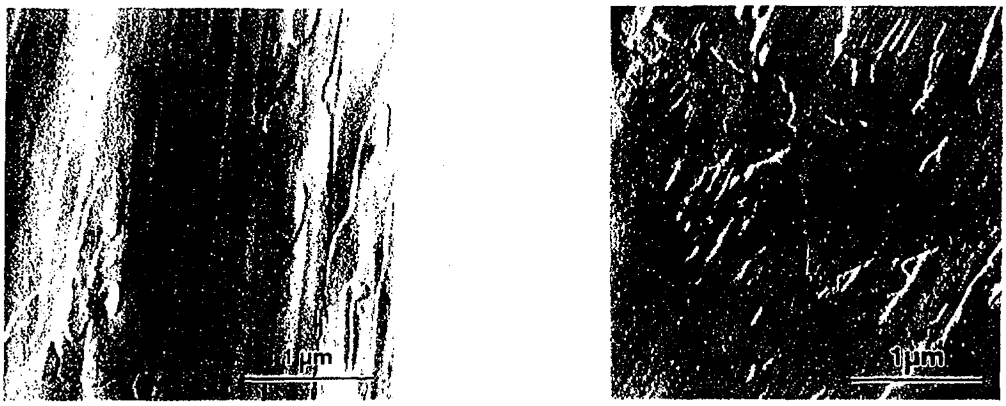
Before degradation **After degradation**

Degradation model



Microfibril crystals appear.

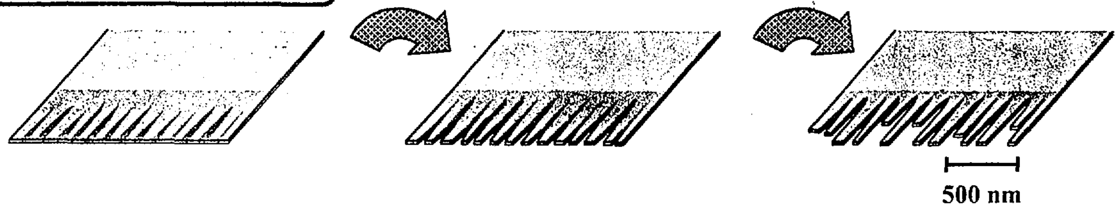
AFM Images of P(3HB-*co*-10mol%-6HHx) Thin Film Before and After Enzymatic Degradation



Before degradation **after degradation**

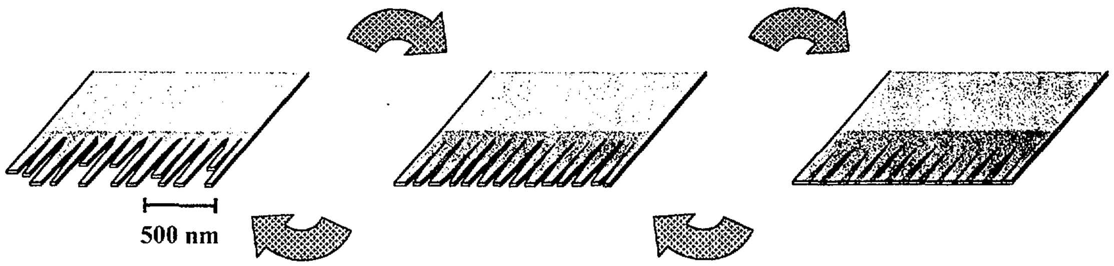
Degradation model

Microfibril crystals appear.



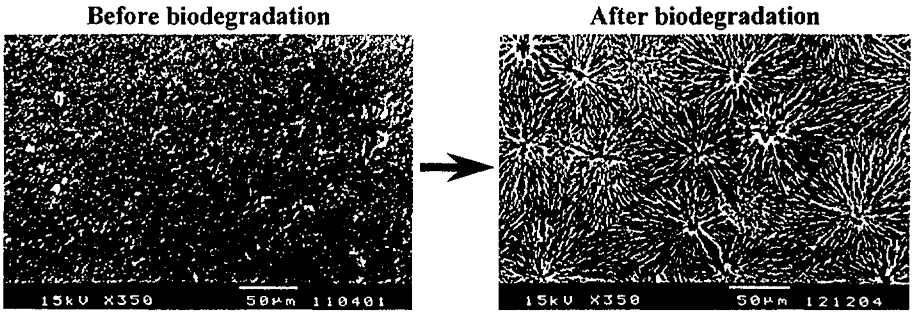
Model for Lamellar Growth and Enzymatic Degradation of PHA Crystals

Lamellar growth model

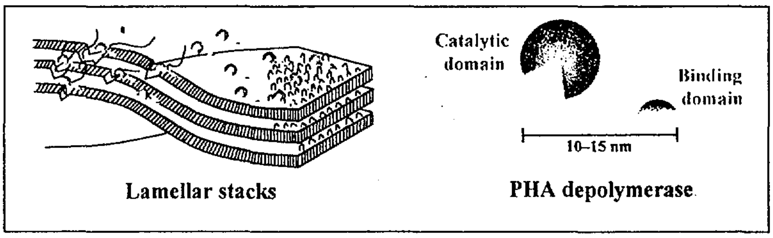


Degradation model

4. Materials Design of PHA Materials

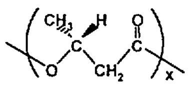

Before biodegradation
After biodegradation

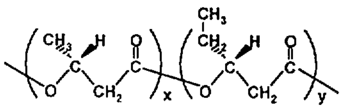
P(3HB) Thick Film

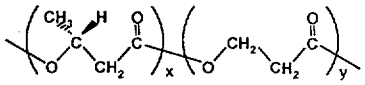


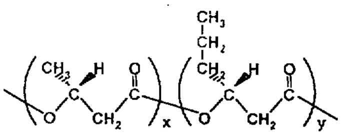
Chemical Structure of Random Copolymers with (*R*)-3-Hydroxybutyric Acid Unit as a Constituent

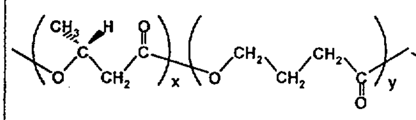
Biosynthetic

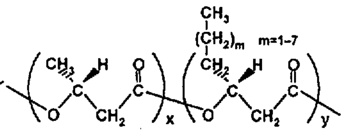

P(3HB)


P(3HB-*co*-3HV)


P(3HB-*co*-3HP)

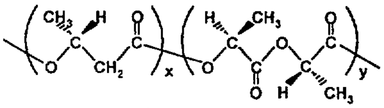

P(3HB-*co*-3HHx)

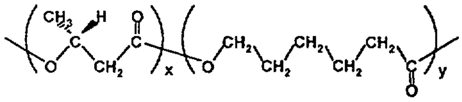

P(3HB-*co*-4HB)



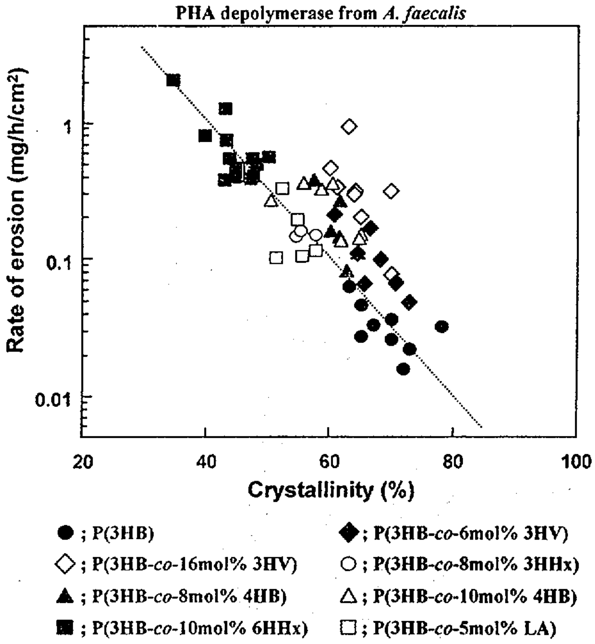
P(3HB-*co*-mcl-3HA)

Chemosynthetic


P(3HB-*co*-LA)

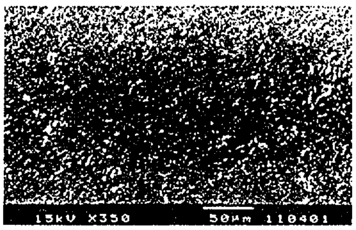

P(3HB-*co*-6HHx)

Relationship between the Rate of Enzymatic Erosion and Crystallinity for Poly(hydroxyalkanoic acids)

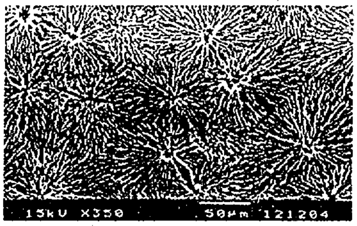


Changes in film surface

Before enzymatic degradation

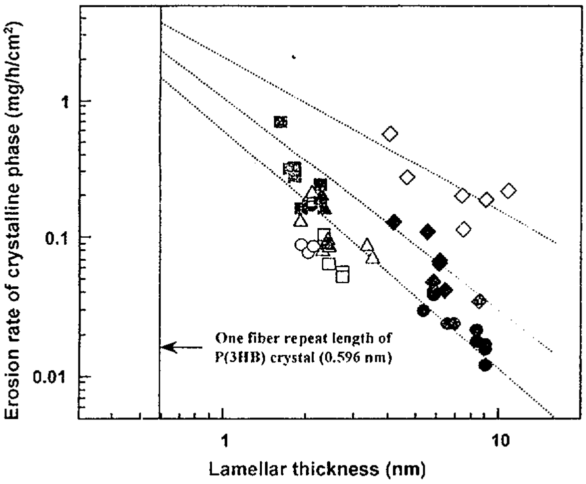


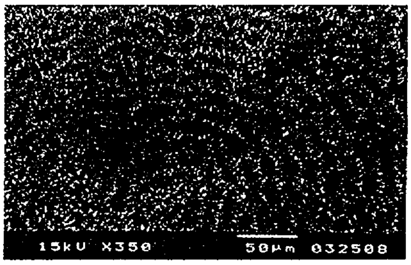
After enzymatic degradation

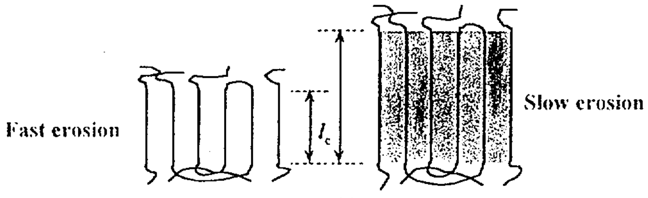


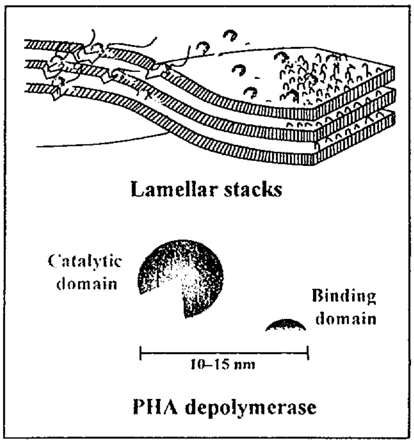
(Kumagai, Kanesawa, & Doi, 1992; Koyama & Doi, 1997; Abe *et al.,* 1998)

Relationship between the Enzymatic Erosion Rate in Crystalline Phase and Lamellar Thickness of Poly(hydroxyalkanoic acids)



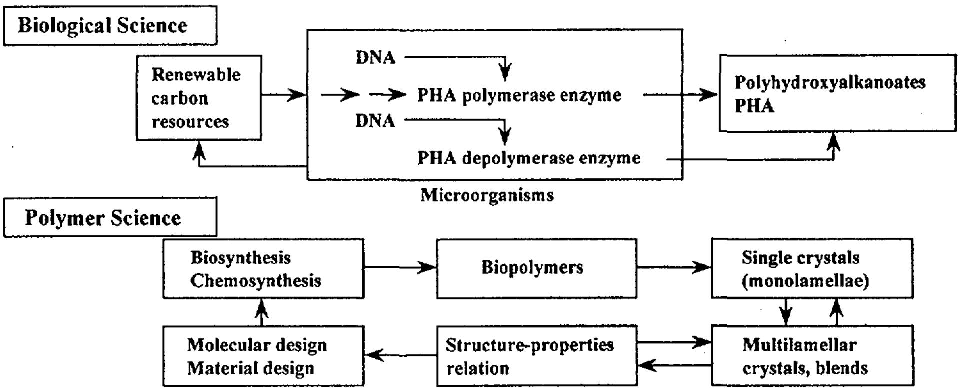






(Abe *et al.,* 1998)

Polymer Chemistry Lab., RIKEN Institute



11. Sustainable Polyhydroxyalkanoate (PHA) Production

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Introduction

Polyhydroxyalkanoates (PHAs), are polyesters formed by many prokaryotic microorganisms when unbalanced nutritional conditions are chosen for the producing cells (1). A general formula for these polymers is given in figure 1. Up to more than 90% of the cell dry weight can be accounted for as polymer (2), when appropriate fermentation conditions are chosen for the accumulating microorganisms. Beside the homo-polyester poly-R-3-hydroxybutanoate, consisting of 3-hydroxybutanoate (3HB) only, two main types of copolyesters can be formed by different microorganisms (3). The first type of PHAs always contains C_3 units in the polymer backbone, but the side chains can contain H, methyl- or ethyl-groups if prepared with microorganisms like *Ralstonia eutropha*, or propyl- to nonyl groups are found in the side chains if the copolyester is prepared with *Pseudomonas oleovorans*. In the latter case branchings (4), double bonds (5), epoxides (6), and aromatic structures (7) can be introduced into the side chain. Furthermore copolyesters containing w-chloroalkanoates (F, Cl, Br) can be produced (8-10). In the case of *P. oleovorans* and other strains from the group of fluorescent pseudomonads PHA formation only occurs, when the organisms are grown either with fatty acids (butanoate to hexadecanoate) or with alkanes (hexane to dodecane). Doi (11) recently reported about synthesis of a copolyester consisting of 3-hydroxybutyrate and 3-hydroxyhexanoate by *Aeromonas cavei*, and Chen (12) isolated a bacterium from oil-contaminated earth able to synthesize the same polyester when fed with glucose and laurylic acid. This copolyester shows an extremely high extension needed to break.

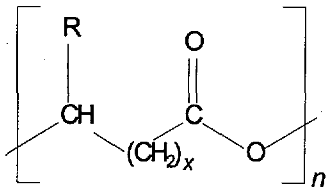

Figure 1: General formula of PHAs

The second type of PHA is a short side chain polyester, containing hydrogen, methyl-, or ethyl groups in the side chains, and having C_3, C_4, and C_5 units in the backbone of the polymer (13,14). Carbohydrates, alcohols, and low fatty acids are typical substrates for growth and PHA formation for these microorganisms. In most cases, cosubstrates have to be fed to the producing cultures as precursors for copolyester formation (14, 15). Typical precursors that have been used are propionate, valerate, or 1,4-butanediol, leading to analogues of 3HB such as 4-, and 5-hydroxyalkanoates.

Formation of random copolyesters results in many physical changes in the PHAs, including liquid-crystalline-amorphous forms, and a variety of piezoelectric, thermoplastic, elastomeric and other properties (16).

The "mixed" polyesters formed depend on the organisms used to produce them, and on the carbon sources and polyester precursors. For PHAs formed by prokaryotes the main physiological role accepted is, that the polyesters function as carbon and energy reserve materials. When growth is limited by exhaustion of nitrogen, phosphate, sulfur, oxygen, etc. in the nutritional broth, excess carbon is channeled into PHAs, leading to polyesters with molecular weights of up to about 3.4 MD (17). Recently other physiological roles have been recognized for PHAs. Relatively small molecular weight PHAs (up to about 35 KD) are incorporated into membranes and their tertiary helical structures (backbone inside) such that ion pores are putatively used for transport of ions into and out of the cells (18-20).

Polyhydroxyalkanoates (PHAs) can be biodegradable substitutes to fossil fuel plastics that can be produced from renewable raw materials such as saccharides, alcohols and low-molecular-weight fatty acids. They are completely degradable to carbon dioxide and water through natural microbiological mineralization. Consequently, neither their production nor their use or degradation have a negative ecological impact. By keeping closed the cycle of production and re-use, PHAs can enable at least part of the polymer-producing industry to switch from ecologically harmful end-of-the-pipe production methods towards sounder technologies.

Kinetics of PHA accumulation

The new findings reported above and those reviewed from the literature point out the existence of three distinct types of growth and PHA accumulation behavior, each one typified here by one or more microorganism-carbon source combinations:

1) PHA synthesis occurs in association with growth (ex.: *A. latus* with sucrose);

2) PHA synthesis occurs in partial association with growth (ex.: *R. eutropha* G^{+3} with glucose, *A. latus* with glucose);

3) PHA is hyperproduced after a carbon starvation period (ex.: *Pseudomonas* 2 F with glucose).

In principle, the three behaviors can be exploited for PHA production in batch culture, but due to its higher productivity, a continuous production process is of higher commercial interest, especially for strains with a high maximum specific growth rate. To prove this point, the overall productivity of a batch system will be compared to that of a continuous culture in the following way (21):

[1]

$$\frac{Pr_{CSTR}}{Pr_{DSTR}} = \ln \frac{X_e}{X_i} + t_0\,\mu_{max}$$

where Pr_{CSTR} and Pr_{DSTR} are the productivities of a continuous stirred-tank reactor (CSTR) and a discontinuous stirred-tank reactor (DSTR), respectively, X_e is the maximum biomass concentration, X_i is the initial biomass concentration, and t_0 is the period of time between the end of a production run and the start of the next one.

The use of values of μ_{max} for *A. latus* and *R. eutropha* G^{+3} and a maximum biomass concentration of 30 gL^{-1} in Eq. 1 gives a productivity ratio of 8.2 with *A. latus* and 5.25 with *R. eutropha* if t_0 is set to a low 10 h. This means that for a fixed desired amount of product per unit of time, the bioreactor volume can be substantially reduced if a continuous culture is chosen over a batch process. From an engineering point of view, the reactor performance would also be easier to control, as lower fermentor volumes lead to less segregation through better mixing at inferior energy expenditure (22).

But if a continuous process is considered, the issue of kinetics must be addressed. The data from our experiments suggest the following possibilities for a PHA production process:

1) an autocatalytic process of biomass growth and polymer production. Example: *A. latus* with glucose;
2) an autocatalytic process of biomass growth and polymer production followed by hyperproduction after carbon starvation. Example: *Pseudomonas* F 2 with glucose;
3) an autocatalytic process of biomass (and PHB) formation followed by a phase of linear PHA accumulation. Example: *A. latus* with glucose, *R. eutropha* G^{+3} with glucose.

Consideration of the basic differences between these scenarii lead to the present proposition that for a multi-stage continuous PHA-production process, the use of a plug-flow tubular reactor, or PFTR (in which Reynolds numbers are large), brings substantial increases in productivity when compared to a system consisting of CSTRs only. Support of this assertion comes from the works of Levenspiel (23), where mean residence times for the two types of reactors are compared under the restriction of a desired goal:

For a CSTR in steady-state, where the concentrations in the reactor are the same as those in the outflow, the mass balance for biomass is given by

$$[2] \qquad F\,(X_i - X_e) + V\,(r_X) = 0$$

where F is the flow rate, X_i is the incoming biomass concentration, X_e is the effluent biomass concentration, V is the reactor volume and r_X is the absolute rate of biomass increase through growth, or dX/dt (amount per unit volume per unit time).

The mean residence time t_{CSTR}, during which X_i is converted to X_e, is therefore simply

$$[3] \qquad t_{CSTR} = \frac{V}{F} = \frac{X_e - X_i}{r_X}$$

The mean residence time necessary for a CSTR to produce an effluent containing the concentration X_e can thus be determined graphically when the relationship between X and $1/r_X$ is known.

In the case of an PFTR, which can be looked upon as a series of small CSTRs, the mean residence time is given by the integration

$$[4] \qquad t_{PFTR} = \int_{X_i}^{X_e} \frac{1}{r_X} \, dX$$

Here again, t can be determined graphically for a known process.

Data from fermentations with *R. eutropha* G^{+3} were used to plot $1/r_X$ as a function of the biomass concentration (5). Graphical determinations of t_{PFTR} and t_{CSTR} revealed that for the autocatalytic process of simple biomass growth, a CSTR is the optimal system. For strains storing PHA growth-associatedly, a CSTR is therefore the best system for growth and PHA storage. If hyperproduction of PHA after a phase of carbon starvation is expected, a two-step continous system, consisting of two CSTRs in series, should be employed. In most cases however, growth is followed by a distinct PHA accumulation phase. This is the case for *R. eutropha* G^{+3}, and a PFTR is clearly the superior solution for the second stage. In other words, a combination of the two systems, i.e., a CSTR followed by a PFTR, allows a minimal total bioreactor volume to yield the same productivity as a two-CSTR arrangement of higher total volume. In the case of *R. eutropha* just described, the ratio t_{CSTR}/t_{PFTR} is 8,9 for the accumulation. A second-stage PFTR needs thus only have 11,4 % the volume of a CSTR to achieve the same results. In the case of *A. latus*, the ratio is 5,1, or a PFTR 19,8 % the size of a CSTR. The CSTR-PFTR arrangement not only guarantee maximum productivity, but also minimizes cosubstrate loss, and might be a tool for enhancing product quality, since very narrow residence time distributions (and therefore uniform cell population) are characteristic of plug-flow tubular reactors (24).

Production of P3HB and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with *Alcaligenes latus* strain DSM 1122, DSM 1123, and DSM 1124

Alcaligenes latus exhibits a behavior different from that of *R. eutropha* in both growth and P3HB accumulation. Its maximum specific growth rate μ_{max} is 0.45 to 0.48 h^{-1}, depending on the nature and the concentration of the carbon source (glucose or sucrose). If sucrose alone is used, P3HB accumulation is almost totally associated to growth (4), and recent research has showed that with glucose as substrate, up to 38 % of the dry biomass can consist of P3HB at the end of a growth phase (25). The maximum specific P3HB production rate $p_{P3HB, max}$ can reach 0.50 h^{-1} during growth on sucrose, whereas a $p_{P3HB, max}$ of 0.29 h^{-1} is attainable with glucose alone. Therefore, cells of *A. latus* contain a high percentage of P3HB (about 60 % with sucrose, 38 % with glucose) even during non-limited multiplication.

In the tables 1 and 2, yields and specific rates for growth and PHA accumulation are shown for glucose and sucrose as pure sugars, and for maltose (starch hydrolysate), green syrup, an intermediate from sucrose production, and for beet molasses. As can be seen, such wastes from agricultural products can successfully be used for PHA production. Yields on the waste products tested are absolutely comparable to those measured for pure carbon sources, but specific rates are normally lower with the waste materials. All data below come from growth and PHA production experiments performed in 10 L volume bioreactors.

Table 1: *A. latus* strains DSM 1122, 1123, and 1124. Yields and specific rates with Glucose or Sucrose as carbon sources

Strains on Glucose	$Y_{X/C}$ **(g/g)**	$Y_{XR/C}$ **(g/g)**	$Y_{X/N}$ **(g/g)**	$Y_{XR/N}$ **(g/g)**	$Y_{P/C}$ **(g/g)**	μ **(h^{-1})**	μ_R **(h^{-1})**	q_P **(h^{-1})**
A. latus DSM 1122	0,49	0,41	2,37	1,5	0,4	0,57	0,6	0,55
A. latus DSM 1123	0,36	0,31	1,12	1,4	0,4	0,48	0,6	0,80
A. latus DSM 1124	0,46	0,33	1,96	1,4	0,4	0,23	0,3	0,25
Strains on Sucrose	$Y_{X/C}$ **(g/g)**	$Y_{XR/C}$ **(g/g)**	$Y_{X/N}$ **(g/g)**	$Y_{XR/N}$ **(g/g)**	$Y_{P/C}$ **(g/g)**	μ **(h^{-1})**	μ_R **(h^{-1})**	q_P **(h^{-1})**
A. latus DSM 1123	0,40	0,21	3,88	1,72	0,35	0,29	0,24	0,55
A. latus DSM 1124	0,53	0,17	5,74	1,79	0,36	0,33	0,26	0,58

The yields are defined as $Y_{X,P/C}$ = g biomass, PHA per g substrate used. Residual biomass X_R is defined as total dry biomass minus its PHA content, the specific growth rate μ (h^{-1}) is equal to $\mu = 1/X\ dX/dt$, and the specific production rate q_P (h^{-1}) is $q_P = 1/X\ dP/dt$.

Production of P3HB and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) from Methanol

Methanol could be used as a carbon source for the production of PHAs wherever it is available in a cheap way. The conversion of methane (natural gas) to methanol is a well known process leading to high yields

Table 2: *A. latus* strains DSM 1122, 1123, and 1124. Yields and specific rates with Maltose, Green syrup, or beet molasses as carbon sources

Strains on Maltose	$Y_{X/C}$ **(g/g)**	$Y_{XR/C}$ **(g/g)**	$Y_{X/N}$ **(g/g)**	$Y_{XR/N}$ **(g/g)**	$Y_{P/C}$ **(g/g)**	μ **(h^{-1})**	μ_R **(h^{-1})**	q_P **(h^{-1})**
A. latus DSM 1123	0,51	0,33	3,31	2,28	0,16	0,13	0,12	----
A. latus DSM 1124	0,52	0,24	4,36	2,06	0,28	0,24	0,19	0,18
Strains on Green Syrup	$Y_{X/C}$ **(g/g)**	$Y_{XR/C}$ **(g/g)**	$Y_{X/N}$ **(g/g)**	$Y_{XR/N}$ **(g/g)**	$Y_{P/C}$ **(g/g)**	μ **(h^{-1})**	μ_R **(h^{-1})**	q_P **(h^{-1})**
A. latus DSM 1123	0,54	0,31	----	----	0,20	0,28	0,28	0,19
A. latus DSM 1124	0,69	0,25	5,44	2,0	0,44	0,34	0,23	0,31
Strains on Molasses	$Y_{X/C}$ **(g/g)**	$Y_{XR/C}$ **(g/g)**	$Y_{X/N}$ **(g/g)**	$Y_{XR/N}$ **(g/g)**	$Y_{P/C}$ **(g/g)**	μ **(h^{-1})**	μ_R **(h^{-1})**	q_P **(h^{-1})**
A. latus DSM 1123	1,09	0,99	----	----	0,19	0,41	0,37	0,02
A. latus DSM 1124	0,90	0,39	4,94	3,09	0,29	0,14	0,14	0,05

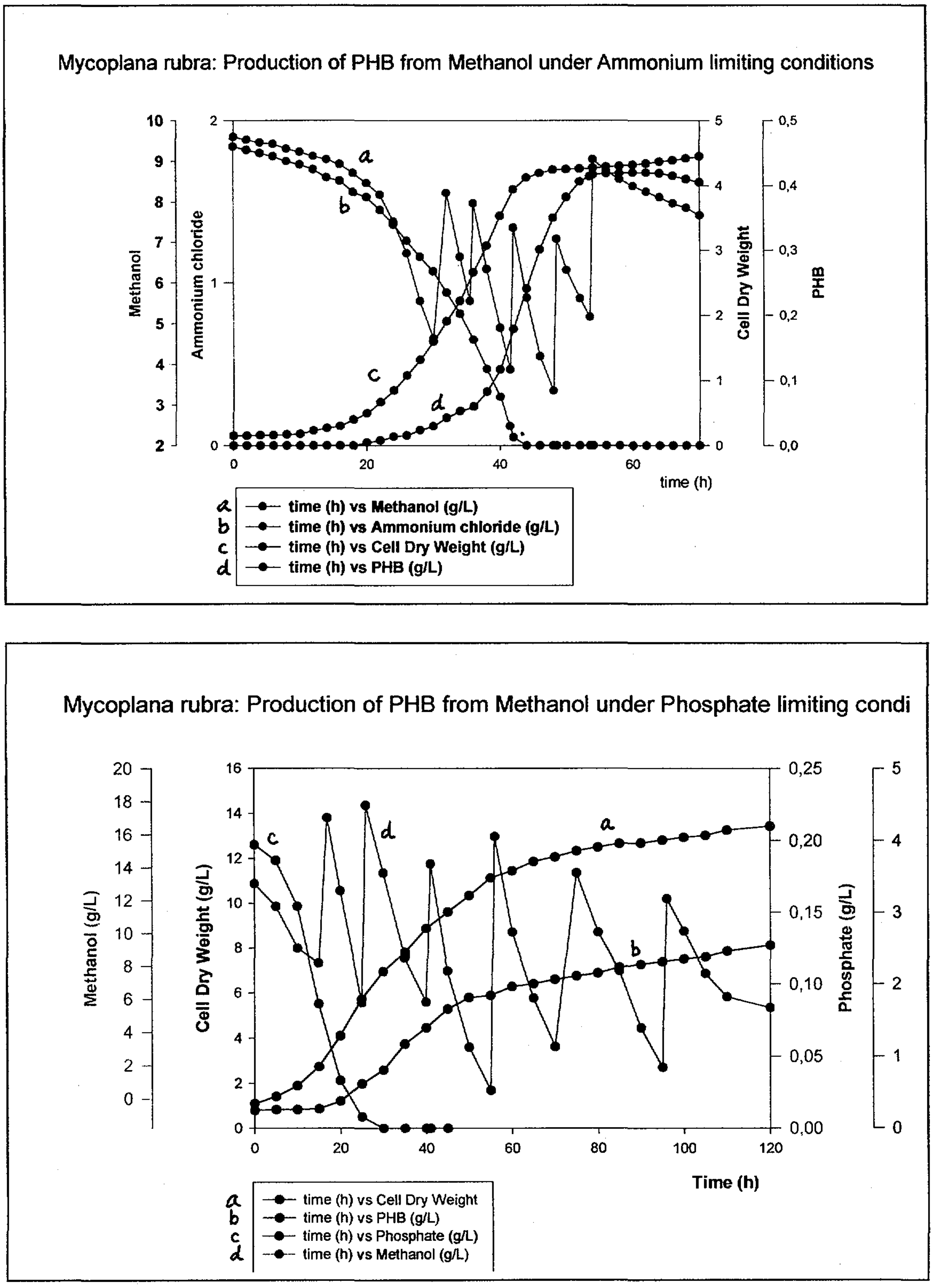

Figure 3: Production of PHB with *Mycoplana rubra* with Ammonium or Phosphate as a growth limiting substrate.

of methanol, and could be a starting point for PHB production applying methylotrophic bacteria as producing organisms. Such microorganisms can use this C_1-compound as a sole carbon and energy source either by the Serine Cycle or by the Ribulose monophosphate pathway. Experimentally, a lot of work has been done using *Methylomonas extorquens, Mycoplana rubra* (Figure 3), and other socalled "pink pseudomonads", utilizing methanol via the serine pathway. As has been shown by different groups, growth limitation by depleting the nitrogen source (NH_4^+) can affect the rate of acetyl-CoA formation and therefore influence the accumulation of PHB in a negative way. Figure 3 shows the results of PHB accumulation by *Mycoplana rubra* as well under nitrogen limiting conditions as under phosphate limitation. For the first case it can be seen that PHB accumulation starts during the growth phase of the organism, but maximum production rate occurs at ammonium concentrations suboptimal for growth (0,05 to 0,15 g/L NH_4Cl). Later, the production rate of PHB declines to zero or even degradation can occur, when the strain is kept under NH_4-limitation. A similar effect can be seen with phosphate as a growth limiting substrate.

Also here, PHB production starts before phosphate is completely depleted, and highest PHB accumulation rates are reached when phosphate concentration is as low as 0,05 – 0,01 g/L phosphate. In contrary to the ammonium limited experiment, the PHB concentration is still rising after phosphate depletion, even though with a lower and constant rate. In order to optimize PHA production rate, this means that as well the concentrations of ammonium as phosphate have to be controlled during the PHA accumulation phase, and a feeding strategy has to be developed that guarantees optimum concentrations.

Similar findings have been published by Suzuki et al. (26) using *Pseudomonas sp.* K as a producing strain. After 170 h of fermentation in a fed-batch system with constant ratio of carbon/nitrogen feeding the total cell concentration in the experiment was 233g/L, the PHB concentration reached was 149 g/L (63,95% of cell dry weight). PHB yield from methanol was 0,20 (g PHB/g methanol).

Production of Poly(3HB-co-4HB) with Ralstonia eutropha G+3

Beside accumulation of homopolymer poly-R-3-hydroxybutyrate *R. eutropha* can also synthesize copolyesters. When feeding 1,4-butanediol, g-butyrolactone, or 4-hydroxy-butyrate (4-HB) as a co-substrate during PHA accumulation phase, a copolyester containing 4-hydroxybutyrate is produced by this strain. This copolyester is of high interest, because even low concentrations of 4-HB in the polyester change dramatically change its physical and mechanical properties (Table 3).

In figure 4, data are presented from a growth and PHA accumulation experiment with this strain, using glucose as a main carbon source and g-butyrolactone as a precursor for copolyester production. As can be seen from the figure, PHA is mainly produced during a storage phase after ammonium sulfate, used as nitrogen source during the growth of the strain was depleted. At this time g-butyrolactone is added to the cultural medium, and copolyester production starts. During this experiment it was planned to produce a copolyester containing 6 to 8% of 4-hydroxybutyrate, and both carbon source concentrations should be

Table 3: Physical and Mechanical Properties of Poly(3-hydroxybutyrate- co-4-hydroxybutyrate) Films at 23 °C (Doi, 1990)

Composition (mol%)		*Crystallinity* (%)	*Density* (g/cm^3)	Stress at Yield (Mpa)	Elongation at Yield (%)	Tensile Strength (Mpa)	Elongation to Break (%)
3HB	4HB						
100	0	60 ± 5	1.250	--	--	43	5
97	3	55 ± 5	n.d.	34	4	28	45
90	10	45 ± 5	1.232	28	5	24	242
84	16	45 ± 5	1.234	19	7	26	444
56	44	15 ± 5	n.d.	--	--	10	511

near a zero level at the end of the experiment. Specific growth rate and biomass yield from glucose during growth phase were rather average, whilst the yield for the P(3-HB) part of the polyester ($Y_{P3HB, glucose}$= 0,46 g/g), calculated from spent glucose is nearby theoretical, and the yield for P(4-HB) in the copolyester ($Y_{P4HB, glucose}$= 0,13 g/g) is as well not bad, but can be improved significantly by optimizing fermentation conditions. After 60 hours the experiment was stopped at a biomass concentration of 9,34 g/L, containing 7,24 g/L of PHA (77,8% of cell dry weight) and 7% of 4-hydroxybutyrate in the copolyester.

Production of medium chain length PHAs with Pseudomonas oleovorans

Another possibility for PHA production from fossil raw materials is given with *Pseudomonas oleovorans* and other members of the "fluorescent pseudomonads group". When such organisms are grown on alkanes or carboxylic acids, high concentrations of PHAs containing C_3 units in the polymer backbone, and propyl- to nonyl groups in the side chains of the copolyesters. The composition of such copolyesters is given in the tables 4 and 5.

Investigations by Huijberts et al. (28) with *P. putida* revealed the synthesis by this micro-organism growing on glucose of PHAs composed of seven different monomers, including units of 3-hydroxydecanoate (3HD; the major constituent), 3-hydroxyhexanoate (3HHx), 3-hydroxyoctanoate (3HO), and saturated and mono-unsaturated monomers of 12 and 14 carbon atoms.

Other unsaturated, medium-side-chain (MSC) PHAs from pseudomonads have been lately reported. Lee and colleagues (29) used *Pseudomonas* sp. A33 and other related organisms isolated by Schirmer et al. (30) to produce various copolyesters. *Pseudomonas* sp. A33 in the presence of 1,3-butanediol stored a PHA of 3HB units and nine other different constituents, including the saturated, 16-carbon 3-hydroxyhexadecanoate (3HHD; 0.2 mol%), and three unsaturated: 3-hydroxydodecenoate (3HDDE; 21.0 mol%), 3-hydroxytetradecenoate (3HTDE; 3.4 mol%), and 3-hydroxyhexadecenoate (3HHDE; 1.4 mol%). The authors used several techniques to demonstrate that this PHA was a real copolymer and not a blend of polymers, but did not determine whether it had a random distribution of monomers or consisted of block structures.

Table 4: PHAs consisting of saturated hydroxyalkanoate units from various alkanes produced with *Pseudomonas oleovorans* (Doi, 27)

Carbon source	PHA content	PHA Composition	(mol% of 3HA unit)					
	(wt%)	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
Hexane	2,0	100	--	--	--	--	--	--
Heptane	11,4	--	100	--	--	--	--	--
Octane	25,3	11	--	89	--	--	--	--
Nonane	24,3	--	37	--	63	--	--	--
Decane	21,9	10	--	66	--	24	--	--
Undecane	14,3	--	23	--	63	--	14	--
Dodecane	5,8	2	--	31	--	31	--	31

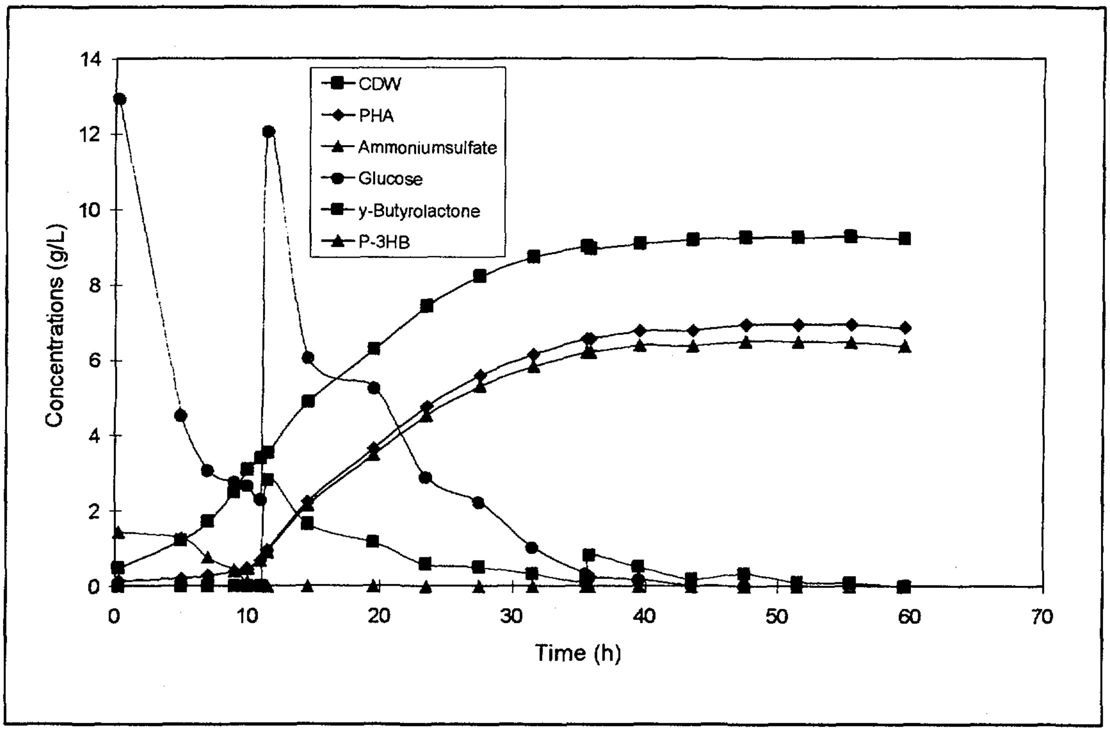

Figure 4: Production of Poly(3HB-*co*-3HV) from glucose and sodium valerate with *Ralstonia eutropha*

Unsaturated, MSC PHAs produced by *P. oleovorans* from n-octane and 1-octene were crosslinked with electron-beam irradiation by de Koning et al. (31). The resulting material had the properties of a true rubber yet retained its biodegradability.

Poly(3-hydroxyalkanoates) with phenyl units as part of the functional group have been produced by *P. oleovorans*. Kim et al. (7) fed the organism with mixtures of 5-phenylvaleric acid and either n-nonanoic acid or n-octanoic acid, to obtain two different polymers, one of 3-hydroxyalkanoate units corresponding to the fed alkanoate, the other of 3-hydroxy-5-phenylvalerate (3H5PV). 3H5PV made up to 40.6 mol% of the total polymer, which reached 31.6% in mass of the CDM. The biomass yield was low however.

Table 5: PHAs consisting of saturated hydroxyalkanoate units from various carboxylic acids produced with *Pseudomonas oleovorans* (Doi, 27)

Carbon source	PHA content (wt%)	PHA Composition (mol% of 3HA unit)						
		C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
3-Hydroxybutanoate	1.2	--	--	22	--	57	--	21
Butanoate	0,6	--	--	--	--	33	--	67
Pentanoate	0,7	--	--	--	--	35	--	65
Hexanoate	3,3	95	--	5	--	--	--	--
Heptanoate	2,3	--	100	--	--	--	--	--
Octanoate	8,7	8	--	91	--	1	--	--
Nonanoate	9,1	--	35	--	65	--	--	--
Decanoate	12,5	8	--	75	--	17	--	--
Undecanoate	9,8	--	28	--	59	--	13	--
Dodecanoate	6,6	6	--	57	--	32	--	5
Tridecanoate	5,4	--	32	--	48	5	14	--
Tetradecanoate	10,6	7	--	59	--	30	--	4
Pentadecanoate	5,3	--	32	--	47	8	13	--
Hexadecanoate	3,4	8	--	50	--	30	--	12
Heptadecanoate	No growth	--	--	--	--	--	--	--
Octadecanoate	No Growth	--	--	--	--	--	--	---

When they supplied 11-cyanoundecanoic acid and n-nonanoic acid as carbon sources for polymer accumulation by *P. oleovorans*, Lenz and co-workers (32) obtained a PHA composed of up to 32 mol% of cyano-containing monomers, most likely of 9-cyano-3-hydroxynonanoate and 7-cyano-3-hydroxyheptanoate. Biomass yield and cyano-unit content increased, but total polymer production decreased, as the proportion of the cyano substrate in the feed mixture increased. In the same series of investigations, a cyano-containing PHA was also produced from a mixture of 11-cyanoundecanoic acid and n-octanoate.

PHAs with halogenated functional groups can be synthesized by *P. oleovorans*. In addition to the chlorinated and fluorinated polymers reported (8, 9, 33), poly(3-hydroxyalkanoate) copolymers containing brominated repeating units have been produced. Kim et al. (10) grew *P. oleovorans* on mixtures of nonanoic or octanoic acid and 6-bromohexanoic acid, 8-bromo-octanoic acid or 11-bromoundecanoic acid. The molar percentage of brominated units in the polymer reached 37.5 % when an equimolar mixture of nonanoic acid and 11-bromoundecanoic acid was used, and PHA and biomass yields increased with increasing length of brominated substrate. All PHAs obtained were random copolymers.

Recently, Bear et al. were able to produce a copolyester containing up to 37 % terminal epoxy groups in the side chains, when *P. oleovorans* was fed with a mixture of 10-epoxyundecanoic acid and sodium octanoate (6).

Downstream processing for PHA isolation

One of the cost factors beside the carbon source and the fermentation process is the isolation of the PHA from the microbial biomass. This step can either be performed either by extracting the polyester from the separated microbial biomass, or by solubilization of the non PHA biomass. A method that has been used quite often in literature is PHA extraction with hot chloroform from dried microbial biomass and precipitation of the polyester by simply adding ethanol. Even though such a procedure is quite simple reutilization of the extracting solvent is not so easy, because separation of chloroform and ethanol by distillation is energetically quite costly. We have therefore tried to simplify this step of solvent reutilization by making use of the advantages of the system chloroform-ethanol-water for such a separation (see Figure 5).

As can be seen from the figure 5, the three components can form either two or three phases depending on the relative concentrations of the components. It is therefore possible to separate $CHCl_3$ from the Chloroform/ethanol mixture by adding water to it: two phases are formed, their composition is shown in

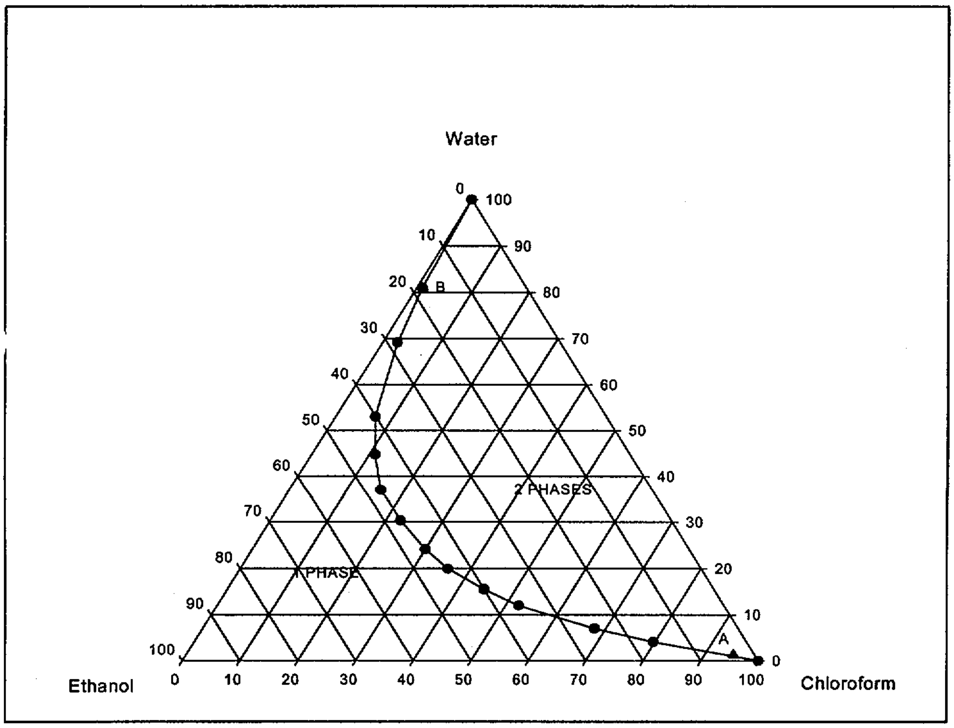

Figure 5: Phase diagram for the system Water – Ethanol – Chloroform

Table 6. It has to be stated that even better yields can be achieved, if the process is run continuously. Phase A can directly be reused for PHA extraction, if wanted (not needed) the water content of phase A can be removed by addition of water-free Na_2SO_4, removal of ethanol is not needed as well, because

technical grade chloroform always contains about 1% of ethanol for stabilization reasons. For the separation of the components in phase B a low energy consuming membrane process can replace distillation.

Table 6: Composition of the Phases A and B for chloroform separation

	Chloroform %	Ethanol %	Water %
Lower Phase (A)	95	3,7	1,3
Upper Phase (B)	1,0	18	81

Recombinant strains for PHA production

As early as 1988 the poly-beta-hydroxybutyrate (PHB) biosynthetic pathway from *Alcaligenes eutrophus* H16 has been cloned and expressed in *Escherichia coli* [34]. Initially, an *A. eutrophus* H16 genomic library was constructed by using cosmid pVK102, and cosmid clones that encoded the PHB biosynthetic pathway were sought by assaying for the first enzyme of the pathway, beta-ketothiolase. Six enzyme-positive clones were identified. Three of these clones manifested acetoacetyl coenzyme A reductase activity, the second enzyme of the biosynthetic pathway, and accumulated PHB. PHB was produced in the cosmid clones at approximately 50% of the level found in *A. eutrophus*. One cosmid clone was subjected to subcloning experiments, and the PHB biosynthetic pathway was isolated on a 5.2-kilobase KpnI-EcoRI fragment. This fragment, when cloned into small multicopy vectors, can direct the synthesis of PHB in *E. coli* to levels approaching 80% of the bacterial cell dry weight.

Similar experiments have been performed and published by Schubert et al.[35]. Eight mutants of *A. eutrophus* defective in the intracellular accumulation of poly-b-hydroxybutyric acid (PHB) were isolated after transposon Tn5 mutagenesis with the suicide vector pSUP5011. EcoRI fragments which harbor Tn5-mob were isolated from pHC79 cosmid gene banks. One of them, PPT1, was used as a probe to detect the intact 12.5-kilobase-pair EcoRI fragment PP1 in a lL47 gene bank of *A. eutrophus* genomic DNA. In six of these mutants (PSI, API, GPI, GPIV, GPV, and GPVI), the insertion of Tn5-mob was physically mapped within a region of approx. 1.2 kilobase pairs in PP1; in mutant API, cointegration of vector DNA has occurred. In two other mutants (GPII and GPIII), most probably only the insertion element had inserted into PP1. All PHB-negative mutants were completely impaired in the formation of active PHB synthase, which was measured by a radiometric assay. In addition, activities of ß-ketothiolase and of NADPH-dependent acetoacetyl CoA (acetoacetyl-CoA) reductase were diminished, whereas the activity of NADH-dependent acetoacetyl-CoA reductase was unaffected. In all PHB-negative mutants, the ability to accumulate PHB was restored upon complementation in trans with PP1. The PHB-synthetic pathway of *A. eutrophus* was heterologously expressed in *E. coli*. Recombinant strains of *E. coli* JM83 and K-12, which harbor pUC9-1::PP1, pSUP202::PP1, or pVK101::PP1, accumulated PHB up to 30% of the cellular dry wt. Crude extracts of these cells had significant activities of the enzymes PHB synthase, ß-ketothiolase, and NADPH-dependent acetoacetyl-CoA reductase. Therefore, PP1 most probably encode all three genes of the PHB-synthetic pathway in *A. eutrophus*. In addition to PHB-negative mutants, mutants were isolated which accumulate PHB at a much lower rate than the wild type does. These PHB-leaky mutants exhibited activities of all three PHB-synthetic enzymes; Tn5-mob had not inserted into PP1, and the phenotype of the wild type could not be restored with fragment PP1. The rationale for this mutant type remains unknown.

Alcaligenes eutrophus transformants AER3, AER4 and AER5 harboring cloned phbCAB, phbAB and phbC genes (from *A. eutrophus* encoding acetyl-CoA-acetyltransferase (EC-2.3.1.16), aceto-acetyl-CoA-reductase and poly-hydroxybutyrate-synthase) introduced via shuttle vector plasmid pKT230) were cultured under various different culture conditions to elucidate the optimal culture conditions for accumulation of poly-beta-hydroxybutyrate (PHB). The transformants showed increased total cell growth and PHB accumulation due to the recombinant enzymes. In batch culture, the transformant synthesized PHB more effectively at the high C/N molar ratio and low C compared to the parent strain. Fed-batch culture was more effective for maximizing PHB biosynthesis compared to the batch culture mode. The plasmid stability was maintained at about 85% after 36 hr and elongated morphological changes of transformant at the early growth stage was noticed. The gene amplification through the transformation of cloned PHB biosynthesis genes in *A. eutrophus* appears to be an excellent method for strain improvement to achieve an effective accumulation of PHB [36].

The increase of gene dosage of the poly(3-hydroxybutyrate) biosynthesis operon in *Ralstonia eutropha* to test whether PHB synthesis rates may be increased by recombinant methods was studied by Jackson and Srienc [37]. The native *R. eutropha* phbCAB operon was inserted into the broad-host-range vector pKT230. This PHB operon-containing plasmid, and a control plasmid containing the identical broad-host-range replicon but not the PHB genes, were transferred to *R. eutropha* H16. Analysis of whole-cell lysates indicated that the strain harboring the operon-containing plasmid possessed ß-ketothiolase and acetoacetyl-CoA reductase specific activities that were 6.0 and 6.2 times elevated, respectively, as compared to the control strain with a single operon. After growth on fructose, PHB synthesis rates were sharply dependent on the type of carbon source offered during the PHB accumulation phase under nitrogen limitation. In the case of the strain harboring the control plasmid, and in comparison to fructose as carbon source, PHB accumulation was 2.15, 2.83, and 2.60 times faster when resuspended in nitrogen-free medium with lactate, acetate, or 3-hydroxybutyrate, respectively. The strain harboring the PHB operon-containing plasmid synthesized PHB at a lower specific rate in each case. During exponential growth on fructose, the strain harboring the control plasmid was again more efficient at forming PHB. These results suggest that increasing the intracellular concentration of PHB precursors may be a superior alternative to raising the levels of PHB enzymes for enhancing PHB productivity in *R. eutropha*.

Recombinant PHA producers seem to have several advantages as PHA producers compared with wild-type PHA-producing bacteria. However, the PHA productivity (amount of PHA produced per unit volume per unit time) obtained with these recombinant E. coli strains has been lower than that obtained with the wild-type bacterium *Alcaligenes latus*. To endow the potentially superior PHA biosynthetic machinery to *E. coli*, the PHA biosynthesis genes from *A. latus* have been cloned [38]. The three PHA biosynthesis genes formed an operon with the order PHA synthase, beta-ketothiolase, and reductase genes and were constitutively expressed from the natural promoter in *E. coli*. Recombinant *E. coli* strains harboring the *A. latus* PHA biosynthesis genes accumulated poly(3-hydroxybutyrate) (PHB), a model PHA product, more efficiently than those harboring the *R. eutropha* genes. With a pH-stat fed-batch culture of recombinant *E. coli* harboring a stable plasmid containing the *A. latus* PHA biosynthesis genes, final cell and PHB concentrations of 194.1 and 141.6 gL^{-1}, respectively, were obtained, resulting in a high productivity of 4.63 g of PHB/liter/h. This improvement should allow recombinant *E. coli* to be used for the production of PHB with a high level of economic competitiveness.

Two types of polyhydroxyalkanoate (PHA) biosynthesis gene loci (phb and pha) of *Pseudomonas sp.* strain 61-3, which produces a blend of poly(3-hydroxybutyrate) [P(3HB)] homopolymer and a random copolymer poly(3-hydroxybutyrate-co-3-hydroxyalkanoate) [P(3HB-co-3HA] consisting of 3HA units of 4 to 12 carbon atoms, were cloned and analyzed at the molecular level [39]. In the phb locus, three open reading frames encoding polyhydroxybutyrate (PHB) synthase (PhbCPs), beta-ketothiolase (PhbAPs), and NADPH-dependent acetoacetyl coenzyme A reductase (PhbBPs) were found. The genetic organization showed a putative promoter region, followed by phbBPs-phbAPs-phbCPs. Upstream from phbBPs was found the phbRPs gene, which exhibits significant similarity to members of the AraC/XylS family of transcriptional activators. The phbRPs gene was found to be transcribed in the opposite direction from the three structural genes. Cloning of phbRPs in a relatively high-copy vector in *Pseudomonas sp.* strain 61-3 elevated the levels of beta-galactosidase activity from a transcriptional phb promoter-lacZ fusion and also enhanced the 3HB fraction in the polyesters synthesized by this strain, suggesting that PhbRPs is a positive regulatory protein controlling the transcription of phbBACPs in this bacterium. In the pha locus, two genes encoding PHA synthases (PhaC1Ps and PhaC2Ps) were flanked by a PHA depolymerase gene (phaZPs), and two adjacent open reading frames (ORF1 and phaDPs), and the gene order was ORF1, phaC1Ps, phaZPs, phaC2Ps, and phaDPs. Heterologous expression of the cloned fragments in PHA-negative mutants of Pseudomonas putida and Ralstonia eutropha revealed that PHB synthase and two PHA synthases of Pseudomonas sp. strain 61-3 were specific for short chain length and both short and medium chain length 3HA units, respectively.

In order to scale up medium-chain-length polyhydroxyalkanoate (mcl-PHA) production in recombinant microorganisms, Prieto et al. [40] generated and investigated different recombinant bacteria containing a stable regulated expression system for phaC1, which encodes one of the mcl-PHA polymerases of *Pseudomonas oleovorans*. The mini-Tn5 system was used as a tool to construct *Escherichia coli* 193MC1 and *P. oleovorans* POMC1, which had stable antibiotic resistance and PHA production phenotypes when they were cultured in a bioreactor in the absence of antibiotic selection. The molecular weight and the polydispersity index of the polymer varied, depending on the inducer level. *E. coli* 193MC1 produced considerably shorter polyesters than *P. oleovorans* produced; the weight average molecular weight ranged from 67,000 to 70,000, and the polydispersity index was 2.7. Lower amounts of inducer added to the media shifted the molecular weight to a higher value and resulted in a broader molecular mass distribution. In addition, it was found that *E. coli* 193MC1 incorporated exclusively the R configuration of the3-hydroxyoctanoate monomer into the polymer, which corroborated the enantioselectivity of the PhaC1 polymerase enzyme.

Interesting results where published by Dennis et al. [41] on the formation of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate). The acetoacetyl-CoA reductase and the polyhydroxy-alkanoate (PHA) synthase from *Ralstonia eutropha* were expressed in *Escherichia coli*, *Klebsiella aerogenes*, and PHA-negative mutants of *R. eutropha* and *Pseudomonas putida*. While expression in *E. coli* strains resulted in the accumulation of poly(3-hydroxybutyrate) [PHB], strains of *R. eutropha*, *P. putida* and *K. aerogenes* accumulated poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) [poly(3HB-co-3HHx)] when even chain fatty acids were provided as carbon source, and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [poly(3HB-co-3HV)] when odd chain fatty acids were provided as carbon source. This suggests that fatty acid degrdation can be directly accessed employing only the acetoacetyl-CoA reductase and the PHA synthase. This is also the first proof that the PHA synthase from *R. eutropha* can incorporate 3-hydroxyhexanoate (3HHx) into PHA and has, therefore, a broader substrate specificity than previously described.

Recombinant strains of *Ralstonia eutropha* PHB-4, which harbored *Aeromonas caviae* polyhydroxyalkanoates (PHA) biosynthesis genes under the control of a promotor for *R. eutropha* phb operon, wereexamined for PHA production from various alkanoic acids [42]. The recombinants produced poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) [P(3HB-co-3HHx)] from hexanoate and octanoate, and poly(3-hydroxybutyrate-co-3-hydroxyvalerate-co-3-hydroxypentanoate) [P(3HB-co-3HV-co-3HHp)] from pentanoate and nonanoate. One of the recombinant strains, *R. eutropha* PHB-4/pJRDBB39d3 harboring ORF1 and PHA synthase gene of *A. caviae* (phaCAc) accumulated copolyesters with much more 3HHx or 3HHp fraction than the other recombinant strains. To investigate the relationship between PHA synthase activity and in vivo PHA biosynthesis in *R. eutropha*, the PHB-4 strains harboring pJRDBB39d13 or pJRDEE32d13 were used, in which the heterologous expression of phaCAc was controlled by promoters for *R. eutropha* phb operon and *A. caviae* pha operon, respectively. The PHA contents and PHA accumulation rates were similar between the two recombinant strains in spite of the quite different levels of PHA synthase activity, indicating that the polymeration step is not the rate-determing one in PHA biosynthesis by *R. eutropha*. The molecular weights of poly(3-hydroxybutyrate) produced by the recombinant strains were also independent of the levels of PHA synthase activity. It was suggested that a chain-transfer agent is generated in *R. eutropha* cells to regulate the chain length of polymers.

In order to produce poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) and poly(3-hydroxyvalerate-co-3-hydroxyheptanoate), the PHA synthase gene (phaCNc) from *Nocardia corallina* was identified in a lambda library on a 6-kb BamHI fragment. A 2.8-kb XhoII subfragment was found to contain the intact PHA synthase. This 2.8-kb fragment was subjected to DNA sequencing and was found to contain the coding region for the PHA synthase and a small downstream open reading frame of unknown function. On the basis of DNA sequence, phaCNc is closest in homology to the PHA synthases (phaCPaI and phaCPaII) of *Pseudomonas aeruginosa* (approximately 41% identity and 55% similarity). The 2.8-kb XhoII fragment containing phaCNc was subcloned into broad host range mobilizable plasmids and transferred into *Escherichia coli*, *Klebsiella aerogenes* (both containing a plasmid bearing phaA and phaB from *Ralstonia eutropha*), and PHA-negative strains of *R. eutropha* and *Pseudomonas putida*. The recombinant strains were grown on various carbon sources and the resulting polymers were analyzed. In these strains, the PHA synthase from N. corallina was able to mediate the production of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) containing high levels of 3-hydroxyhexanoate when grown on hexanoate and larger even-chain fatty acids and poly(3-hydroxyvalerate-co-3-hydroxyheptanoate) containing high levels of 3-hydroxyheptanoate when grown on heptanoate or larger odd-chain fatty acids [43].

Another approach towards production of mcl PHAs from recombinant E. coli was shown by Doi's group[44]. The *Escherichia coli* 3-ketoacyl-ACP reductase gene (fabGEc) was cloned using a PCR technique to investigate the metabolic link between fatty acid metabolism and polyhydroxyalkanoate (PHA) production.Three plasmids resppectively harboring fabGEc and the poly-3-hydroxyalkanoate synthesis genes phaCAc and phaC1Ps from *Aeromonas caviae* and *Pseudomonas sp.* 61-3 resp. were constructed and introduced into *E. coli* HB101 strain. On a two-stage cultivation using dodecanoate as the sole carbon source, recombinant *E. coli* HB101 strains harboring fabGEc and phaC genes accumulated PHA copolymers (about 8 wt% of dry cell weight) consisting of several (R)-3-hydroxyalkanoate units of C4, C6, C8, and C10. It was suggested that overexpression of the fabGEc gene leads to the supply of (R)-3-hydroxyacyl-CoA for PHA synthesis via fatty acid degradation.

In Vitro Production of PHAs

Beside the studies of PHA production in fermentation processes applying living microorganisms also in vitro systems may be used in future. A combined chemical and enzymatical procedure has been developed to synthesize macroscopic poly[(R)-3-hydroxybutyrate] (PHB) granules in vitro. The granules form in a matter of minutes when purified polyhydroxyalkanoate (PHA) synthase from Alcaligenes eutrophus is exposed to synthetically prepared (R)-3-hydroxybutyryl CoA, thereby establishing the minimal requirements for PHB granule formation. The artificial granules are spherical with diams. of up to 3 mm and significantly larger than their native counterparts (0.5 mm). The isolated PHB was characterized by ^{1}H and ^{13}C NMR, gel-permeation chromatography, and chemical analysis.

The in vitro polymerization system yields PHB with a molecular mass > 10.10^6 Da, exceeding by an order of magnitude the mass of PHBs typically extracted from microorganisms. It was demonstrated that the molecular mass of the polymer can be controlled by the initial PHA synthase concentration. Preliminary kinetic analysis of de novo granule formation confirms earlier findings of a lag time for the enzyme but suggests the involvement of an additional granule assembly step. Minimal requirements for substrate recognition were investigated. Since substrate analogs lacking the adenosine 3',5'-bisphosphate moiety of (R)-3-hydroxybutyryl CoA were not accepted by the PHA synthase, the authors provide evidence that this structural element of the substrate is essential for catalysis [45].

Additional work in this field was performed by Lenz et al. [46], showing the effectivity of glycerol on stabilizing the polymerase after purification and on eliminating the lag phase in in vitro polymerization reactions of 3-hydroxybutyl CoA (HBCoA), and 3-hydroxyvaleryl CoA (HVCoA). K_M values were determined for the activity of the polymerase with both HBCoA and HVCoA, and the rates of propagation for both monomers were estimated. With a racemic mixture of HBCoA, the enzyme polymerized only the [R] monomer.

Production of PHAs with transgenic plants

The obtainment of polyhydroxyalkanoates from genetically modified crop plants represents a drastic change in methodology. With this strategy, the steps necessary to procure the substrates used in a fermentative process are no longer required, as naturally occuring carbon dioxide and sunlight serve as carbon and energy sources, respectively. While this field of research is still in its infancy, progress since the initial trials has shown the concept to be promising. The first investigations reported on the use of the the plant *Arabidopsis thaliana* harboring the PHA genes of *R. eutropha.*

Poirier et al. [47] reported the successful expression of the *R. eutropha* genes encoding acetoacetyl-CoA reductase and PHA synthase in the cytoplasm of *A. thaliana.* The 3-ketothiolase gene is endogenous in plant cytoplasm. These experiments resulted in P(3HB) synthesis in the cytoplasm, nucleus and vacuoles of all plant tissue, but in low amounts and at the cost of stunted growth and poor seed production. This was attributed to the diversion toward polymer accumulation of acetyl-CoA normally channelled into essential metabolic pathways.

The second phase of research [48] has focused on the targeting of the PHA pathway to a specific subcellular compartment, the plastid, where biosynthesis of triglycerides from acetyl-CoA normally occurs. All three genes needed be cloned in this case, and this led to the accumulation of high levels of P(3HB) with few deleterious effects on the growth or fertility of the hosts. The homopolymer was stored within plastids to up to 14% of the dry mass of the plants (a 100-fold increase from expression in the cytoplasm) in the form of granules of size and appearance similar to those of bacterial PHA inclusions.

The genes encoding acetoacetyl-CoA reductase and PHA synthase from *R. eutropha* were expressed in in cotton (*Gossypium barbadense* L. cv Sea Island) fibers. Transgenic plants containing both enzymes produced PHA in the fibers, since b-ketothiolase activity is present in cotton fibers [49]. The presence of P(3HB) granules in transgenic fibers resulted in measurable changes of thermal properties, the fibers exhibited better insulating characteristics. The rate of heat uptake and cooling was slower in transgenic fibers, resulting in higher heat capacity [50].

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12. Production of Polyhydroxyalkanoates by Metabolically Engineered Escherichia coli Strains

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Polyhydroxyalkanoates (PHAs) are synthesized by numerous microorganisms as an energy and/or reducing power reserve material usually when there is growth limiting nutrient in the presence of excess carbon source. PHAs have been attracting much attention due to their potential to be used as completely biodegradable thermoplastics and elastomers. However, the production cost of PHAs is rather high compared with other polymeric materials, which has been hampering their use in a wide range of applications. Numerous cultivation strategies employing various microorganisms have been developed during the last 10 years or so towards the goal of achieving high PHA productivity and thus lower production cost. One of the most successful systems for the production of PHAs was that using recombinant *Escherichia coli* harboring heterologous PHA biosynthesis machinery.

Metabolically engineered *E. coli* strains harboring a multi-copy plasmid containing the *Ralstonia eutropha* PHA biosynthesis genes have been employed for the production of poly(3-hydroxybutyrate), PHB. Nutrient feeding strategies were developed for the production of PHB to a concentration greater than 100 g/L with productivity greater than 3 g/L-h by fed-batch culture. The new strategy of applying oxygen limitation for the more efficient production of PHB was developed, and was used to produce PHB with the productivity as high as 3.8 g/L-h. Several other recombinant *E. coli* strains were developed using the new PHA biosynthesis genes cloned from *Alcaligenes latus*. It was found that these recombinant *E. coli* strains could produce PHB more efficiently than the recombinant strains containing the *R. eutropha* PHA biosynthesis genes. Several other systematic pathway manipulations were made to allow *E. coli* to produce novel PHA copolymers. These studies suggested that metabolic engineering can be employed to efficiently channel the pathway intermediates towards the synthesis of PHAs of desired characteristics. Advantages of employing recombinant *E. coli* for the production of PHAs will also be discussed.

Production of Polyhydroxyalkanoates by Metabolically Engineered E.coli Strains

Sang Yup Lee

Metabolic and Biomolecular Engineering National Res. Lab.

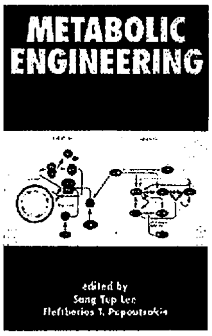
Dept. Chemical Engineering and BioProcess Eng. Res. Center

KAIST

Korea Advanced Institute of Science & Technology

한국과학기술원

To achieve our objective...


METABOLIC ENGINEERING

edited by
Sang Yup Lee
Eleftherios T. Papoutsakis

Metabolic Engineering

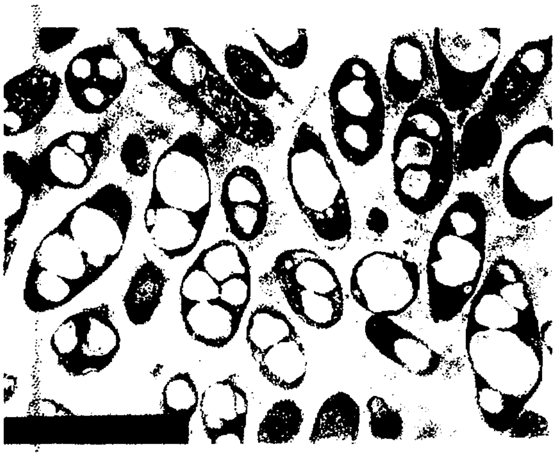
Purposeful modification of metabolic network to achieve...

1. Enhanced production of metabolites and other biologicals that are already produced by host organism
2. Production of modified or new metabolites and other biologicals that are new to the host organism
3. Broadening the substrate utilization range
4. Designing improved or new metabolic pathways for degradation of various chemicals, especially xenobiotics
5. Modification of cell properties that facilitate bioprocessing (fermentation and product recovery)

Lee, S.Y. and Papoutsakis, E.T.(1999) Metabolic Engineering, Marcel Dekker, USA

Polyhydroxyalkanoates (PHAs)

- Energy/carbon/reducing power storage material
- Intracellularly accumulated as distinct granules by numerous microorganisms
- Synthesized usually when an essential nutritional component is limiting in the presence of excess carbon source



Properties of Polyhydroxyalkanoates (PHAs)

Completely biodegradable

Produced from renewable resources

Thermoplastic or elastomer

Biocompatible and non-toxic

Optically active (enantiomerically pure in R-configuration)

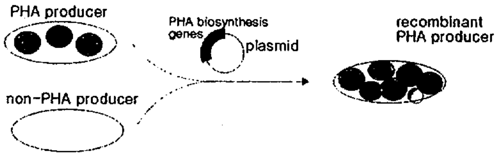
Polyhydroxyalkanoates (PHAs)

- Short-chain-length (SCL) PHA
  - consisting of 3-5 carbon atoms
  - high degree of crystallinity
  - P(3HB): brittle and stiff, similar to polypropylene
- Medium-chain-length (MCL) PHA
  - consisting of 6-14 carbon atoms
  - elastomers with low crystallinity
  - substitutes for conventional nondegradable elastomers

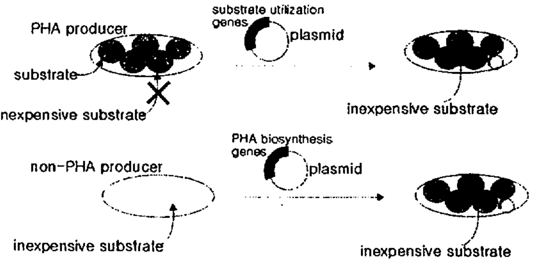
KAIST

Metabolic Engineering of PHA Producers

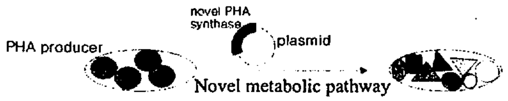
(a) Enhancing PHA production



(b) Broadening utilizable substrate range



(c) Producing novel PHA



Objective: Cost effective production of PHA

1. Bacterial strain

2. Fermentation

- batch, fed-batch, continuous
- inexpensive carbon source
  - glucose, sucrose, fatty acids, methanol,
- high PHA content (target: > 80%)
- high PHA productivity
- high PHA concentration
- high PHA yield
  - no waste of carbon (e.g. exopolysaccharides

3. Recovery

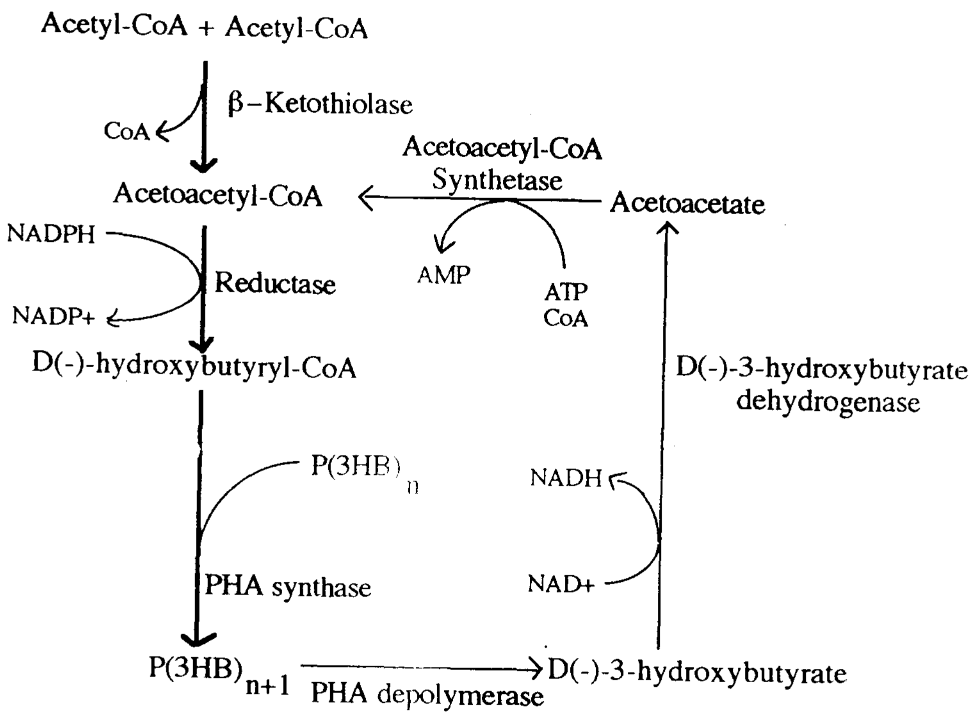
- easy cell disruption
- digestion of non-PHA w/o degradation of PHA

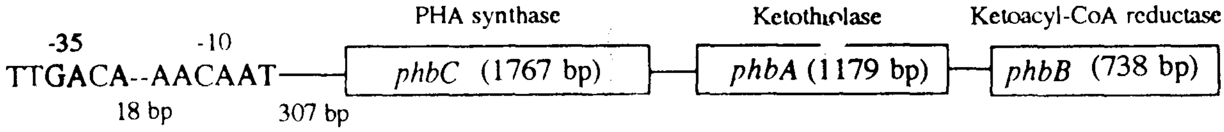
Candidates:

Ralstonia eutropha
Alcaligenes latus
Azotobacter vinelandii
Methylotrophs & Pseudomonads
Recombinant bacteria (*Escherichia coli*)

Lee, S.Y. (1996) TIBTECH 14: 431-438

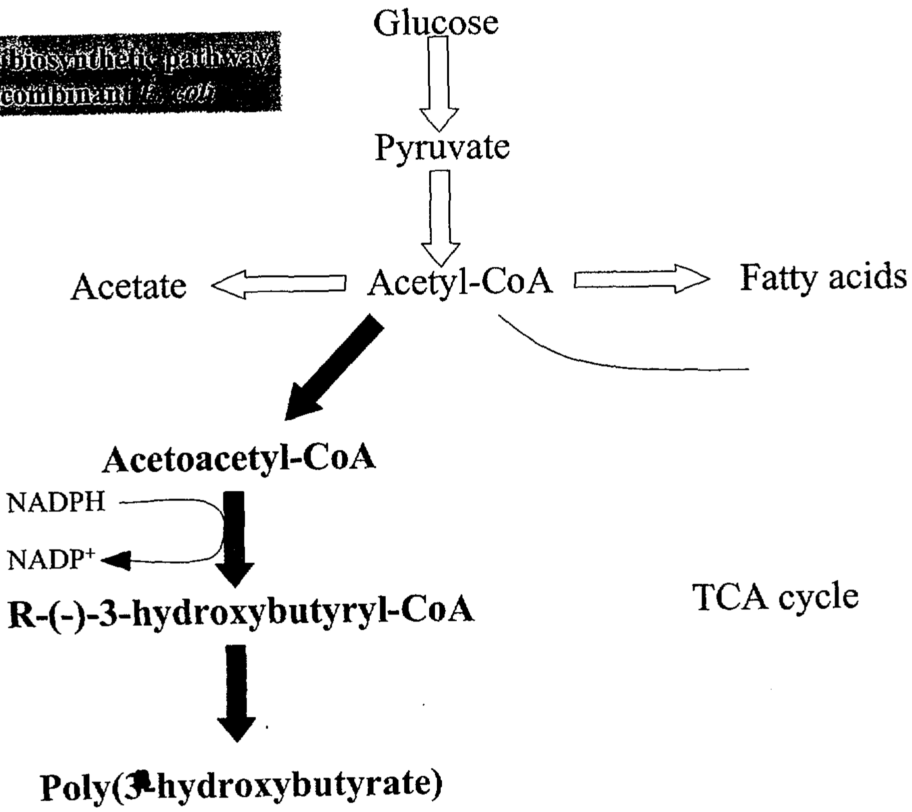
P(3HB) Synthesis and Degradation in *A. eutrophus*



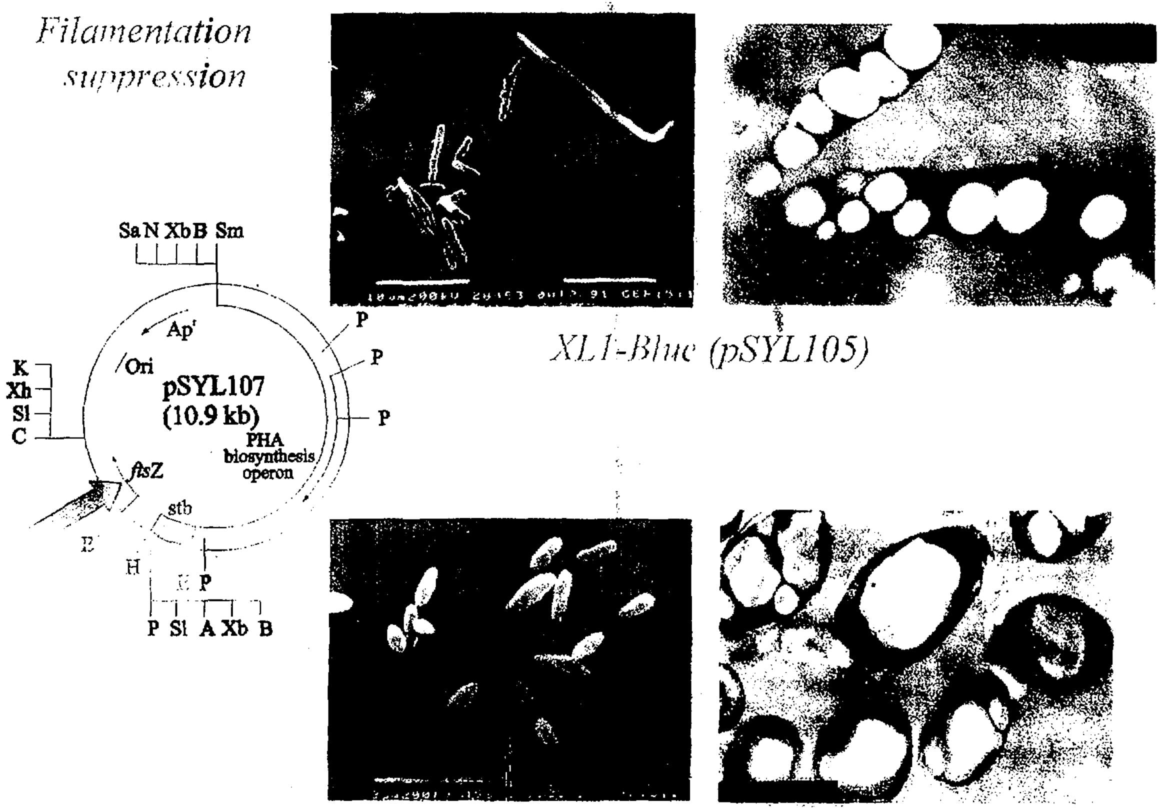


Organization of the PHA biosynthetic genes from *Alcaligenes eutrophus* H16

PHB biosynthetic pathway
in recombinant *E. coli*



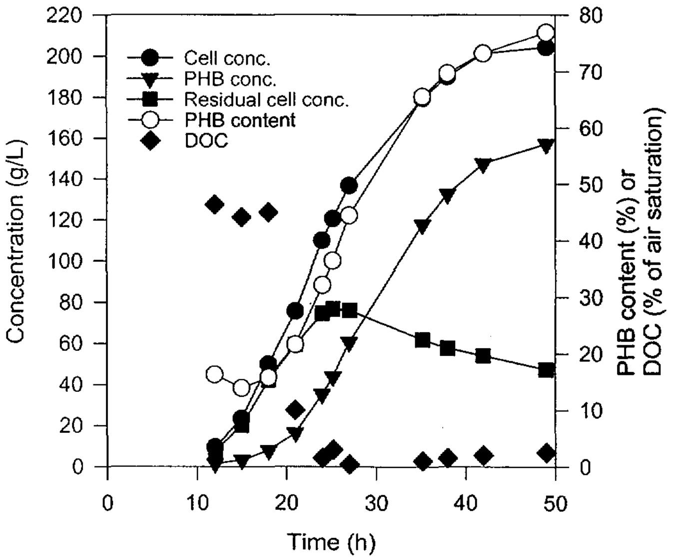
Filamentation suppression



XL1-Blue (pSYL105)

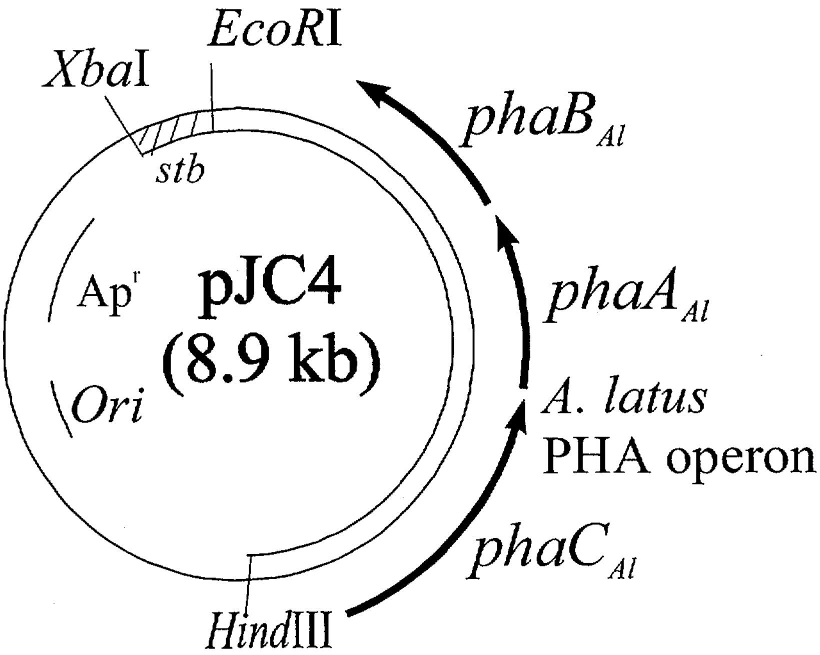
XL1-Blue (pSYL107)

Fed-batch culture of XL1-Blue (pSYL107) in a defined-medium under low DOC (1-3% of air saturation)

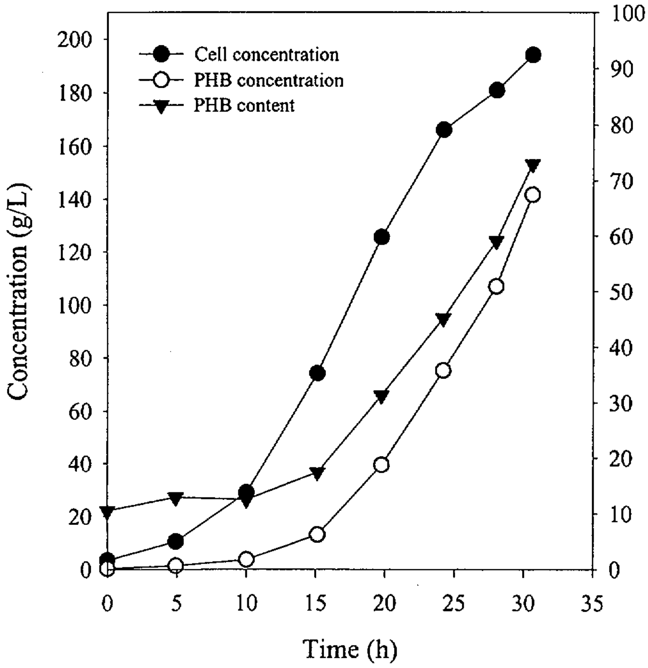


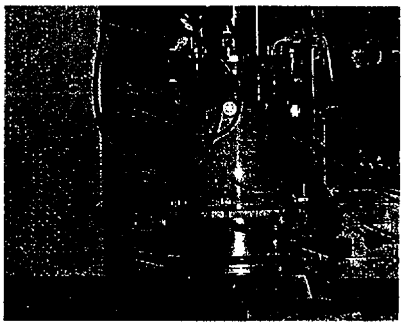
205 g DCW/L
158 g PHB/L
77% of DCW
3.2 g PHB/L-h

▫ A new plasmid for PHA production in *E.coli*



Fed-batch culture of recombinant *E.coli* XL1-Blue (pJC4)





Final values:
CDW: 197 g/L
PHB: 142 g/L
Content: 72%
Productivity: 4.63 g/L-h

Recovery of P(3HB) from recombinant *E. coli* by simple chemical digestion

Recovery cost can be up to 50% of the total operating cost

Methods that have been used....

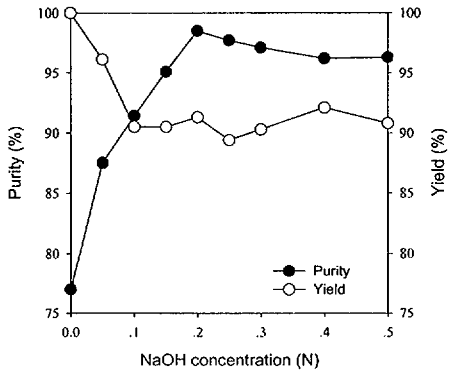
Solvent extraction
Enzymatic digestion ⇒
Surfactant-hypochlorite digestion

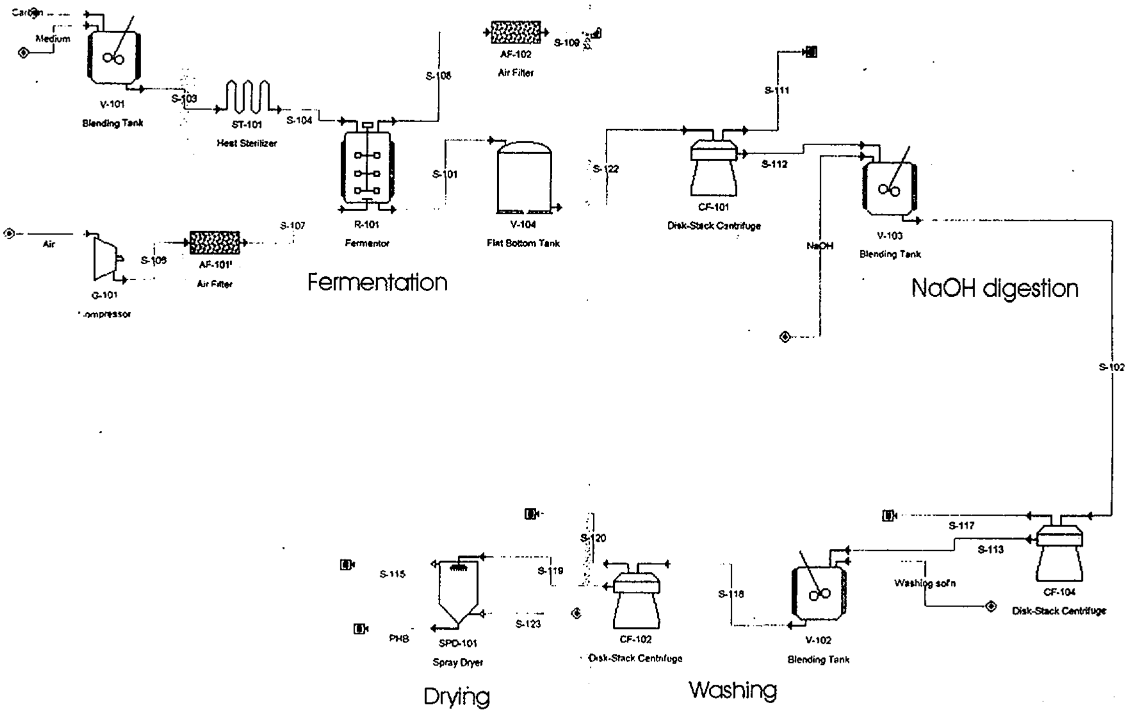
Difficult
Expensive
Inefficient

New simple chemical digestion method

50 g CDW/L of recombinant *E. coli*
P(3HB) content of 77%
Digest with 0.2 N NaOH at 30 °C for 1 hr

P(3HB) having purity of 99%
and yield of 92%





Removal of endotoxin during the recovery of PHA by gram negative bacteria

(Collaboration with Dr. K. Han, LG Chem) **FDA: 5 EU/kg body weight**

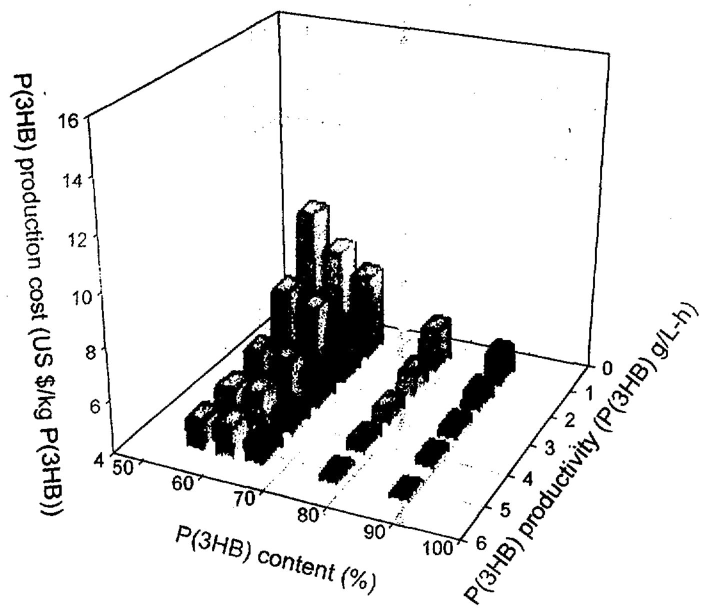
Limulus amebocyte lysate gel clot method

- ***Ralstonia eutropha*** **and** ***Alcaligenes latus***
  - Chloroform extraction results in endotoxin level of less than 10 EU/g PHB.

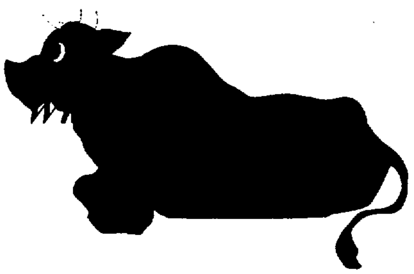
- **Recombinant** ***Escherichia coli*** harboring heterologous PHA biosynthesis genes
  - Digestion with 2N NaOH for 1 hr.
  - Endotoxin level of less than **1 EU/g PHB** (from 2 x 10^7 EU/g)

Sensitivity analysis: P(3HB) production by recombinant E. coli

Production scale: 100,000 ton/yr
Recovery by simple chemical digestion



whey



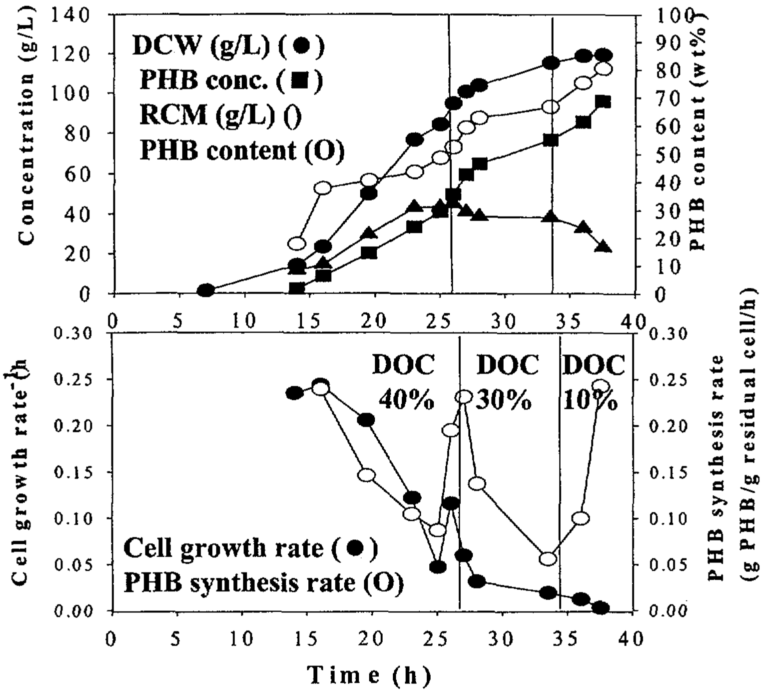
- 4.5% (w/v) lactose
- 0.8% (w/v) protein
- 1.0% (w/v) salts
- 0.1-0.8% (w/v) lactate

- 26 million tonnes of whey produced per year in USA
- High BOD -----> environmental problem

Table 2. Comparison of recombinant *E. coli* strains for PHB production from whey using the "optimal" whey concentration determined by screening studies.

Strain	Whey Conc. (g/L)	Cell Mass (g/L)	PHB Conc. (g/L)	PHB Content (% w/w)
DSM499 (pSYL105)	20	1.1	0.07	6.7
DSM499 (pSYL107)	40	6.3	2.6	42
DSM6056 (pSYL105)	30	1.2	0.06	4.9
DSM6056 (pSYL107)	30	2.1	0.35	17
KCTC2223 (pSYL105)	40	6.0	0.48	8.0
KCTC2223 (pSYL107)	10	2.3	0.06	2.6
GCSC6197 (pSYL107)	35	2.6	0.9	35
GCSC3121 (pSYL107)	35	2.9	1.2	41
GCSC2507 (pSYL107)	70	6.9	3.5	51
GCSC6572 (pSYL107)	35	2.5	1.1	44
GCSC4401 (pSYL107)	30	5.7	4.5	79
✓ GCSC6576 (pSYL107)	30	6.4	5.2	81

PHB from whey (280 g/L lactose)



No culture broth removal !

Cell conc. : 119.5 g/L
PHB conc. : 96.2 g/L
PHB content : 80.0 wt%
PHB productivity:
2.57 g/L/h

Advantages of employing recombinant E. coli

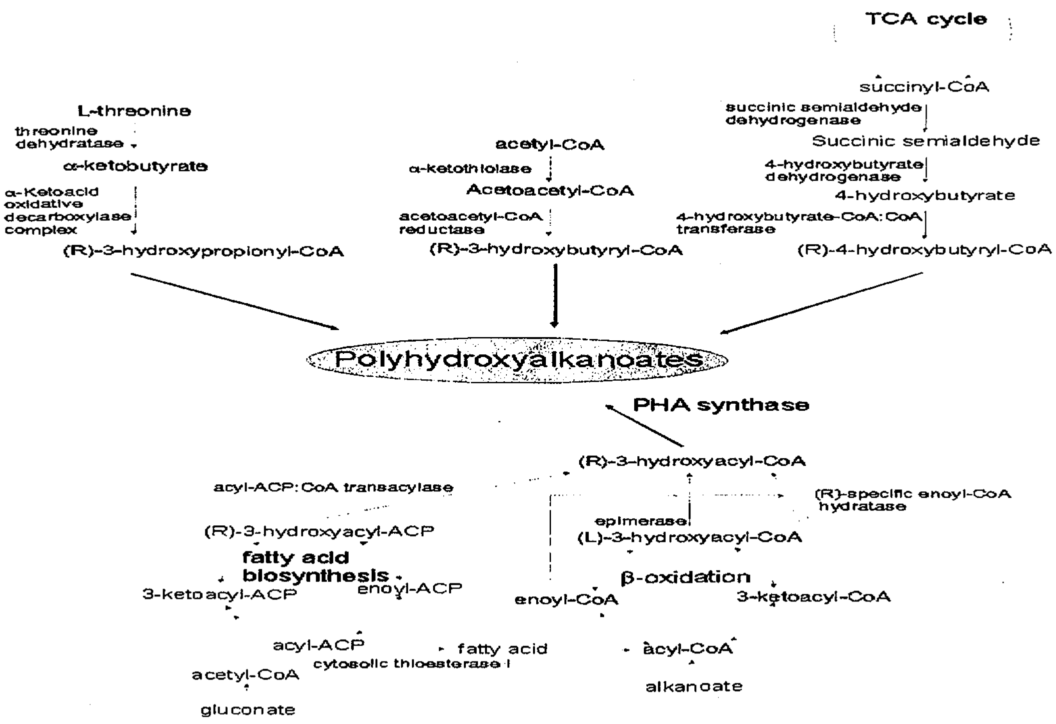
- high PHA conc. (160 g PHB/L)
- high PHA content (85%)
- high PHA productivity (5 g PHB/L-h)

- lack of PHA depolymerase

- fragility of cells after PHA accumulation
- less degradation of PHA during recovery → **Efficient recovery**
- larger granule size

- a number of utilizable carbon substrates → **Inexpensive carbon substrate**

Metabolic Pathways Generating Various Monomers



TCA cycle

succinyl-CoA

succinic semialdehyde dehydrogenase

Succinic semialdehyde

4-hydroxybutyrate dehydrogenase

4-hydroxybutyrate

4-hydroxybutyrate-CoA:CoA transferase

(R)-4-hydroxybutyryl-CoA

L-threonine

threonine dehydratase

α-ketobutyrate

α-Ketoacid oxidative decarboxylase complex

(R)-3-hydroxypropionyl-CoA

acetyl-CoA

α-ketothiolase

Acetoacetyl-CoA

acetoacetyl-CoA reductase

(R)-3-hydroxybutyryl-CoA

Polyhydroxyalkanoates

PHA synthase

(R)-3-hydroxyacyl-CoA

acyl-ACP:CoA transacylase

(R)-specific enoyl-CoA hydratase

epimerase

(R)-3-hydroxyacyl-ACP

(L)-3-hydroxyacyl-CoA

fatty acid biosynthesis

β-oxidation

3-ketoacyl-ACP

enoyl-ACP

enoyl-CoA

3-ketoacyl-CoA

acyl-ACP

fatty acid

acyl-CoA

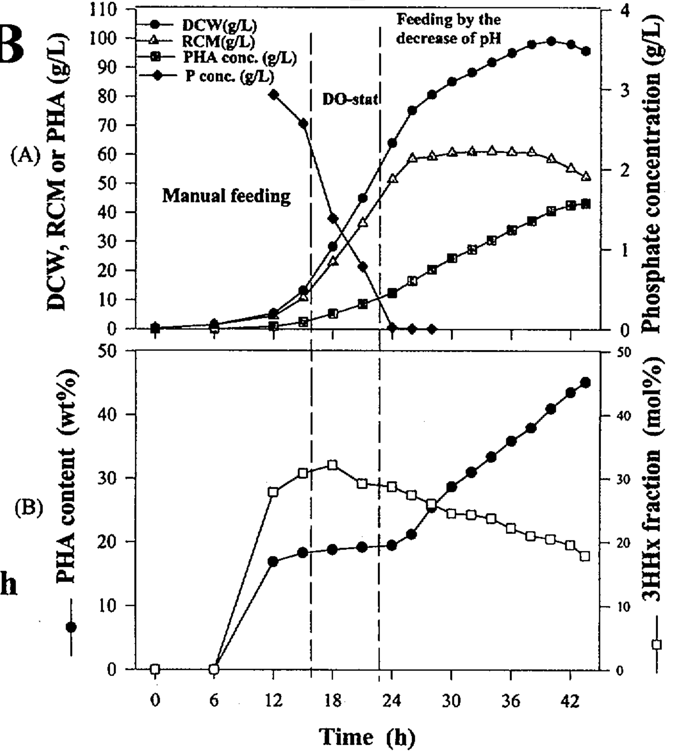
cytosolic thioesterase I

acetyl-CoA

alkanoate

gluconate

Fed-batch culture of *A. hydrophila* Fermentation B



DCW : 95.7 g/L

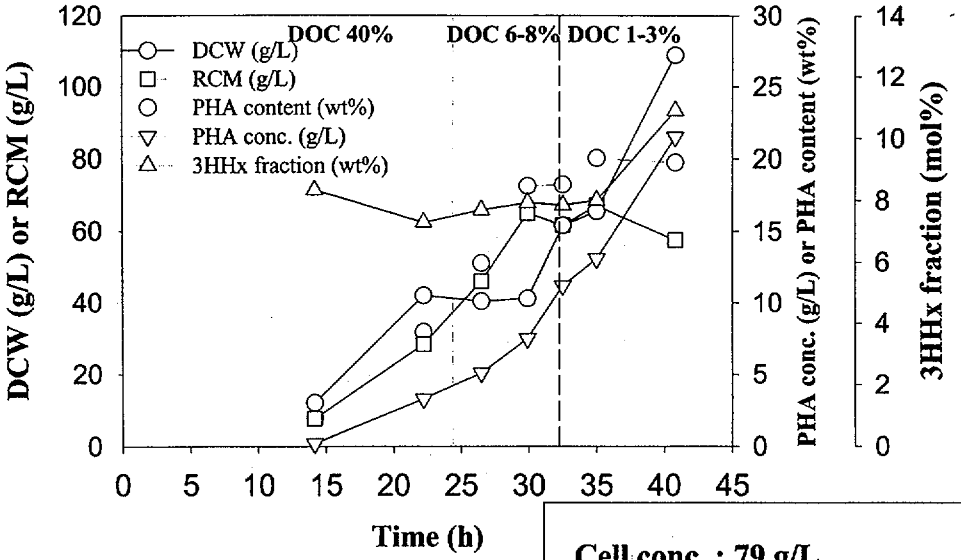
PHA conc. : 43.3 g/L

PHA content : 45.2 wt%

HHx fraction : 17.5 mol%

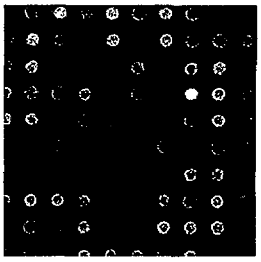
PHA productivity : 1.01 g/L/h

Time profiles of Fed-batch culture of *E. coli* LS5218 (prTrp3A-CnJBOF1)



Cell conc. : 79 g/L
PHA conc. : 21.5 g/L
PHA content : 27.2%
HHx fraction :9.7 mol%
PHA Productivity: 0.51 g PHA/L-h

DNA chip



- DNA chip (DNA microarray)
  - High density array of DNA of known sequences on a solid support
  - It allows analysis of large amount of information coming out of the genome project in a relatively short time.

- Applications
  - Gene expression monitoring

    --- **Transcriptome analysis**, Pharmacogenomics
  - Detection of Mutations and analysis of polymorphism & phenotype

    --- genetic diagnosis and prognosis

Work in progress....

Global transcriptome and proteome monitoring

↓

MFA, MCA and MNA

↓

Optimized metabolic pathway for PHA copolymer production

↓

Super PHA producer!!!

Session 3; EDPs Based on Aliphatic Polyesters

13. CELGREEN®: Daicel's Biodegradable Plastics

Masanori Ito

Celgreen Business Development, Planning & Development Group, Daicel Chemical Ind. Ltd., Japan
[E-mail: ms_ito@daicel.co.jp]

Daicel is manufacturing 1)Polycaprolactone by semi-commercial plant, 2) Cellulose acetate by commercial plant, 3)Aliphatic polyesters (under R & D).

CELGREEN is the registered trade mark of Daicel's biodegradable plastics, which are 'environmentally friendly' and can be degraded by microorganisms in natural environment. Daicel is currently offering two types of products, cellulose acetate type (PCA) and polycaprolactone type (PH, PHB). CELGREEN PCA type has characteristics of high clarity, high strength and high viscosity. CELGREEN PH type has characteristics of good miscibility with other polymers, high strength and high elongation. CELGREEN PHB type has improved heat-resistance property compared with CELGREEN PH type.

CELGREEN can be processed by extrusion molding, injection molding, and blow molding under the proper temperature conditions and gives moldings, films and sheets products.

CELGREEN can be degraded by microorganisms in water (fresh water, seawater and sewage), soil, or compost.

CELGREEN PCA is useful for the usage field of Polystyrene and CELGREEN PH and PHB for Polyolefin PE and PP.

Daicel is now focusing on marketing mulch-film and compost bag in Japan.

Detail of the actual applications of the CELGREEN products will be presented.

Daicel's Activities

1989 Joined 'Biodegradable Plastics Society'

- Chairperson : Akiro Kojima (Daicel Chemical Ind., on June, 1995)
- Evaluation of biodegradability in natural environment
  (Field Test)

1990 Joined the MITI project { RITE (Research Institute of
Innovative Technology for the Earth) }

- Development of biodegradable plastics by technologies of molecular design and controlled polymerization(Chemical synthesis)

Direct synthesis of Polyglicolide (Single-step synthesis with inexpensive materials ($CO+CH_2O$))

Synthesis of Polyesters (SDM+1, 4-BD)

SDM :Dimethylsuccinate (Methylacryate + CO + CH_3OH)
1, 4-BD :1, 4-Butanediol

Manufacturing :

1)	Polycaprolactone	: Semicommercial plant in Otake city
2)	Cellulose acetate	: Commercial plant in Himeji city
3)	Aliphatic polyester	: Under R & D

Evaluation of biodegradability :

1) Evaluation in natural environment
   - Soil burial test
   - Water immersion test (in the river and sea)

2) Evaluation with microorganisms (Activated sludge)
   - Standard sludge (OECD 301C)
   - Sludge of municipal sewage works in Himeji city
     (JIS K6951, ISO 14852)

PRODUCT TYPES AND PROPERTIES

CELGREEN has both cellulose acetate type (PCA) and polycaprolactone type (,)

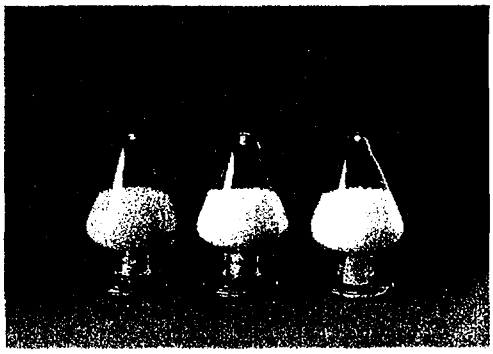
PCA type has characteristics of high clarity, high strength and high viscosity.
type has characteristics of good miscibility with other polymers, high strength and high elongation.
type is improved the heat-resistance property of type.

Please use properly these types of plastics for each use.

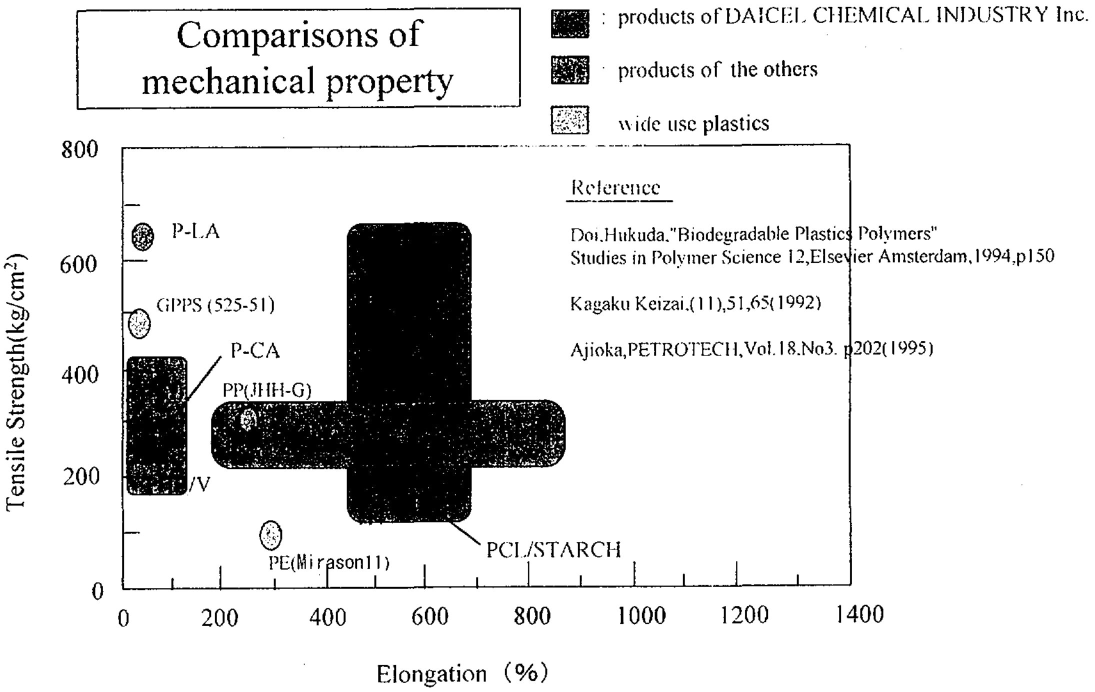
PROPERTIES OF MOLDED PRODUCTS

[illegible]	[illegible]	[illegible]	[illegible]					
			PCA00	PCA02	PCA05	PHB02	PHB05	PH7
Density	g /cm³		1.26	1.25	1.22	1.21	1.22	1.14
MFR (190℃-2160 g)	g /10min	K7210	0.3	1.5	4.5	2.7	6.1	1.7
Tensile Strength at Yield	kg/cm²	K7113	330	240	180	260	280	200
Tensile Strength at Break	kg/cm²	K7113	360	270	220	370	370	690
Elongation at Break	%	K7113	53	62	72	360	370	780
Tensile Modulus	kg/cm²	K7113	3200	2400	1800	2700	2600	2300
Flexural Strength	kg/cm²	K7203	460	310	240	260	270	380
Flexural Modulus	kg/cm²	K7203	14800	11000	8800	5800	5800	4500
Izod Impact Strength (Notched)	kg cm/cm	K7110	15	12	10	49	39	N.B.
Heat Distortion Temperature (18.6kg/cm²)	℃	K7207	59	53	51	50	51	47
(4.6kg/cm²)		K7207	81	77	71	64	72	56
Vicat Softening Temperature	℃	K7206	110	111	104	103	106	55

Note : These values are typical data and are not guaranteed.



Comparisons of mechanical property



Reference

Doi,Hukuda,"Biodegradable Plastics Polymers" Studies in Polymer Science 12,Elsevier Amsterdam,1994,p150

Kagaku Keizai,(11),51,65(1992)

Ajioka,PETROTECH,Vol.18,No3. p202(1995)

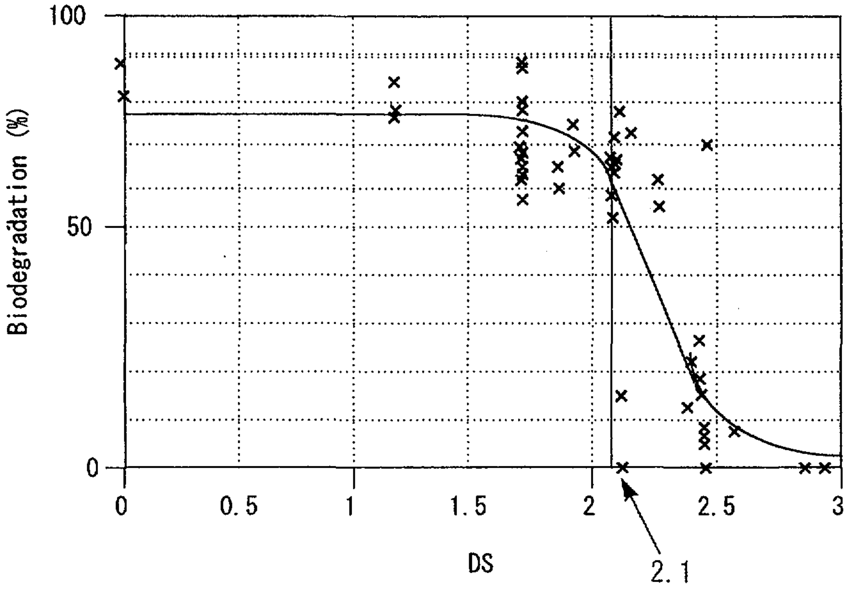
Cellulose $\xrightarrow{\text{acetylation}}$ Cellulose acetate

Use of Cellulose acetate

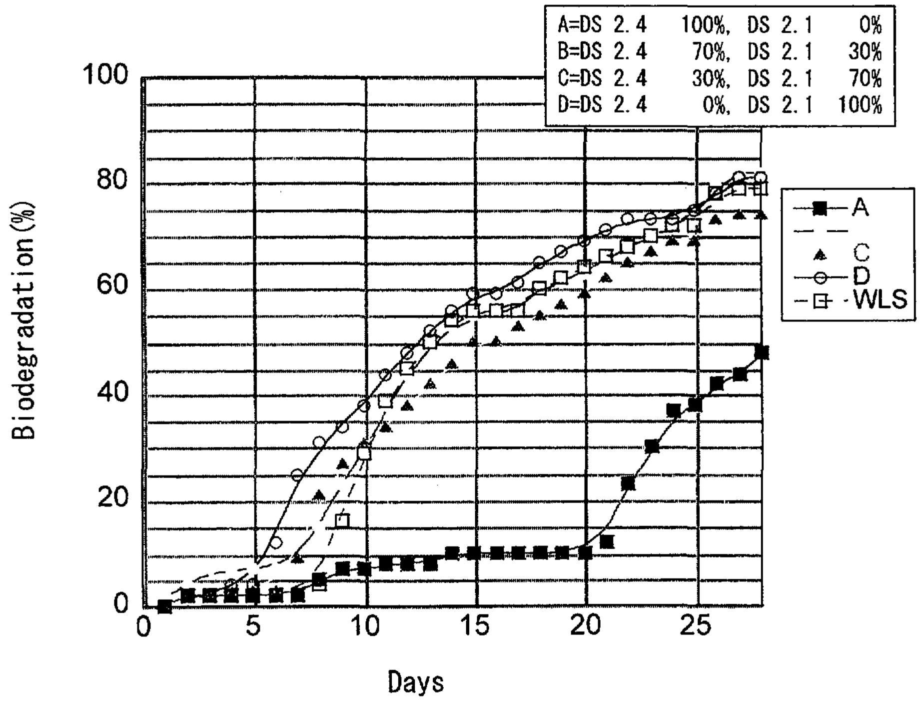
- photographic film
- cigarette filter
- packaging film
- fiber
- moldable plastics

Biodegradation of Cellulose acetate

(Using activated sludge in Aboshi plant)

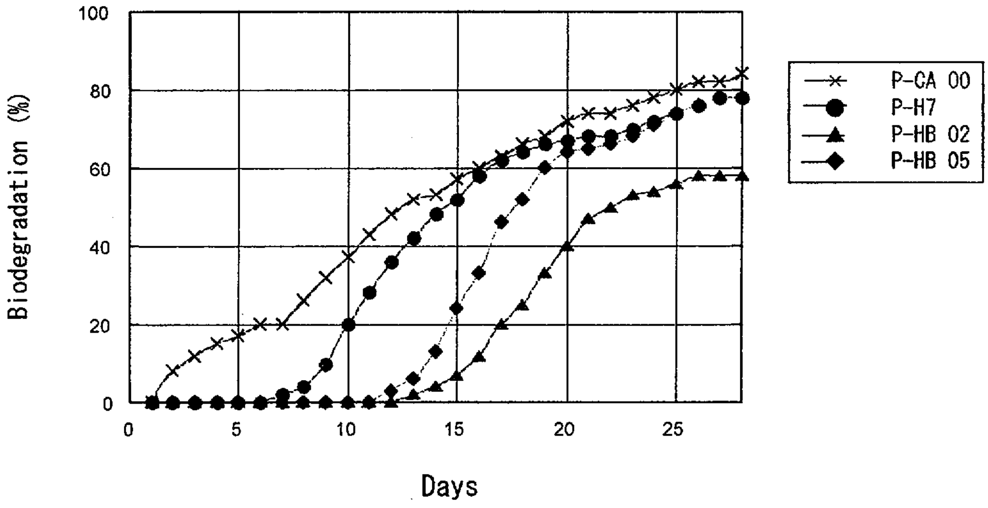


Biodegradation of Mixture of DS 2.14 and 2.45 CA



Biodegradation of P-CA and P-HB

P-CA : Cellulose acetate compounds
P-HB : Aliphatic polyester compounds

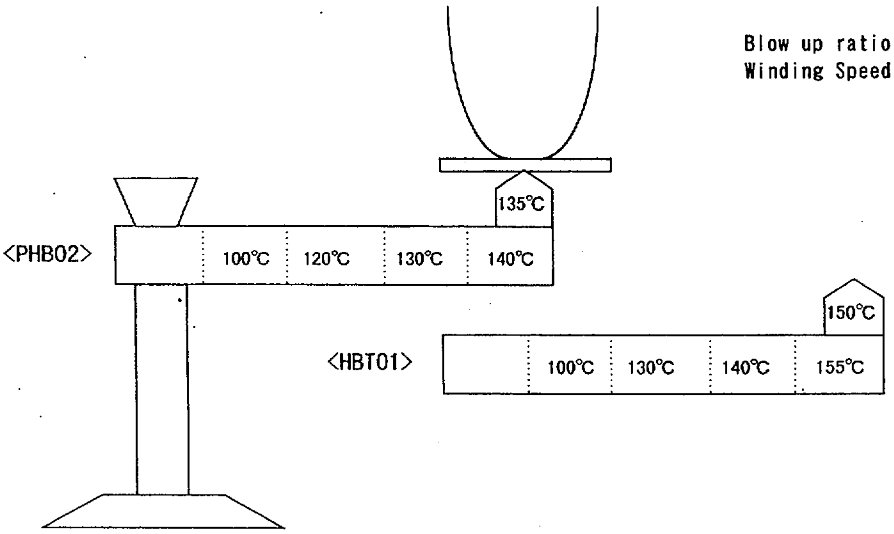


(Using returned sludge of municipal sewage works)

Forming Processes and Applications

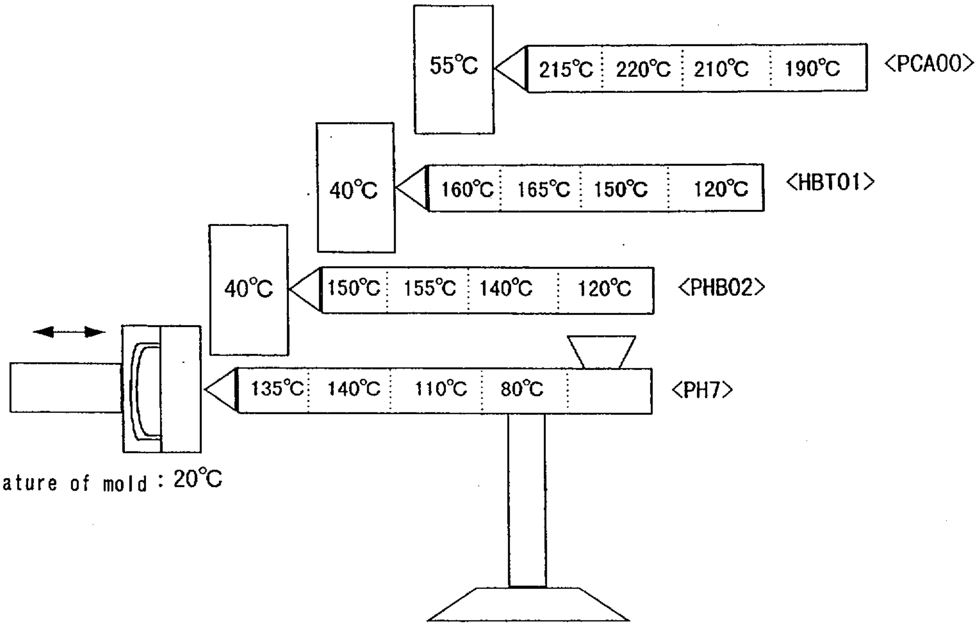
Forming Processes	Application Products	Celgreen® PCA	Celgreen® PHB	Celgreen® PH
Injection molding	Pots , Golf tees	◎	○	△
Inflation molding	Mulchingfilm	△	◎	△
T-dye Extrusion molding	Sheets ,	◎	◎	○
	Nets	×	◎	×
Blow Molding	Bottles	△	○	△
Extrusion Foaming	Loose Fill, Sheets	×	○	△
Fiber	Mono , multi-filament	△	△	△
Thermo forming	Trays , Packages	△	○	△
Ultrasonic adhesion	Brief case	×	○	○
Heat seal adhesion	Bags	×	○	○

Inflation molding processing conditions
(PCA, HBT, PHB, PH)



Blow up ratio: 2- 4 times
Winding Speed:20-30 m/min.

Injection molding processing conditions
(PHB, HBT)



Temperature of mold : 20℃

Application Areas Desired by Society
(Suggestion of the Committee)

Report "The Age of New Plastics"
by the Study Committee for the Practical Use of Biodegradable Plastics

1. Areas in which Biodegradable Plastics are Used in the Environment

1) Materials for agriculture, forestry, and fisheries
Mulchfilm, transplant seedling pot, fishing net, fishing line, etc.

2) Environmental construction materials
Planting of trees in deserts and wasteland, industrial water-holding seat, soil, vegetation netting, etc.

3) Outdoor leisure goods, etc..
Disposable goods used for golf, fishing, marine sports, mountain climbing, etc..

2. Applications where Recycling are Difficult

1) Food packagings and containers

Removals of stains and organic matters after use is extremely difficult for many types of food packagings and containers. The required resources for the removals are huge.

Trays of perishable foods, lunch boxes, instant food containers, fast food containers, etc.

2) Sanitary goods

Products which present sanitary problems

Paper diapers, sanitary goods, disposable razors, toothbrushes, etc.

3) Construction materials

Construction materials which cannot be easily separated from other construction wastes

Heat-insulators, civil engineering formwork in mountain and sea areas that are difficult to access, soil retention, etc.

3. Applications Effective for Composting

1) Some food packagings and containers
2) Bags for kitchen refuse (garbage bags, draining bags, etc.)

4. Applications that Use the Functions other than Biodegradability

1) In vivo degradation and absorption
   Example : Surgical thread, fracture-stabilizing material, nonwoven fabric, medical films, etc.

2) Slow release
   Example : Materials used to coat pharmaceuticals (drug delivery system), agricultural chemicals, fertilizers, etc.

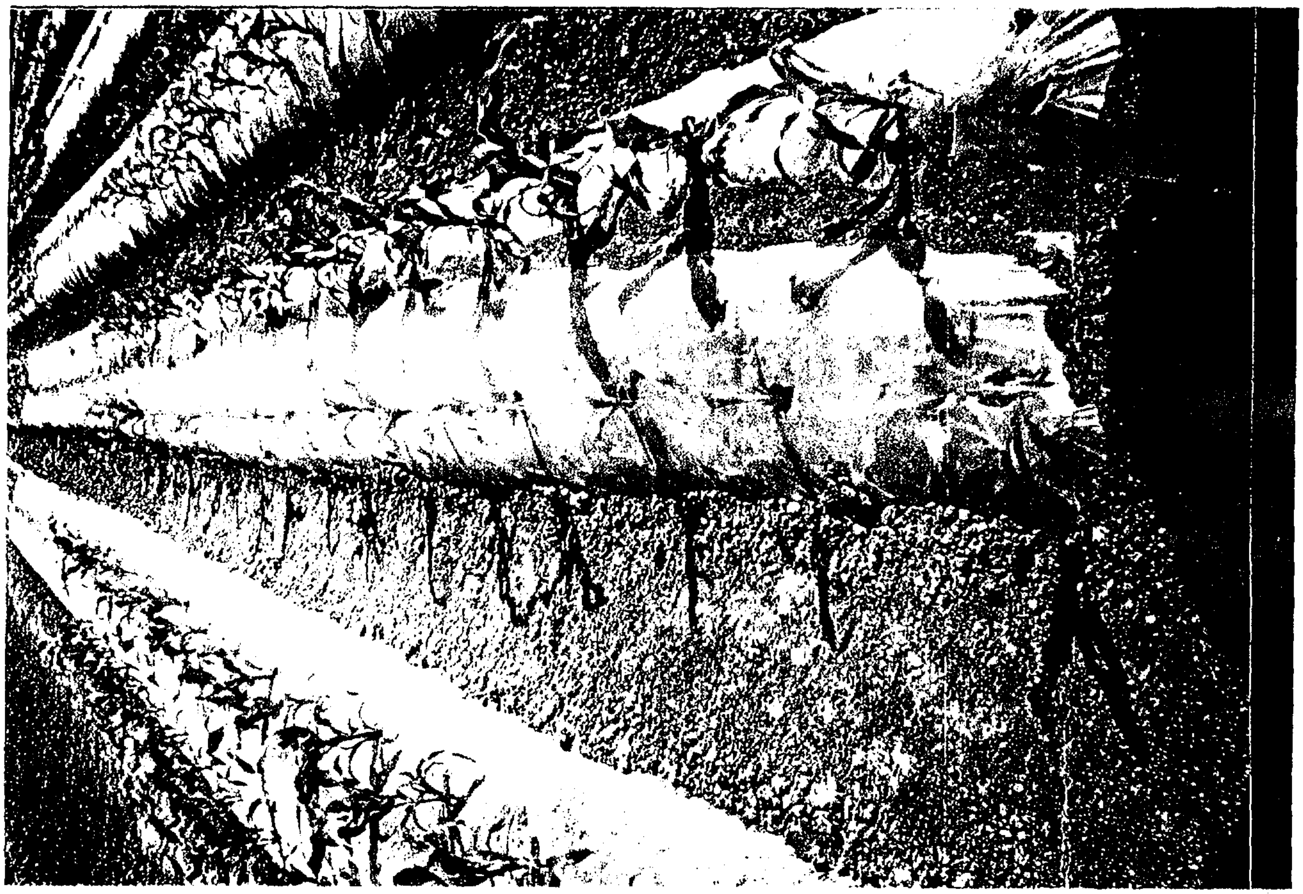
3) Water retention and absorption
   Example : Biodegradable materials that have enough levels of water retention and absorption for afforestation of desert and wasteland, etc.

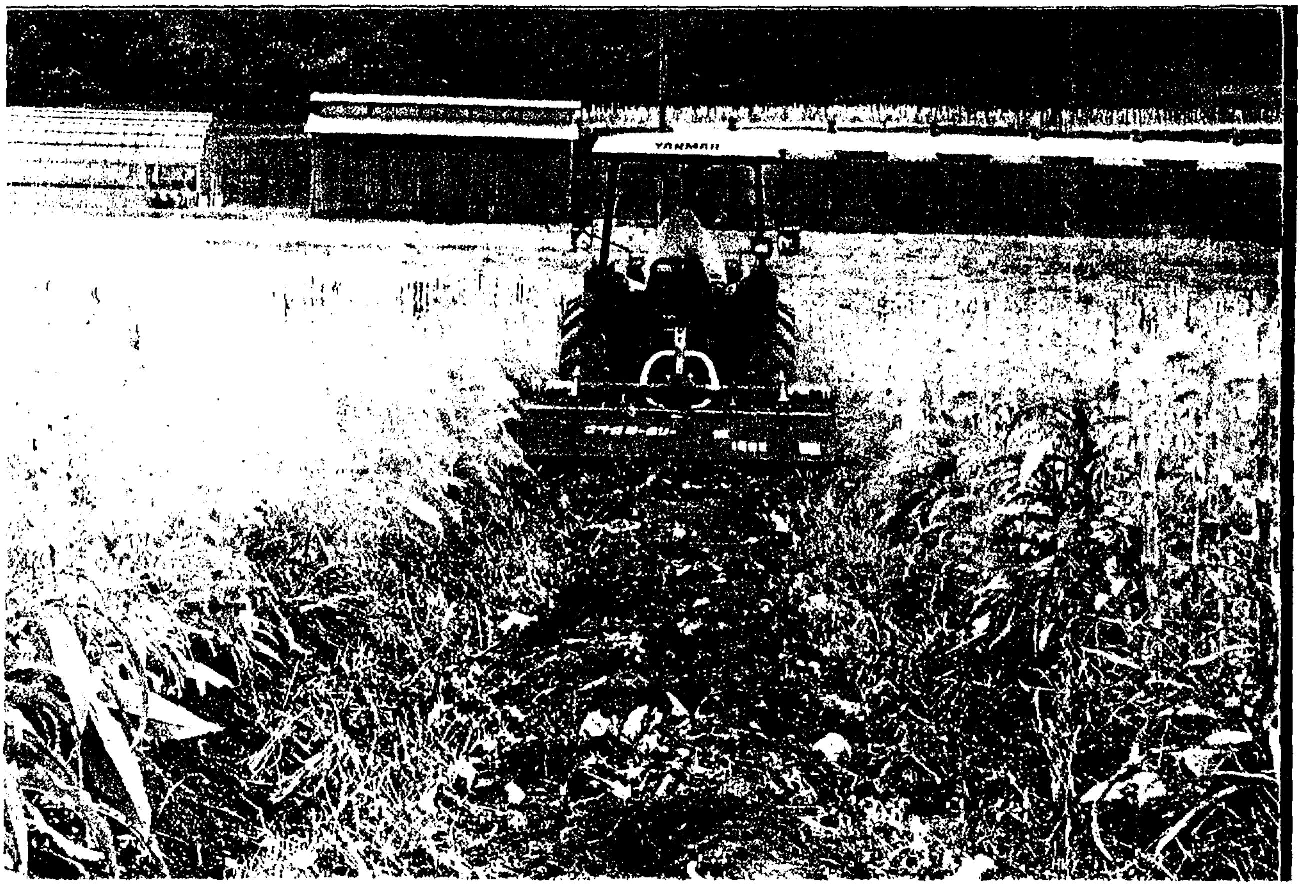
4) Low oxygen permeability and non-absorptivity
   Example : food packagings, inner coating of beverage pack, etc.

5) Low melting point
   Example : Adhesives used for during packaging, binding, and bag-making.

Market potential on the field of agriculture
(In Japan, 1996)

Products	Tons/Year	Raw Materials
Mulchfilms	53, 500	LDPE
Pots	10, 000	LDPE
Nets (Bags)	6, 500	LDPE
Bands	8, 700	PP
Nonwoven fabrics	3, 800	PP, PET
Stretch films	12, 100	PVC




YANMAR

14. Morphology and Degradable Behavior of Various Aliphatic Polyesters

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Aliphatic polyester derived from diols and diacids have great potentials to replace no-biodegradable plastics. However, some features of aliphatic polyesters are yet to meet the requirements to be used as commercial materials. In general, aliphatic polyesters have low melting point and inferior physical properties, e.g. heat resistance and mechanical strength compared to other commercial polymers. Thus, to improve the physical properties, polyesters introduced by various functional groups and copolyesters/blends with other commercial polymers have been investigated.[1]

Most of the biodegradable synthetic polymers contain hydrolysable groups along the main chains. It is known that the biodegradation of such polymers proceeds through hydrolysis and oxidation. Degradation of polymers depends not only on experimental parameters such as pH, ionic strength, temperature and implantation site, but also on polymer characteristics such as molecular weight, molecular weight distribution, morphology, additives, size, chemical composition and configurational structures.[2]

Introduction of various functional group into the back-bone of aliphatic polyester can affect on the degradable properties and its mechanisms because they have their own functional properties and can change microstructure of main polymers. Also, the blend or copolymers of aliphatic polyesters with aromatic component have been investigated to improve thermal durability and mechanical properties. All these concepts of deformation from the homo aliphatic polyesters were based on the chemical or microstructural changes which will be prefer to control biodegradability and mechanical properties. Especially, microstructure of polymers was very important parameter and not yet revealed its obvious relationship with degradability.

In this work, homo aliphatic polyesters and aliphatic/aromatic copolyester were investigated through their degradability, thermal properties and morphological parameters. The effects of various factors on degradability were presented and discussed on the base of experimental results.

Reference

1. Eui Sang Yoo, Seung Soon Im, *Macromol. Symp.* **118** (1997) 739
2. M. Vert, *Macromol. Chem. Macromol. Symp.* **6**(1986) 109

Morphology and Degradable Behavior of Various Aliphatic Polyester

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Department of Textile & Polymer Engineering, College of Engineering

Hanyang University, Seungdong-Ku, Heangdang-dong, Seoul, 133-791,

KOREA

Contents

Factors which can effect biodegradabilities

I .chemical structure of polymer

[Total structure]
- aliphatic> alicyclic> aromatic
- linear chain> branch(>?) cross-linking
- saturated bond> unsaturated bond
- Low MW> high MW
- MW distribution
  wide(>?) narrow

[main chain]
- aliphatic ester linkage
- peptide linkage
- ether linkage
- amide linkage

[Superstructure]
- amorphous> crystalline
- degree of orientation
- low Tm> high Tm

II. Physical chemical Properties

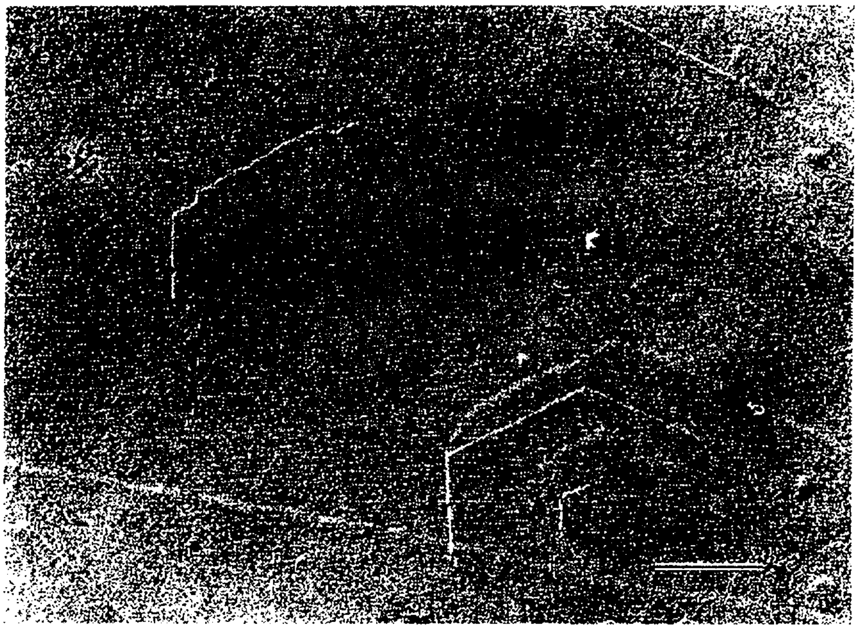
[Shape . Size]
- powder> film> bulk

[Microorganism . Enzyme susceptibility]
- water-soluble> water-swellable> water-resistant
- hydrophilic> hydrophobic

PBS Single Crystal Lamellae and Spherulite

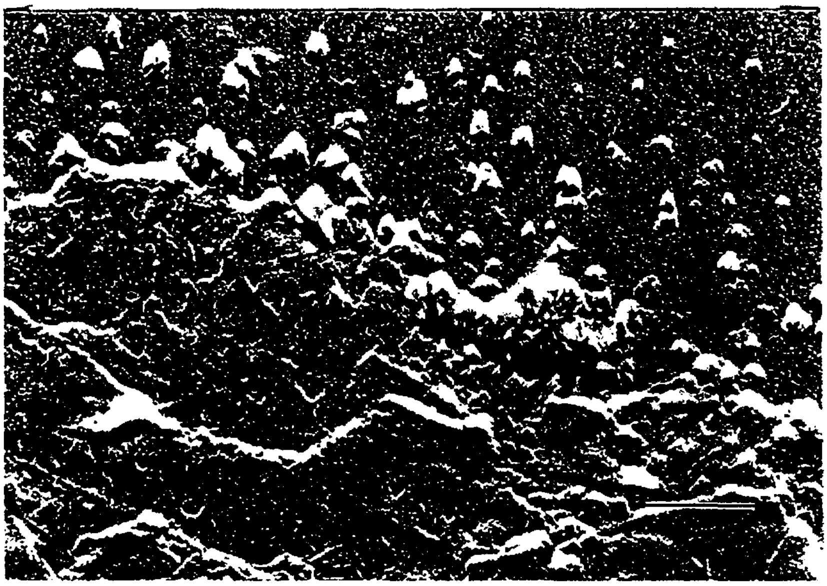
- PBS : Poly(butylene succinate)
  $-(-O(CH2)_4-OCO-(CH2)_4-2-CO-)n-$
- Crystallographic Unit Cell
  Monoclinic
  a = 5.23 Å, b = 9.08 Å, c = 10.79 Å
  β = 123.87°
- Single crystal grown in solution
  leaf-like lamella at 60℃ and terrace-like lamella at 65℃
- Chains of PBS are oriented perpendicular to the basal plane of the single crystal lamellae, since the corresponding electron diffraction patterns give the *hk*0 net.
- Spherulite morphology depending on the crystallization temperature
  Double ringed pattern above 60℃ and single ringed pattern under 60℃ were observed.

Electron micrograph(0.4㎛ scale bar) of PBS terrace type lamellar crystallized at 65 ℃

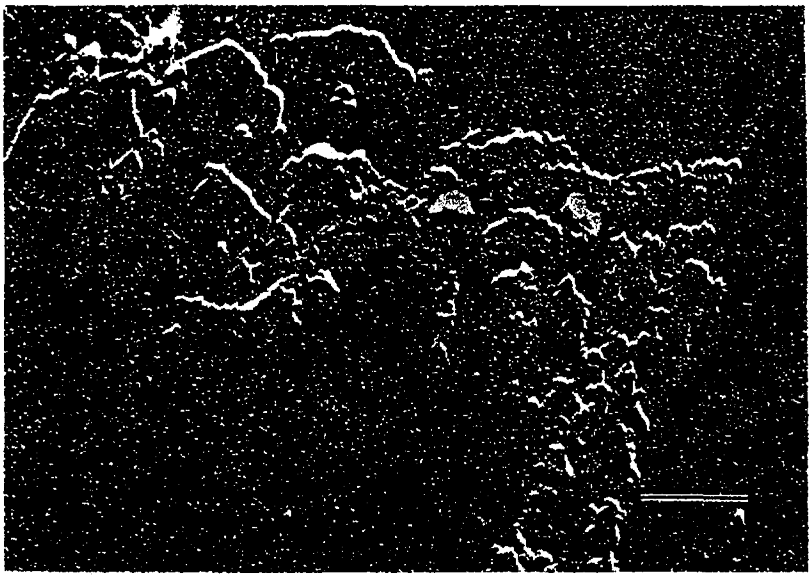


Electron micrograph(0.38 ㎛ scale bar) of PBS lamellar after dipping in buffer solution for 30 min

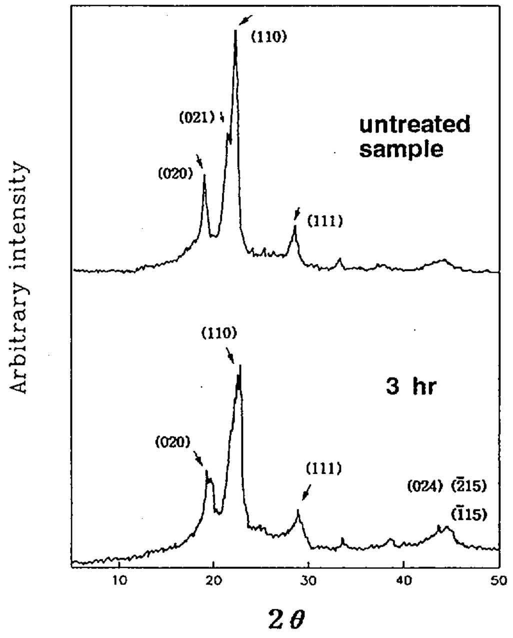
Electron micrograph(0.38 μm scale bar) of PBS lamellar after dipping in buffer solution for 90 min



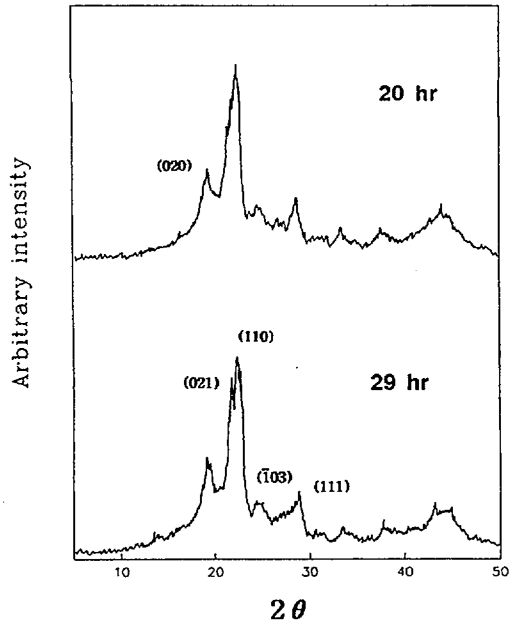
Electron micrograph(1 μm scale bar) of PBS lamellar after dipping in buffer solution for 180 min



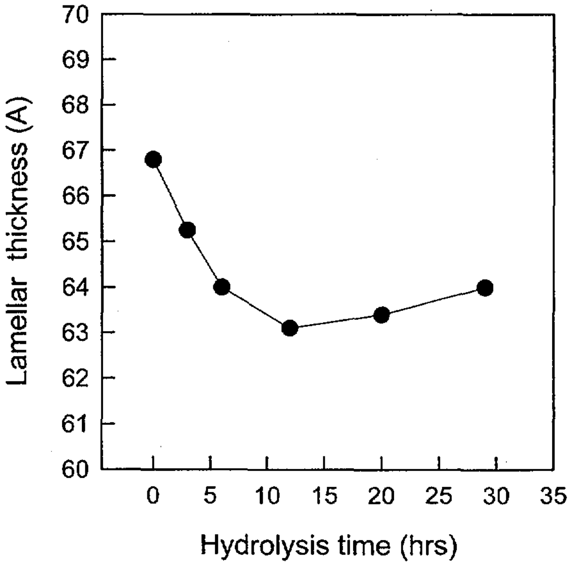
Wide angle X-ray diffraction pattern of untreated and hydrolyzed PTMS single crystal lamellar after dipping in buffer solution



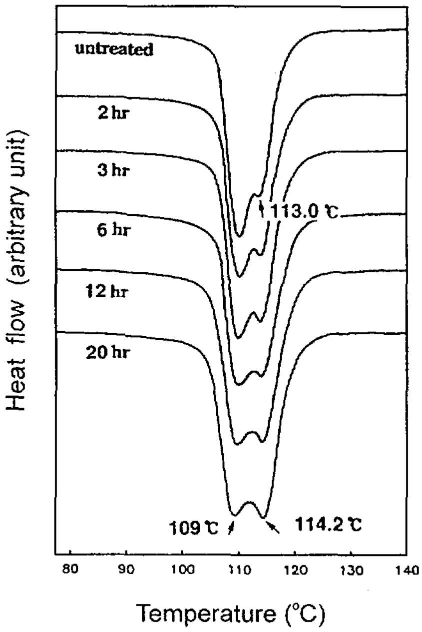
Wide angle X-ray diffraction pattern of untreated and hydrolyzed PTMS single crystal lamellar after dipping in buffer solution



Relationship between lamellar thickness and hydrolysis time in the buffer solution



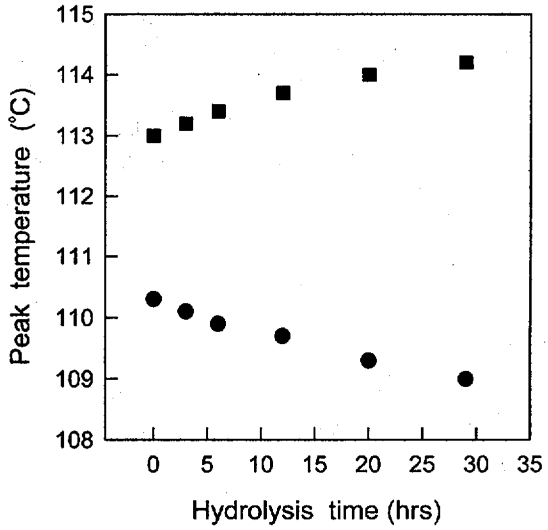
DSC thermograms of PBS single crystal lamellae with various hydrolysis time



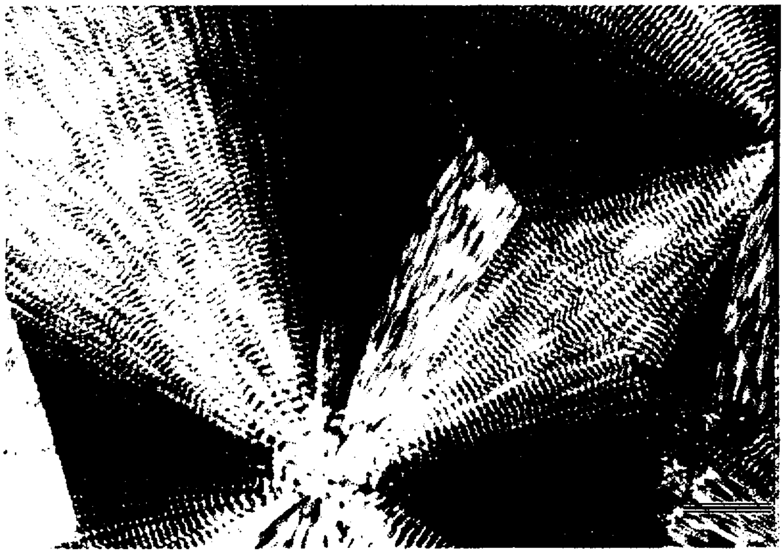
"Melting behavior of poly(butylene succinate) during heating scan by DSC"
J.Polym. Sci. Part B: Polymer Physics, **37**, 1366-1375 (1999)

Relationship between peak temperature of

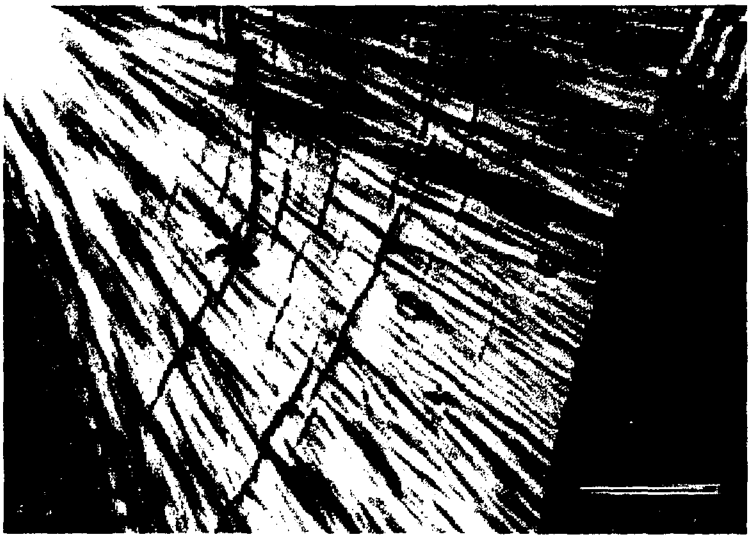
- ■ *high melt endotherm*
- ● *low melt endotherm*



Optical micrograph (9 μm scale bar) of PBS spherulites grown at 80 ℃



Optical micrograph (3 μm scale bar) of PBS spherulites after hydrolysis in buffer solution for 3 hrs



PBS/PBT random & block Copolymer

1. *Synthesis of PBS/PBT Random Copolymers*

Step 1.

DMT +SA + BD PBS/PBT Co-oligomers

Step 2.

PBS/PBT Co-oligomers PBS/PBT Copolymers

2. *Synthesis of PBS/PBT Block Copolymers*

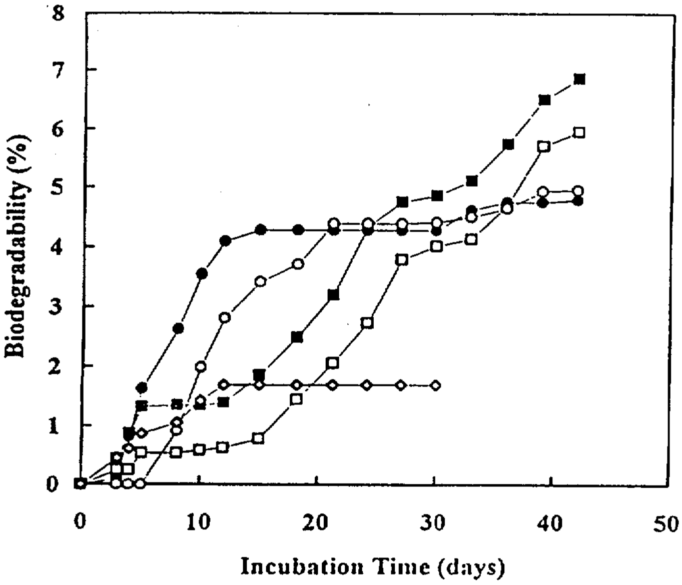
PBS homopolymer
\+ PBS/PBT block copolymer
PBT homopolymer

Probability, Block Length and Degree of Randomness(B) of PBS/PBT Random Copolymer

Copolymer	Terephthalate unit	Probability of finding of unit		Block length		Degree of randomness
	Mol%	P_{ST}	P_{TS}	Ln_S	Ln_T	B
PBS	0.0	0.000	–	–	–	–
ST1	10.8	0.129	0.897	7.735	1.115	1.026
ST2	23.8	0.254	0.774	3.390	1.292	1.028
ST3	41.0	0.398	0.625	2.514	1.601	1.023
ST4	52.0	0.529	0.492	1.890	2.031	1.021
ST5	65.8	0.661	0.371	1.514	2.697	1.032
ST6	83.9	0.821	0.193	1.218	5.192	1.014
ST7	92.1	0.878	0.087	1.139	11.519	0.965
PBT	100	–	0.000	–	–	–

Biodegradability calculated from the amount of carbon dioxide produced by enzyme hydrolysis of different incubation time in P(BS-co-BT) system at 37 ℃;

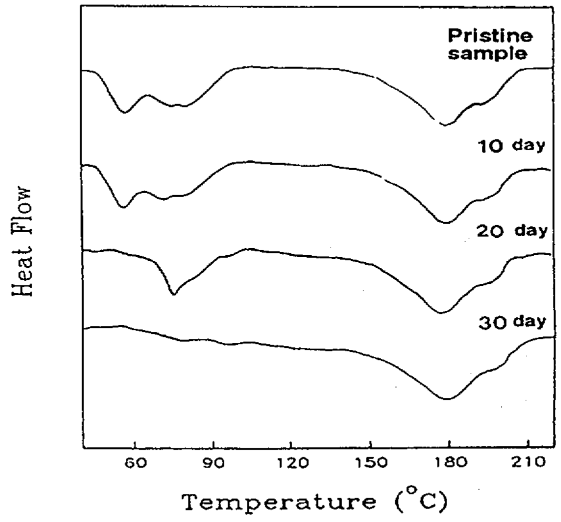
PBS (■), ST2(□), ST3(●), ST5(○), ST6(◇).



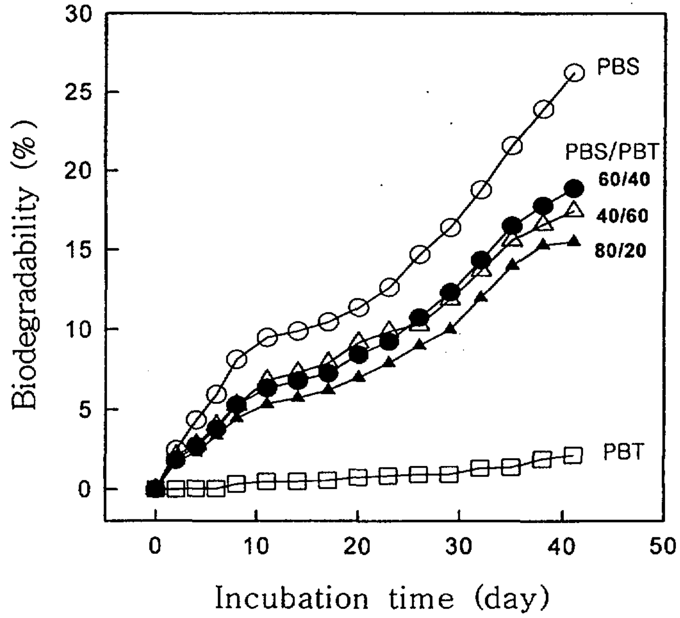
The sequence distribution parameters, crystallinity and biodegradability in PBS/PBT block copolymers

Sample Code	PBS/PBT	Reaction time (min)	Crystalli -nity(Xc)	Xc(PBS)/ Xc(PBT)	1/A	Ln_S	Ln_T	B	Degradability after40days (%)	Degradability of PBS
B2	80/20	0	31.7	95	2.8	16.70	3.24	0.42	8.41	9.76
		10	27.7	96	2.4	11.53	2.71	0.46	9.97	11.92
		40	26.0	100	2.0	7.44	1.85	0.63	15.52	18.79
B4	60/40	20	34.3	33.4	2.3	16.82	7.52	0.19	15.07	21.52
		40	29.8	-	1.7	6.92	3.96	0.40	18.95	28.48
		60	18.9	-	-	5.15	3.58	0.47	23.24	38.34
B6	40/60	20	29.3	45.6	2.6	14.10	21.71	0.12	12.68	32.77
		40	28.4	-	-	5.77	7.76	0.30	17.47	42.27
		60	28.0	-	-	3.57	4.97	0.48	19.17	47.73

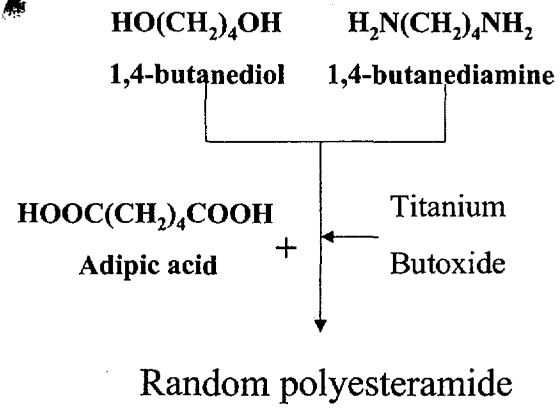
DSC thermograms of PBS/PBT=60/40 reacted for 40min at a given degradation time



Biodegeadability of PTMS/PTMT block copolymers with different composition, as a function of incubation time. Transesterification reaction time is 40 min.

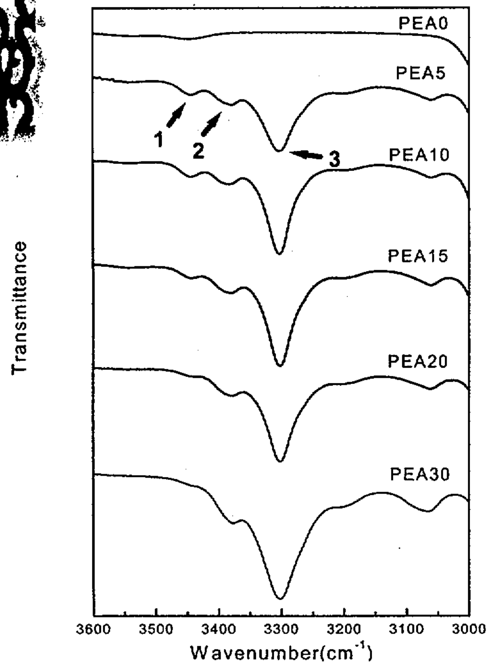


Polyester-amide



Sample No.	*Mole ratio of butanediol/butanediamine*
PEA0	***100/0***
PEA10	***90/10***
PEA15	***85/15***
PEA20	***80/20***
PEA30	***70/30***

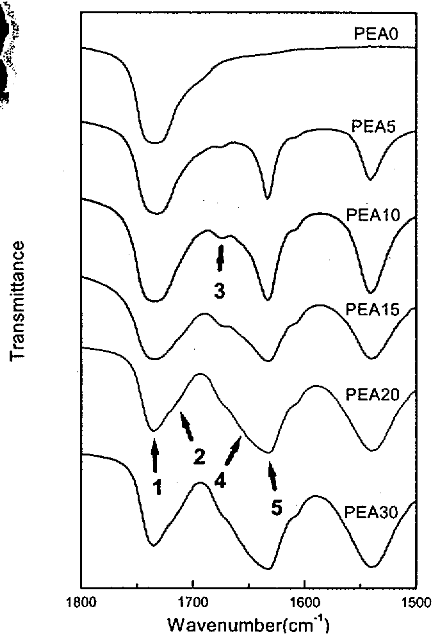
FT-IR spectra of polyester-amide in the regions of 3500-3100cm^{-1}



Peak assignments of NH groups

Peak No.1	Assignment of NH groups	Wavenumber[cm^{-1}]
1	Free NH groups	3345 – 3442
2	H-bonded amide-ester	3385 – 3382
3	H-bonded amide-amide	3305 – 3300

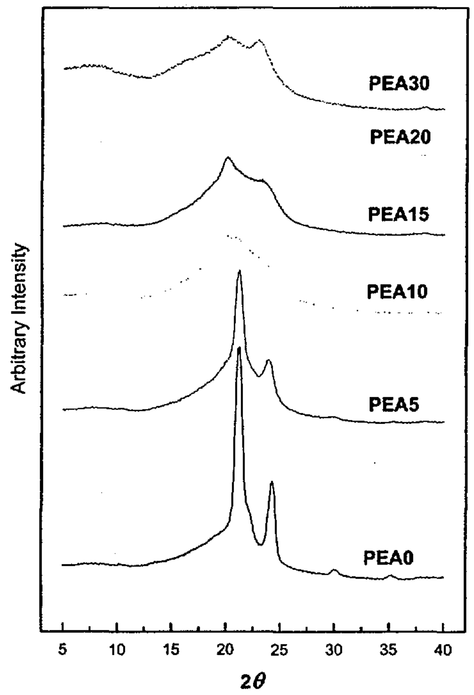
FT-IR spectra of polyester-amide in the regions of 1800-1500cm^{-1}



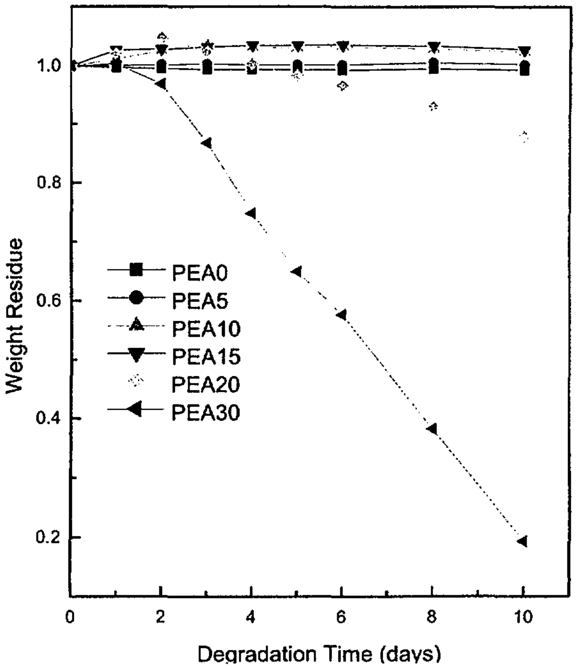
Peak assignments of C=O groups

Peak No.	Assignment of CO groups	Wavenumber[cm^{-1}]
1	Free C=O ester group	1740 – 1735
2	H-bonded C=O ester group	1715 – 1700
3	Free C=O Amide group	1675 – 1670
4	Disordered H-bonded C=O Amide group	1650 – 1638
5	Ordered H-bonded C=O Amide group	1635 -1630

Normalized WAXD profiles of PEA series



Weight remains of PEA series hydrolized in pH 11 buffer solution at 25 ℃ for 10 days



Microstructural Changes during Biodegradation

- Effect of Molecular Orientation

◈ Material

Poly (ε-caprolactone)

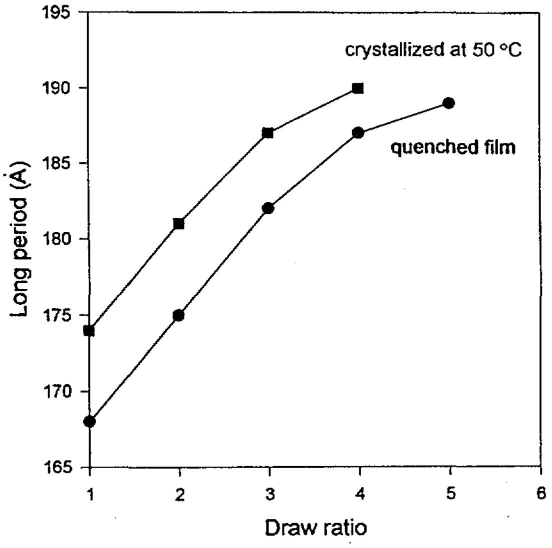
◈ Experimental

Optical Microscopy

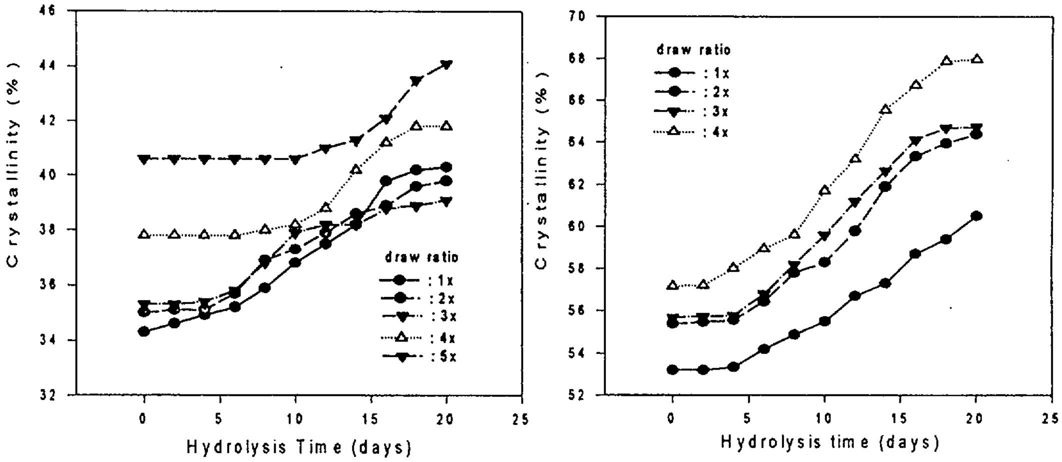
Wide and Small angle X-ray Scattering method

DSC, etc.

Variation of long period for PCL films with different draw ratio. The values are obtained by applying the Bragg equation to the peak positions of the Lorentz corrected SAXS intensity profiles



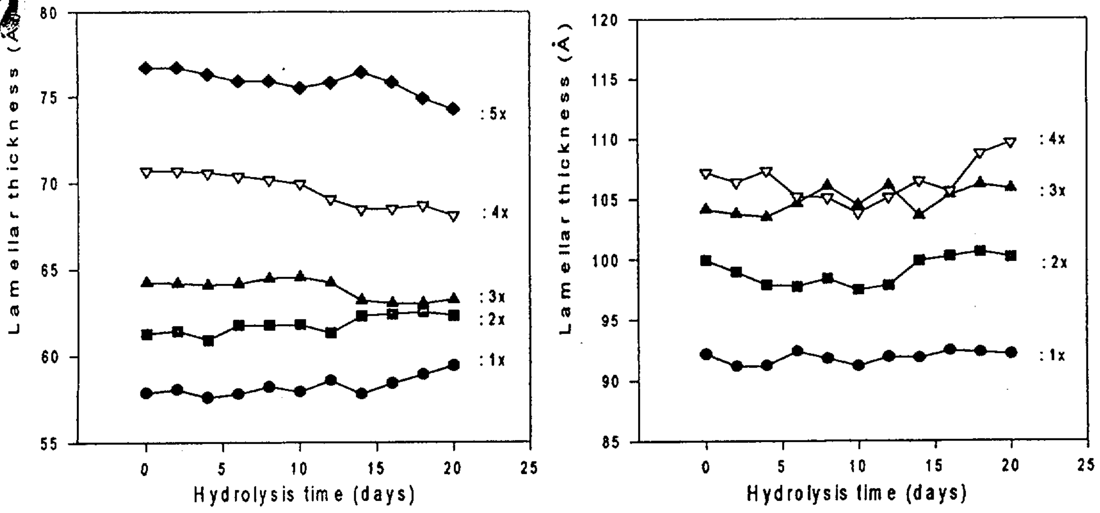
Crystallinity of (a) quenched and (b) the 50 ℃ crystallized films Calculated from the WAXS intensity profiles for samples with different draw ratio



(a)

(b)

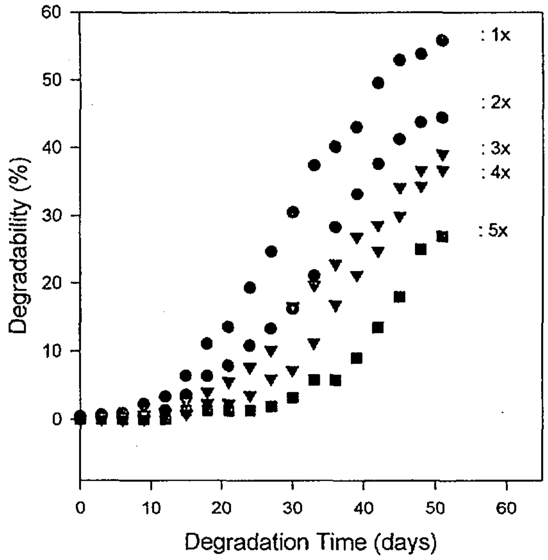
Variation of long period for (a) quenched and (b) 50 ℃ crystallized PCL films depending on hydroysis time. The thickness were calculated from the values of long period and crystallinity



(a)

(b)

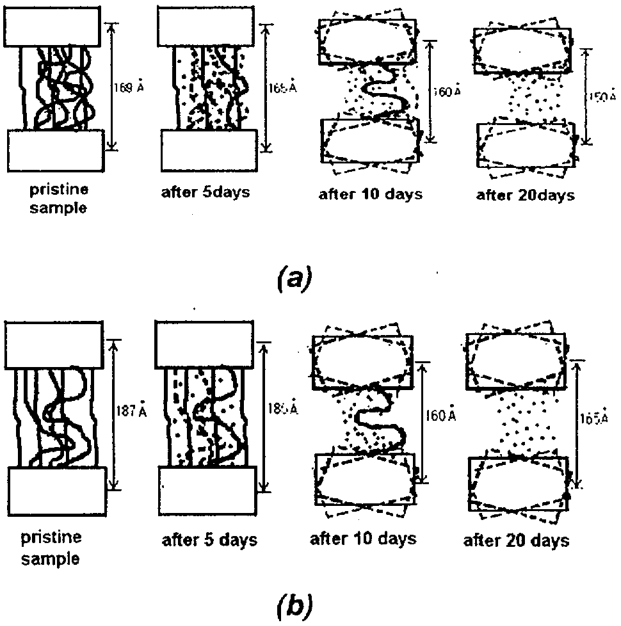
Biodegradability of quenched PCL films with various draw ratio. Biodegradation test was performed in activated sludge



Fine structures of drawn PCL films before and after biodegradation in activated sludge measured by wide- and small-angle X-ray diffractometer

Draw ratio	Degradation	Quenched film					Annealed film (50℃)				
		Crystallinity (%)	Crystallite Sizes (Å)			Crystal Volume (Å^3)	Crystallinity (%)	Crystallite Sizes (Å)			Crysta Volum (Å^3)
			L(110)	L(200)	Lamellar thickness			L(110)	L(200)	Lamellar thickness	
1 (undrawn)	Before	34.3	73.6	68.7	57.6	349,500	53.2	83.7	72.6	92.5	674.5
	After	31.8	69.2	63.1	53.1	277,800	50.1	77.6	69.4	83.6	540.2
2	Before	35.1	68.6	65.5	61.4	331,000	55.4	78.6	70.4	100.3	666.0
	After	33.6	62.1	61.3	55.4	253,000	51.2	75.2	67.6	91.2	556.3
3	Before	35.3	67.7	63.8	64.2	332,700	55.7	71.8	68.7	104.2	616.8
	After	32.1	62.2	58.6	60.1	262,900	51.3	67.2	66.2	91.4	487.9
4	Before	37.8	65.8	61.8	70.6	344,500	57.1	70.3	65.6	108.5	600.4
	After	34.5	58.4	54.3	64.3	244,700	52.4	67.6	63.7	93.6	483.7
5	Before	40.6	64.9	60.5	76.7	361,400	-				
	After	33.4	57.1	55.4	69.6	264,200					

Schematic diagrams of the changes occurred to the lamellar morphology of PCL films on hydrolysis; (a) model for lower drawn film (b) model for higher drawn film



Conclusion

◈ Not only amorphous structure but also crystalline structure (etc. perfectness and size) affect the biodegradability of crystalline polymers

◈ The biodegradability of polymers could be controlled with the microstructural design of amorphous and crystalline region.

◈ Microstructure is a key factor for biodegradation management and it can be controlled by sequence distribution in the copolymer system.

15. The Biodegradation of Poly(tetramethylene succinate-co-tetramethylene adipate) Through Water-Soluble Products

Eiichi Kitakuni*[1], Katsuyuki Yoshikawa[1], Katsuharu Nakano[1], Junji Sasuga[1], Masayoshi Nobiki[1], Ryoji Ishioka[2] & Yoshiyuki Yakabe[3]
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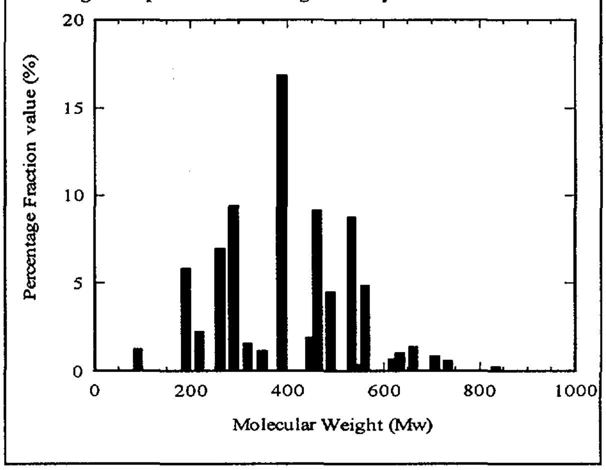
[E-mail: kitakuni@ctl.sdk.co.jp]

Abstract

The environmental impact of non-biodegradable waste polymer materials has become steadily more acute. They finally end up in the municipal solid waste stream. The biodegradable polyesters are expected to reduce the amount of waste and come to hold public attention. However, the polyesters are likely to produce water-soluble intermediates during the degradation, which might diffuse and remain in an environment until they are completely digested. To assess the environmental impact of the intermediates is necessarily required to determine whether the biodegradable polyesters are capable of solving the posed problem before they are widely demanded and consumed in our daily life.

We previously showed that some water-soluble oligomers could be readily obtained from Poly (tetramethylene succinate-co-tetramethylene adipate) (PBSA) by enzymatic hydrolysis [1]. The oligomers were considered the intermediate products liberated from the polymer by the work of extracellular enzymes. Figure shows the composition of all the hydrolysates experimentally obtained from PBSA by using *Chromobacterium* extracellular lipase. They were identified by high performance liquid chromatography / mass spectrometry (HPLC/MS) and ^{1}H-NMR, revealing that 28 oligomer species were liberated from PBSA in all. Moreover, 20 species of them were the polyester-based compounds of monomer units, but another 8 species were small amounts of the diurethane compounds.

Fig. Composition of the oligomers hydrolized from PBSA



We also focused on the two oligomers typical of the chemical structure which were Bis(hydroxybutyl) succinate (BSB) and Bis(hydroxybutyl) hexamethylene dicarbamate (BHB). Their biodegradability was examined for 28 days in the activated sludge, revealing that the final conversion rate of constituent carbon to carbon dioxide was estimated at 80mol% for BSB and 10mol% for BHB. The amount of carbon remaining in the undegraded BHB was 20mol% and the other BHB might have been converted to dissolved carbon compounds. In the presence of BSB, the biodegradability of BHB was increased by about 1.5 times. It suggested that BSB induced a growth of microorganisms and helped BHB degradation. This is consistent with the observation that the biodegradation of BHB in native soil reached over 60% for 60days.

References

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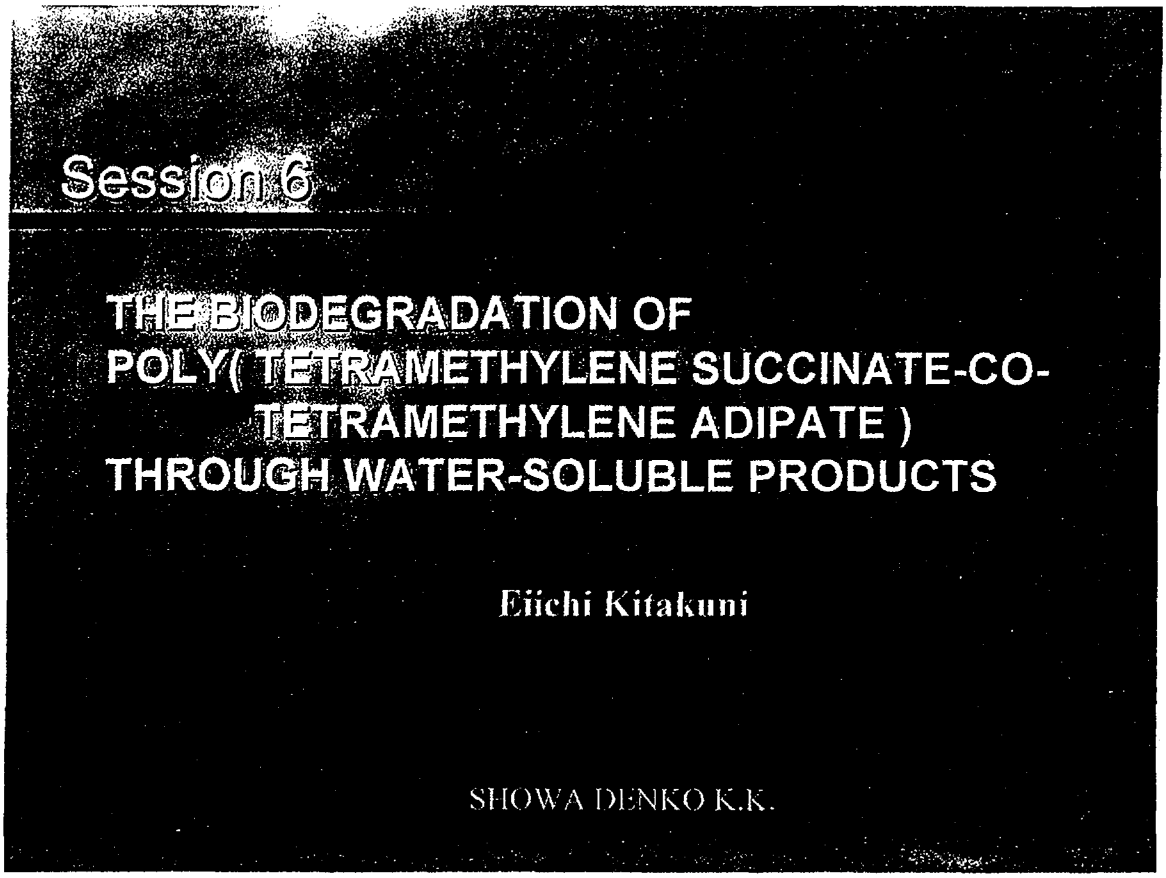
2. E. Kitakuni, K. Yoshikawa, K. Nakano, J. Sasuga, M. Nobiki, H. Naoi, Y. Yokota, R. Ishioka, Y. Yakabe. 2000. The Biodegradation of Poly(tetramethylene succinate-co-tetramethylene adipate) and Poly(tetramethylene succinate) through water-soluble products. *Environmental toxicology and chemistry.* in press.

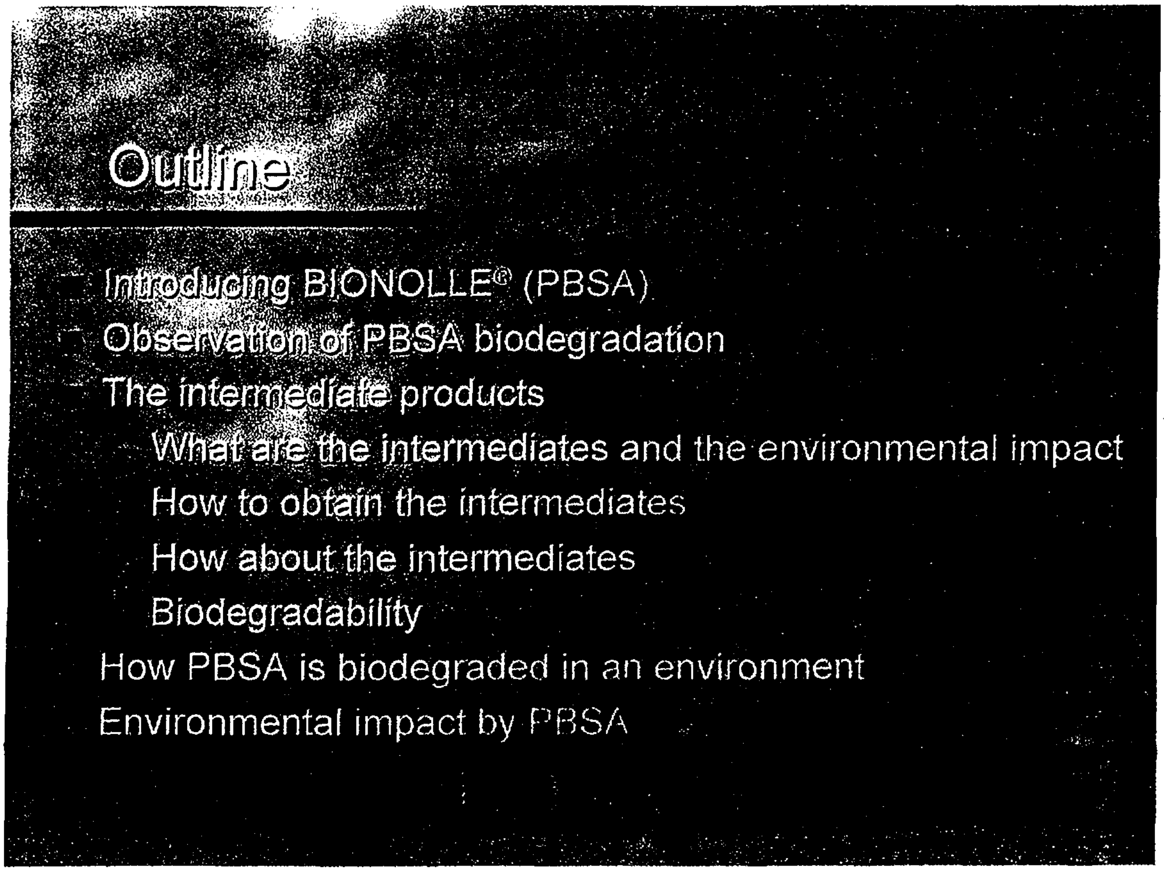


Session 6

THE BIODEGRADATION OF POLY(TETRAMETHYLENE SUCCINATE-CO-TETRAMETHYLENE ADIPATE) THROUGH WATER-SOLUBLE PRODUCTS

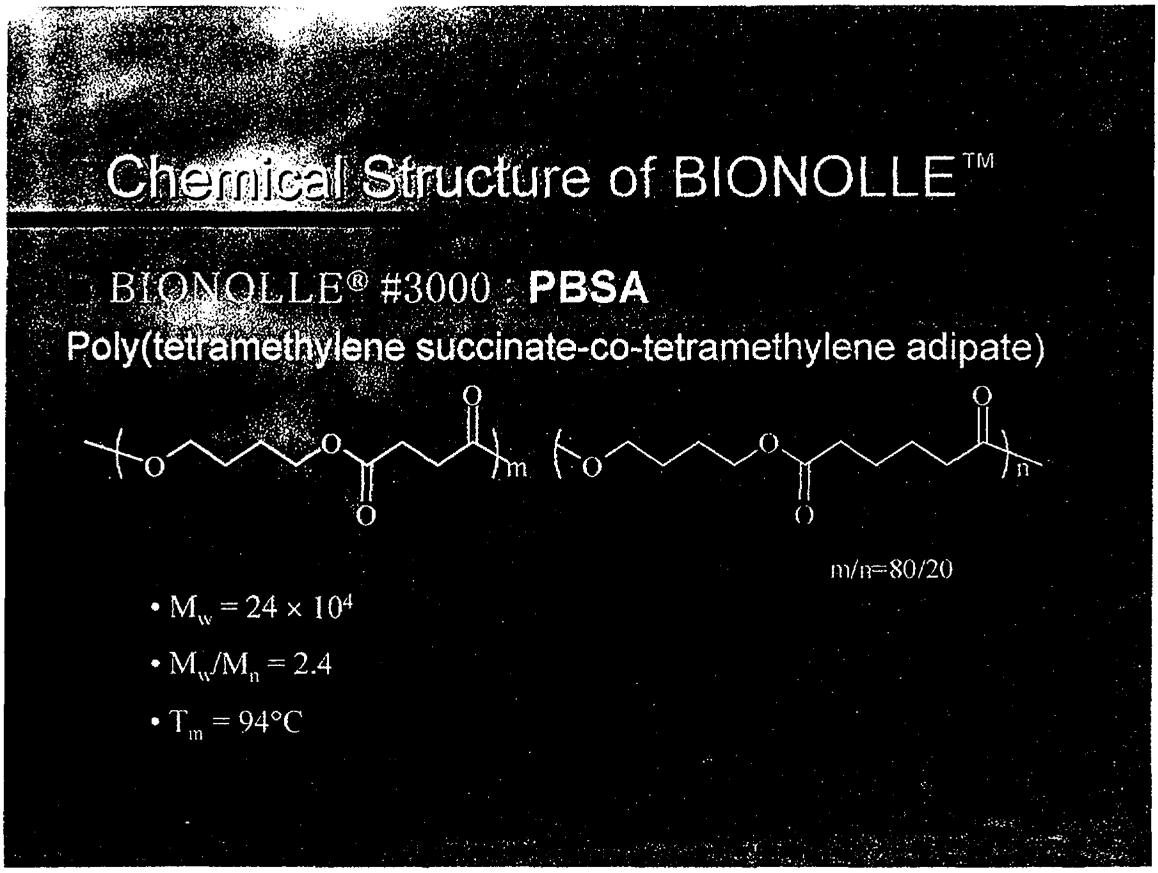
Eiichi Kitakuni

SHOWA DENKO K.K.



Outline

- Introducing BIONOLLE® (PBSA)
- Observation of PBSA biodegradation
- The intermediate products
  - What are the intermediates and the environmental impact
  - How to obtain the intermediates
  - How about the intermediates
  - Biodegradability
- How PBSA is biodegraded in an environment
- Environmental impact by PBSA



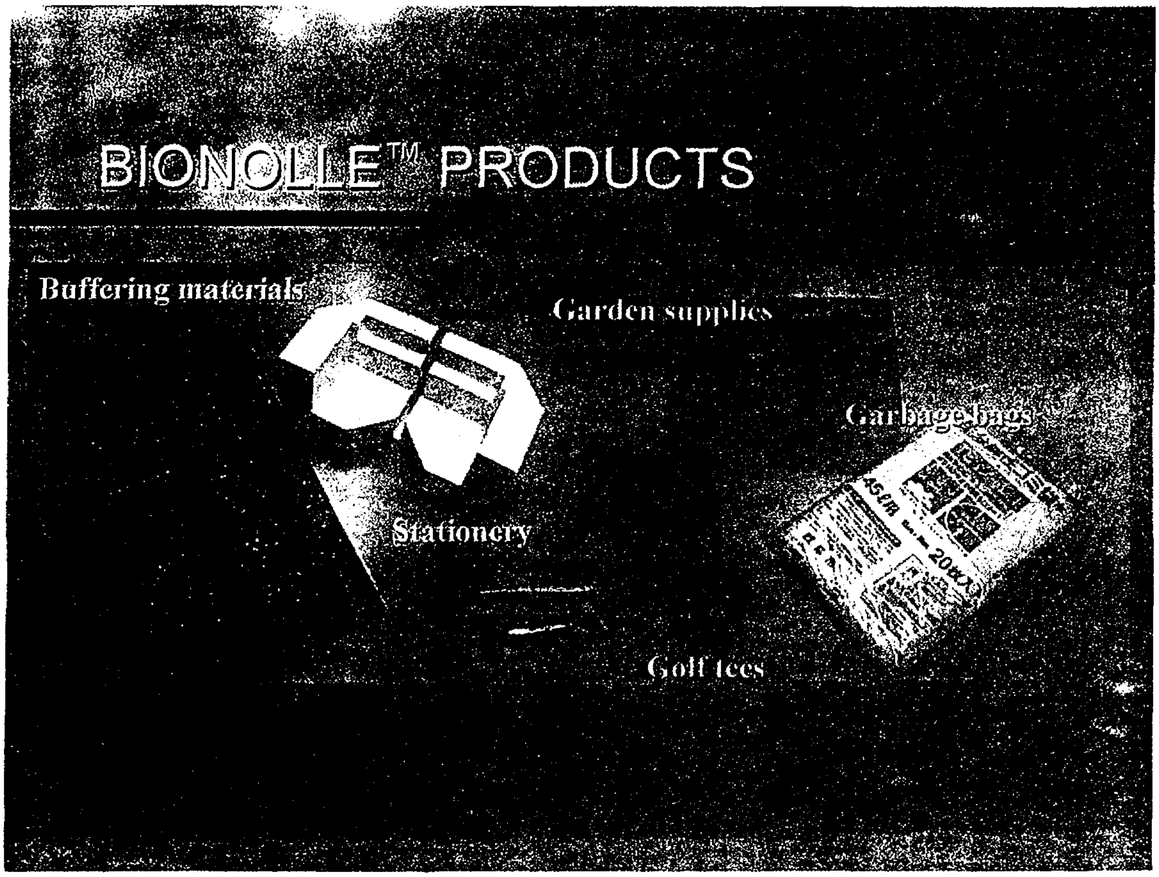
Chemical Structure of BIONOLLE™

BIONOLLE® #3000 : **PBSA**

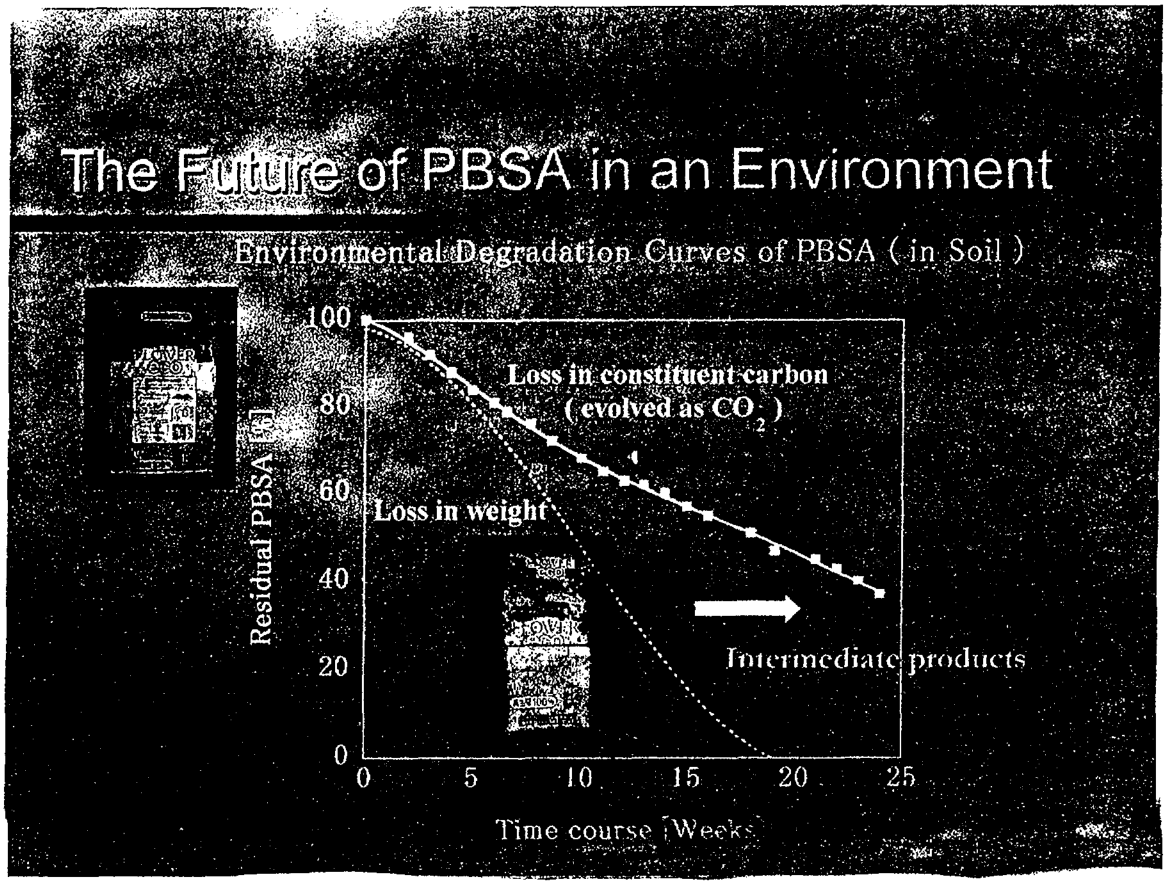
Poly(tetramethylene succinate-co-tetramethylene adipate)

m/n=80/20

- $M_w = 24 \times 10^4$
- $M_w/M_n = 2.4$
- $T_m = 94°C$

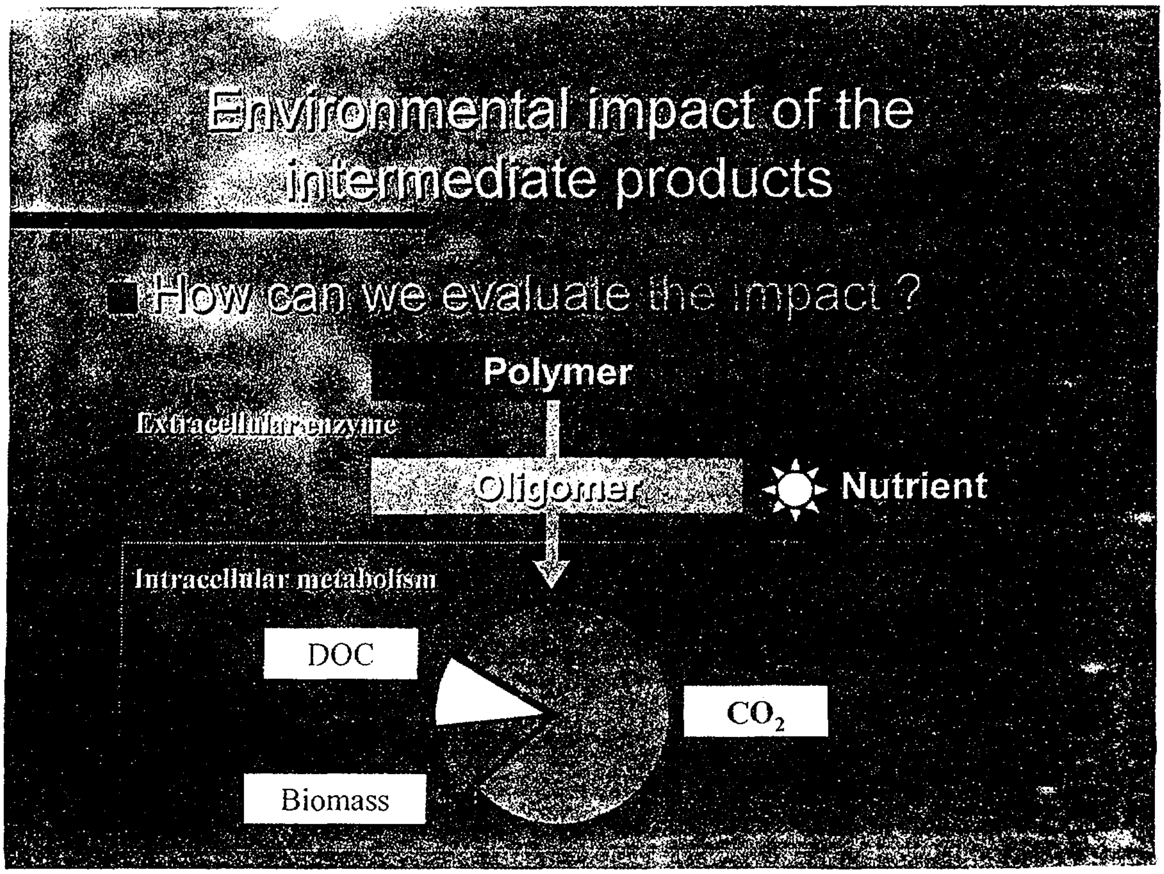


BIONOLLE™ PRODUCTS



The Future of PBSA in an Environment

Environmental Degradation Curves of PBSA (in Soil)



Environmental impact of the intermediate products

- How can we evaluate the impact ?

Polymer

Extracellular enzyme

Oligomer

Nutrient

Intracellular metabolism

DOC

CO_2

Biomass

To obtain the oligomers

In an Environment

In the Laboratory

High Polymer (PBSA)

Extracellular enzymes

Derived from Microorganism living in
Soil, Fresh water, Sea etc.

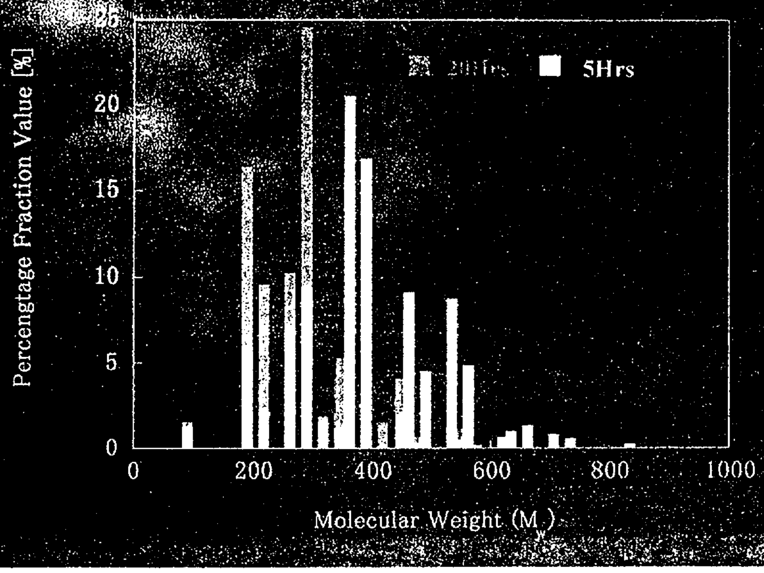
Commercial enzyme

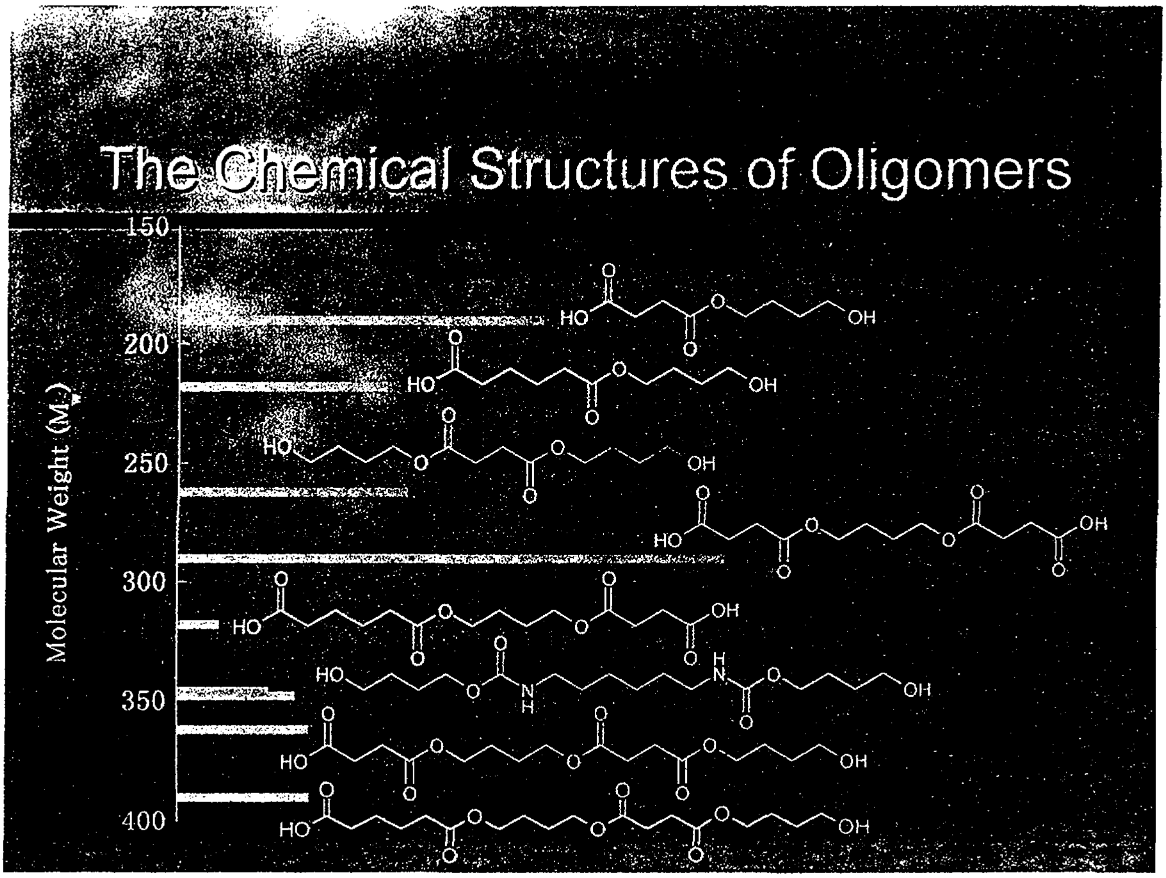
Lipase Type XII
Chromobacterium visosum

Oligomers

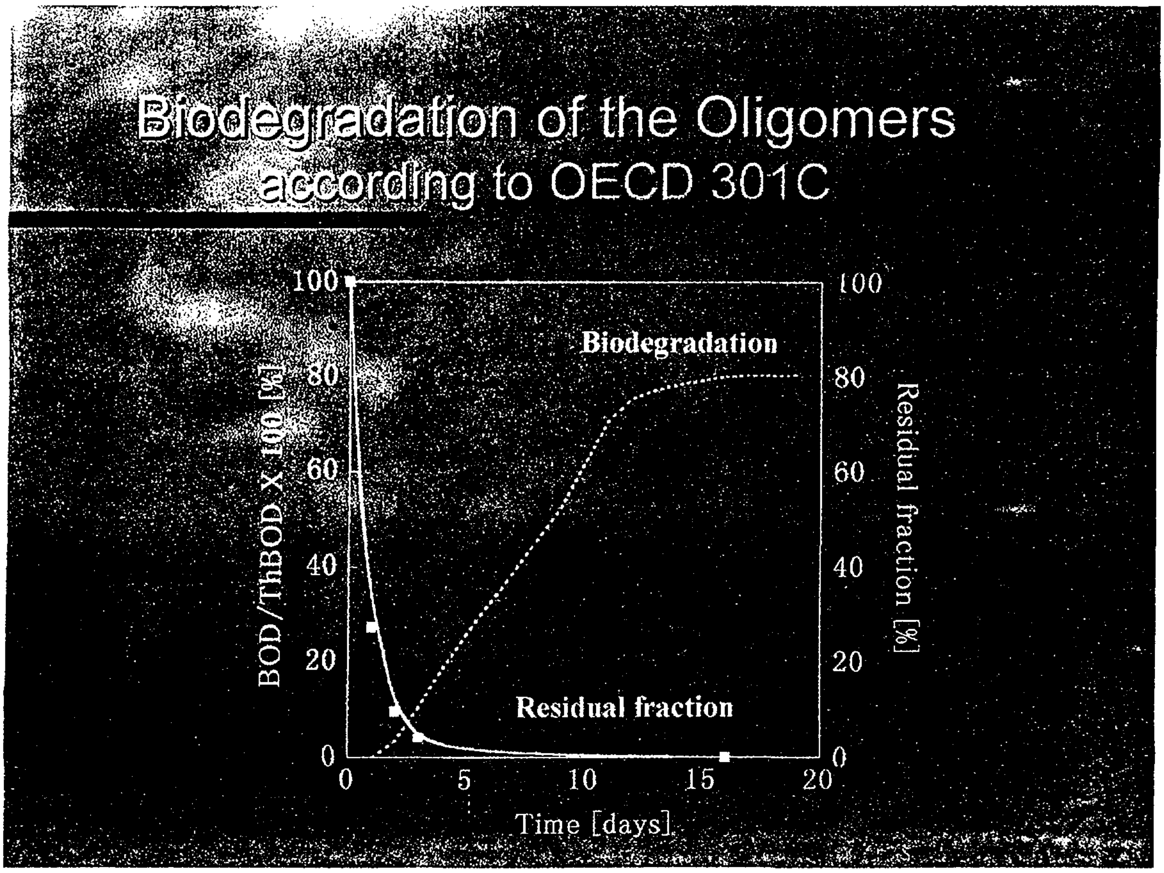
The Water-Soluble Oligomers hydrolyzed from PBSA

Composition of the Water-Soluble Oligomers after 5Hrs and 20Hrs of the enzymatic hydrolysis

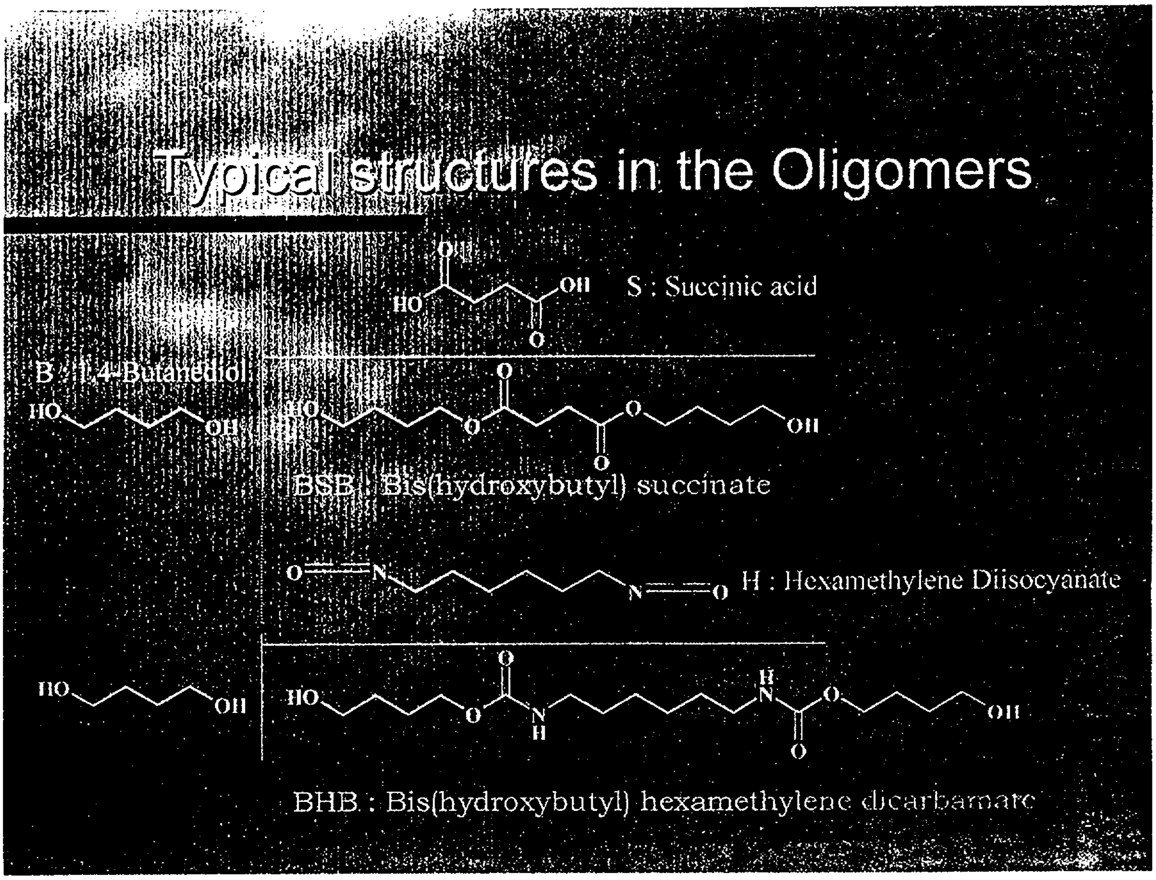




The Chemical Structures of Oligomers



Biodegradation of the Oligomers according to OECD 301C



Typical structures in the Oligomers

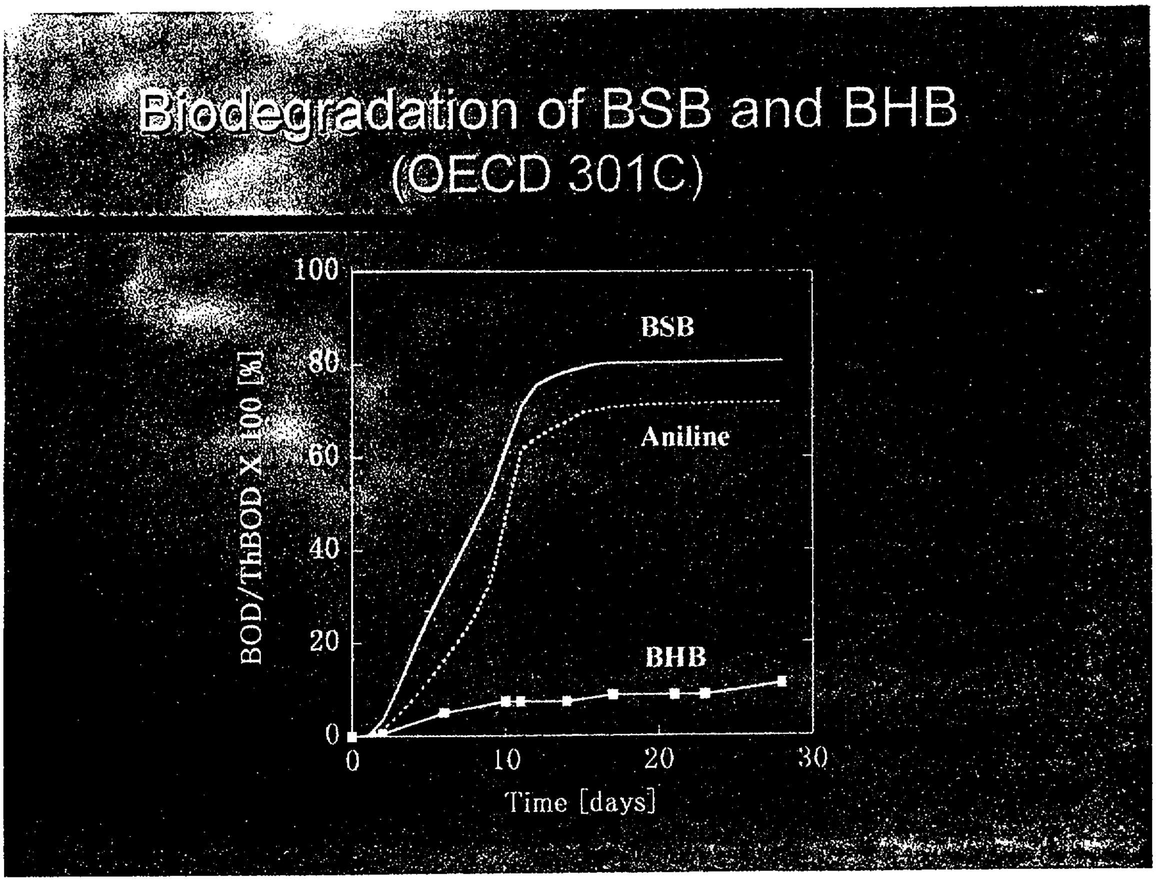
S : Succinic acid

B : 1,4-Butanediol

BSB : Bis(hydroxybutyl) succinate

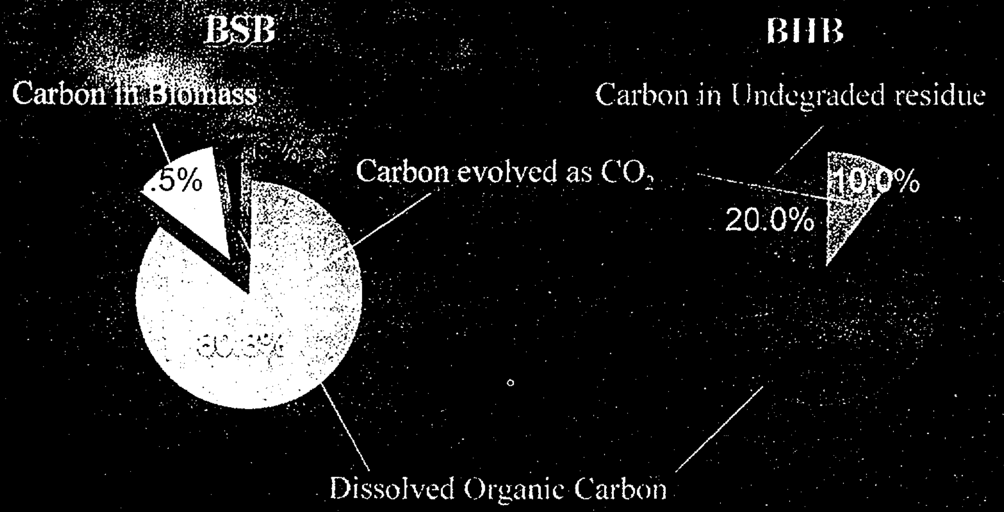
H : Hexamethylene Diisocyanate

BHB : Bis(hydroxybutyl) hexamethylene dicarbamate

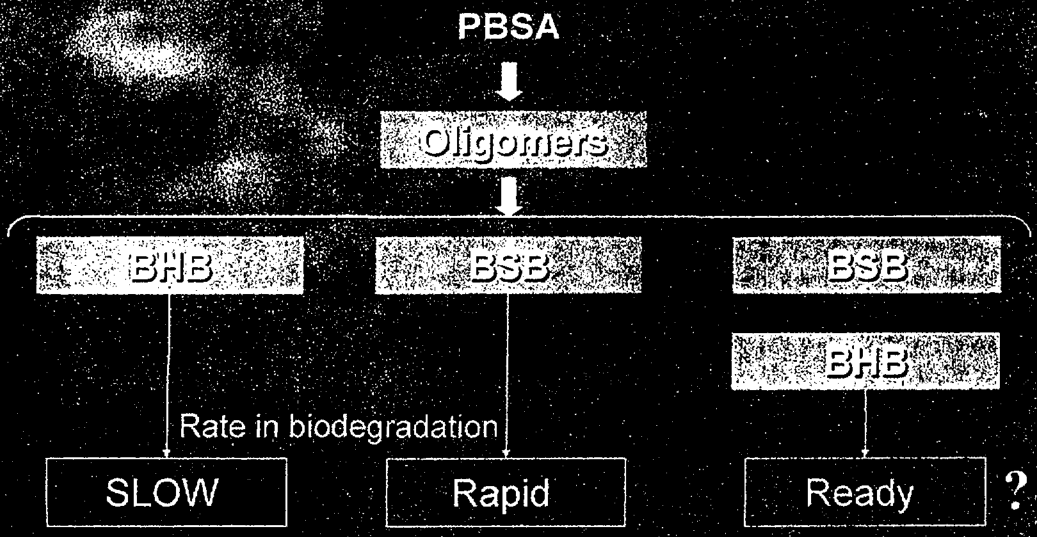


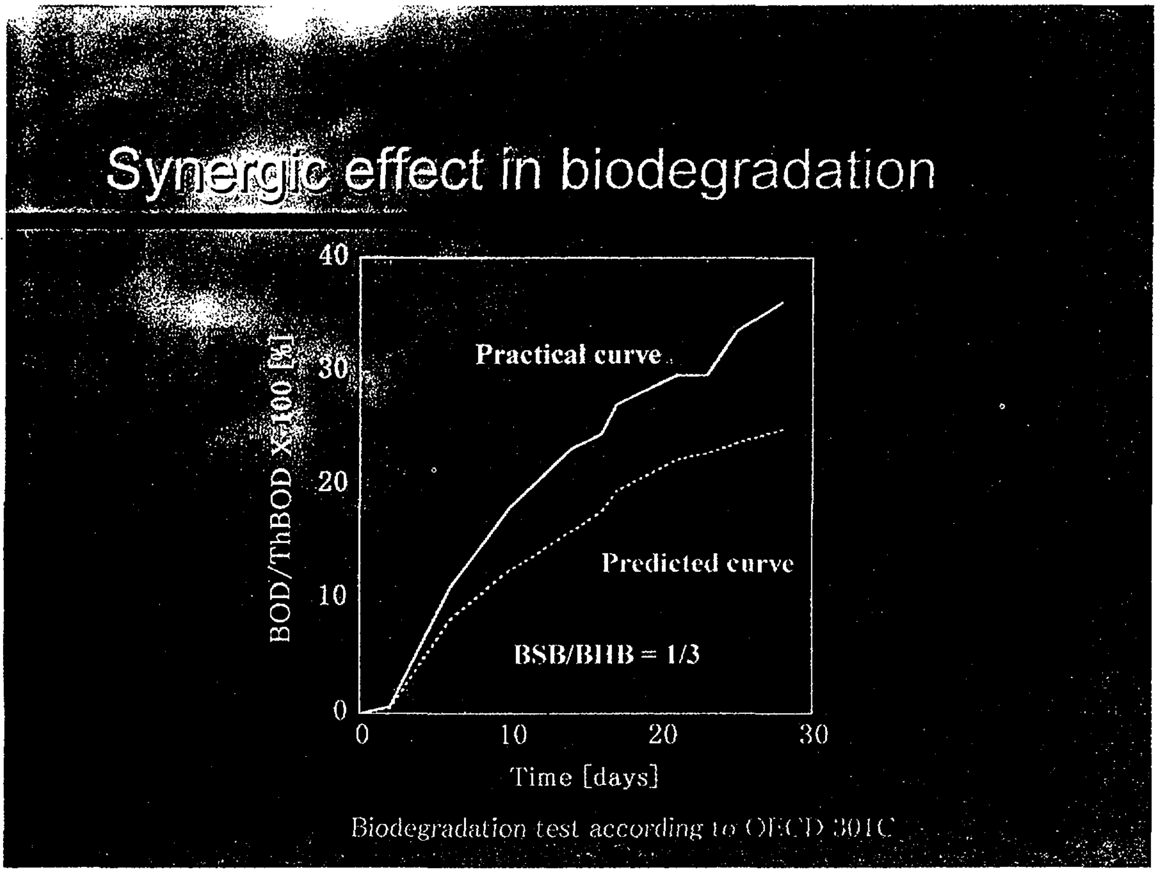
Biodegradation of BSB and BHB (OECD 301C)

Comparision of the Carbon Balance between BSB and BHB



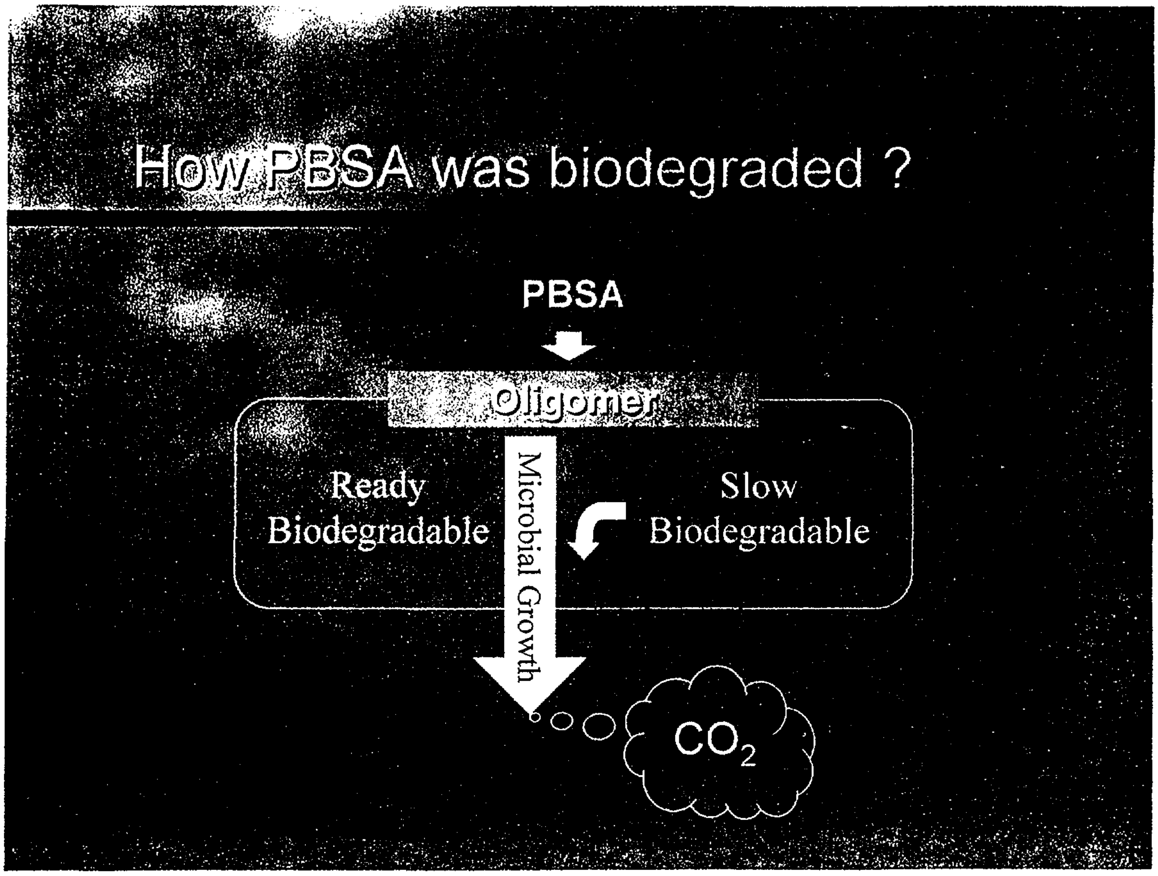
Why PBSA was ready biodegradable?





Synergic effect in biodegradation

Biodegradation test according to OECD 301C



How PBSA was biodegraded ?

PBSA

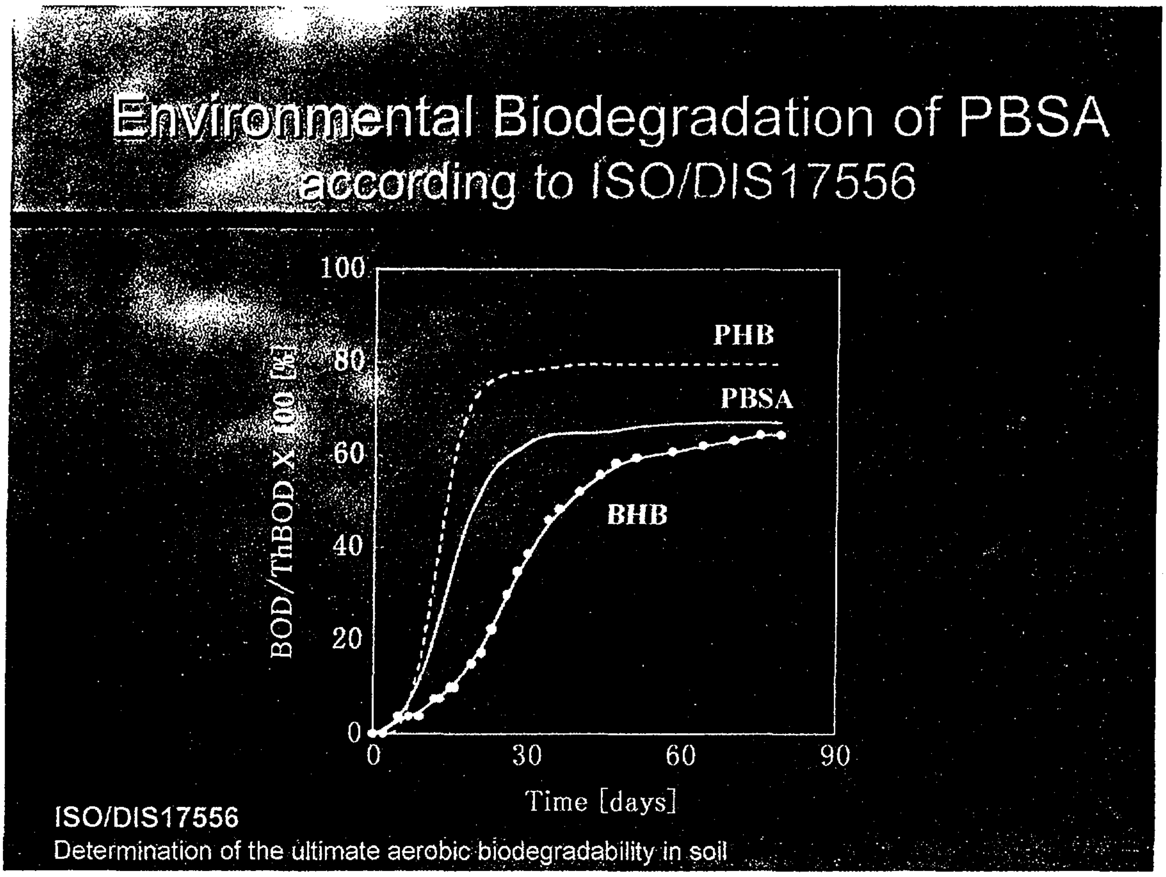
Oligomer

Ready
Biodegradable

Microbial Growth

Slow
Biodegradable

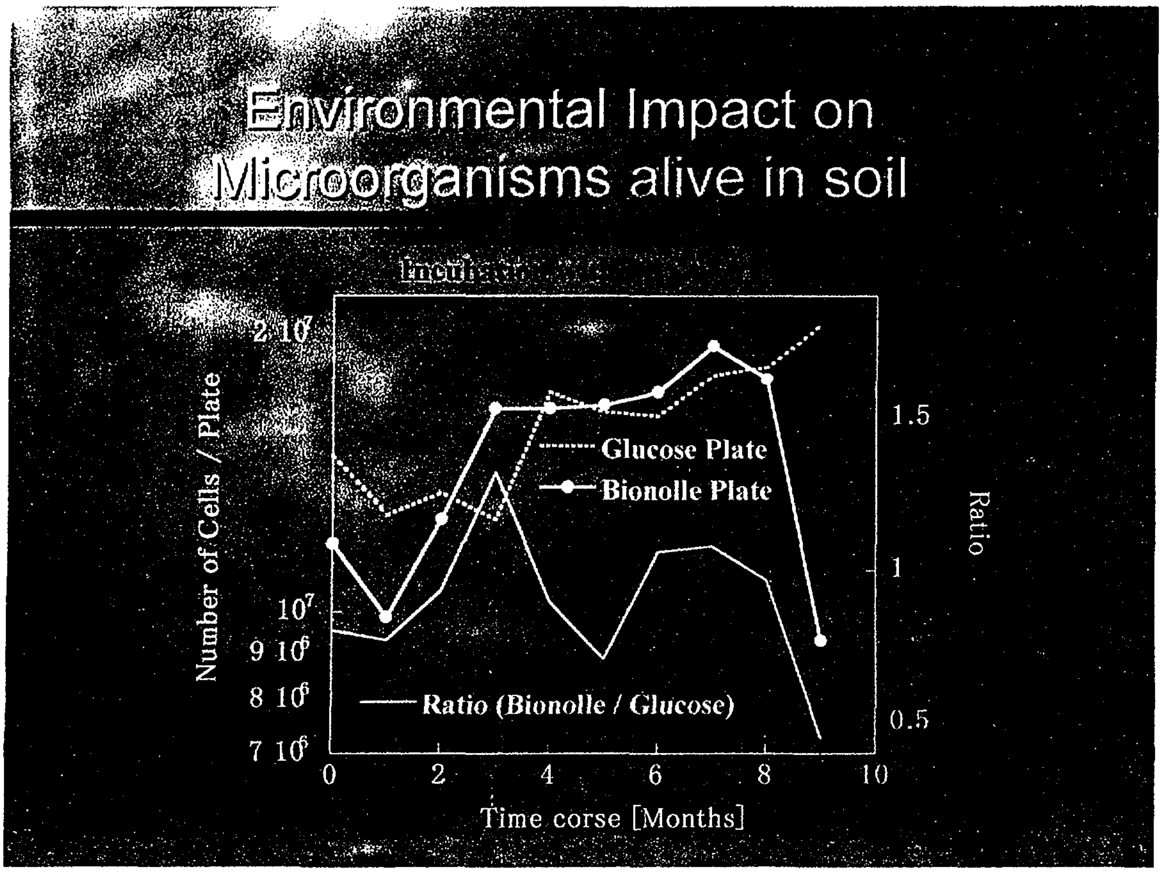
CO_2



Environmental Biodegradation of PBSA according to ISO/DIS17556

ISO/DIS17556

Determination of the ultimate aerobic biodegradability in soil



Environmental Impact on Microorganisms alive in soil

Summary & Conclusions

- PBSA was enzymatically hydrolyzed into the water-soluble oligomers
- The obtained oligomers was classified into the polyester-based compounds or the diurethan compounds
- The oligomers showed ready-biodegradability as a whole
- Typical two oligomers was chemically synthethized and evaluated of their biodegradabilities
- The polyester-based oligomers would promote the microbial growth and help the biodegradation of diurethane oligomers
- Microorganisms could keep conditioning to degrade PBSA while PBSA was present in the environment

Acknowledgements

- Many scientists have contributed to the study:

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Yoshiyuki Yakabe

16. Synthesis of High Molecular Weight Aliphatic PBS/PBA and Their Properties

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Intrduction

Degradable aliphatic polyesters have received much attention because they can replace nondegradable polymers that cause ecological problems. The aliphatic polyesters from the combinations of aliphatic diols and dicarboxylic acids such as ethylene glycol/succinic acid (SCA), 1,4-butane diol (1,4-BD)/SCA, 1,4-BD/adipic acid (ADC), and so on decompose rather easily and produce less harmful chemical fragments under natural circumstances. In spite of the practical significance, however, the aliphatic polyesters have difficulties in fabrication because of their low melt viscosity [1]. To solve these drawbacks associated with melt processing, lots of attempts have been made to increase the molecular weight of the polymer through a coupling or branching reaction between a suitable chain branching agent and the polymer [2]. This work presents the synthesis of high molecular weight poly(butylene succinates) (PBS) and poly(butylene adipates) (PBA) and their tensile properties. We also describe their degradation behavior in a buffer solution.

Results and Discussion

PBS and PBA prepolymers were prepared by the melt condensation polymerization of either 1,4-BD and SCA or 1,4-BD and ADC in the presence of titanium (VI) isoproxide catalyst. The prepolymers reacted again with 1,4-BD or SCA to produce the corresponding prepolymers with hydroxyl or carboxylic acid group at both ends of the polymer chain. Finally, high molecular weight linear or branched aliphatic polyesters such as PBS and PBA were synthesized either by a coupling reaction between the prepolymers with hydroxyl or carboxylic acid group, or by a branching reaction between the prepolymer with carboxylic acid group and glycerol, a branching agent. We also established the optimum conditions for the preparation of the high molecular weight polymers. The weight average molecular weight of the prepared linear and branched polyesters was in the range of 100,000 to 330,000. From a Instron test, the resulting films prepared from the high molecular weight polymers had much better tensile properties in strength, elongation at break and toughness than those of low molecular weight polymers. In addition, we carried out in-vitro degradation test in a buffer solution of pH 4, 7, or 10 at 25 ℃ to investigate degradation behavior of the PBS films. From a SEM analysis, their hydrolytic rate was found to be dependent not only on the pH of buffer solution but on the molecular weight of the films.

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Background

Every year, several hundred thousand tons of plastic products are discarded into marine and earth environments, causing the death of numerous animals. Recently, there has been a growing demand for biodegradable plastics as a solution to ecological and environmental problems.

Conventional Biodegradable Polymers

- **Poly(ε -caprolactone)**
- **Poly hydroxy butyrates** etc.
- **Aliphatic polyesters**

Applications

- **Surgical casting materials**
- **Disposable products**
- **Biodegradable films**

Disadvantages

- **Limited applications**
- **High cost**
- low melt viscosity
  ↓
  poor molding properties
- low heat stability

•High-Molecular-Weight Aliphatic Polyesters

- **Poly(butylene adipate)**
- **Poly(butylene succinate)**
- **Poly(ethylene adipate)**
- **Poly(ethylene succinate)**

} Bronolle® Series
(Prepared by Showha Highpolymer Co.)
Ref). U.S. Pat. 5306787 (1994).
5310782 (1994).
5436056 (1995).

•Applications

- **Films**
- **Blown bottles**
- **Foamed sheet**
- **Highly expanded foam**
- **Cellular fibrillated materials**

•Advantages

- **Good mechanical properties** ; High toughness, high strength and high elongation
- **Easier producing method** ; Chemosynthetic method rather than controlled fermentation method of PHB
- **Relatively low cost**

* High melt viscosity
↓
Good molding properties

Objectives

- **Examination of optimum condition for the preparation of high-molecular-weight linear or branched PBS and PBA.**
- **Investigation of mechanical properties of linear or branched PBS and PBA with different molecular weight.**
- **In-vitro degradation test in a buffer solution.**

Table 1. Preparation of Carboxylic Acid or Hydroxyl Group Terminated Linear PBS

Polymer	Reaction Time (hr)	Conversion (%)	η^{a}	$\overline{M_n}^{b}$	$\overline{M_w}^{b}$	PDI ^{b}	Tm	Tg
HOOC-PBS-COOH	6	72	0.54	25,100	68,700	2.74		
	6	64	0.56	26,400	63,900	2.42		
	9	76	1.12	84,600	167,700	1.98	113	-40
HO-PBS-OH	5	73	0.13	3,300	6,600	2.00		
	9	81	1.01	49,200	123,400	2.51		

[a] Inherent viscosity (η) was measured in $CHCl_3$ (0.5 g/dL) at 25 °C.

[b] [redacted] measured in $CHCl_3$ solvent by GPC.

polymerization temp.: 230° (at 0.5 torr)

Table 2. Preparation of High Molecular Weight Linear PBS by a Coupling Reaction

Polymer		Reaction Temp. (℃)	Yield (%)	η	$\overline{M}_n$	$\overline{M}_w$	PDI
HOOC-PBS-COOH	HO-PBS-OH						
η 0.54	η 0.13	210	86	1.84	102,500	205,500	2.00
		230	73	1.96	108,800	213,300	1.96
η 0.54	η 1.01	210	91	1.19	64,500	142,100	2.20
		230	88	1.40	96,300	192,500	2.0
η 1.12	η 1.01	210	91	1.19	63,600	134,400	2.11
		230	85	1.50	81,300	167,700	2.06

Polymn time : 3 hrs at 0.5 torr.
TIP : 0.3 wt% vs. prepolymers

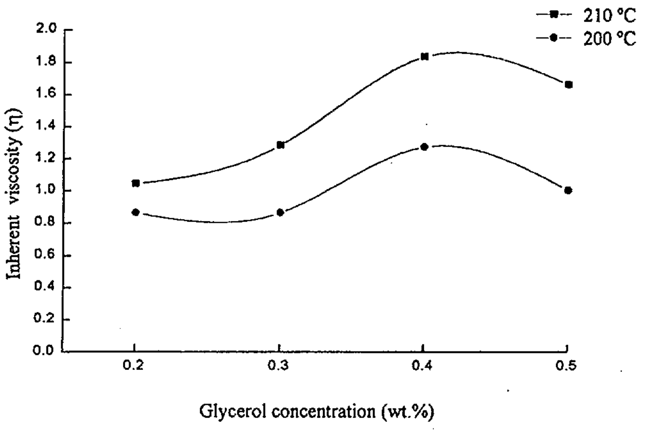


Fig. 1. Influence of glycerol concentration on the molecular weight of the branched PBS.

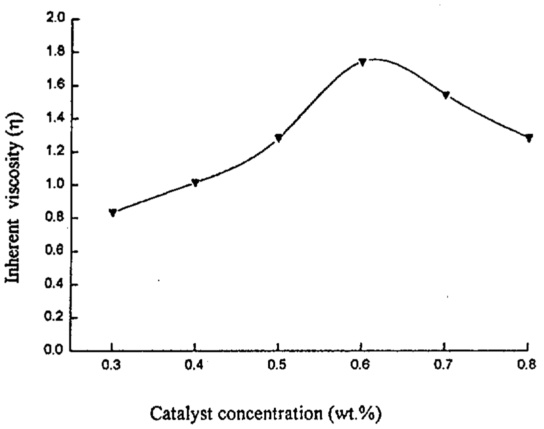


Fig. 2. Influence of Catalyst Concentration on the molecular weight of the branched PBS.

Table 5. Tensile Properties of PBS Films [a]

Polymer	I.V	$\overline{M_w}$	Thickness (μm)	Modulus (MPa)	Tensile Strength (MPa)	Strain at Break (%)	Toughness (Mpa)
HO-PBS-OH	1.01	123,400	25	204	14	55	10
Linear PBS	1.93	213,300	25	508	22	110	24
Branched PBS	1.04	126,100	25	170	17	55	9
Branched PBS	1.96	219,600	30	180	24	120	22

[a] The PBS thin films (5.0 × 60.0 mm) were cast [illegible] from their 5 wt.% chloroform solutions. Tensile test was performed at a strain rate of 10 mm/min with a load cell of 10 N at 15 °C.

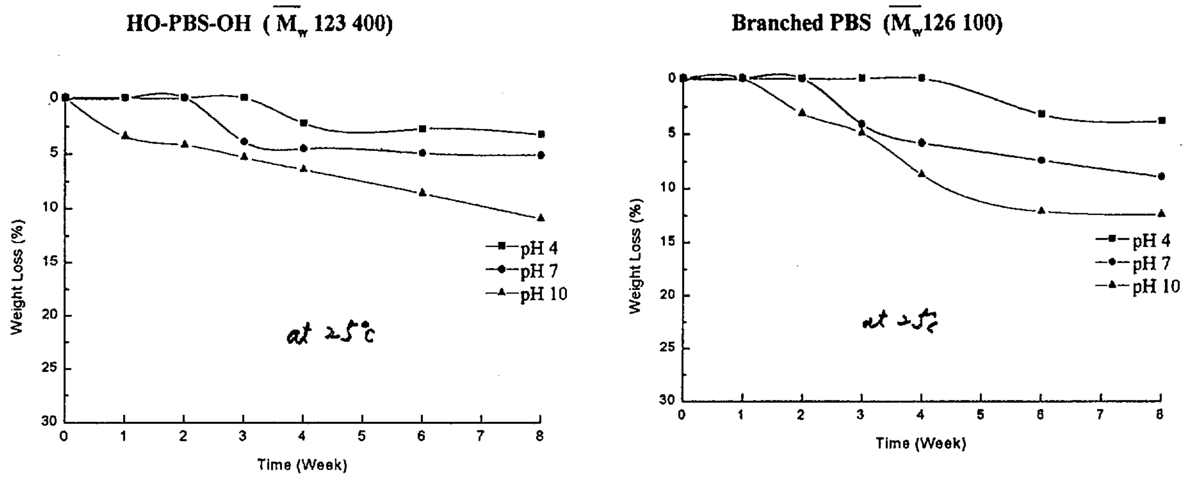


Fig. 3. Effect of pH on the Weight Loss of PBS at 25°C.

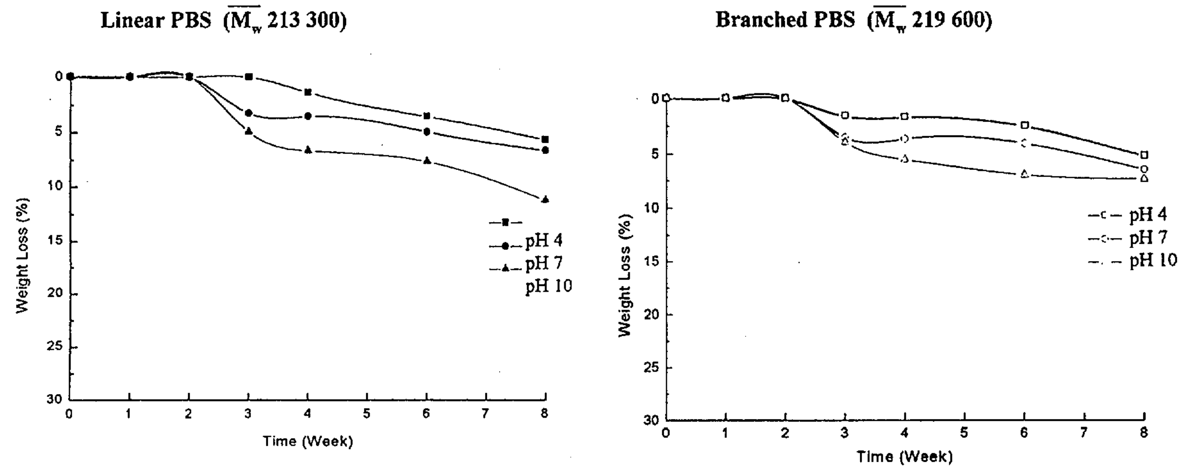


Fig 4. Effect of pH on the Weight Loss of PBS at 25°C.

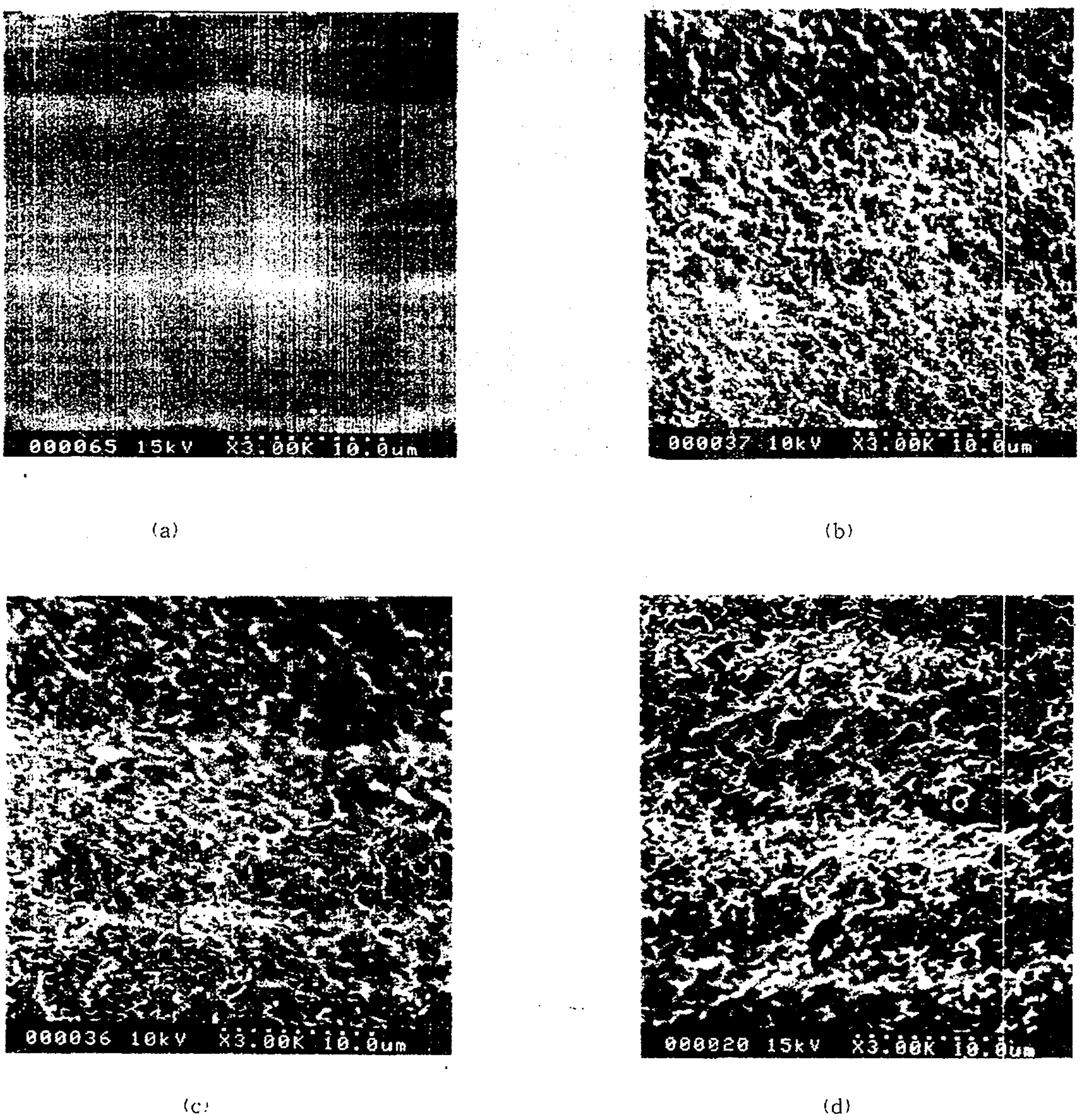
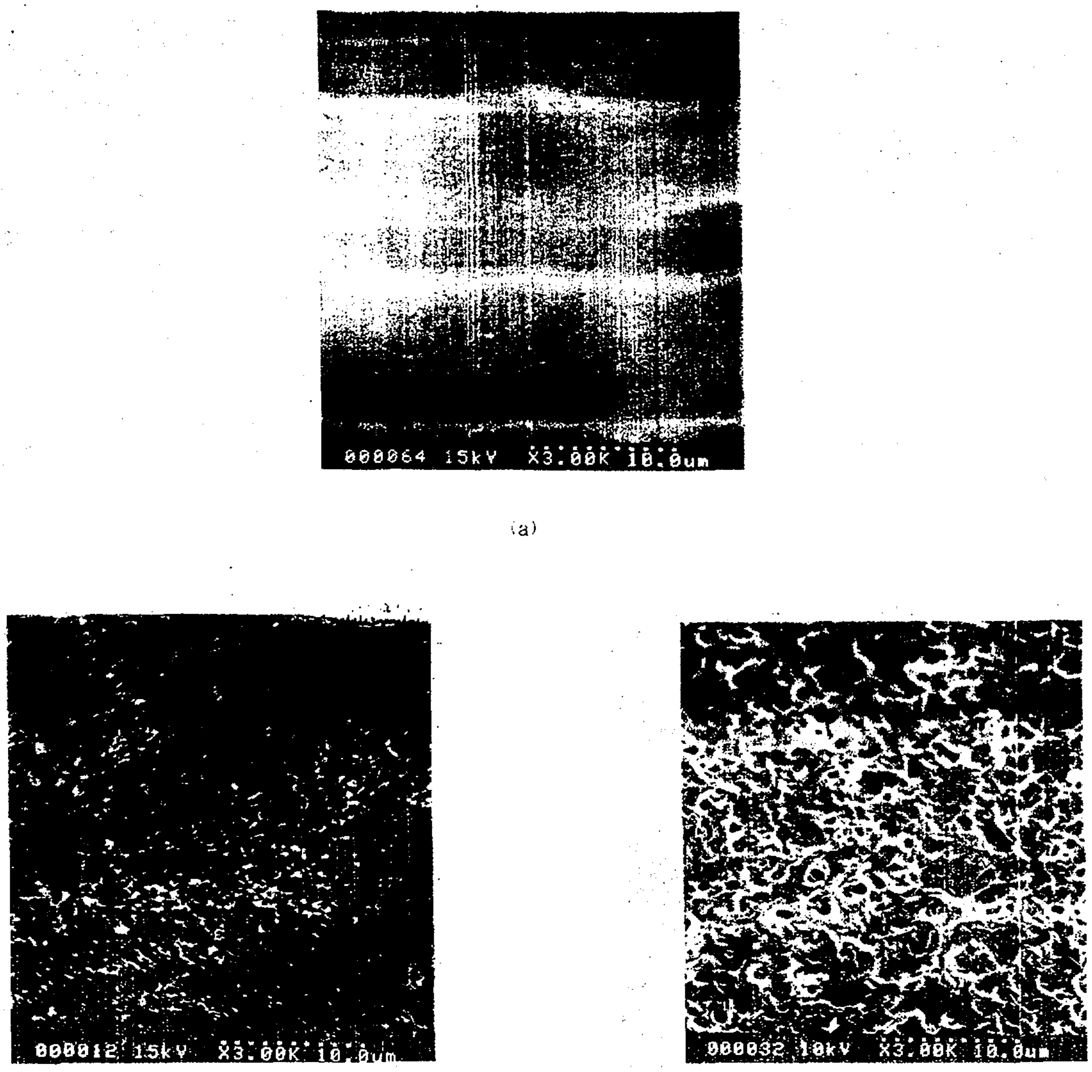


Fig. 6. Scanning electron micrographs of branched PBS (I.V 1.96): (a) before hydrolysis; (b) after hydrolysis for 4weeks at pH 4; (c) after hydrolysis for 4weeks at pH 7; (d) after hydrolysis for 4weeks at pH 10; film thickness, 30 ㎛.



(a)

(b)

(c)

Fig. 7. Scanning electron micrographs of HO-PBS-OH (I.V 1.01): (a) before hydrolysis; (b) after hydrolysis for 4weeks; (c) after hydrolysis for 8weeks at pH 4; film thickness, 30 ㎛.

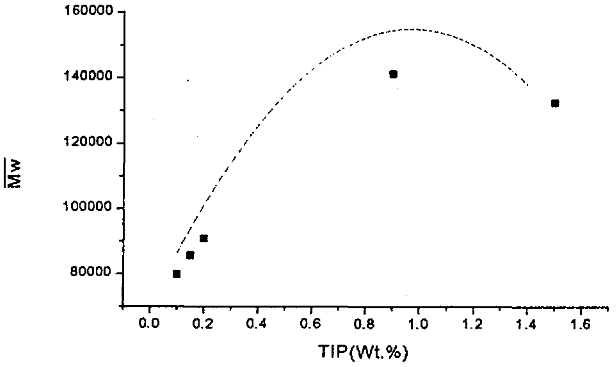


Fig. 8. Effect of TIP concentration on the molecular weight of branched PBA.

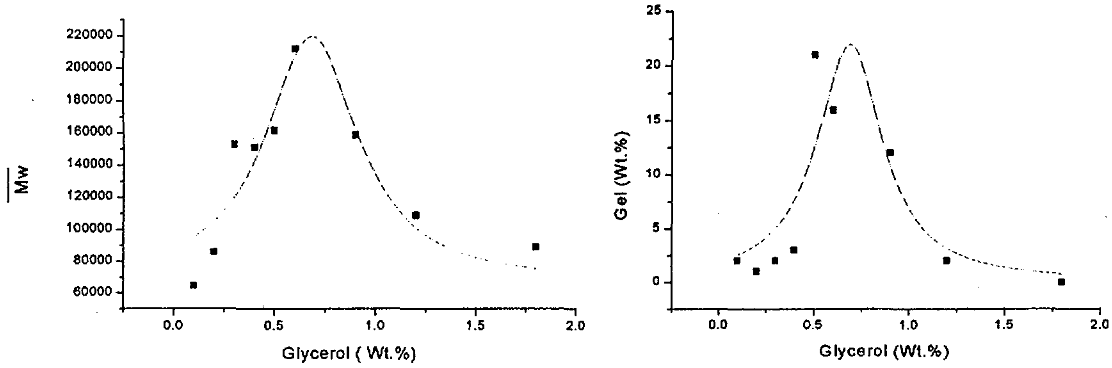


Fig. 9. Effect of glycerol concentration on the molecular weight of branched PBA.

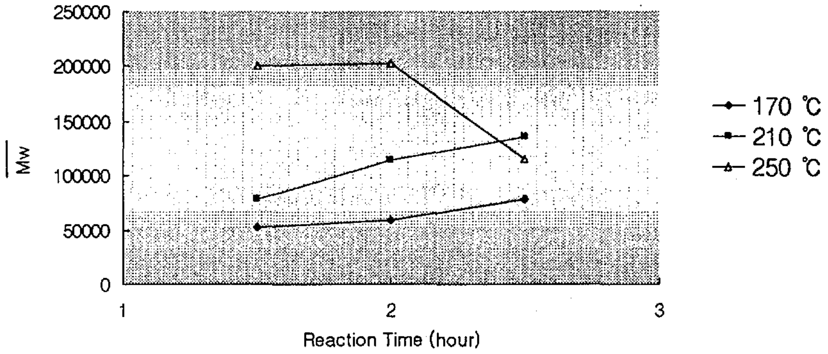


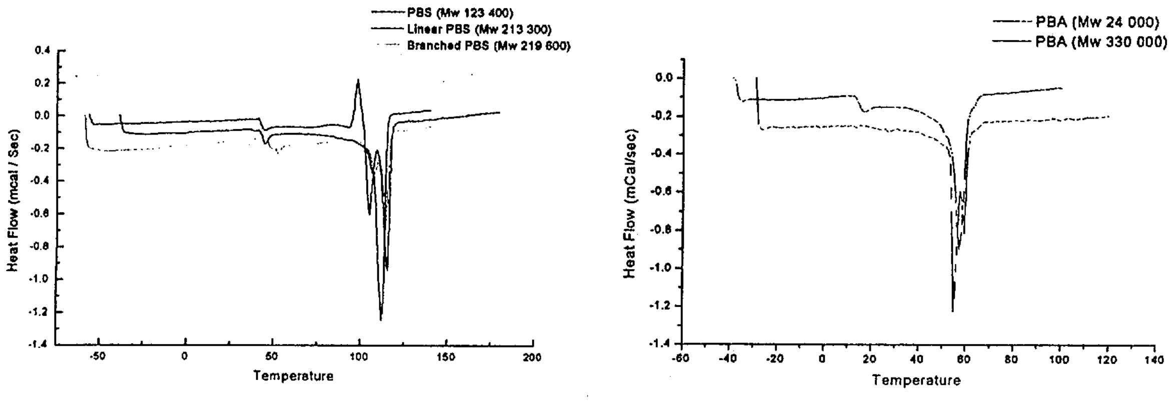
Fig. 10. Effect of reaction time and temperature on the molecular weight of branched PBA.

Table 9. Influence of different branching agents on the molecular weight of branched PBA

Branched[a] PBA	**PBA (Wt.)**	**Branching Agent (Wt.% to PBA)**	**TIP (Wt. % to PBA)**	**Yield (%)**	**Gel (%)**	**$\overline{Mn}$[b]**	**$\overline{Mw}$[c]**	**PDI**
PC8-G-06	1.00	Glycerol 0.60	0.30	65	19	52100	135100	2.59
PC8-P-01	1.00	Pentaerythritol 0.60	0.30	68	8	57500	183300	3.19

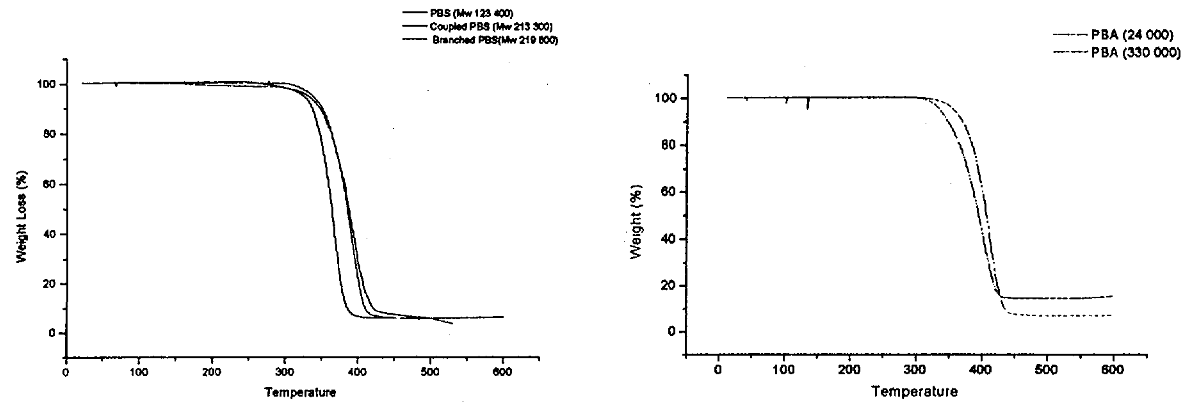
[a] Reaction time & temperature were 2.5 h and 210 ℃, respectively.

[b,c] Measured by GPC with THF solution (10 mg/ 5 mL).



PBS **PBA**

Fig. 11. DSC Thermograms of PBA and PBS (Scanning rate ; 5.0 ℃/min).



PBS **PBA**

Fig. 12. TGA Thermograms of PBS and PBA (Scanning rate ; 10.0 ℃/min).

Table 11. Tensile properties of linear and branched PBA

PBA	I.V.^{a}	$\overline{Mn}^b$	$\overline{Mw}^c$	PDI	Thickness (μM)	Tensile Strength (MPa)	Strain at Break (%)	Modulus (MPa)	Toughness (MPa)
PC2	0.53	23000	39200	1.70	15	6.0	2.92	493	0.061
PC3	0.65	27600	45200	1.64	15	11.6	5.97	420	0.327
PC1	0.87	41800	73700	1.76	15	17.5	36.9	568	4.94
PC2-G-05	1.37	69700	165600	2.38	20	19.9	547	421	82.5
PC3-G-07	1.48	61900	211900	3.42	20	17.7	584	328	73.5
PC1-G-01	1.62	67400	237600	3.53	20	23.5	531	450	90.5

[a] Inherent Viscosity was measured in $CHCl_3$ solution(0.5 g/dL) at 25 ℃.

[b,c] Measured by GPC with THF solution (10 mg/ 5 mL).

Film dimension : 5 mm x 60 mm.

Crosshead speed : 20 mm/min.

Summary

- We prepared PBS and PBA prepolymers by the melt condensation polymerization of either 1,4-butanediol and succinic acid or 1,4-butanediol and adipic acid in the presence of TIP as a catalyst.
- The prepolymers reacted with 1,4-butanediol or succinic acid to produce the corresponding prepolymers with hydroxyl or carboxylic acid group at both ends of the polymer chain.
- High-molecular-weight branched PBS and PBA were prepared by the branching reaction between the prepolymer with carboxylic acid group and glycerol, as a branching agent.
- We also established the optimum conditions for the preparation of the branched PBS and PBA.
- The weight average molecular weight of the aliphatic polyesters was in the range of 100,000 to 230,000.
- The resulting films prepared from the high-molecular-weight polymers had much better tensile properties in strength, elongation at break and toughness than those of low molecular weight polymers.
- In-vitro degradation test for PBS was carried out in a buffer solution of pH 4, 7 or 10 at 25 °C.
- From a SEM analysis, the hydrolytic rate was found to be dependent not only on the pH of buffer solution but on the molecular weight of the film.

17. Properties and Applications of Aliphatic and Aromatic/Aliphatic Polyesters "EnPol"

Dong-Hoon Kim
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[E-mail: irekim@hitel.net]

Majority of people would agree on the fact that biodegradable polymers applied in agricultural mulch film, golf tee, disposable cutlery, compost and garbage bags, fishing nets and etc. can decrease remarkably the environmental problems caused by conventional non-biodegradable polymers.

There were many attempts worldwide in the 1970's, 1980's and 1990's for the usage of biodegradable polymers for the above applications. However, it was not successful on the matter of consumption rate of biodegradable polymers (18,000 MT/year at year 1998) compared to the conventional commodity plastics (approximately 100,000,000 MT/year at year 1998). Experts estimate the optimum consumption ratio of biodegradable polymers among the commodity plastic materials as 10～30%. Therefore, there should be the biodegradable polymers market of at least 10 million metric tons per year worldwide at the moment.

The limited small market of biodegradable polymers is mainly due to the inferior physical properties, poor processibility and high price of biodegradable polymers.

IRe Chemical Ltd. was founded for the purpose of contributing to the field of environmentally friendly biodegradable polymers by solving the above drawbacks of biodegradable polymers, and at the same time for the purpose of synthesizing and applying the advanced synthetic polymers for medical applications.

EnPol, trade mark of IRe Chemical Ltd., polymers are commercially available biodegradable aliphatic or aromatic/aliphatic polyester that are stable in the atmosphere but biologically decompose in compost, in soil, in fresh water and in the sea.

EnPol is produced through the condensation polymerization of aliphatic glycols with aliphatic or combination of aliphatic/aromatic dicarboxylic acids.

EnPol polymers are developed and produced mainly for disposal by composting, in-soil degradation, and in-lake·sea degradation. Living microorganisms transform EnPol polymers into biomass, carbon dioxide and water. EnPol polymers are completely decomposed in normal composting operations without any harmful by-products. EnPol polymers are harmless to the environment at every stage of the decomposition process.

- EnPol polymers are safe for incineration. Combustion of EnPol polymer does not yield any toxic gas or residues.
- EnPol polymers are processable with conventional plastic extrusion equipments.
- EnPol polymers are recyclable. EnPol polymers can be recycled several times for most of the conventional plastic processing equipments.
- EnPol polymers have a good printability even without surface-treatment.

EnPol has superior processability, physical properties and broad application spectrum according to its wide range of grades. The grades of EnPol covers wide range of melting temperature from 60℃ to 118℃. Especially the G8000 grade series of EnPol, produced through combination of aromatic/aliphatic dicarboxylic acids in the acids part of condensation polymerization, has a superior tear strength and thus can be considered as a best candidate material for agricultural applications such as mulch film and pot. The biodegradability of the G8000 series can be adjusted according to each application through the IRe's catalyst and process technology. At the presentation, characteristics of EnPol grades, focusing G8000 series, and its applications will be discussed.

IRe Chemical Ltd.

What should be the world-wide market of biodegradable polymers now?

Experts estimate the optimum consumption ratio of biodegradable polymers among the commodity plastic materials as 10 to 30% of them (approx. 100,000,000 MT/year in 1998).

The limited small market of biodegradable polymers is mainly due to the inferior physical properties, poor processability and high price of biodegradable polymers.

IRe Chemical Ltd. was founded for the purpose of contributing to the field of environmentally friendly biodegradable polymers by solving the above drawbacks of biodegradable polymers, and at the same time for the purpose of synthesizing and applying the advanced synthetic polymers for medical applications.

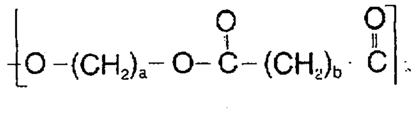
General Descriptions

EnPol polymers, produced through the polycondensation reaction of glycols and dicarboxylic acids with IRe's self-developed catalyst and process technology, are biodegradable aliphatic polyester resins.

EnPol polymers are stable in the atmosphere, but biological decomposition commences when exposed to bacteria or fungi, and moisture. Living micro-organisms transform EnPol polymers into carbon dioxide and water. EnPol polymers are completely decomposed in normal composting conditions without any harmful by-products, and harmless to the environment at every stage of the decomposition process.

The properties of EnPol polymers are diverse and adjustable similar to those of conventional plastic materials such as PE, PP and PS.

< Main unit of EnPol >



$$\left[O-(CH_2)_a-O-\overset{\overset{O}{\|}}{C}-(CH_2)_b\cdot\overset{\overset{O}{\|}}{C} \right]$$

Characteristics (I)

Biodegradable:

EnPol polymers are fully biodegradable aliphatic polyester. Living micro-organisms transform EnPol polymers into carbon dioxide and water without any harmful by-products.

Incineration:

EnPol polymers are safe for incineration. Combustion of EnPol polymers does not yield any toxic gas or residues.

Recyclable:

EnPol polymers are recyclable. EnPol polymers are thermoplastic and can be recycled several times for most of the conventional plastic processing equipments.

Printability:

Printability of EnPol polymers is good even without surface treatment.

Characteristics (II)

Food contact application:

EnPol polymers meet the FDA specifications for food contact applications (FDA extraction studies done in accordance with CFR 21 § 177.1520)

Medical device application:

EnPol polymers meet the USP spec. for medical applications (Analysis studies done in accordance with USP 23 <661> for physicochemical tests)

*** Customer grade:**

EnPol series have wide spectrum of grades through IRe's unique self-developed process & catalyst technology. Current conventional plastics can be replaced by EnPol polymers in most applications.

Customer grades are available for specific applications from diverse combinations of EnPol polymers.

Renewing interest in Agricultural-Based Feedstocks

CMR(Chemical Market Reporter) FOCUS REPORT
November 9, 1998

Chemical companies and research groups are building platforms for the commercialization of chemicals using carbohydrate-based feedstocks.

MBI has been working for an economical route to succinic acid which starts with glucose. Succinic acid, a feedstock analog to maleic anhydride, can be used as a raw material for 1,4-butane diol, tetrahydrofuran, L-lysine and adipic acid. Current biological processes can produce succinic acid for 25 cents per pound, according to Dr. Zeikus, with glucose feedstock costing roughly 8 cents per pound. Dr. Zeikus says that at 20 cents per pound, succinic acid can compete with maleic anhydride. "Our ultimate target is to see succinate at 16 cents a pound," he adds. "At 25 cents per pound, succinic acid can serve as a specialty chemical substitute for petroleum-based succinic acid in food and pharmaceutical ingredients; surfactants and detergents; green solvents and biodegradable plastics."

Processing of EnPol

EnPol polymers can be processed with conventional plastic processing equipments:

- **Inflation (Blown) film extrusion**
- **T-die cast film extrusion**
- **Injection molding**
- **Blow molding**
- **Tube extrusion**
- **Sheet extrusion & Thermoforming**
- **Mono and multi-filament**
- **Foamed sheet, Foamed molding**
- **Spinning (Fiber)**
- **Spun-bonded nonwovens**
- **Lamination**
- **Paper (Board) coating**
- **Extrusion coating**

Applications of EnPol

Disposable goods
cup, knife, spoon, fork, razor, straw, diaper

Paper (or board) coating
disposable bowl, cup, pot, tray, etc.

Agriculture and Horticulture
mulch film, plant pot, rope or string, clip,
matrix for controlled release of fertilizer/pesticides

Bottle
bottle for shampoo, detergent, medicine, cosmetic, beverage, etc.

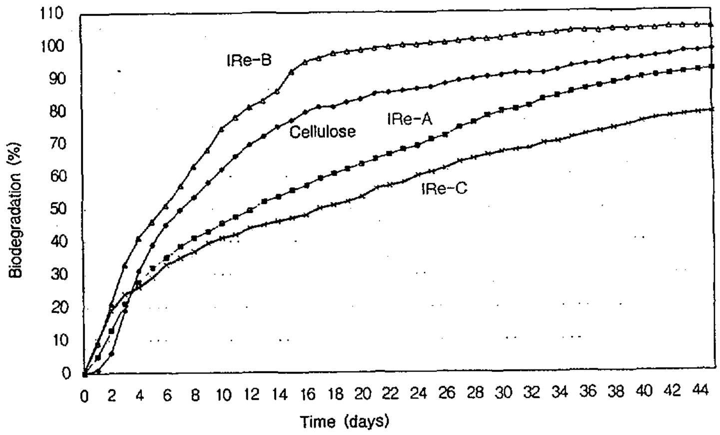
Packaging
loose-fill packaging, shrinkable film, etc.

Medical
injection syringe, mouthpiece for endoscopy, casting tape (gyps), etc.

Miscellaneous
film and rope for protecting roots in plant move, golf-tee, fishline, net, etc.

Biodegradability of EnPol

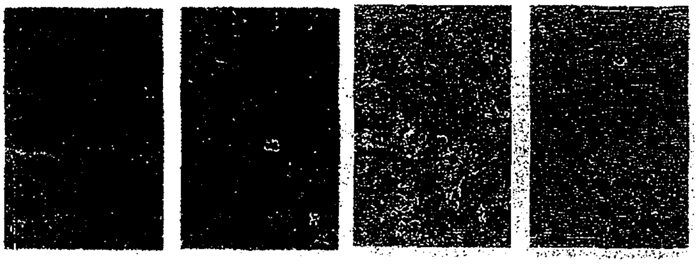
- ISO DIS 14855 under controlled composting condition
- Tested by Organic Waste Systems[O.W.S.n.v.](Belgium)
- Reference material : powdered cellulose



※ The different patterns of biodegradation process of EnPol series shown above demonstrate the availability of the controlled time frame of biodegradation which is required for certain applications.

Soil Burial Field Test

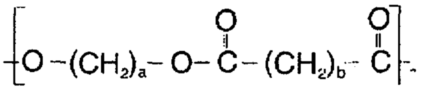
- Grade: EnPol G4000
- Sample: 35 ㎛ thickness blown film
- Test: August, 1997 (Ansan-City, Kyunggi-Do, Korea)



●Before Test
●After 7days
●After 15days
●After 30days

EnPol G8000 Grade

(Aromatic/Aliphatic polyester)



$$\left[O-(CH_2)_a-O-\overset{O}{\overset{\|}{C}}-(CH_2)_b-\overset{O}{\overset{\|}{C}} \right]$$

Biodegradability Comparison between PBS & Aro/Ali

day	PBS	Aro/Ali
	% CO_2 produced	% CO_2 produced
3	0.4	0.4
10	7.3	3.2
17	11.2	14.7
24	12.8	18.3
40	29.6	36.2
50	39.1	52.5
56	41.9	64.9

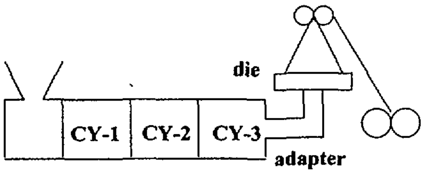
EnPol™ Grades & Applications

Grade	Melting Temp. (℃)	MI @190℃, 2160g (g/10min)	Applications
G2000	60	< 1.5 @120℃, 2160g	low melting temperature applications, inner (sealing) layer of coextrusion film
G2600	56 ~ 60	< 1.5 @120℃, 2160g	
G4000	95 ~ 100	4 ±1.5	packaging film, plastic bag, air-cushion (blister) film
G4025	80 ~ 95	4 ±1.5	
G4600	92 ~ 95	4 ±1.5	
G4625	80 ~ 92	4 ±1.5	
G5000	110 ~ 120	15 ~ 25	injection molding
G5100	110 ~ 120	10 ±2	melt coating, tube, fiber
G5200	110 ~ 120	3 ±1.5	plastic bottles, monofilament
G5300	110 ~ 120	< 3	sheet & vacuam forming
G5000 T20*)	110~120	15~25	injection molding
G5000 T40	110~120	15~25	injection molding
G5000 T50	110~120	15~25	injection molding
G8000	95~100	3~6	agricultural film, shrink film
G8000 C05)	*95~100*	5 ±2	agricultural film, plastic bag
G8000 C07	95 ~ 100	5 ±2	agricultural film
G8000 C25	95 ~ 100	5 ±2	agricultural film, plastic bag

*) T means talc-filled grade, C means calcium carbonate-filled grade.

Recommended processing temp. conditions

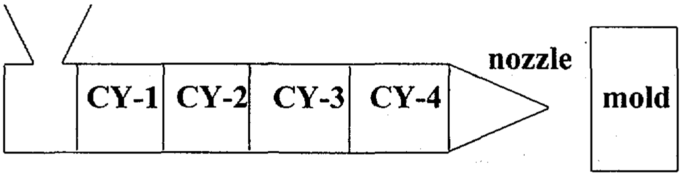
① **Inflation (Blown) Film**



Grade	CY-1	CY-2	CY-3	adapter	die
G4000	150℃	160℃	160℃	155℃	155℃
G4600	140℃	155℃	155℃	150℃	150℃
G8000	140℃	155℃	155℃	150℃	150℃
G8000-C series	140℃	150℃	150℃	150℃	150℃

* It is recommended to set the temperature within ±10℃ of the above recommended values.

② Injection Molding



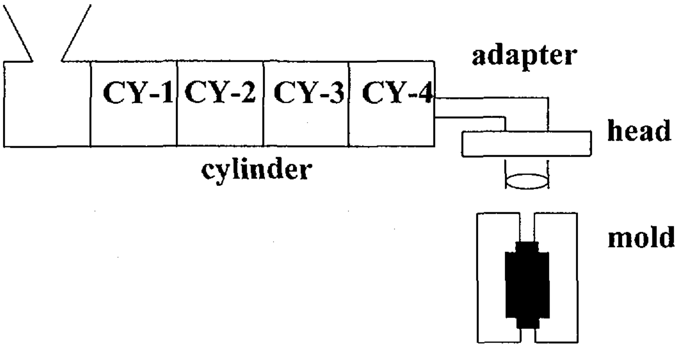
Grade	CY-1	CY-2	CY-3	CY-4	nozzle	mold
G5000	160℃	170℃	170℃	170℃	160℃	10~25℃
G5000-T series	160℃	175℃	175℃	175℃	165℃	10~25℃

* The injection grades have excellent miscibility and mechanical compatibility with fillers (limestone, talc and starch).

* Physical properties of injection grades can be adjusted to behave similar with conventional plastic materials (PE~PS).

* It is recommended to set the temperature within ±10℃ of the above recommended values.

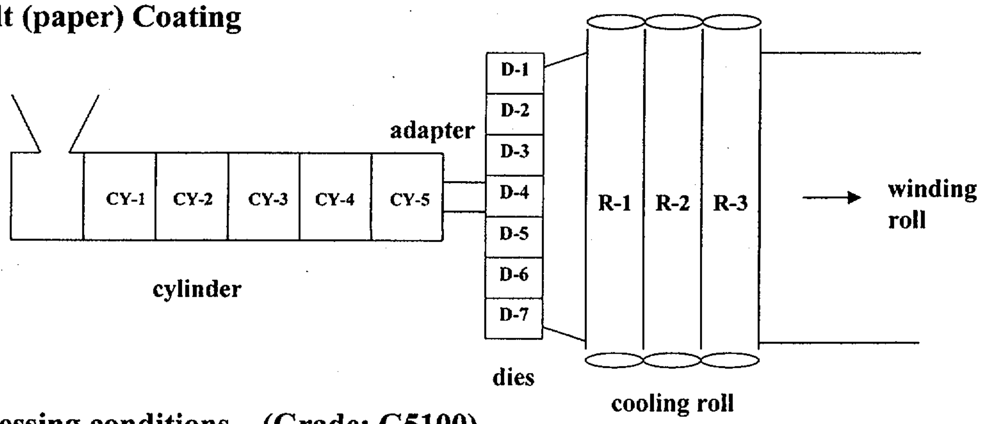
③ Blow Molding (Bottles)



Grade	CY-1	CY-2	CY-3	CY-4	adapter	head
G5200	140℃	140℃	140℃	140℃	145℃	140℃

* It is recommended to set the temperature within ±10℃ of the above recommended values.

④ Melt (paper) Coating



Processing conditions (Grade: G5100)

Extruder rpm = 350
Line Speed : 55m/min
CY-1/CY-2/CY-3/CY-4/CY-5 = 121/195/211/210/221(℃)
adapter temperature = 220(℃)
D-1/D-2/D-3/D-4/D-5/D-6/D-7 = 244/251/254/256/254/251/244(℃)
cooling roll, R-1/R-2/R-3 = 50/50/50(℃)

Procedure for cleaning the processing equipment

(Replacing the existing conventional resin with EnPol)

① Method Ⅰ

- Heat-up the processing equipments which containing the existing resin.
- When the processing temperature for the existing resin is reached, disassemble the die and die-head and clean it.
- Charge the EnPol resin.
- After purging for about 15 minutes, set the cylinder temperature for the processing of EnPol resin.
- When the processing temperature for EnPol is reached, assemble the die and die-head.
- When the processing temperature for EnPol is completely reached, start the production of EnPol film.

② Method Ⅱ

- Heat-up the processing equipments which containing the existing resin.
- When the processing temperature for the existing resin is reached, charge the EnPol resin.
- After purging for about 10 minutes, set the cylinder temperature for the processing of EnPol resin.
- When the processing temperature in cylinder parts for EnPol resin are reached, set the die temperature for the processing of EnPol resin.
- When the processing temperatures at all parts for EnPol resin are reached, start the production of EnPol film.

* It is recommended to purge at lower screw rpm when changing the existing resin with EnPol resin to save the EnPol.

Recommended drying conditions

Grade	Drying Temperature	Time for Drying
EnPol-G2000	50℃	4 hours
EnPol-G2600	45℃	4 hours
EnPol-G4000	65℃	4 hours
EnPol-G4600	60℃	4 hours
EnPol-G5000	80℃	4 hours
EnPol-G8000	60℃	4 hours

IRe Chemical Ltd.

Thank you,

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Web site : www.irechem.co.kr

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Session 4; EDPs Based on Starch and Miscellaneous

18. Properties and Industrial Applications of Mater-Bi Starch-based Materials

Giovanni Ghislandi and Catia Bastioli

Novamont S.p.A., Italy

[E-mail: gghislandi@materbi.com]

Mater-Bi is a new generation of bioplastics, produced by Novamont, derived mainly from renewable resources, able to significantly the environmental impact in terms of energy consumption and green-house effect in specific application, to perform as traditional plastics when in use, and completely biodegradable within a composting cycle.

Today Mater-Bi starch-based bioplastics are used in specific application where biodegradability is required such as the sectors of composting (bags and sacks), fast food tableware (cups, cutlery, plates, straws etc.), packaging (soluble foams for industrial packaging, film wrapping, laminated paper, food containers), agriculture (much film, nursery pots, plant labels), hygiene (diaper back sheet, cotton swabs).

Moreover new sectors are growing outside biodegradability, driven by improved technical performances; versus traditional materials, as in the case of biofillers for tires or chewable items for pets.

The properties and the cost-performance ratio achieved by these products in certain applications and the new product under development give more confidence in the future possibilities of Mater-Bi.

The market of starch-based bioplastics counts for about 20000 ton/year, with a strong incidence of soluble foams for packaging and films. Novamont is one of the main players.

Bioplastics from renewable origin, either biodegradable of non degradable, still constitute a niche market which requires high efforts in the areas of material and application development; the technical and economical breakthroughs achieved in the last three years, however, open new possibilities for such products in the mass markets.

This paper will review the recent achievements of Mater-Bi products in terms of applications, in-use performance, biodegradation behavior and environmental impact.

"PROPERTIES AND INDUSTRIAL
APPLICATIONS OF MATER-BI
STARCH-BASED MATERIALS"

G.GHISLANDI C.BASTIOLI
NOVAMONT S.p.A.
w.w.w. materbi.com
ICS-UNIDO SEOUL
September 19-22, 2000

NOVAMONT INTRODUCTION

START-UP ("THE LIVING CHEMISTRY" PROJECT)
IN 1989 AS RESEARCH CENTER FROM A BRANCH OF DONEGANI INSTITUTE, THE MONTEDISON'S CORPORATE RESEARCH CENTER

OBJECTIVE
INTEGRATE AGRICULTURE, CHEMISTRY AND ENVIRONMENT TO ENGINEER NEW MATERIALS:
- MAINLY FROM RENEWABLE RESOURCES
- WITH MINIMAL ENVIRONMENTAL IMPACT
- WITH THE SAME CHARACTERISTICS OF PLASTICS
- COMPLETELY BIODEGRADABLE WITHIN A COMPOSTING CYCLE

RESULTS
MATER-BI STARCH-BASED MATERIALS AS THE RESULTS OF THE PROJECT "THE LIVING CHEMISTRY" + aggiunta slide

Mater-Bi

is a new generation of bioplastics derived mainly from renewable resources, able to significantly reduce the environmental impact in terms of energy consumption and green-house effect in specific applications, to perform as traditional plastics when in use, and to completely biodegrade within a composting cycle (45 days)

NOVAMONT INTRODUCTION

STRUCTURE

- 90 EMPLOYEES: > 1/3 DEDICATED TO R&D
- A RESEARCH CENTER AT CUSTOMERS' DISPOSAL
- A NETWORK OF DISTRIBUTORS ACTIVE IN EUROPE, USA, JAPAN AND AUSTRALIA
- PRODUCTION CAPACITY:
  - * PRESENT: 2 LINES FOR A TOTAL CAPACITY INCLUDING LICENCING ACTIVITY OF 18000 TON/YEAR

EXPERIENCE

10 YEARS IN RESEARCH, APPLICATION DEVELOPMENT, PRODUCTION AND MARKETING WITH A CONTINOUS AND SIGNIFICANT GROWTH IN THE SECTOR GUARANTEE THE INDUSTRIAL LEVEL ACHIEVED BY MATER-BI PRODUCTS

NOVAMONT CONTRIBUTION TO THE SECTOR OF BIODEGRADABLE MATERIALS

Scientific contribution

- NOVAMONT IS INTERNATIONALLY RECOGNIZED AS A PIONEER IN THE FIELD OF BIODEGRADABLE MATERIALS SINCE 1989

  Patents and Publications

  - ✻ *~ 60 PATENTS AND PATENT APPLICATIONS; 36 FILED BY NOVAMONT; ~ 20 ACQUIRED FROM WARNER-LAMBERT WITH RELATED WORLD-WIDE LICENCES*
  - ✻ *90 ARTICLES AND PARTICIPATIONS TO INTERNATIONAL MEETINGS*
  - ✻ *5 AWARDS*

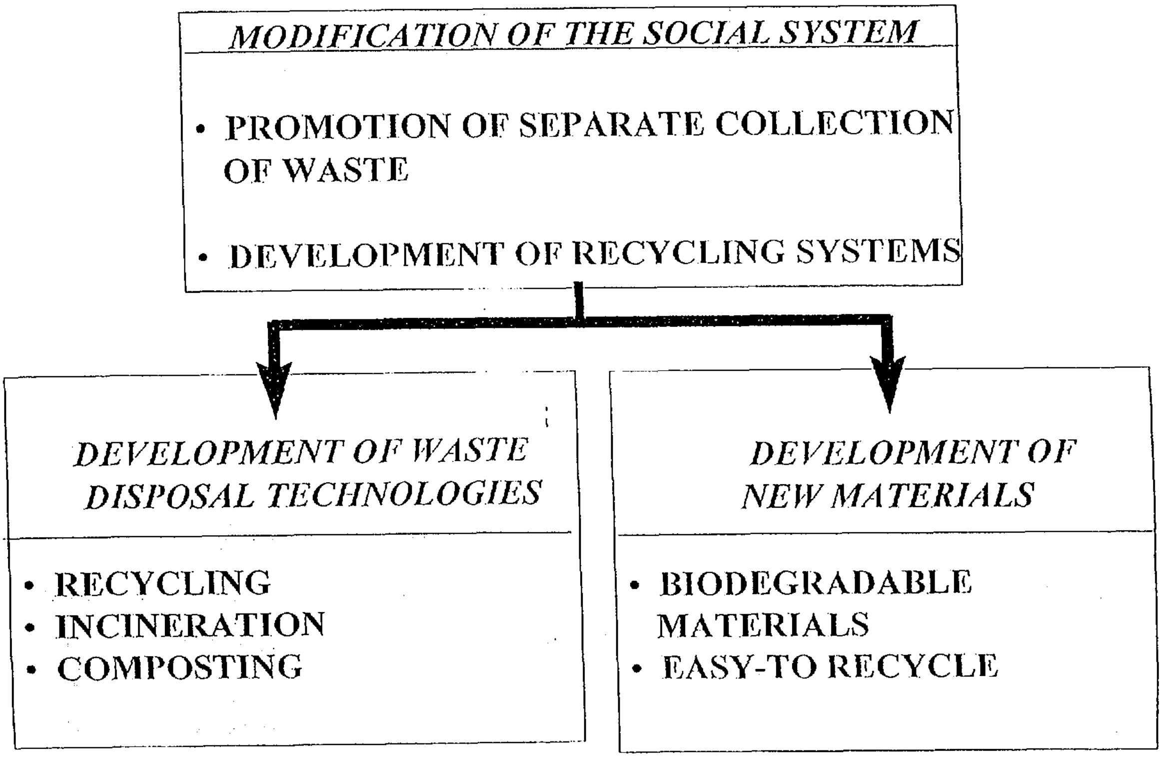
Standars and norms

- NOVAMONT IS MEMBER OF INTERNATIONAL COMMITTEES LIKE ASTM/ISR, CEN, ORCA, AND CONTRIBUTED TO THE PREPARATION OF NEW STANDARDS AND REGULATIONS ON BIODEGRADABLE MATERIALS

Separate collection

- NOVAMONT HAS BEEN WORKING WITH CUSTOMERS AND COMMUNITIES TO IDENTIFY TAILOR MADE COLLECTION SYSTEMS SINCE 1992

APPROACH TO THE WASTE DISPOSAL PROBLEM



MODIFICATION OF THE SOCIAL SYSTEM

- PROMOTION OF SEPARATE COLLECTION OF WASTE
- DEVELOPMENT OF RECYCLING SYSTEMS

DEVELOPMENT OF WASTE DISPOSAL TECHNOLOGIES

- RECYCLING
- INCINERATION
- COMPOSTING

DEVELOPMENT OF NEW MATERIALS

- BIODEGRADABLE MATERIALS
- EASY-TO RECYCLE

WHAT BIODEGRADABLE MATERIALS ARE

- NEW MATERIALS AT AN EMBRYONIC STATE OF DEVELOPMENT WITH:
    - * MORE FAVORABLE ENVIRONMENTAL IMPACT IN COMPARISON WITH TRADITIONAL MATERIALS
    - * IN-USE PROPERTIES SIMILAR TO TRADITIONAL PLASTICS
    - * BIODEGRADABILITY AS PAPER

WHY STARCH

- LOW COST
- AVAILABLE IN LARGE QUANTITIES FROM MAIS, POTATOES, WHEAT AND OTHER SOURCES
- BIODEGRADABLE IN DIFFERENT ENVIRONMENTS
- BIODEGRADABLE AND INCINERABLE WITH RECYCLING OF THE ATMOSPHERIC CO_2 (LCA)

▼

IDEAL RAW MATERIAL FOR COMPLETELY
BIODEGRADABLE PRODUCTS

BIODEGRADATION

$$\text{MATERIAL} + \underset{\text{AEROBIC}}{\text{BIOMASS}} \xrightarrow[H_2O]{O_2} CO_2 + H_2O + \text{BIOMASS}$$

$$\text{MATERIAL} + \underset{\text{ANAEROBIC}}{\text{BIOMASS}} \xrightarrow[H_2O]{} CO_2 + CH_4 + \text{BIOMASS}$$

BIODEGRADATION

- COMPOSTING PLANT
- SEWAGE SLUDGE

TYPICAL APPLICATION SECTORS FOR RENEWABLE PRODUCTS

- **BIODEGRADABILITY AS A FUNCTIONAL CHARACTERISTIC**
- **ENVIRONMENTAL AND OR TECHNICAL PERFORMANCES SUPERIOR OR DIFFERENT IN COMPARISON WITH STANDARD MATERIALS**

WHY MATER-BI

- IN NATURE STARCH IS A RESERVE OF ENERGY FOR VEGETABLES
  - * IT HAS NOT STRUCTURAL PROPERTIES
  - * IT IS NOT RESISTENTE TO WATER
- MATER-BI HAS BEEN ENGINEERED TO OVERCOME THESE LIMITS

HOW MATER-BI CAN BE OBTAINED

CRYSTALLINE STARCH FROM CORN, POTATOES OR WHEAT

DESTRUCTURIZATION OF STARCH AND TRANSFORMATION IN THERMOPLASTIC STARCH

COMPLEXATION OF DESTRUCTURIZED STARCH AT DIFFERENT EXTENT IN PRESENCE OF SPECIFIC NATURAL AND SYNTHETIC POLYMERS

METHODS AND CRITERIA

METHODS

- ISO 14851 AND 14852: METHOD TO MEASURE BIODEGRADABILITY OF PLASTIC MATERIALS IN AN ACQUEOUS ENVIRONMENT
- ISO 14855: METHOD TO MEASURE BODEGRADABILITY OF PLASTIC MATERIALS IN A COMPOSTING ENVIRONMENT.

CRITERIA

- CEN BIODEGRADATION OF 90% IN 6 MONTHS TIME
  METHOD USED: ISO 14855 MOSTLY
- ASTM TWO OPTIONS:
  - BIODEGRADATION OF 90% FOR BLEND, IN 6 MONTHS TIME
  - BIODEGRADATION OF 60% FOR PURE POLYMERS (I.E. HOMOPOLYMER AND COPOLYMER), IN 6 MONTHS TIME.

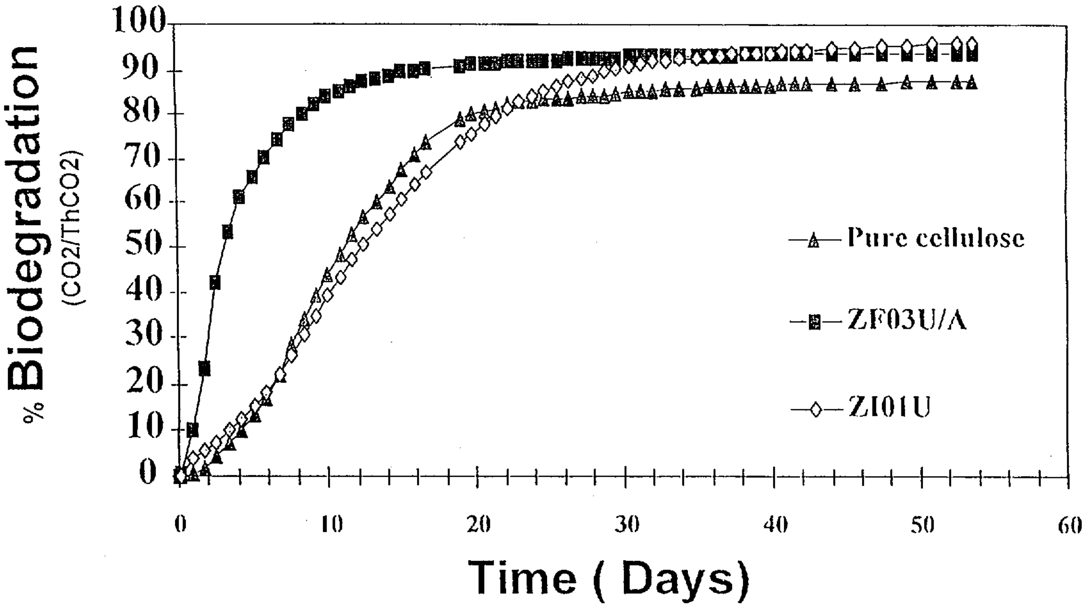
  METHOD USED: ISO 14855
- DIN SAME OF ASTM BUT USING ISO 14851/2/5 METHODS.

WHY BIODEGRADATION?

- ONLY *COMPLETELY BIODEGRADABLE AND COMPOSTABLE* PLASTIC PRODUCTS CAN SERIOUSLY HELP TO GRADUALLY REDUCE THE ENVIRONMENTAL IMPACT OF TRADITIONAL PLASTIC LIKE PE, PP AND PS

- TO HAVE A SOIL NOT VISUALLY OR CHEMICALLY CONTAMINATED BY TRADITIONAL PLASTICS WHICH CAN ALTERATE THE QUALITY OF FOOD CULTIVATIONS

AEROBIC BIODEGRADATION UNDER CONTROLLED COMPOSTING CONDITIONS ISO 14855



APPLICATIONS

NON BIODEGRADABLE PRODUCTS:

- BIOFILLERS FOR TIRES

BIODEGRADABLE PRODUCTS:

* PACKAGING:	BAGS AND SACKS, WRAPPINGS, FOAMS (LOOSE FILLERS)
* CATERING:	CUPS, PLATES, TRAYS, CUTLERY, STRAWS, ETC.
* HYGIENE:	- DIAPER BACKSHEETS, - COTTON SWABS
* AGRICULTURE:	MULCH FILM, TWINES , NURSERY POTS, NETS, ETC.

MATER-BI BAGS USED BY COMMUNITIES FOR THE SEPARATE COLLECTION OF ORGANIC AND YARD WASTE

SHOPPING BAG MADE OF MATER-BI

per chi ama la natura

Morbida due veli

CARTA

Toilette

La Carta Toilette Esselunga ***per chi ama la natura*** è davvero ecologica perchè è stata studiata per garantire il rispetto dell'ambiente in cui viviamo. Infatti:

- è prodotta esclusivamente con **fibre di cellulosa rigenerate e purificate,** ottenute da carta riciclata selezionata.
- Viene purificata per mezzo di una **tecnologia innovativa che non utilizza sostanze dannose per l'ambiente.**
- **È confezionata in un materiale speciale**, il Mater-Bi, a base di amido di mais **completamente biodegradabile** (D.M. 7/12-1990).
- È proposta in **4 maxi-rotoli**, lunghi più del doppio di un normale rotolo, per **occupare meno spazio e ridurre i volumi da trasportare.**

Morbida e resistente, la Carta Toilette Esselunga ***per chi ama la natura*** è un prodotto di qualità ad un prezzo conveniente tutto l'anno.

confezione realizzata in Mater-Bi

Mater-Bi

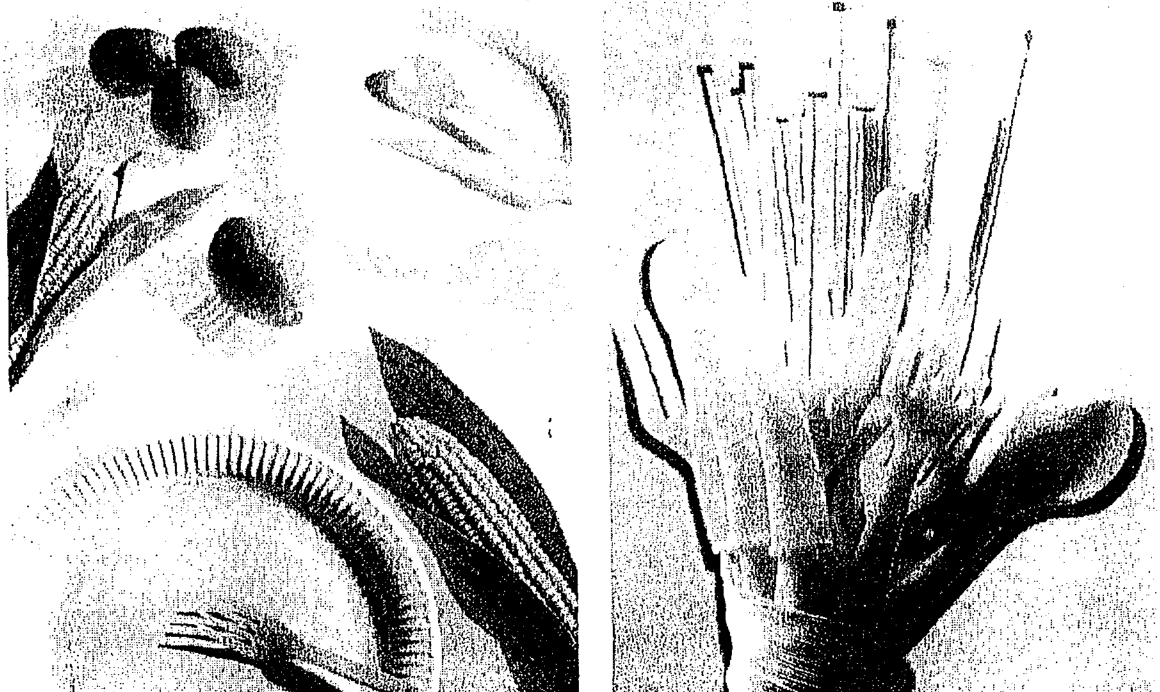
marchio registrato della Novamont S.p.A.

CARATTERISTICHE TECNICHE (per rotolo)	
Veli	2
Strappi	500
Peso	195 g
Lunghezza	60 m
Materiale	cellulosa riciclata

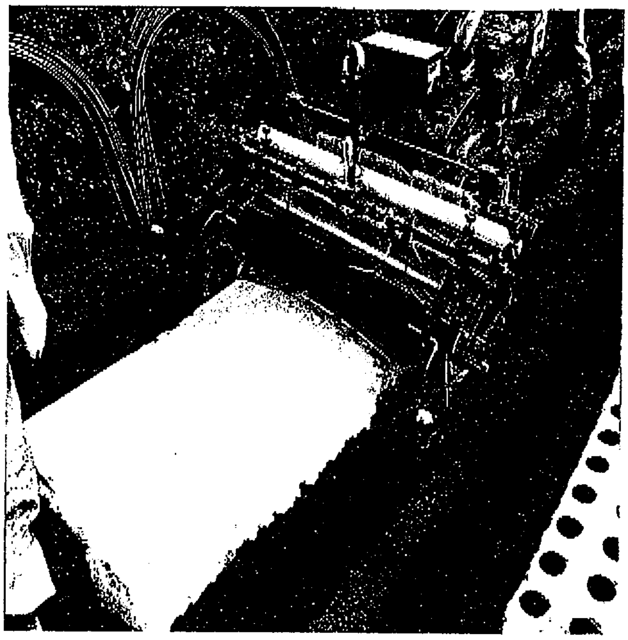
Tolleranza ± 5%

LOOSE FILLERS MADE OF MATER-BI

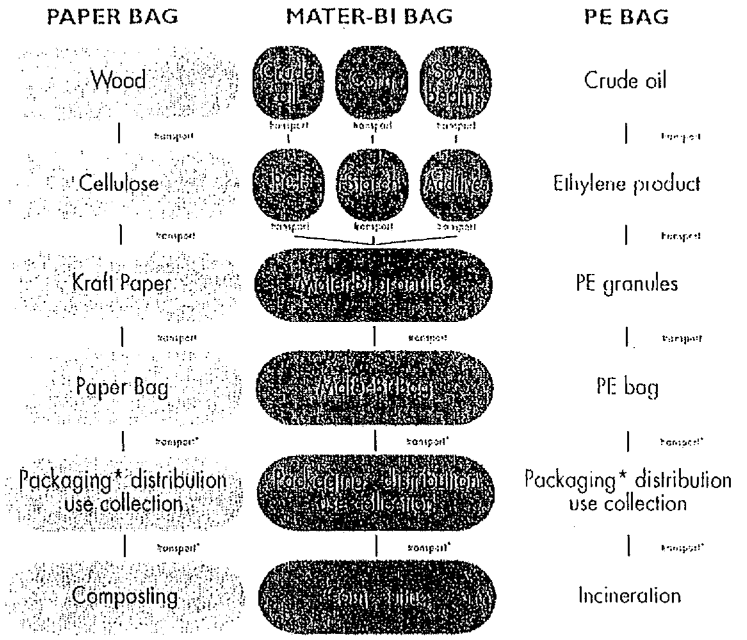
CUTLERY, CUPS AND PAPER LAMINATED PLATES MADE OF MATER-BI



MULCH FILM MADE OF MATER-BI



LCA: STEPS OF THE PRODUCTION CHAIN



*Not considered in the LCA

LIFE CYCLE ANALYSIS OF COMPOSTING BAGS (COMPOSTO, SWITZERLAND-JUNE 1998)

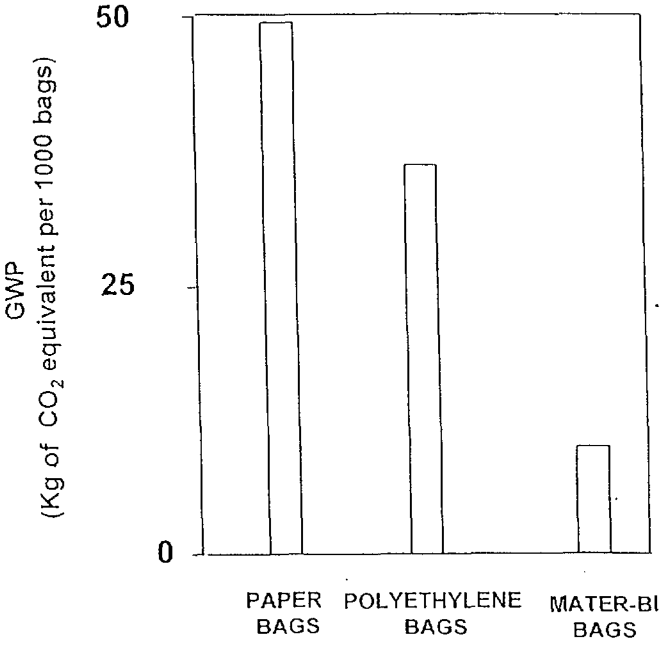
COMPARED BAGS (1000 BAGS/TYPE)

- MATER-BI BAGS (STARCH-PCL) 10 LT (9.2 gr/bag)
- HDPE BAGS 10 LT (7.2 gr/bag)
- NON BLEACHED PAPER BAGS (59.6 gr/bag)

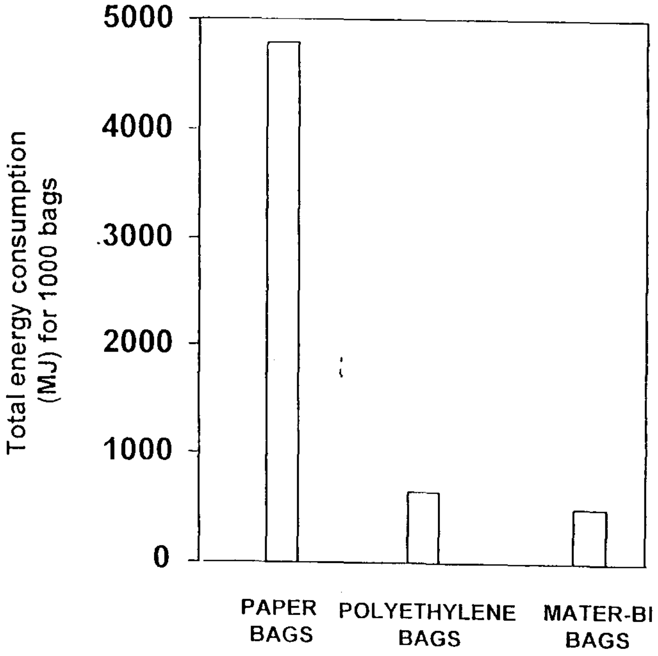
GENERAL ASSUMPTIONS

- DATA OF ENERGY CONSUMPTION AND ENVIRONMENTAL IMPACT CALCULATED CONSIDERING THE PRESENT LOGISTIC SITUATION OF RAW MATERIALS AND FINISHED PRODUCTS WITH TRANSPORTATION TO SWITZERLAND
- THE EVALUATION INCLUDES RAW MATERIALS ACQUISITION, PRODUCTION, PROCESSING AND DISPOSAL OF BAGS, AS WELL AS TRANSPORTATION
- PE BAGS SUPPOSED TO BE INCINERATED FREE FROM ANY FOOD RESIDUE
- MATER-BI AND PAPER BAGS SUPPOSTED TO BE COMPOSTED TOGETHER WITH FOOD WASTE
- DATA CONCERNING STARCH, PE AND PAPER TAKEN FROM BUWAL DATA BASE

GLOBAL WARMING POTENTIAL OF PAPER, PE AND MATER-BI BAGS*



TOTAL ENERGY CONSUMPTION OF PAPER, PE AND MATER-BI BAGS



CONCLUSIONS

A SIGNIFICANT GROWTH OF BIODEGRADABLE MATERIALS WITH REAL BENEFITS FOR THE ENVIRONMENT IS TIED TO:

- STANDARDS ON BIODEGRADABILITY AND COMPOSTABILITY WHICH GUARANTEE THE ABSENCE OF RESIDUAL SYNTHETIC PRODUCTS IN THE COMPOST
- PROMOTION OF BIODEGRADABLE MATERIALS WITH ENVIRONMENTAL IMPACT LOWER THAN TRADITIONAL MATERIALS WITH PARTICULAR ATTENTION TO CO_2 EVOLUTION
- GROWTH OF SEPARATE COLLECTION OF ORGANIC AND YARD WASTE AND OF RELATED COMPOSTING INFRASTRUCTURES
- PROMOTION OF THE CONCEPT THAT COST OF DISPOSAL IS AN INTEGRANT AND RELEVANT COMPONENT OF A PRODUCT'S COST

▼

THE LEGISLATIVE ATTENTION CAN SIGNIFICANTLY INFLUENCE THE BUSINESS DEVELOPMENT

ORGANIC WASTE SEPARATE COLLECTION

- CRITICAL WASTE FOR LANDFILL MANAGEMENT
- CANNOT BE INCINERATED (WATER)
- RETURN THE ORGANIC WASTE CONTENT TO THE SOIL
- QUALITY COMPOST:
  BUSINESS OPPORTUNITY

THE SEPARATE COLLECTION ORGANIZATION IN U.S.

(ONLY YARD WASTE)

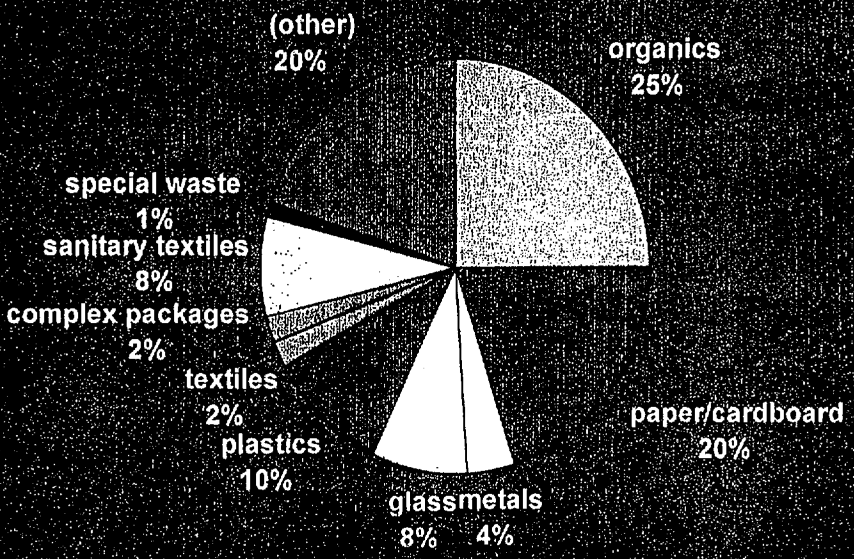
- ***SYSTEM***

DOOR TO DOOR
  PRIVATE 120 LT BIN
  PUBLIC 120 LT. BIN

- ***FREQUENCY***

SMALL TOWNS	1-2/WEEK
BIG CITIES	2-3/WEEK

TYPICAL URBAN WASTE COMPOSITION IN EUROPE



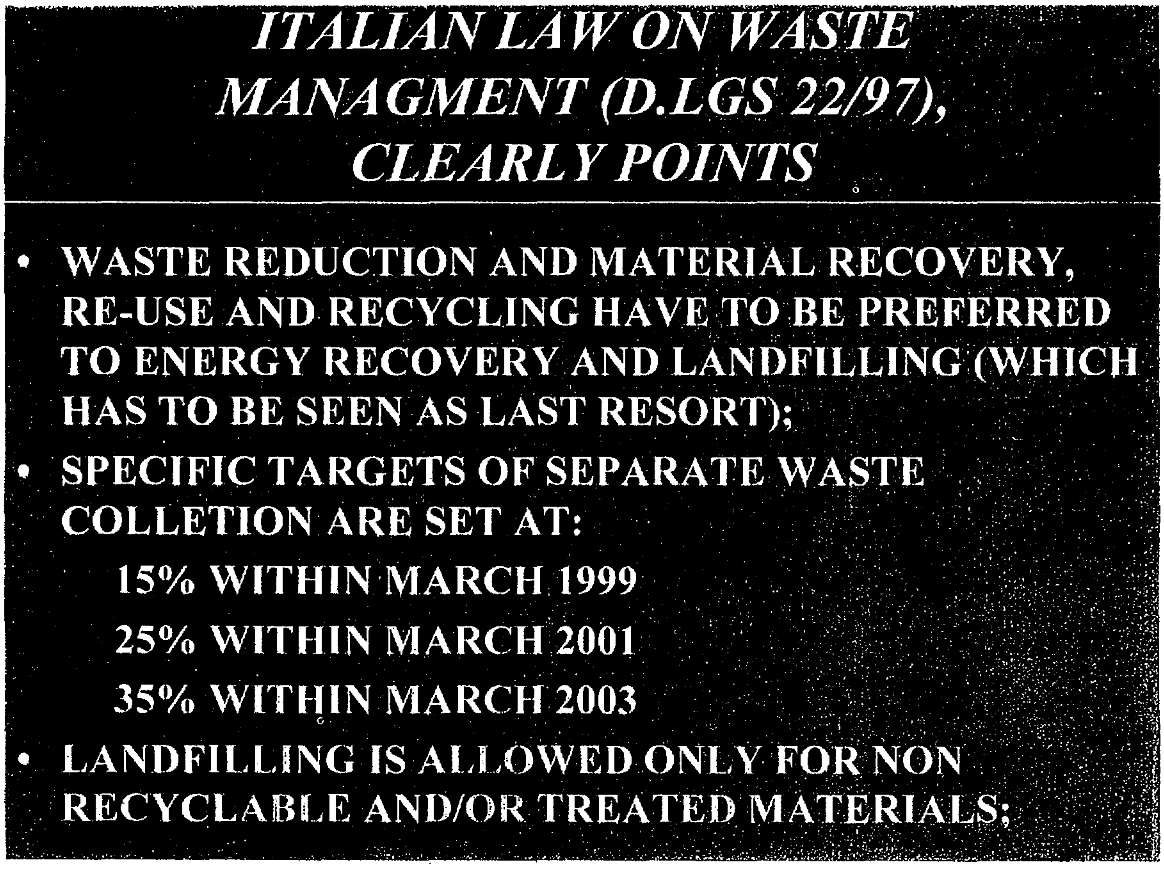
THE SEPARATE COLLECTION ORGANIZATION IN EUROPE (KITCHEN AND YARD WASTE)

- ***SYSTEM***

HOUSEHOLD: WASTE SEPARATION
CENTRAL DUMP: COLLECTION
TRANSPORT/DISTIDUTION IN DIFFERENT RECYCLING/TREATMENT PLANTS

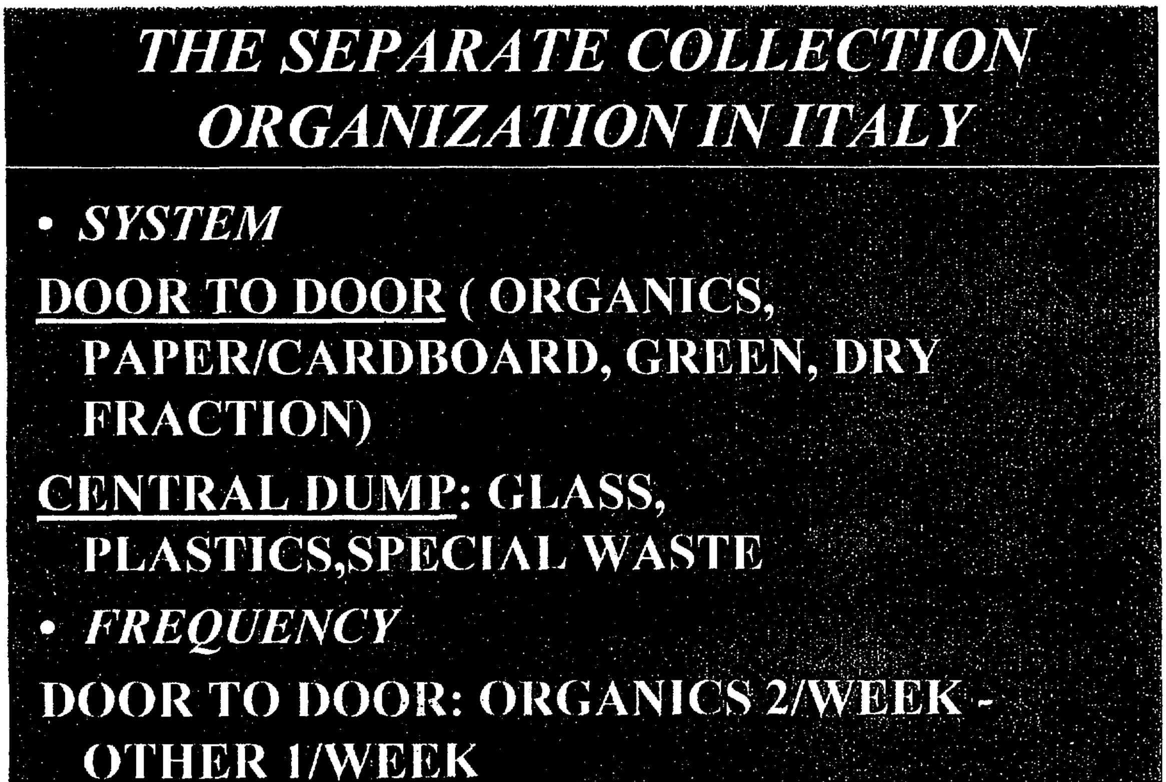
- ***FREQUENCY***

1/WEEK



ITALIAN LAW ON WASTE MANAGMENT (D.LGS 22/97), CLEARLY POINTS

- WASTE REDUCTION AND MATERIAL RECOVERY, RE-USE AND RECYCLING HAVE TO BE PREFERRED TO ENERGY RECOVERY AND LANDFILLING (WHICH HAS TO BE SEEN AS LAST RESORT);
- SPECIFIC TARGETS OF SEPARATE WASTE COLLETION ARE SET AT:
  - 15% WITHIN MARCH 1999
  - 25% WITHIN MARCH 2001
  - 35% WITHIN MARCH 2003
- LANDFILLING IS ALLOWED ONLY FOR NON RECYCLABLE AND/OR TREATED MATERIALS;



THE SEPARATE COLLECTION ORGANIZATION IN ITALY

- *SYSTEM*

DOOR TO DOOR (ORGANICS, PAPER/CARDBOARD, GREEN, DRY FRACTION)

CENTRAL DUMP: GLASS, PLASTICS,SPECIAL WASTE

- *FREQUENCY*

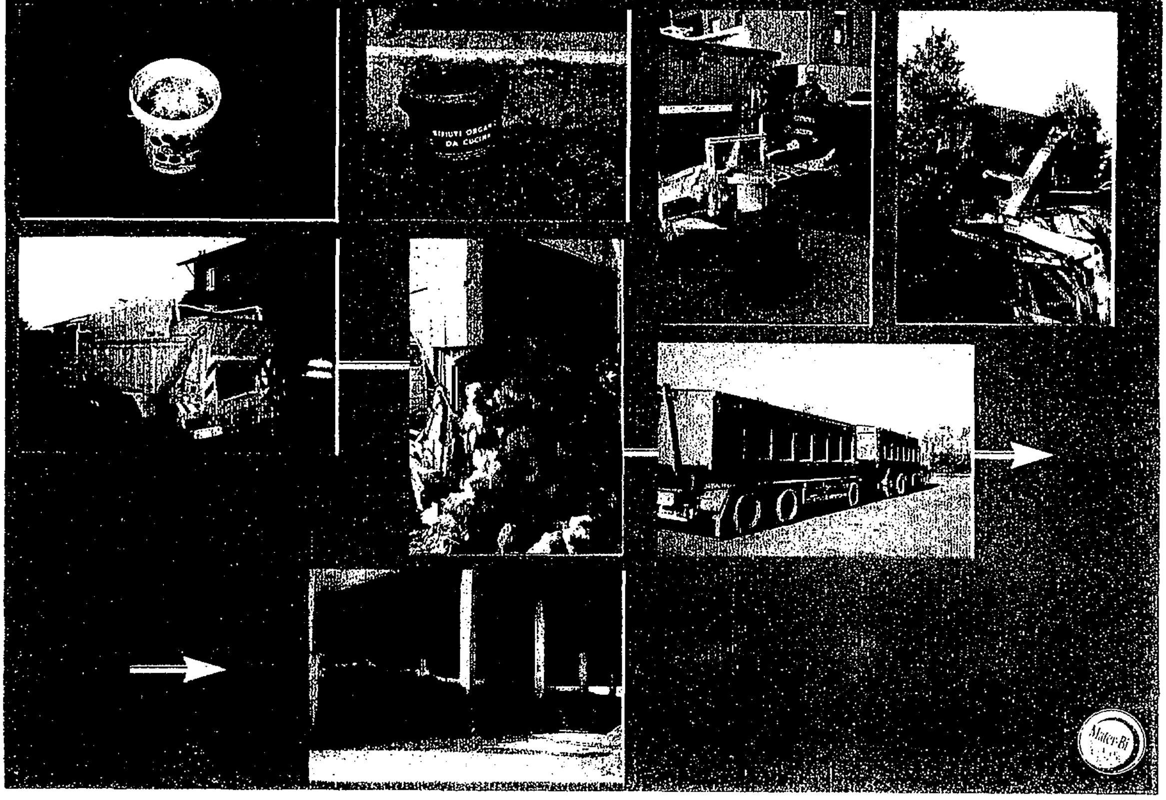
DOOR TO DOOR: ORGANICS 2/WEEK - OTHER 1/WEEK

CENTRAL DRUMP: 1/WEEK

ITALIAN SITUATION

- MORE THAN 600 COMMUNITIES, 5 MILLIONS OF CITIZENS, EQUAL TO THE 10% OF THE ITALIAN POPULATION ARE SEPARATING THE ORGANIC WASTE WITH BIODEGRADABLE BAGS
- MORE THAN 100 COMPOSTING PLANTS RUNNING
- 1.500.000 TONS OF ORGANIC WASTE TREATED

SEPARATE COLLECTION OF ORGANIC WASTE - ITALY



COMPOSTING BAGS WITH MATER-BI Z GRADES

BIODEGRADABLE/COMPOSTABLE AS PAPER

MECHANICAL PROPERTIES SIMILAR TO LDPE

WATER RESISTENCE

ODOR BARRIER

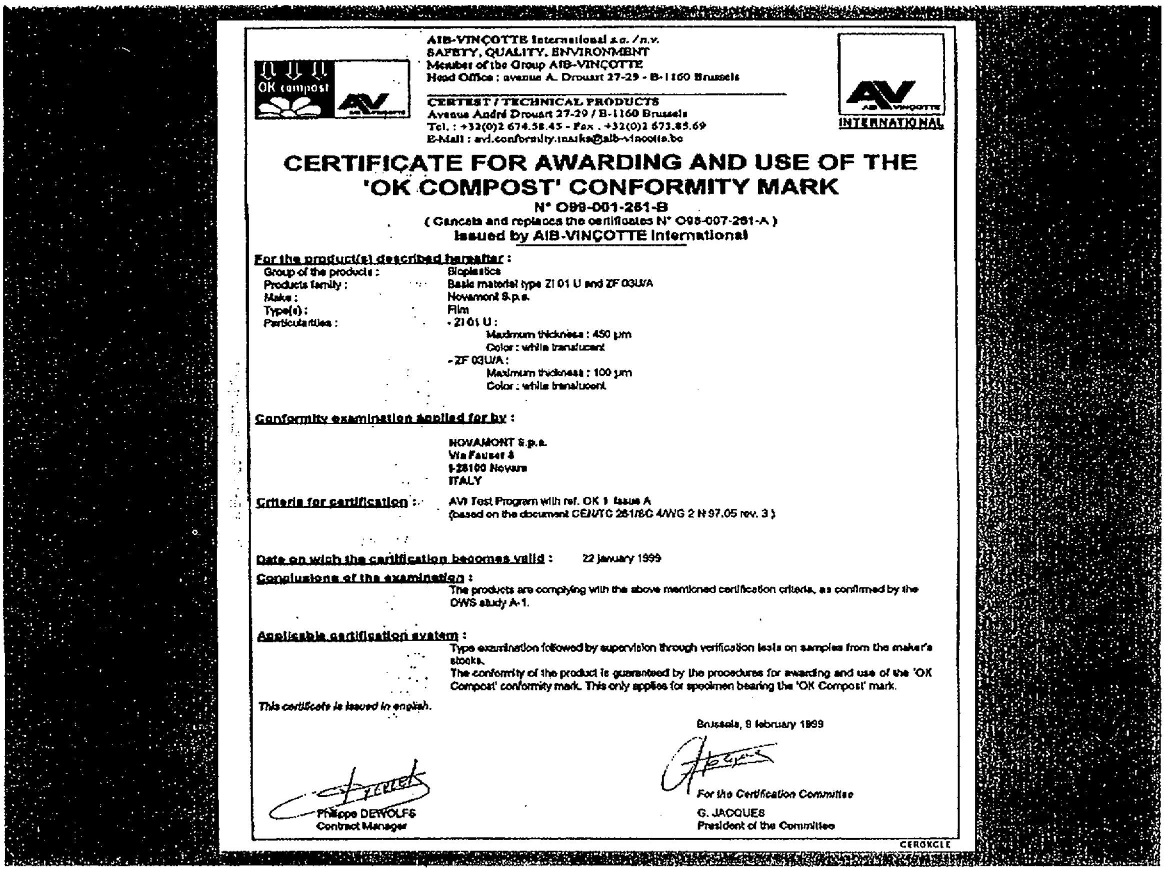
TRASPARENCY

LOW VOLUME

COMPARISON OF BAGS IN TERMS OF ENVIRONMENTAL PROFILE (Impact categories of ECO-Indicator 95)

Impact Category	Mater-Bi Bag in comparison with paper bag.	Mater-Bi Bag in comparison with PE bag*.	Mater-Bi Bag in comparison with PE bag including residue organic combustion**.
Energy	++	O	+
Global warming	++	++	++
Acidification	+	O	++
Nitrification	++	O	+
Ozone creation	++	+	++
Toxic to air	+	+	++
Toxic to water	--	O	-
Radiation	--	--	++
Deposited waste	+		O

* PE bags incinerated without any organic waste residual.
** PE bags incenerated with organic waste residual.



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E-Mail : avi.conformity.marks@aib-vincotte.be

CERTIFICATE FOR AWARDING AND USE OF THE 'OK COMPOST' CONFORMITY MARK

N° O98-001-261-B

(Cancels and replaces the certificates N° O98-007-261-A)

Issued by AIB-VINÇOTTE International

For the product(s) described hereafter :

Group of the products : Bioplastics
Products family : Basic material type ZI 01 U and ZF 03U/A
Make : Novamont S.p.a.
Type(s) : Film
Particularities :
- ZI 01 U :
  - Maximum thickness : 450 µm
  - Color : white translucent
- ZF 03U/A :
  - Maximum thickness : 100 µm
  - Color : white translucent

Conformity examination applied for by :

NOVAMONT S.p.a.
Via Fauser 8
I-28100 Novara
ITALY

Criteria for certification : AVI Test Program with ref. OK 1 Issue A
(based on the document CEN/TC 261/SC 4/WG 2 N 97.05 rev. 3)

Date on wich the certification becomes valid : 22 january 1999

Conclusions of the examination :

The products are complying with the above mentioned certification criteria, as confirmed by the OWS study A-1.

Applicable certification system :

Type examination followed by supervision through verification tests on samples from the maker's stocks.

The conformity of the product is guaranteed by the procedures for awarding and use of the 'OK Compost' conformity mark. This only applies for specimen bearing the 'OK Compost' mark.

This certificate is issued in english.

Brussels, 9 february 1999

Philippe DEWOLFS
Contract Manager

For the Certification Committee
G. JACQUES
President of the Committee

CEROXCLE

19. Degradable Plastics from Polyolefins: Evaluations & Applications

David M. Wiles[1], **Joo Fai Tung**[2], **Gerald Scott**[3] **and Graham Swift**[4]
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[3]Aston University, UK; [4]G.S.P.C. Inc., USA
[E-mail: epicanada@epi-global.com]

Introduction

There is increasing concern in many parts of the world that discarded packaging made of plastic is accumulating at an alarming rate, and that inadequate methods exist for disposing of this waste material. Even though plastics, compared to other packaging materials, provide advantages from both an energy and an environmental point of view, it is felt at least by some politicians that the use of plastic packaging should be regulated.

The concept of biodegradable plastics has been with us for some time now, and there have been two distinctly different approaches to producing such materials. On the one hand, huge investments have been made and are being made to perfect the preparation and use of plastics derived from naturally-occurring or biologically-produced polymers. It is considered by some that such materials are inherently biodegradable and therefore do not present a disposal problem. While such an assumption is difficult to defend, there are also problems with cost, fabrication, and above all with energy requirements to produce these polymers. Indeed, there is a growing body of knowledge (1,2) that indicates that biologically-produced polymers cannot provide the environmental advantages that have been claimed for them. On the other hand, technologies have been developed to convert polyolefins from materials that are microbially inert into materials that are totally degradable following normal usage, and after being discarded in a variety of environments. This approach combines the cost/performance advantages of the polylefins with the added useful property of not accumulating in the environment. There is no requirement for legislative limitations to the use and disposal of environmentally degradable polyolefin packaging materials.

Controlled Conversion

In brief, the durability of polyethylene (PE) , as an example, is established when the integrity of the molecules of which it consists is maintained. The normal situation is that oxidative degradation (random, chain-scission events in the presence of oxygen) will eventually occur such that the molar mass is reduced, the tensile properties decrease, the material becomes brittle and undergoes fragmentation. Concomitantly the material becomes water-wettable owing to the incorporation of oxygen-containing groups in the partially degraded molecules. Details of the sequence of reactions, collectively referred to as oxidative degradation, have been summarized in numerous publications (e.g., 3,4). The sequence can be initiated by mechanical stress, by UV light or by heat, for example (see Figure 1). The individual steps are almost identical regardless of what initiates the process which, in the absence of inhibitory factors or agents, is a branching chain reaction. The overall process is inevitable, and it occurs at a rate that depends on the environment but is normally much too slow to be a significant factor in reducing the build-up of waste plastics in landfill, agriculture, or composting operations, or in litter control. In all of these situations, PE that undergoes the conventional process of oxidative degradation much more rapidly than normal can be very useful. The additional factor of biodegradability is also very important, and PE molecules that have undergone oxidative degradation are, in fact, biodegradable (5,6). The technology developed by EPI Environmental Products Inc. enables the production of oxo-biodegradable polyolefins (7,8) which meet the requirements by means of a two-stage process.

It is mandatory, of course, that plastic packaging remains stable through processing, storage, and use. In other words, the lifetime must be controlled in such a way that the 2-stage process of oxo-biodegradation does not start until the plastic is discarded. Enhanced photodegradation can be obtained by ensuring sensitivity to unfiltered terrestrial sunlight. Enhanced susceptibility to thermal oxidation requires a rather more subtle approach because simply increasing sensitivity to heat is not acceptable. The polymer would not survive conventional processing and fabrication procedures. The technology developed by EPI enables the production of oxo-biodegradable polyolefins with controlled lifetimes. These lifetimes can be varied from short (weeks) to long (months/years) depending on the service life required by the application.

Evaluation and Testing

As with any novel technology, it has been necessary to evaluate thoroughly polyolefin packaging and containers based on EPI totally degradable plastic additive (TDPA™) formulations to ensure that controlled lifetimes are obtained, in keeping with end-use requirements. Processing with standard equipment at normal speeds produces materials that have been shown (largely using accepted ASTM test methods) to undergo enhanced rates of molar mass reduction (GPC, MI), loss of tensile properties and oxidation (FTIR spectroscopy) as a result of simulated or actual outdoor exposure. The conditions used were consistent with landfill, agricultural or litter situations (8). Additional third-party trials have shown that EPI – based polyolefin products provide superior performance as agricultural mulch films, disposable cutlery, and compost bags. In a commercial composting operation, EPI-based PE bags contributed to the production of top quality compost that easily passed all the eco-toxicity tests. Bread bags based on EPI's TDPA™ technology have obtained complete food contact certification.

Applications

Landfill Disposal: It is common practice in many countries that most packaging films and containers have a rather short use-life (weeks, months) following which the material is discarded and ends up in a landfill. Notwithstanding the wide variation in climate and waste disposal practices in different parts of the world, used packaging plastics normally persist for a very long time in a landfill. This contributes both to a reduction in the useful life of a landfill (premature filling) and to a very significant lengthening of the time period before the filled and capped site can be used for any other purpose. This arises because prolonged anaerobic biodegradation, methane production and mechanical instability persist at the site. The inherently slow abiotic oxidation of food wrap, carrier bags and packaging plastics is exacerbated by the common practice of wrapping or enclosing food waste in such discarded plastics, as well as in trash bags. This "encapsulation" of readily biodegradable food waste, paper and the like seriously retards the assimilation of these materials by microbes as a result of restricting the ingress of water and air. It seems that packaging made from conventional polyolefins will persist for many decades in a landfill, and this creates problems.

In contrast, the use of polyolefins based on TDPA™ formulations for food wraps and bags, for example, for virtually all packaging applications, as well as for daily landfill covers, solves numerous problems. As a result largely of the warmth generated microbially in a landfill, EPI-based products undergo oxidative degradation at a modest rate (instead of at an extremely slow rate) and become brittle. Under the influence of the mechanical stress that is characteristic of landfill compaction, the brittle films, bags and other packaging break into fragments thus allowing the vertical movement of gases and liquids through the landfill contents. This increases the rate of biodegradation of food waste and paper, for example, that is enclosed within or under plastic film. There are significant environmental advantages in having as much biodegradation as possible occur aerobically, instead of anaerobically, because the latter produces methane (more damaging as a "greenhouse gas" than CO_2) and prolongs the biodegradation process by an order of magnitude or more.

Agricultural Mulch: In the growing of soft fruits and vegetables, as well as forage crops, the use of thin plastic mulch films is commonplace in many parts of the world to reduce the requirements for moisture and fertilizer, to suppress weeds, and to increase crop yield. There is a chronic problem, however, with the disposal of the contaminated (dirt, vegetation) in tact mulch films at the end of the growing season. Comprehensive field trials have demonstrated the advantages of using oxo-biodegradable PE films that are based on EPI TDPA™ formulations. They become brittle towards the end of the growing season and the fragments can be dispersed in the soil, using conventional cultivation equipment, to continue undergoing the two-stage degradation process referred to earlier. Other types of products suitable for additional applications in agriculture/horticulture are under development.

Composting: This technology is one of the most useful ways of converting food waste and garden waste into materials which have considerable value as fertilizers, soil improvers, and the like. A commercial composting operation is typically large and quite sophisticated. The standards for the best quality products from such operations are recognized to be high. Among the contaminants to be avoided are any that could interfere with the biodegradation of the normal organic input
(e.g., waste food, grass, leaves) and any that do not biodegrade during the procedure, and any that produce products which are toxic to subsequent seed germination and plant growth. Although there are no toxic by-products associated with PE, for example, the persistence of normal PE film, bags, etc., throughout the composting process would visibly contaminate the product, for which there would therefore not be a market. In contrast, PE based on EPI technology, being oxo-biodegradable, undergoes extensive oxidative degradation as a result of the relatively high temperatures during composting, and the partially degraded molecules in the film fragments become water-wettable and biodegradable long before they become water-soluble. The use of EPI-based oxo-biodegradable compost bags contributes to the production of high quality compost that passes all the ecotoxicity tests.

Summary

Many markets exist for plastics having all the useful characteristics, including reasonable costs, for which the polyolefins are well recognized. In a significant proportion of these markets, however, the added property of environmental degradability is a particularly noteworthy feature. Of course conventional polyolefins are bioinert but technology has been developed during the past decade by EPI Environmental Products Inc. to covert conventional PE into degradable plastics by means of a two-stage oxo-biodegradation procedure. Additional degradable products based on polypropylene have been and are being developed, and degradable polystyrene has also been produced. It must be emphasized that all these materials have a controlled lifetime that can be varied according to the requirements of the marketplace.

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Figure 1. The Abiotic Oxidative Degradation of Polyethylene

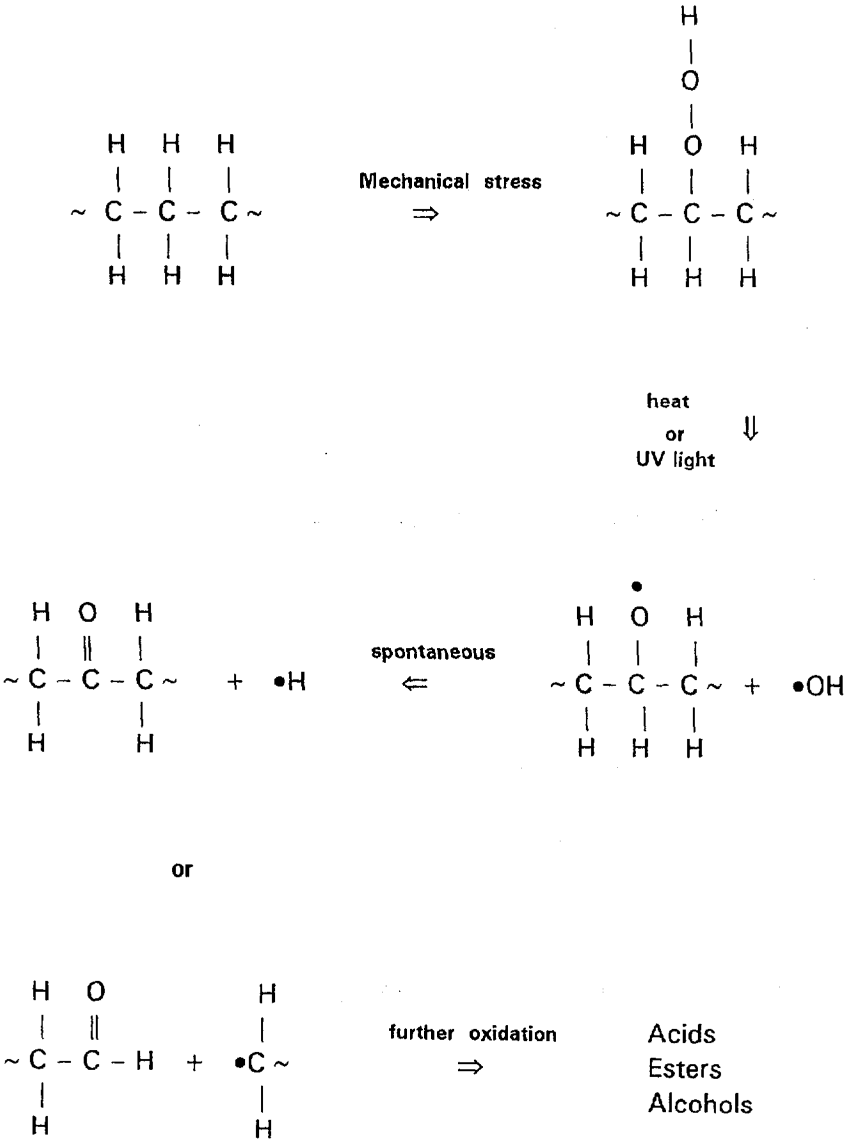

Table 1: Degradation of Enviro® Cover Daily Landfill Cover (LLDPE and LDPE blend) during 3 winter months in Western Canada

PE film sample	*Melt Index (g/10 min)*	*TBS* (MPa)*	*EaB** (%)*	*Carbonyl Index (@ 1715 cm^{-1})*
Control film (unexposed)	0.44	24.5	550	0.18
1 m below surface	0 .55	14.0	450	0.26
2m below surface	0.72	8.0	130	0.42

*tensile breaking strength
**elongation at break

Table 2: Degradation of Enviro® Cover Daily Landfill Cover (LLDPE and LDPE blend) during Oct. to Dec., 1998 in China

PE film sample	*TBS* (MPa)*	*EaB** (%)*	*Carbonyl Index (@ 1715 cm^{-1})*
Control film (unexposed)	24.0	480	0.24
On the surface	12.7	90	0.45
20 cm below surface	22.6	450	0.26
2 m below surface	10.1	40	0.59

*tensile breaking strength
** elongation at break

20. Development and Application of STARATE Series Product

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1. Introduction to the Company

The industrialization project involving 10,000-ton modified starch (SMA) and biodegradable functional plastics products which are now being developed by the Danhai Company with an investment of 1.94 million yuan Ren Min Bi is one of the 20 major projects to industrialize scientific and technological achievements at Tianjin. This project has been decided by China's State Planning Commission to be a demonstration project to popularize the industrialization of our country's major scientific and technological achievements.

At present, our company already has an annual productive capacity of 30,000 tons of the master batch of biodegradable plastics and 10,000 tons of biodegradable plastics products. It is expected that after the project has been fully carried out in 2001, we will have achieved an annual productive capacity of 30,000 tons of biodegradable (plastics) master batch and 30,000 tons of relevant products. Over the years, our company has been developing and forging ahead through abiding by the spirit of always striving to be the topmost enterprise in our country. Our biodegradable plastics master batch has been accredited to be one of the major new biosynthetic products of the national grade. Our company has also been awarded the authentication of being one of Tianjin's high-tech enterprise, and our products have been accredited the trademarks of China's national environmental protection. Furthermore, they have been awarded the credit of bearing the trademarks of products manufactured by adopting international standards. I am proud to say that ours is the largest enterprise in China for the production of degradable plastics.

At the present time, when the human race steps into the 21st century, it is our common duty and obligation to care for the ecological environment with which we all concern our selves and protect the globe that humanity jointly owns. There was an article captioned 'Will the operation of the 21st century rely on the "Green gold" (i.e. agricultural products) or "Black gold" (i.e. petroleum products)? ' in an American newspaper, *Today's America*, of February 1, 1999. It emphasizes that the economy of every country in the world has been encumbered by the shortage of petroleum. And there is the possibility that agricultural crops will gradually replace petroleum and become the material sources from which all such matters ranging from fuel to plastics can be obtained. The "black gold" will

probably be superceded by the "green gold". The ultimate goal of our company to develop the STARATE Series products is to replace the unrenewable resources by the rapidly renewable resources and contribute to the improvement of the living environment of the human race.

2. The Advanced Nature of the Technology

The STARATE Biodegradable Master batch is a novel type of composite material which has been developed and produced mainly from denatured starch (SMA). Its technological characteristics are as follows:

(1) The starch in liquid state is dehydrated in a vacuum. Then the dehydrated starch is made fine to have the diameter of each particle fall below 8μm, so as to extend the activated surfaces of the starch particles and improve the degree of activation of the starch.

(2) Under certain specific conditions, in adding the self-made DH denatured agent to denature the starch by covering it with hydroxyl, the chain structure of the starch molecules will be altered and its dispersion in the resin will be heightened. It will reduce the difference in nature between the various compositions of the stench - polyethylene resin blending setup and increase the quantity of the additives of the denatured starch (SMA) in the master batch up to 80%.

(3) The assisting additives, including the denatured starch, the chemical degradation promoters, pro-oxidation agents, special purpose cross-linking agents etc. can ensure the manufactured products' degradation by microbes and assimilation with the soil without any additional source of carbon. Therefore, the products have fine degradation properties .

(4) The melt milling under high shearing force makes the different components of the starch polyethylene resin composite system bland together organically, and the plasticity become more uniform.

(5) The super fine hydroxyl –covered denatured starch is of fine quality and reasonable price. Such expensive chemical materials (EAA) ,which are necessary in manufacturing ordinary degradable master batches, have been dispensed with, thus making the cost of the master batch much lower.

The uniqueness of this design has ensured the exquisite blending of the mechanics property of the products during use and their property of biodegradation after use which makes "STARATE" biodegradable master batches outstrip other similar products.

We have applied for an invention patent in China for the method for the preparation of STARATE biodegradable master batches.

3. An Introduction To The Products

(1) STARATE biodegradable masterbatches

The Danhai Company is now manufacturing seven series of ten assortments of biodegradable master batch, including different grades of packaging films, mulch films, fiber-class special purpose resin, foaming-class special purpose resin, special purpose resin for seedlings raising bowls, special purpose resin for high starch powder and special purpose resin for sheet materials. They are widely used in civil packaging, industrial packaging, one-off medical hygienic films, agricultural mulch films, injection-molded products, non-woven cloths, and foaming materials etc. Their prescriptions may be adjusted to meet the customers' demand in order to help the products claim uniqueness in the market.

The different classes of biodegradable products manufactured by our company are as follows :

a. Packaging Film Class: BM1130, BM1140, BM1150, BM1160
b. Mulch Film Class: DM2150
c. Fiber Class: XZ5220, XZ5250
d. Foaming Class: FM3150, FM3170, FM3350
e. Seedlings Raising Bowls: Special Use: YZ6150
f. High Starch Special Use: NZ4150

The STARATE biodegradable master batch and special purpose resin are granular in external appearance with regular forms and uniform size. The color of the granule varies form gray to light yellow. Their physical and chemical indices are shown in Table1.

Item	BM				DM	XZ		FM		YZ
	BM1130	BM1140	BM1150	BM1160	DM2150	XZ5220	XZ5250	FM3150	FM3170	YZ6150
Starch content %	28 ± 2	38 ± 2	48 ± 2	57 ± 2	48 ± 2	20 ± 2	50 ± 2	50 ± 2	70 ± 2	50 ± 2
SMA content, %	40 ± 2	53 ± 2	65 ± 2	80 ± 2	65 ± 2	25 ± 2	58 ± 2	65 ± 2	80 ± 2	65 ± 2
MFI,g/min	0.3±0.2	0.5±0.2	0.7±0.2	2.5±0.5	8.0±2.0	35±5	40±7	5±3	2.0±0.5	2.5±0.5
Volatility,%	1.5±0.5	2.0±0.5	3.0±0.5	3.0±0.5	3.0±0.5	1.5±0.5	2.5±0.5	2.5±0.5	5 ± 1	2.5±0.5
Density,g/cm^3	1.05±0.05	1.07±0.05	1.10±0.05	1.15±0.05	1.10±0.05	0.95±0.05	1.05±0.05	1.10±0.05	1.20±0.05	1.05±0.05

Table 1 The Physical and Chemical Indices of STARATE Biodegradable masterbatches.

The enterprise standard of Q/12XJ3882-1999 of Tjianjin Danhai Co., Ltd is implemented in manufacturing the above products.

2.The biodegradable agricultural mulch film

The biodegradable agricultural mulch film produced by Danhai Co. is made by using our STARATE biodegradable master batch. The product which is 0.008

mm thick has as much as 40% of the masterbatch added to it. The product whose thickness is 0.020 mm, has as much as 60% of the masterbatch added to it. Both the exterior and physical properties of the product conform to the standard requirements.

The physical indices of the biodegradable mulch film containing 40% of the masterbatch are shown in table2.

Item	Index							
	0.02mm thick		0.014mm thick		0.012mm thick		0.008mm thick	
		First Class Products		First Class Products		First Class Products		First Class Products
Tensile strength, N TD, MD≥	2.5	2.3	2.0	1.7	1.6	1.3	1.3	1.0
Breakdown elongation %, TD, MD≥	220	180	200	150	160	120	120	100
Right angle tearing strength TD, MD≥	1.0	0.9	0.8	0.7	0.6	0.5	0.5	0.4

In 1998 and 1999, our company covered an experimental plot of farmland with a biodegradable mulch film having a thickness of 0.008mm and 40% of the masterbatch content. After 60 days, we found that some parts of the film area had began to degrade. And 100 days later, large areas of it degraded. And 180 days later, there was complete degradation. A biodegradable test was done to this product according to the international standard of ISO846-1996 (Plastics—The determination of the action under the effect of fungi and microbes---by using the method of inspection by direct observation or the method of evaluation by measuring the changes in quality or substance). The breed level of microorganisms reached Level 4 after 28 days, which means that the area covered by the microorganisms on the sample surface exceeded 50%. This fact illustrates the fine biodegradability of the product.

The different indices of the 0.02mm thick biodegradable mulch film containing 60% of the masterbatch are shown in Table 3.

Table3

No.	Evaluation Item	Test method	Unit	Index
1	Thickness	GB/T6672	μ m	20±2
2	Density	GB/T1033 B	g/cm3	1.02
3	Haziness	GB/T2410-89	%	84.1
4	Melting point	GB/T13464-92	° C	117
5	Ash content	bum for 2h,550° C	%	0.14
6	Tensile load	GB/T13022-91	N	MD2.9, TD23
7	Breakdown elongation rate	GB/T13022-91	%	MD530, TD760
8	Right angle tearing load	QB/T1130-91	N	MD1.1, TD1.7
9	Cadmium content in the material	atom absorption	ppm	<0.5
10	Lead content in the material	atom absorption	ppm	<1
11	Heavy metal dissolved out (Pb base)	GB/T5009.60-96	ppm	<1
12	Consumption of potassium permanganate	GB/T5009.60-96	mg/l	1.58

13	Biodegradability Rate	ASTMD 5338-92	%	37.10
14	Mass change rate	ASTMD 5338-92	%	13.23

The biodegradable agricultural mulch film and the ordinary polyethylene mulch film have similar functions of increasing output, preserving heat and moisture in the soil. Besides, their prescriptions can be adjusted subject to the requirements of the differences in regions, climatic conditions and crop application so as to effectively control the introduction period of degradation and the rate of degradation. In Heilongjiang Province from 1997 to 1999 and in Xinjiang Province from 1999 to 2000, the 0.008mm thick biodegradable mulch film containing 35% of STARATE biodegradable masterbatch was used. The introduction period was commonly 40 to 90 days. The product met the requirements of the customers' use, and good economic as well as social benefits were obtained.

After three years of field tracing experimentation, we have obtained, from the Agricultural Reclamation and Cultivation Bureau of Heilongjiang Province, the permission to enter the market and allow the various farms in that province to popularize the use of the biodegradable mulch films produced by Danhai Company. Furthermore, the biodegradable masterbatches and biodegradable mulch films produced by our company have been batch exported to Japan since 1999.

It has been proved by practice that the remnant amount of the mulch film left in the soil after degradation does not caused any physical pollution with regard to the ratios in the entity, i.e. the ratio of the soil content to its density and the small openings in the soil. The mulch film will finally return to nature and assimilate with the soil. There will not be any bad influence on the next season's cultivation.

This product is being manufactured by adopting the enterprise standard Q/12 XJ3829-1999 of Tianjin Danhai Company. And in 1999, the company was granted a Certificate of Products Adopting International Trademarks by Tianjin Technical Supervision Bureau.

The photos taken by means of an electronic microscope lens and the descriptions of the agricultural mulch films with different starch content are shown below.

The original state of the mulch film with 40% of starch content.

Photo 1

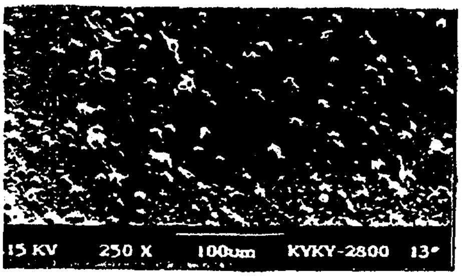

Photo 1 is a picture of the original state of the film with 40% of the masterbatch content, taken by an electronic microscope lens. From this picture we can see that the film contains a great amount of starch granules, which are quite compatible with the polyethylene. The granule's surface is smooth and the granules are distributed evenly. The diameter of the granule is <8 μm

State I of the film with 40% of the masterbatch content after degradation

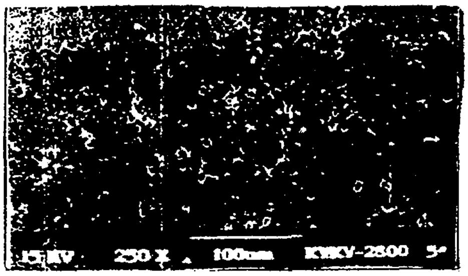

Photo 2

This is a picture of the film with 40% of the masterbatch after degradation. The starch granules in the film are entirely consumed, leaving only a certain number of holes.

State II of the film with 40% of the masterbatch content after degradation

Photo 3

This enlarged photo shows that during the degradation, the structure of the polythene film has been destroyed and cracks and holes have appeared, which illustrates that the polythene has undergone a certain degree of degradation.

The original state of the film with 60% of the master batch content

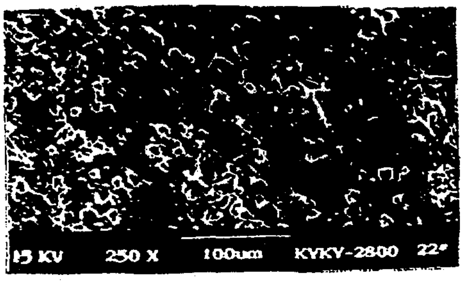

Photo 4

This is a picture taken with an electronic microscope lens of the original state of a film with 60% , of the master batch content.

The number of starch granules on the surface of the films is clearly greater than that on the surface of the film with 40% of the master batch content. The starch is distributed evenly. The surface of the granule is round and smooth. The compatibility of the starch with the polythene is fine.

State I of the film with 60% of the master batch content after degradation

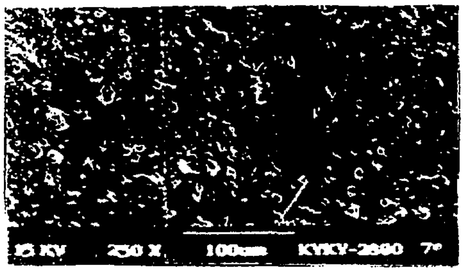

Photo 5

This picture shows the state of the film with 60% of the master batch content after degradation. A great amount of holes has appeared on the surface of the film. The number of holes is much greater than that on the film with 40% of the masterbatch. This illustrates that the starch has been effectively utilized, leaving only the remnants of the film with polythene.

State II of the film with 60% of the masterbatch content after degradation

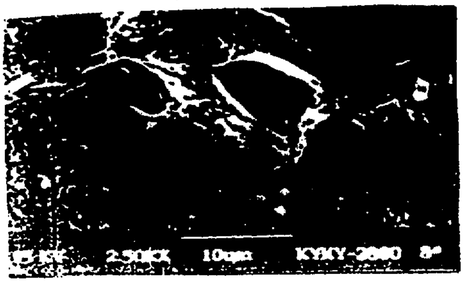

Photo 6

In this enlarged picture we can see a lot of holes on the film. It shows that the polythene has undergone a relatively large degree of degradation.

(3) The Biodegradable Packaging Film Products

The biodegradable packaging film products manufactured with our company's STARATE masterbatch are divided into two large categories: civil packaging films and industrial packaging films

As far as the usage of degradable film products for packaging is concerned, a fine mechanical property and biodegradability are an important combination of specific characteristics. It ensures the film's excellent tensile strength and breakdown elongation as well as the film's degradation within a specified period of time when it will become fragments which are harmless to the environment. These tiny pieces will eventually be consumed by the environment, thus protecting the ecological environment.

① The indices of the external appearance, width and thickness of the biodegradable packaging film are the same as the indices of the ordinary packaging film products and conform to the requirements of the standards of QB/T2461-1999 and GB/T4456-1999

② The indices of the physical properties of the biodegradable film products with different masterbatch contents are not the same. The results are shown in Table 4.

Table 4 A list of the indices of the properties of the biodegradable packaging film products with different masterbatch contents.

F120A:7042: denatured starch SMA	thickness μ m	film weight g/m²	tensile strength MPa		Breakdown elongation %		Dart drop	Ultimate weight load
			MD	TD	MD	TD	30g	kg
65:15:20	25±3	21.1	34.5	35.7	495	430	Break0/10	10
55:15:20	25±3	22.1	34.5	32.4	420	555	Break0/10	9
45:15:40	25±3	22.1	24.4	25.6	395	480	Break0/10	8
35:15:50	25±3	21.9	21.1	27.4	400	510	Break0/10	7
25:15:60	25±3	20.4	23.8	18.7	440	580	Break0/10	6
20:10:70	25±3	21.3	20.1	15.7	395	618	Break0/10	5
10:10:80	25±3	22.3	15.3	12.2	440	585	Break0/10	4
10:0:90	25±3	21.3	14.2	11.2	400	555	Break0/10	3

Table 4 shows that the physical strength in the film product changes with the increase of the quality of the biodegradable masterbatch added to it i.e. the change in its physical strength is due to an increase in the content of the starch in the film product. However, even though the content of the masterbatch is as high as 90%, the physical as well as mechanical properties of the film product can still meet the requirements of standard GB/T4456-1996. Furthermore, Table 4 shows only the results of our comparative experiments. If some adjustments of the brand of the polyethylene resin and the composition of the prescription are made, it will have an impact on the mechanical and physical properties of the film products.

③ We have made some analyses of the surface of a packaging film product, which contains 80% of the masterbatch, with an electronic microscope lens before and after degradation. We have found that the surface of the original sample film is uneven, the starch granules are completely covered by the polyethylene and the condition of the commixture is fine. After degradation the starch on the surface of the film has been entirely degraded. The remainder of the polyethylene surface has already been seriously damaged. A lot of holes, cracks and bits of polythene pieces can be seen on it. An enlargement of the sampling portion can help us observe such a change more clearly. This proves that the polyethylene has also undergone degradation to a certain extent. As time goes by, the degree of degradation will be gradually extended, ranging from the loss of its physical properties to the further transition from a high molecular compound to a low molecular compound. In the end, it will become tiny molecules that can be dissolved and assimilated by the environment.

④ The biodegradable film for foodstuff packaging produced by our company conforms to the stipulation of GB9687. It has been granted No.3241 Sanitation Permit by Tianjin Public Health Bureau.

Our company's STARTATE biodegradable film for foodstuff packaging was

accredited "A Product Bearing the Trademark of National Environmental Protection" by China Environmental Protection Symbol Authentication Commission. And in 1999, it was awarded the Certificate for Adopting the Trademark of International Standard Product by Tianjin Technological Supervision Bureau.

4. The Research and Development of the Second Generation STARATE Products

(1) The one-off biodegradable non-woven fabrics_ the fiber grade special purpose resin.

The one-off biodegradable non-woven fabrics_ the fiber grade special purpose resin is a new high-tech material of environmental protection type. It is a special purpose resin used for manufacturing biodegradable fibers which are mainly used for making one-off products of non-woven fabrics, such as diapers, urinary incontinence underpants for old people, feminine sanitary napkins etc. and such medical items as costumes and cover cloths to be used during an operation or surgery, gauze masks, bedclothes used in the wards, bacteria-proof curtain cloths, pillow-cases and chest scarfs .

It is commonly known that most of the fabrics material used at present in making non-woven fabrics are polyester, nylon, polypropylene, Es, viscose rayon etc. Most of the fibers are high polymers which cannot be degraded within a short time except viscose rayon which belongs to natural cellulose and is degradable. Such products made of one-off non-woven fabrics can also cause serious environ-mental pollution. In addition, the waste disposal by burning of the products made of one-off non-woven fabrics for medical use will produce a great amount of harmful gases, while the high heat will pollute the atmosphere as well.

The second generation STARATE products_ the one-off biodegradable non-woven cloths.

The second generation STARATE product developed by Tianjin Danhai Co., Ltd - the one-off biodegradable non-woven cloth - fiber grade special purpose resin. This special purpose resin is made by adopting the super fine starch treatment technology and associating it with the hydroxyl- cover starch denature technology at the same time, which can improve the activity of the denature starch SMA, change the chain structure of the starch molecules, so that it can combine with the regular polypropylene molecules organically. The biodegradable fiber made of such special purpose resin is an ideal material for making disposable non-woven cloths, which can effectively prevent the pollution of the urban environment and atmosphere by the one-off non-woven cloths. In putting this product on the market, it signifies that synthetic fibers are being

developed more in the direction of functionalism and a new member is added to the functional fiber family. Not only will it contribute to the betterment of the lives of the human race and environmental protection, but also help to reveal to us that the product has a huge market potential. We have already applied for an invention patent for the technique of producing the special purpose resin for making biodegradable fibers.

(2) The biodegradable polythene foaming materials

Foaming materials are being widely used for packaging various kinds of precision instruments, handicraft articles, fruits and breakables because of their light weight, fine resistivity and their properties of sound and thermal insulation.

However, the widespread use of foaming packaging materials has caused many problems with respect to environmental protection. This is mainly due to such materials' low density and large size. They make up a very large portion of the urban wastes. Moreover, they can neither be consumed by the environment after use nor be degraded in several hundred years. So, it is even more important to endow the foaming packaging material with biodegradable properties. This has aroused the increased attention of the public.

As far as such degradable products are concerned, there is still a gap in our country. Tianjin Danhai Company has taken advantage of this opportunity and fully utilized its dominant position with regard to the technique of denaturing and filling starch to produce a kind of starch-type biodegradable material with greater starch content and fine degradable effect. And at the same time, the processing technology of the product is suited to that of the foaming packaging materials at the present stage. Therefore, it is of great significance to the speeding up of the replacement of one-off non-degradable products widely in use now. It has been clearly pointed out in Item 58 of A Catalogue of Backward Production Capacity, Technologies and Products to be Eliminated issued by our National Committee of Economy and Trade in 1999, that disposable foaming products should be eliminated us soon as possible. This measure has brought very great economic losses to the enterprise that produce foaming materials, while the production of the one-off biodegradable polythene foaming master batch will bring them a chance to adjust their products' structure. This is an innovation and revolution in foaming products, which belong to one of the four major varieties of plastics products. We believe that the biodegradable foaming products will become an important integral part of products made with foaming materials in the near future.

3. The biodegradable nutrition type seedling-raising bowls

Our company did researches on and developed one-off degradable nutrition-type seedling-raising bowls on the original basis of the technology for manufacturing the master batch. In view of the characteristics of the seedling raising bowls, we added chemical degradation promoters which contained nitrogen to provide the bowls with nutrients containing nitrogen (such as fertilizers), which are beneficial to the growth of the crops. Such nutrients will be released gradually in pace with the growth of the crops' root systems and promote the healthy growth of the crops. Besides, these bowls can be moved easily during planting. They can degrade naturally after use. They can be used to raise sprouts and move seedlings. Their strength conforms to requirements and their price is equal to that of the common polythene. Furthermore, in due time, they can degrade and break up into tiny fragments which are harmless to the soil. And with the passing of time, they will assimilate into the soil which not only can raise the survival rate of the crops but also be greatly favorable to the protection of the agricultural ecological environment. In this respect, they are favorably received by the great farming community.

The degradable nutrition-type seedling raising bowls have not only offered convenience to agriculture and forestry and the planting of flowers and plants in horticulture by the introduction of a new type of cultivation, but also brought about great economic benefits. Furthermore, as the content of the denatured starch in such a seedling raising bowl is as high as 85%, the actual content of the plastics material is only around 15%. Therefore, it is also a kind of product with outstanding environmental protection properties. Our country's western regions have been experiencing the threat of dust and sand blown by the wind, and drought. The loss of water in the soil and land erosion have been serious there, while arable land is comparatively scarce. Both the germination rate and survival rate of crops are relatively low. The seedling-raising bowls produced by our company have very high capacity for preserving moisture. And they are rich in nutrients. They can be used both to preserve soil moisture and provide the nutrients required for the crops to grow. They can also improve the soil, raise the crops germination rate as well as survival rate. In the wake of the shift of the strategic focal point of our country's economic development toward. The western provinces, that vast expanse of land will surely provide us with a gigantic market.

(4) The HZ4000 series high starch content special purpose resin

In recent years, the "White Pollution" has been "a persistent ailment" in almost every large cities in our country and overseas. The problems that the people of the whole world are universally concerned with are firstly, How to harness the " white pollution"?, secondly, How to protect our ecological environment?, and thirdly, How to raise the people's living standard? These are the difficult problems which urgently need to be solved.

Item 17 of the Law of Environmental Control of Solid Wastes in the People's Republic of China stipulates that in manufacturing the products the principle of their being easy to be processed, ultilized and disposed of or assimilated into the

environment should be adopted. There are 37 cities in China which have already issued documents concerning 'the control of the white pollution' and formulated measures to control the 'white pollution'.

In our research we have discovered that the higher the starch content in the product is, the sooner its degradation will take place, the result of degradation will be better, and it will be less harmful to the environment. That is why we have developed the STARATE HZ4000 series high starch content special purpose resin. And we are using this special purpose resin to produce biodegradable packaging materials, which have both fine degradability and definite mechanical strength. They are able to meet the requirements of the customers' use and achieve the goal of making the solid wastes and discarded objects small in volume and quantity as well as letting them be transformed into resources and innocuous stuff.

When the starch content is lower than 40%, the starch and polyethylene can disperse continuously. The more uniform the dispersion is, the better the structural properties will be. When the starch content exceeds 50%, it is difficult for the product to take shape and its physical strength will drop a great deal. In order to solve this problem, we have processed the denatured starch with special technology to raise the compatibility of the base resin and the denatured starch, thus improving the mechanical strength of the product.

The main ingredients of this product:

Denatured starch SMA 64%,
High polymer resin 36%.

This product can be used as agricultural mulch film, life preservation film and packaging material.

(5) One-off Plant Fiber Tableware and Drinking Utensils

The public is paying more and more close attention to the effect of polystyrene foaming-type tableware and drinking utensils to the environment. The large amount of one-off foaming plastics tableware and drinking utensils used extensively by the catering industry cannot be eliminated and assimilated into the environment. A portion of them are littered in urban districts, scenic spots and places of tourist attraction, around and in bodies of water, such as lakes and ponds, along either side of railroad tracks and highways etc.

They have seriously affected the sights and polluted the environment. It has been found out through investigation that in Beijing the output of civil wastes reaches 12,000 tons per day and 140,000 tons a year, 3% of which consists of waste plastics. The total amount of civil wastes in Shanghai per day is 11,000 tons, and 290,000 tons a year, 7% of which consists of waste plastics. Due to the difficulty in collecting and high cost in recycling the large quantity of foaming plastics tableware and drinking utensils, Item 58 of A Catalogue of Backward Productive Capacities, Technologies and Products to be Eliminated issued by the Committee for National Economy and Trade of China on January 22nd,1999, states clearly that disposable foaming products should be eliminated as soon as possible.

The second generation STARATE products developed by Tianjin Danhai Company: The one-off plant fiber tableware and drinking utencils are produced by using plant fibers and denatured starch (SMA) as their main materials, together with many kinds of edible additives. They are then pressed, foamed and shaped. These products have fine external appearances, high strength, light weight and are of low costs. They can hold food in both liquid and solid states such as: cooker rice, vegetables, fruits, beverages and so on. They can be turned into fodder of poultry and fishes. They exhibit an incomparable vitality. The entirely new STARATE one-off plant fiber tableware and drinking utensils are ideal substitutes for their foaming plastics counterparts. This is the inevitable trend of the development of foodstuff packaging.

The one-off plant fiber tableware and drinking utensils developed by Tianjin Danhai Company are in conformity with the requirements of our national standard, the General Technical Conditions of Disposable Tableware and Drinking Utensils. Furthermore, the new types of biodegradable plastics produced by Tianjin Danhai Company also include special purpose materials for injection molding and suction molding plastics sheets. These are used to produce such plastics products which are discarded after being used only once, for example, containers or battles for lubricants and farm chemicals, trays, clothes-hangers, gold ball stands and whatnot. It is quite possible that China will join the WTO this year and our company's STARATE series products will enter the international market and take part in global competition with their advantageous factors of low prices, fine applicability and biodegradable functions.

As our company is an enterprise engaging in the production, research and development of biodegradable plastics and undertaking a demonstration engineering project of the industrialization of our country's major scientific and technological achievements, we will maintain and foster our company's enterprising spirit of "always striving to be topmost", and bring benefit to humanity. We pledge ourselves to contribute to the cause of environmental protection of China and, hopefully, of the world, and the preservation of the living environment of the entire human race.

21. Development of Biodegradable Biomedical Fibers

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Summary

Shanghai Donghua University and Shanghai Tianchun Biomaterial Ltd. Company began researching Biomedical Degradable Fibers in 1980, and developed commercialized products by 1998. Shanghai Tianqing Ltd. Co. and Shanghai Tianchun Biomaterial Ltd. Co. pioneered the development of Chitin and PGLA fiber systems in China and continues to be a leader in these field. Biomedical fibers are a combination of medical science and material science, connected with industrial textiles as well as medical materials and are developing into one of the most dynamic sectors in the world. Biomedical degradable fibers technology has been available to Chinese scientists for over twenty years. The three main categories; i.e. the chitin system, the polylactide system, and the polyglycolide system, all developed rapidly due to the fact that they are fully natural circulated biodegradable synthetic fibers and thus hold many potential uses. These fibers are products of lactic acid and glycolide acid (produced using starch from corn, etc.), and chitin (derived from crab and shrimp shells). From an environmental perspective, the use of crab and shrimp shells is beneficial turning a valueless substance into a priceless treasure of the human race.

CHITIN FIBER SYSTEM

Chitin is the second most abundant natural polymer. Chitin and its derivatives are non-toxic and have good biological compatibility, anti-bacterial properties, and thus can be used internally and externally. They have been found suitable in producing biodegradable pharmaceutical carriers, and acting as a blood coagulant. They have also been found to be useful in chelating heavy metal ions, as a wound-healing accelerator, for specialized clothing, and for sutures used in surgical procedures.

POLYLACTIDE AND POLYGLYCOLIDE SYSTEM

Polylactide fibers (PLA), polyglycolide fibers (PGA), and the poly [lactide -co- glycolide] (PGLA) copolymer have the highest melting point among biodegradable fibers developed so far. As a result, they can be integrated into various fiber forms such as multi-filament, monofilament, staple fiber, spun bond, etc. The strength and elongation of the fiber can be widely controlled by the processing conditions, so the products of the PLA, PGA, and PGLA are absorbed as desired. Because the raw material involved in PLA, PGA, and PGLA products are also present in the human body, they do not have any overt effects on human physiology and are widely used in surgery, dentistry, orthopedics, oculistics, gynecology, industry, agriculture and so on.

The resource of the biodegradable biomedical fibers is rich, renewable, and natural. Their fibers have unique properties, which can be easily extended into three-dimensional structures of woven, knitted, and non-woven fabrics. Such providence should be taken full advantage of in the interest of protecting our environment and caring for the health of human beings.

Chapter 3:
Plastic Waste Treatments and EDP in Each Country

22. Plastic Waste Management and Plastic Reuse in Austria and Germany

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The quantity of packaging materials used in developed countries can still be considered as very high. Figure 1 shows that 350 to 730 kg per year and capita have been used in western countries in 1995, the average was about 430 kg. Only part of the materials used for packaging consists of plastic packaging (about 30% of the total in EU countries, see Figure 2), but due to its low density, plastic packaging materials remain a problem that has to be solved.

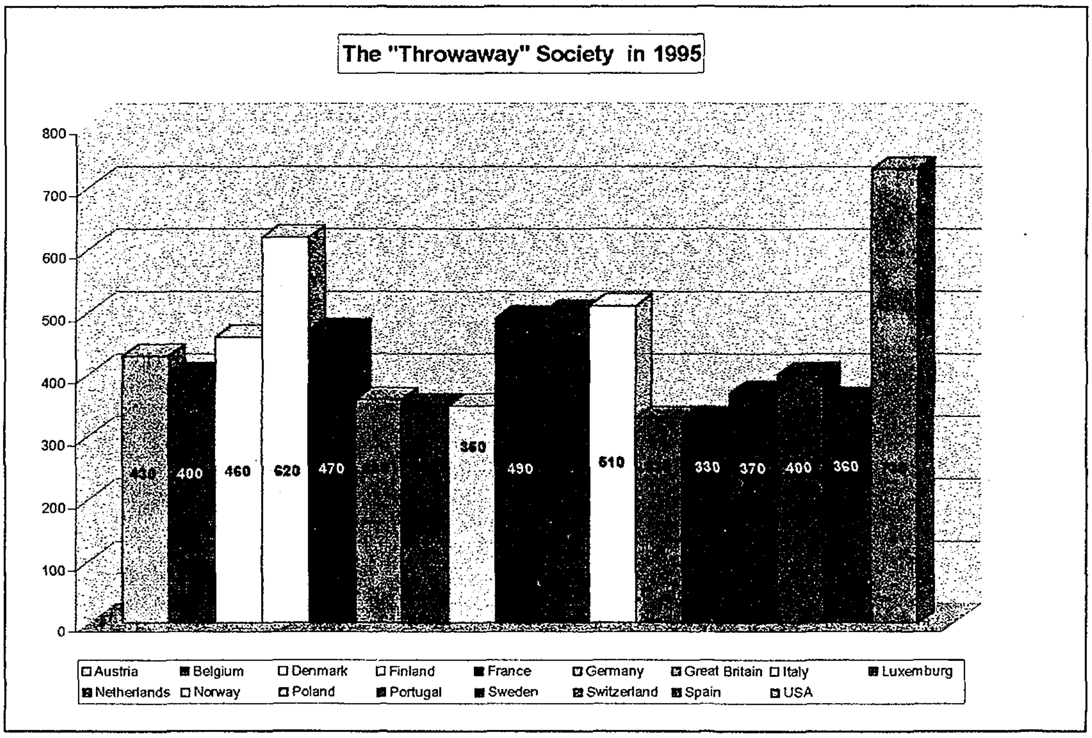


Figure 1: Quantities of packaging materials (kg per capita) used in various countries in 1995

Plastic packaging materials (in kg) used per capita in European countries (1995) was about 149 kg in average per year. In Austria this value was lower than the average (about 20 kg less), and the Netherlands had the highest consumption of such materials (210 kg). Details about the use of plastic packaging materials are given in Figure 2. It can be stated that the quantities shown for European countries are in the same range as those that can be found for other highly industrially developed countries of the western world: the higher living standard is the more plastic materials are used for packaging purposes. For Austria it has to be mentioned, that living standard is as high as in Germany or the Netherlands for example, but plastic packaging consumption per capita and year is 20 kg lower than the European average.

This shows that our strict laws have influenced the consumers behavior, even though we have such directives only since 1993.

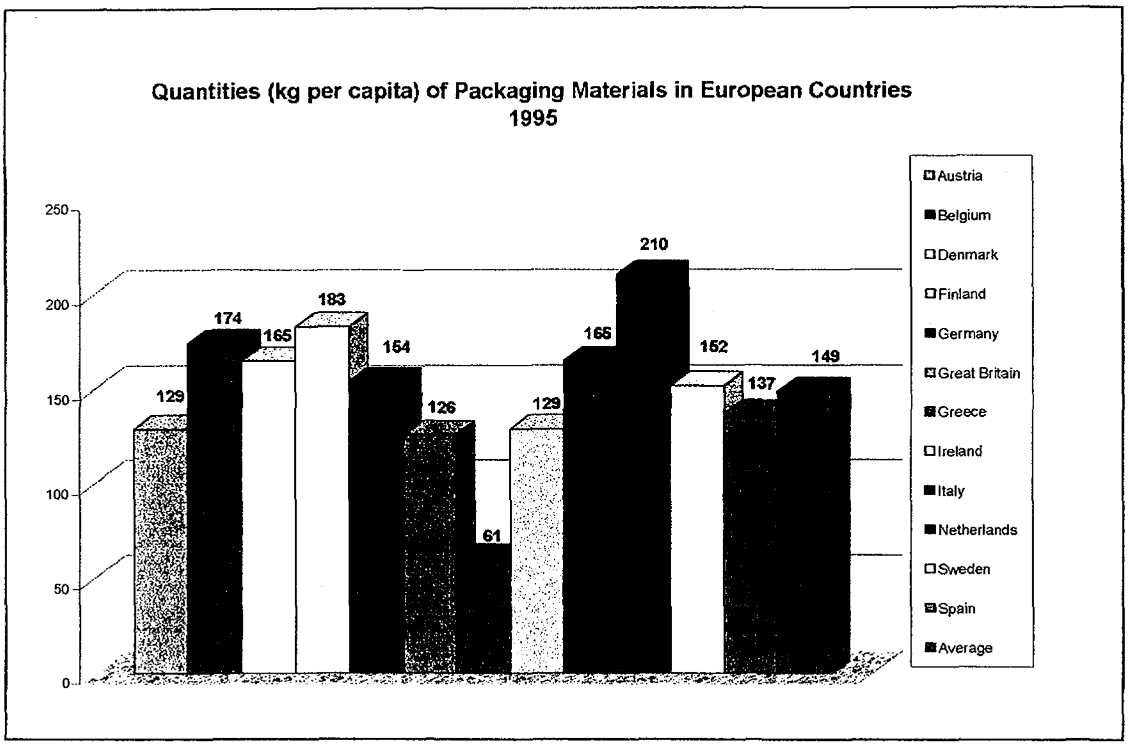


Figure 2: Quantities of plastic packaging materials used in European countries in 1995 in kg per capita and year.

Rising quantities of plastic waste materials have started to raise a problem in Austria in the early 90s. As can be seen from Table 1, a total of 763500 tons of plastic waste had to be handled in 1994. Part of this material was sorted (~ 6%) and/or reutilized directly (~ 1%) even then, part was used at least for energy recovery, but the main part was buried in controlled landfills (~75%).

Due to strict regulation by the Austrian Packaging Ordinance (Law since 1993) and due to the fact that municipal solid waste incineration was not accepted any longer as a form of energy recovery, plastic packaging waste has to be collected and recycled throughout this country. All producers and importers of packed goods, fillers, and packers are responsible for collection and recovery of their packaging. In 1998 not more than 90.000 tons of plastic waste

Table 1: Treatment of Plastic Waste (in tons) in Austria (1994)

Plastic Waste Treatment	tons
Reutilization of Sorted Plastics	44200
Reutilization of Mixed Plastics	5000
Energy Recovery from Heating of Mixed Plastics	27000
Energy Recovery from Municipal Incineration Plants	44200
Stored Plastic Waste	42400
Exported Plastic Waste	11800
Controlled Landfilling	558900
Total Plastic Waste	763500

may be landfilled, and in 2001 this quantity will be further reduced to 60.000 tons per year. Moreover, the share percentage of mechanical recycling is individually fixed for several packaging materials (Table 2).

Table 2: Fixed share percentages (1997) for mechanical recycling for several packaging materials. Percentages related to the total amount of transport and sales packaging

Materials	**% mechanical recycling**
Paper, cardboard, paperboard and corrugated board	90
Glass	93
Ceramics	95
Metals	95
Plastics	**40**
Cardboard composite drinks packaging	40
Other composites	40

Table 3: ARA fees for packaging materials in the years 1998 and 1999

	Fees in US$ per kg (excluding VAT)	
Packaging Materials	**01.01.1998 to 31.12.1998**	**1.1.1999 to 31.12.1999**
Selling Packages from Paper, Cardboard and corrugated board	0.18	0.18
Transport Packages from Paper, Cardboard and corrugated board	0.09	0.09
One-way Packages from Glass	0.10	0.10
Reusable Glass Packages	0.02	0.02
Wood	0.03	0.025
Ceramics	0.32	0.32
Ferrometals (low volume >10 L)	0.44	0.44
Ferrometals (high volume <10 L)	0.22	0.22
Aluminum	0.51	0.51
Textiles	1.34	1.31
Plastics, low quantity(> 1.5 m^2 or > 0.15 kg)	**1.56**	**1.45**
Plastics, high quantity (< 1.5 m^2 or < 0.15 kg) (hollow bodies <5 L, Films < 1.5 m^2 or <0.15 kg, EPS <0.1 kg)	**0,87**	**0.68**
Plastic compounds (excl. Tetrapacs)	**1.50**	**1.40**
Plastic shrink films L(L)DPE (< 1.5 m^2) LDPE **Tray films (< 0.25 m^2, min. 60 m)** **Industrial hollow bodies (HDPE, PP, < 5 L)** **Bags (LDPE, PE/PP, < 25 L)**	**0.54**	**0.41**

A system (ARA) has been set up since for effective recovery, sorting, and recycling of waste packaging materials. Packaging material as well from households as from the industry have to be collected and recovered, and both, mechanical recycling and the energy recovery is accepted for further treatment of plastic-packaging. The ARA (ARA = Altstoff Recycling Austria)is comprised of three privately operating non-profit organizations. They are independent of each other and organize the collection and/or recycling of the collected material based on efficiency, cost-effectiveness, and ecology. In this system ARA signs license contracts to all relevant companies, collects license-fees and transfers the money to ARGEV and ÖKK. ARGEV organizes as well collection as sorting of plastic packaging items, whilst execution lies in the hands of different disposal companies, that are contract partners. ÖKK organizes, coordinates, and controls the recovery of all collected plastic-packaging materials. Recovery itself is executed in seven national and two international plants situated in Switzerland and in the Netherlands.

It is quite clear, that such systems will only run, if they are accepted by the public. It is therefore of utmost importance that containers are available in a high number, and they must be in walking distance to public households. Table 4 shows the situation in Austria.

Table 4: Attainability of Collection Containers for Households (%) in Austria (1996 Public Survey Results)

Distance Province	5-15 Minutes to walk	Up to 5 Minutes to walk	In House / outside of the House	More than 15 Minutes to walk	Unknown	Dont know
Burgenland	38,4	46,3	4,9	8,2	1,8	0,4
Carinthia	20,3	39,5	20,4	11,4	7,7	0,7
Lower Austria	11,6	24,4	54,2	3,2	5,2	1,4
Upper Austria	14,8	27,4	30,2	19,8	5,3	2,6
Salzburg	19,4	30,5	27,3	11,9	9,4	1,5
Styria	10,8	31,4	42,7	9,3	5,1	0,7
Tyrol	25,2	42,1	12,0	13,7	6,2	0,9
Vorarlberg	22,6	57,2	8,6	5,7	5,2	0,7
Vienna	15,5	51,1	16,1	1,5	10,6	5,7
Austria	16,2	37,1	29,0	8,4	6,9	2,4

There are, of course remarkable costs for maintaining this system, and they are financed by fees that have to be paid for the packaging waste. The expenses for collection, recovery and organizational costs are subsequently allocated to the license-tariffs based on expected annually required financial resources. Actual fees are shown in Table 3.

License tariffs are divided into three groups, depending on the volumes of waste plastic packaging items. In1997 about 83000 tons of plastic packages have been collected, and the total of the fees for plastic packaging was as high as 1485 Million ATS (~125 Million $US). The fees collected have been spent as is shown in table 5.

Table 5: Money spent for collection sorting, and recycling in the ARA -system (1997)

ARA System	**Million US$**	**% Fees**
Organization (ARA)	6,25	5
Collection and Sorting (ARGEV)	87,5	70
Recovery (ÖKK)	31,25	25
Total	125,00	100

In 1997 a total of 83.416 tons of plastic waste has been collected in Austria , corresponding to 37,9 % of the total plastic waste. 45% (table 6) of this collected waste could be reused, the rest (46101 tons) was used for energy recovery under strict governmental regulation and control.

Table 6: Collected and recycled Plastic Waste Materials in Austria in 1996 and 1997

Types	*Quality*	*Output 1996 (tons)*	*Output 1997 (tons)*
HDPE bottles	**sorted**	**3070**	**2758**
HDPE buckets	**sorted**	**805**	**927**
HDPE cans	**sorted**	**1009**	**1176**
HDPE hollow bodies	**mixed**	**598**	**342**
PET bottles	**sorted**	**3687**	**4513**
PS/PP	**mixed**	**2462**	**2265**
LDPE films	**transparent, not printed**	**2483**	**7497**
LDPE films	**colored or printed**	**19731**	**13545**
LLDPE films	**transparent, not printed**	**1577**	**2242**
Pharma blisters		**0**	**101**
EPS/XPS		**1213**	**1139**
Textile		**34**	**0**
Mixed plastics		**45669**	**46101**
Tetrapacs		**732**	**810**
TOTAL		**83070**	**83416**

It is interesting to note, that plastic packaging waste collection does not function equally well in all Austrian provinces. Best results come from medium industrialized provinces (Lower Austria, Upper Austria, Styria), while results in the highly industrialized city of Vienna are rather low (figures 3 and 4).

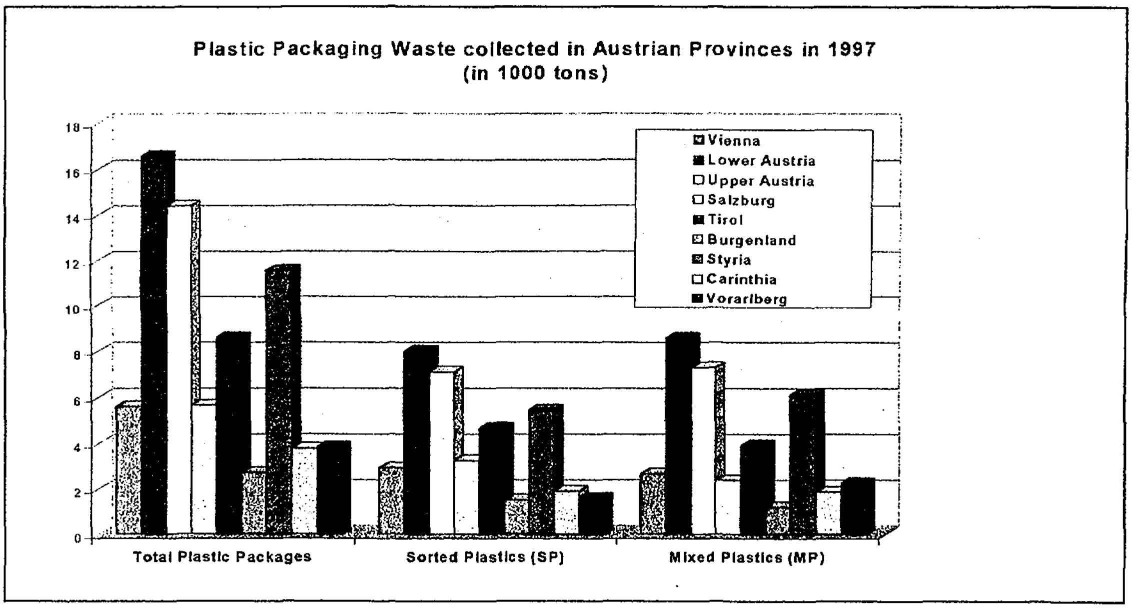


Figure 3: Plastic Waste collection in Austrian Provinces

Incineration of plastic packaging waste is of course of interest for energy recovery from such materials. Heating values are compared in Figure 5. However, there are concerns in our country due to possibly higher risks when mixed municipal waste is incinerated. Therefore municipal waste incineration plants are not accepted for energy recovery in Austria, and strict requirements (Table 7) have to be followed for specialized plants, having the allowance for plastic waste incineration (Table 7).

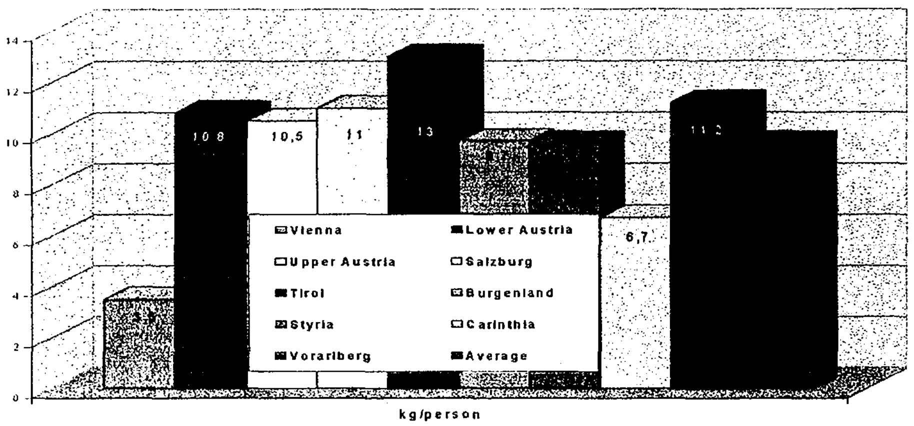


Figure 4: Plastic Packaging Waste Collection 1997 per capita in Austrian Provinces

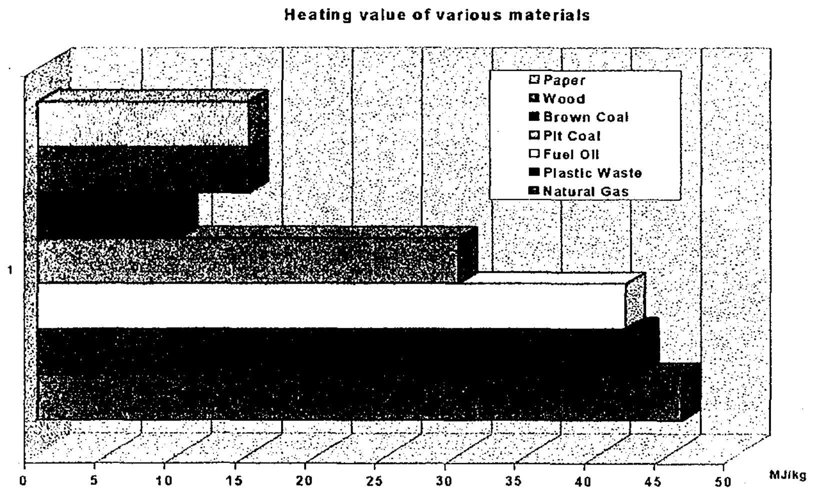


Figure 5: Heating values for various combustible materials

Table 7: Requirements for Energy Recovery from Plastic Waste

- **Observance of Emission Standards**
- **No Increase of Emissions of Harmful Substances**
- **A Maximum Emission of 0,1 ng Dioxin TE/m^3 allowed**
- **Direct Substitution of Conventional Fuels by Packaging Waste and therefore Reduction of the Consumption of Natural Resources has to be proved**
- **Optimum Recovery of the Energy has to be proved**
- **Defined Quality of the Material to be Incinerated is needed**

Table 8: Energy Recovery from the Mixed-Plastic-Fraction in Austria

1994: Cement producers started adaptation of their plants for the use of shredded plastic waste (mixed fraction)

1998: 3 cement factories started to use about 25.000 tons of shredded plastic packaging waste per year

1996: Construction of a fluidized bed incineration power plant to produce low-cost energy for a fiber-producing company.

1999: A total of 96.000 tons of shredded plastic packaging has been used for energy production in this plant

In future, the areas for land filling will be further reduced and the percentage of plastic waste to be recycled has to be increased further.

Despite the fact that research work for development of Environmentally Degradable Plastics (EDP) is performed in Austria since 1975, only low quantities of environmentally degradable plastics packaging material are used (e.g. Mater-Bi) up to now. Because they are not collected separately from other plastic packaging, hardly any data are available about quantities in use. They just do not show up in the official statistic data. There is still no announcement if such materials will be integrated into the Austrian Packaging Ordinance with a special legislation in the future. The reason for this are the concerns, that others than degradable plastics might end up as well in the compostable fraction of the municipal waste that is collected and treated separately in our country.

In Germany, a very similar approach exists, the Dual System with its Green Dot as the financing symbol. It was founded in 1990 as a Company for waste avoidance and recovery of secondary raw material. In 1991 the German "Ordinance on the Avoiding of Packaging Waste" came into force, obliging manufacturers and the retail trade to take back sales packaging after use and to forward it for recycling.

Figure 6: The Green Dot, financing symbol and protected trademark of the Dual System Germany.

In August 1991 the Dual System started its operation by organizing used packaging collection and sorting on a private basis. 400 companies joined the Dual System as shareholders, and the "Green Dot" (Figure 6) got attached as a licensing mark to packaging of the licensees. The development of forwarding sales packaging (in 10^3 t) for recycling in Germany in the years 1991 – 1998 is shown in figure 7.

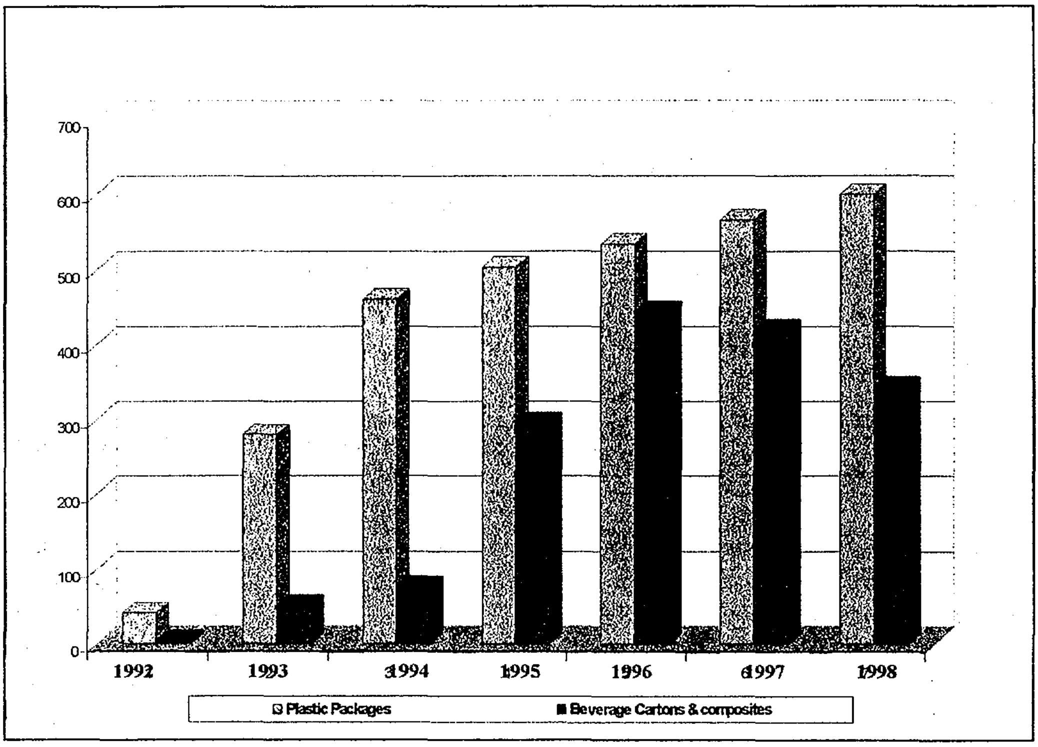


Figure 7: Sales Packaging (in 10^3 t) forwarded for recycling in Germany 1991 – 1998

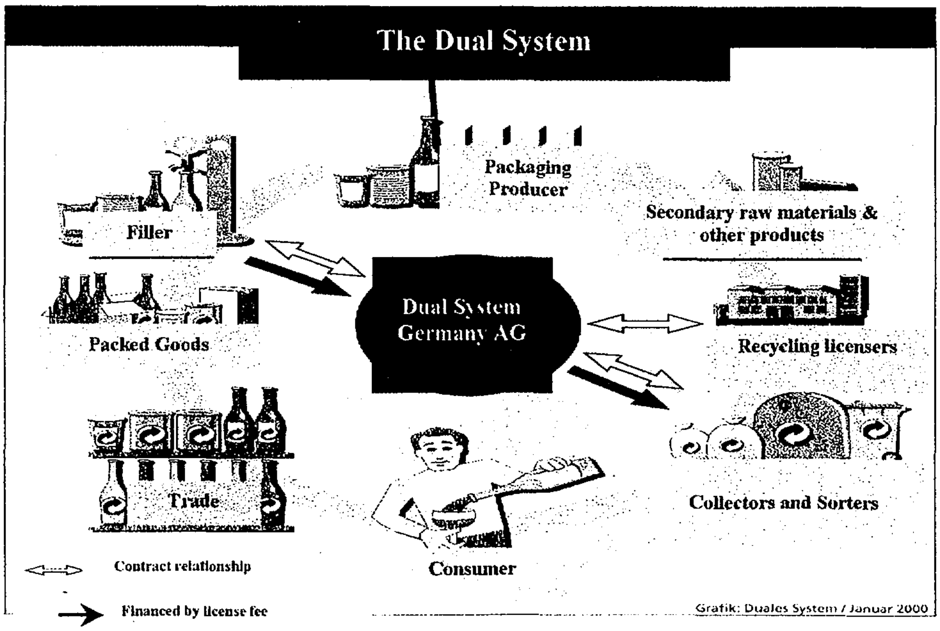


Figure 8: Dual System Germany: the way how it works.

Above figure 8 shows that the system is functioning in the same way as was shown earlier for Austria. Packaging producers sell their systems to fillers, the packed goods are distributed to the consumers via trading, and the consumers do a first sorting into different fractions in the households. These fractions are collected, further sorted, and forwarded to recycling companies, that produce secondary raw materials for the packaging producers as well as other products. The Dual System Germany AG, as a company of shareholders centrally maintains contract relationships as well to the fillers as to the collection and sorting companies and recycling licensers, and the fees collected from the fillers is used to cover the costs for collection and sorting.

In this story of success, the number of licensees has raised from about 3700 in 1991 to 18666 in the last year, and the public acceptation is as high as it is in Austria. In 1999, per capita 77,7 kg of package materials have been collected and sorted in Germany, a quantity that has been much higher than the thresholds set by the German Package ordinance (figure 9).

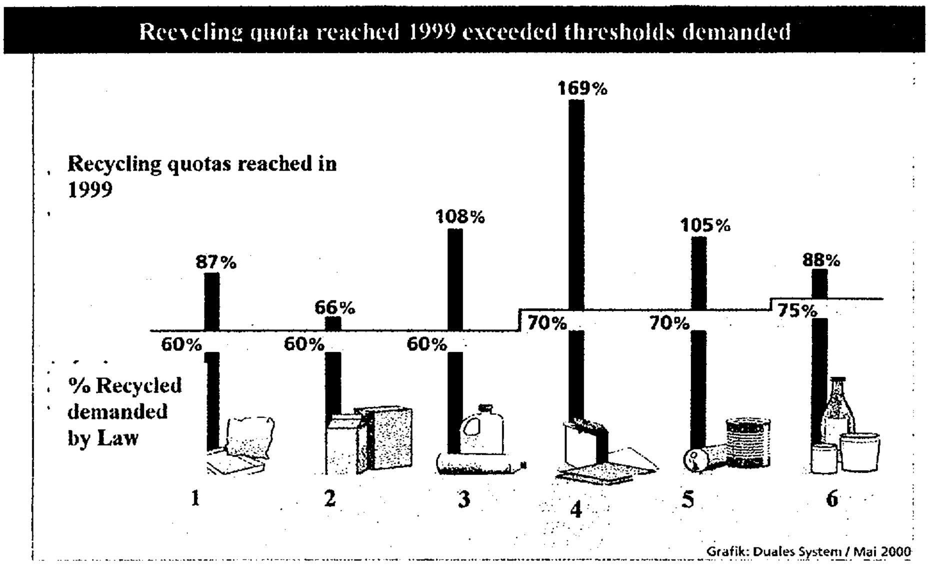


Figure 9: The German Packaging Ordinance limits for recycling have been exceeded in 1999.
1: Aluminum 2: Compounds 3: Plastics 4: Paper & cardboard
5: Tinplate 6: Glass

On the European level, the European Parliament and Council Directive 94/62/EC on packaging and packaging waste came into force. Its key issue is that each member state must take measures to set-up take-back, collection and recovery systems for used packaging by the year 2001. Part of the European countries have therefore decided to use the same system as Germany, and they as well use the "Green Dot" as a sign. Figure 10 shows this international packaging recycling in Europe, and the countries that are using the "Green Dot" in the meantime. The recycling quota are higher than 50 % in 5 European countries now, for another eight countries they are between 18 and 42%, for Portugal and Spain material recycling quota are below 5 %. Details are given in figure 11.

Figure 10: The "Green Dot" Countries in Europe

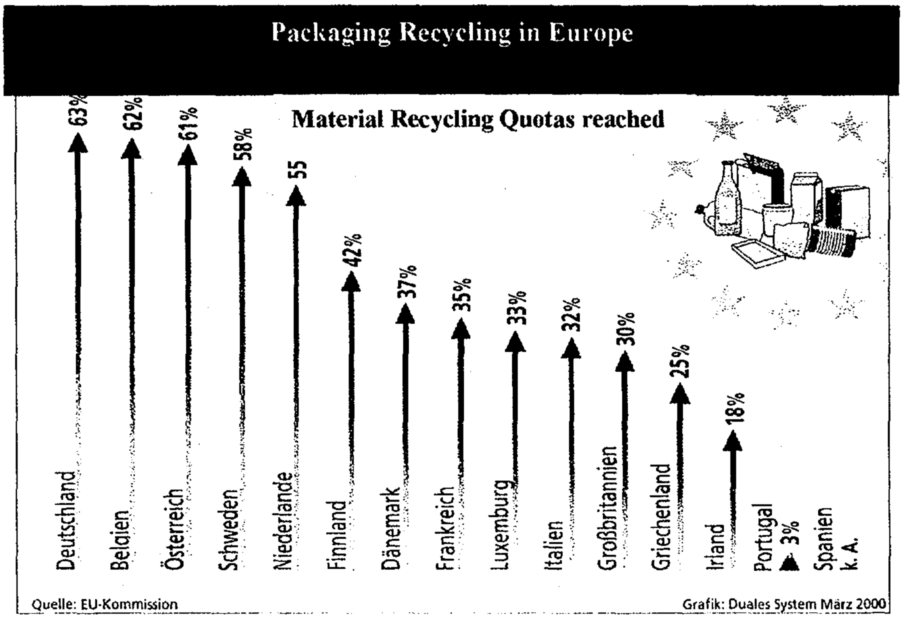


Figure 11: Material Recycling Quota (in %) reached in European Countries

23. Plastic Waste Management and Environmentally Degradable Plastics in Slovakia

Dusan Bakos

Faculty of Chemical Technology, Slovak University of Technology, Slovakia

[E-mail: bakos-cvt.stuba.sk]

Plastic Waste Management

The increasing consumption of plastics with increased production and usage, in both the industrial and consumer markets, is reflected in the amount and composition of plastic waste. Slovakia, with its 5.5 million population has extensive developed chemical industry where an important part belongs to production of plastics and plastic products. The most important chemical companies producing or processing plastics in Slovakia are Slovnaft (polyolefins), Plastika Nitra (processing polyolefins - pipes), Chemical Plant Novaky (PVC, PVAc, PVA), PCHZ Zilina (PMMA, polyamide 6), Matador Púchov (tyres), Duslo Sala (PVAc), etc.

In 1998 Slovakia produced 1.7 million tons of municipal solid waste. This means the amount 322.6 kg per capita, from which only 7.78 kg has been separated and collected. From the composition of municipal solid waste 15 % of the waste stream is plastic waste. Municipal polymer waste management is the area in which the most significant progress has been observed during the last few years after implementation of the "Program of waste management in the Slovak Republic". At the present time, 64.22 % of municipal solid waste is deposited in landfill sites, 10 % is incinerated, and 8 % is reused (i.e., composted).

The most important consequences of the waste management program are activities associated with collection and separation of municipal waste. In this area a good deal of technical and educational effort has been invested. In spite of this and the advanced regulation system (similar to or approaching the most strict European standards), the results are not straightforward. This has political (threat from a further unemployment increase after restrictions of production), economic (is not strong enough to force environmental actions), and different local reasons (consequences of society transition). The percentage of plastics separated from waste stream is far less than in western European countries, where in general 10 % of plastic waste is separated.

Concerning to plastics, the attention is mainly focused on recycling. Each of above mentioned polymer producers in Slovakia have their own waste management program and have rigorous in house recycling policies. Slovnaft can be considered to be the leading company in this field with its comprehensive "Program of Waste Management of the Slovnaft Joint Stock Company". This program is fully in line with, and in some areas exceeds, Slovak Government Legislation, which stipulates that all polymer waste formed during processing operations must be recycled.

The major tasks in this field in the short to medium term can be listed as follows:

1. Recycling of producer/processor and municipally arising PET waste is becoming an increasingly urgent issue.
2. Efforts to devise economically and environmentally acceptable recycling routes, and to find alternative applications for recycled plastics must be stepped up.
3. Increased monitoring of plastic waste in Slovakia should be carried out in closer cooperation with surrounding European countries.

Environmentally Degradable Plastics

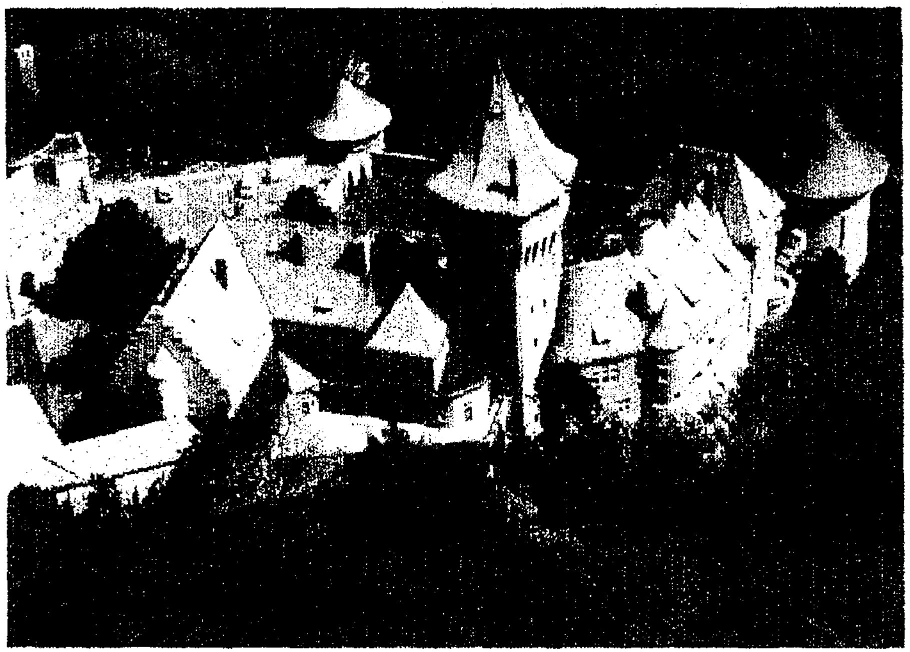
The progress has been attained in EDP plastics legislative in Slovakia just this year. In the frame of the National Program of Environmental Evaluation and Labeling of Products, the regulation for biodegradable plastic packaging materials has been adopted. This is promising, and we expect supporting of research and all activities in this field by governmental institutions. Economically less favorable but environmentally more friendly materials can be applied if the loss due to production is covered from external, mainly governmental funds, or if public consumers are willing to accept higher prices for certain products because they are aware of other benefits.

At present, the only production of environmentally degradable plastics in Slovakia is production of modified PVA with collagen hydrolysate in the forms of blow-extruded films and fibers (Selekt, Bucany). The production is based on domestic PVA polymer which production has started in 1999 in Chemical Plant, Novaky. Not only biodegradation of this material belongs to the main criteria for application. In many cases the solubility of modified PVA products is determinative for applications. Moreover, the utilization of reprocessing leather industry waste in form of collagen hydrolysate gives valuable product for different applications in agriculture and forestry.

Considerable research is going on in Slovakia to develop environmentally degradable plastics, mostly based on blends of biodegradable polymers. The research on biodegradable plastics is mainly undertaken at the Slovak University of Technology, Faculty of Chemical Technology and at the Polymer Institute of the Slovak Academy of Sciences. The activities at the Slovak University of Technology are focused on PVA and PVA modifications and blends. Great effort is given to the development of special biomaterials for medical applications, mainly to prostheses and biosynthetic skin substitute.

The research at the Polymer Institute of Slovak Academy of Science on EDPs proceeds in two directions. First, the blends of poly(hydroxy butyrates) are investigated with the aim of increasing ductility and impact resistance, and decreasing the price of the material. Chemical modification is extensively studied and apart from other reactions, crosslinking iniciated by organic peroxides is applied for the improvement of compatibility of blends with other polymers. Second, mixtures of polyolefins with biodegradable fillers are investigated. Besides starch, extensive research is carried out on compositions of LDPE and PP with organic fillers such as wood flour, milled dry grass, aspen fibers, and recycled paper. It is worth mentioning that the original material has been developed and patented at VUSAPL Nitra. It is PE foil for agricultural use based on LDPE and starch.

ICS - UNIDO
International Workshop on Environmentally Degradable Plastics
Smolenice, Slovak Republic, October 4 - 8,1999



COUNTRY OF PARTICIPANTS
Austria
Belarus
Belgium
Bulgaria
Canada
Czech Republic
Egypt
France
Germany
Hungary
Italy
Poland
Romania
Slovak Republic
Switzerland
The Netherlands
Ukraine
USA
Yugoslavia

Country Reports
The Cuurent State in Polymer Wastes Accumulation, Inceneration and Recycling in **Ukraine** - *P. Zamotaev*
Recent Achievements in Recycling of Plastic Wastes in **Bulgaria** - *K. Troev*
The Problems of Recycling Polymer Waste in Republic of **Belarus** - *V.M. Shapovalov*
Plastic Waste Management and Environmentally Degradable Plastics in **Hungary** - *B. Pukanszky*
Plastc Waste Management and Environmentally Degradable Plastics in **Poland** - *M. Kowalczuk*
Management and Reuse of Plastic Waste in **Austria** - *G. Braunegg*
Plastic Waste Management in **Czech Republic** - *K. Kolomaznik*

ICS - UNIDO
International Workshop on Environmentally Degradable Plastics
Smolenice, Slovak Republic, October 4 - 8,1999

EAST-WEST MEETING

Smolenice, October 5-7, 2000

Contract Research between East and West European Countries

Common Projects an Orientation to Applied Polymer Research in the Frame of EU Funding

PROJECTS

Starch based fillers for Applications in Rubber

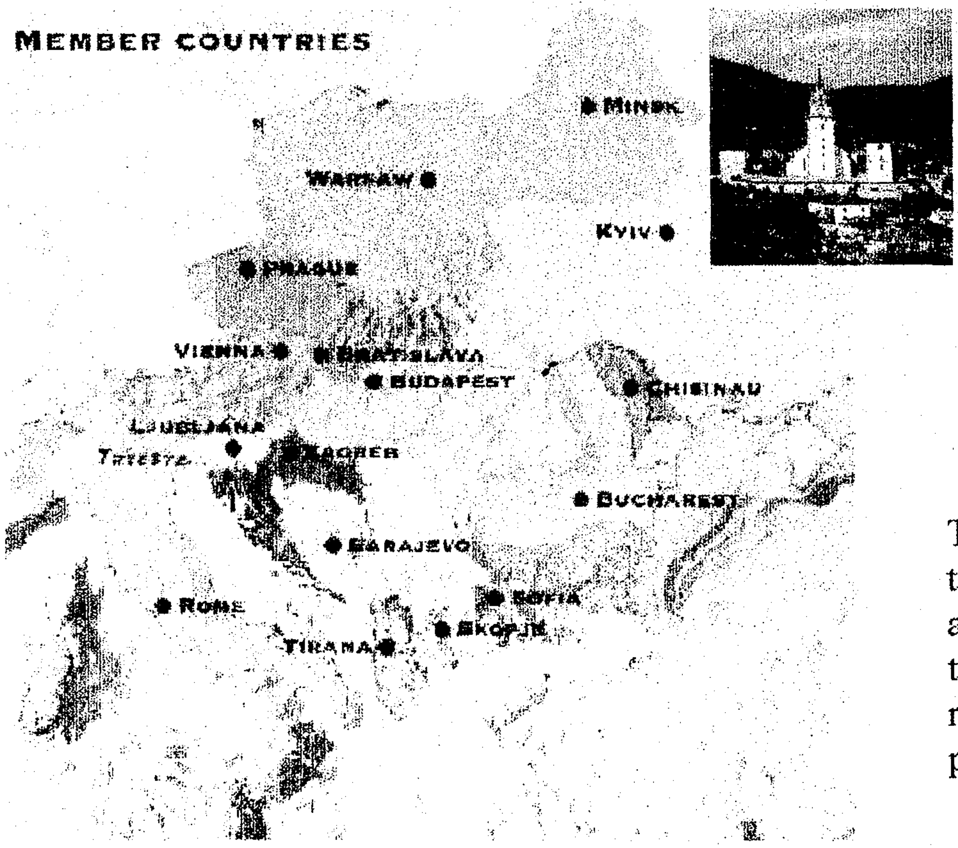
Switzerland, Slovak Republic, Germany

Biodegradable materials based on Collagen Hydrolysate

Italy, Slovak Republic, USA
ICS-UNIDO
(Prefissibility Study)

ICS - UNIDO
International Workshop on Environmentally Degradable Plastics
Smolenice, Slovak Republic, October 4 - 8,1999

FOCAL POINT - ENVIRONMENTALLY DEGRADABLE POLYMERS
Co-operation in the Middle and East Europe



MEMORANDUM OF ESTABLISHMENT
of the
CENTRE OF EXCELLENCE
(FOCAL POINT)
for
Environmentally Degradable Plastics
in Bratislava, Slovakia

The objectives are to transfer know-how and technology in favour of the countries of Middle and East Europe and disseminate scientific and technological information through consultancy and related activities on environmentally degradable polymers to enhance quality of life.

ICS - UNIDO
International Workshop on Environmentally Degradable Plastics:
Industrial Development and Application
Hanyang University, Seoul, Korea, September 19 - 22, 2000

PLASTIC WASTE MANAGEMNT IN SLOVAKIA

SPRAVA O STAVE
ZIVOTNEHO PROSTREDIA
SLOVENSKEJ REPUBLIKY
V ROKU [illegible]

Programme of waste management in the Slovak Republic

1998 **1.8 million tonnes of municipal solid waste**

322.6 kg per capita, and only 7.78 kg separated and collected

Deposition in landfill sites	**64.3 %**
Incineration	**10.0 %**
Reuse	**8.0 %**

Polymer consumption in Central Europe by country

	Thousand Tonnes	%
Poland	1117	49.6
Hungary	420	18.7
Czech Republic	395	17.5
Slovakia	187	8.3
Romania	135	6.0

Polymer consumption in Central Europe by polymer

	Thousand Tonnes
PE	794
PVC	478
PP	451
PS	277
PET	157
Construct	48

PLASTIC WASTE MANAGEMNT IN SLOVAKIA

RECYCLING

Slovak Government Legislation:

„All polymer waste formed during processing operation must be recycled“

The major tasks in plastics recycling:

Recycling of producer/processor and municipally sourced PET waste is becoming an increasingly urgent issue.

Efforts to device economically and environmentally acceptable recycling routs, and to find alternative applications for recycled plastics must be stepped up.

Increased monitoring of plastics waste in Slovakia should be carried out in closer cooperation with surrounding European countries.

ICS - UNIDO
International Workshop on Environmentally Degradable Plastics:
Industrial Development and Application
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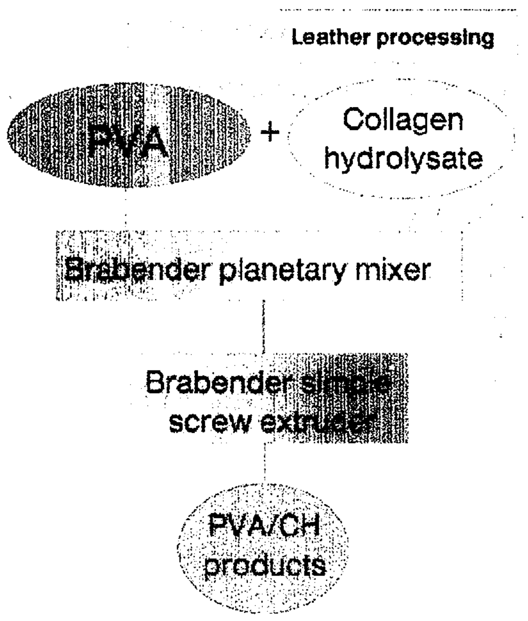
ENVIRONMENTALLY DEGRADABLE PLASTICS IN SLOVAKIA

INDUSTRIAL PRODUCTION: PVA (The Chemical Plant Novaky)
PVA products, PVA modified with collagen hydrolysate
(SELEKT Bucany)

RESEARCH: Polymer Institute of the Slovak Academy of Science, Bratislava
Faculty of Chemical Technology of the Slovak University of Technology in Bratislava
VUSAPL Nitra

- PVA/ collagen hydrolysate blends - cooperation with PVA producer
- Polyhydroxybutyrate and blends with PVA (compatibility improving by chemical modification, crosslinking iniciated by organic peroxides)
- Polyolefins mixtures with biodegradable fillers (starch, wood flour, aspen fibres, recycled paper, milled dry grass)
- Biomaterials based on collagen and hyaluronan (biosynthetic skin substitute, bone filling composites with hydroxyapatite)

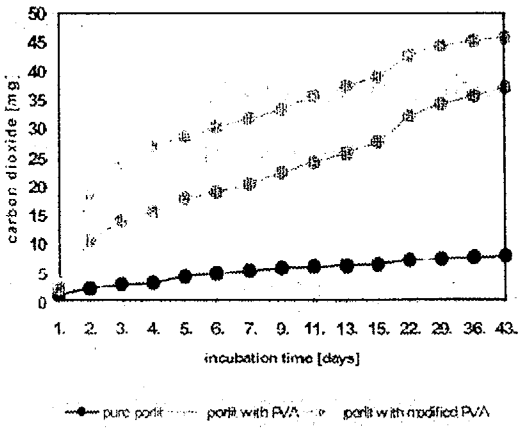
PVA/Collagen Hydrolysate Blends



Collagen hydrolysate improve two significant properties **solubility and biodegradability**, while main mechanical propertiesdo not fall off.

The study focused on:

- Optimisation of blend composition (PVA, CH, glycerol, other additives)
- Blend treating process (pre-treating in mixer, extrusion, torque measurement)
- Structure versus properties of films (IR, NMR, DSC measurements, solubility, mechanical properties, biodegradability)
- Structure versus properties of fibres (DSC measurements, mechanical properties)



24. Biodegradable Plastics Industry in Japan - Past, Present and Future -

Kazushi Ohshima
Biodegradable Plastics Society, Japan
[E-mail:Ohshima@jba.or.jp], [URL: http://www.bpsweb.net]

Reflecting the fact that biodegradable plastics (BPs) are one of the materials available for the design of the sustainable environment, BPs are called "GreenPla" in Japan. Although in the past, the market for BPs was not so large, it has now begun to grow, particularly since 1998 (60 tons in 1992, 1,600-2,000 tons in 1998 and 2,500-3,000 tons in 1999).

The present market is mainly composed of:

- Poly(butylene succinate) : "Bionolle" of Showa HighPolymer Co.
- Poly(caprolactone) : "Celgreen" of Daicel Chemical Industries Ltd.
- Poly(lactic acid) : "NatureWorks" of Cargill Dow Polymers Co.
  "Lacty" of Shimadzu Co.
  "Lacea" of Mitsui Chem. Inc.

and

- Starch : Japan Corn Starch Co., Nihon Shokuhin Kako Co. and Nissei Co.

or

- Starch blended with poly(caprolactone) :
  "Mater-Bi" of Novamont Co. via Nippon Gohsei Co.

for mulch films, seedling pots, composting bags and other miscellaneous applications.

In this paper, the past and present BP industry in Japan is reviewed with a view to illustrating its possible future:

1. Past and Present Status of the BP Industry in Japan
    - Commercially Available BPs and Market Size
    - Application Field Characteristics in Japan
    - Unsolved Technical Problems for Expanding the Market
    - Certification System
2. New Comers into the Japanese Market
3. Future of the BP Industry in Japan
    - Market Size
    - Application Field

BPS

UNIDO-ICS EDP WorkShop 2K, Korea, *Sep.19th – 22nd 2K*

Biodegradable Plastics Industry in Japan

- Past, Present and Future -

1. Biodegradable Plastics Society, BPS
2. Market Development in Japan

Kazushi Ohshima, BPS

BPS

UNIDO-ICS EDP WorkShop 2K, Korea
Biodegradable Plastics Industry in Japan - *Past, Present and Future* -

1. Biodegradable Plastics Society, BPS

- Role and Activities -

- Mission
- Members
- Organization
- Activities
  - Evaluation Method Development
  - Model Program : Compost Bag, Mulch Film
  - Self-Regulation Rule for Food Packaging
  - Certification System

UNIDO-ICS EDP WorkShop 2K Korea
Biodegradable Plastics Industry in Japan - Past, Present and Future -

1. BPS:Mission

- established in *October 1989*
- Mission:

  To *establish all about Technology* of biodegradable Plastics

  and

  To *lead an extensive, commercial Use* of biodegradable Plastics

Note:
Based on BPS's policy, we take interests only in biodegradable plastics

---

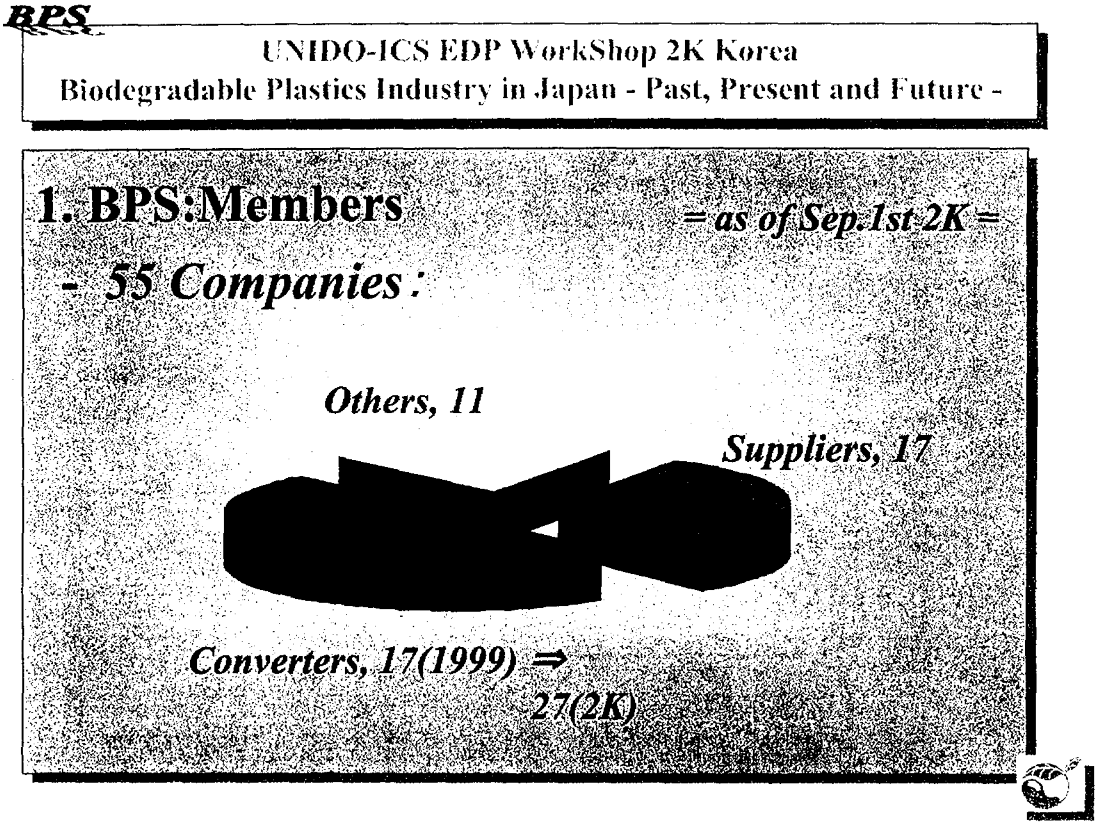
= *Please Note* =

**In Japan, since December 1995,
"Pet" Name of "biodegradable Plastics" is**

GreenPla ®

（"グリーンプラ"）

**, that means
"*green* (:environmentally friendly)" plastics.**



UNIDO-ICS EDP WorkShop 2K Korea
Biodegradable Plastics Industry in Japan - Past, Present and Future -

1. BPS:Members

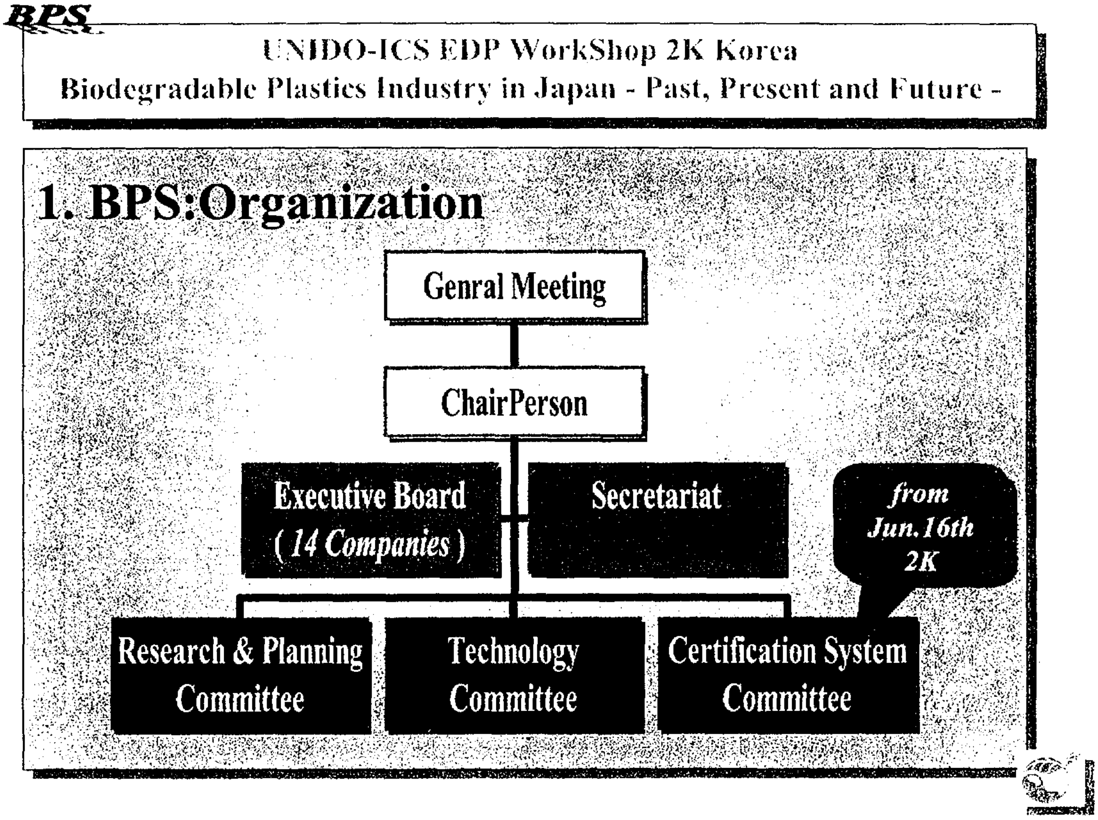
= as of Sep.1st 2K =

- *55 Companies:*

Others, 11

Suppliers, 17

Converters, 17(1999) ⇒ 27(2K)



UNIDO-ICS EDP WorkShop 2K Korea
Biodegradable Plastics Industry in Japan - Past, Present and Future -

1. BPS:Organization

Genral Meeting

ChairPerson

Executive Board
(*14 Companies*)

Secretariat

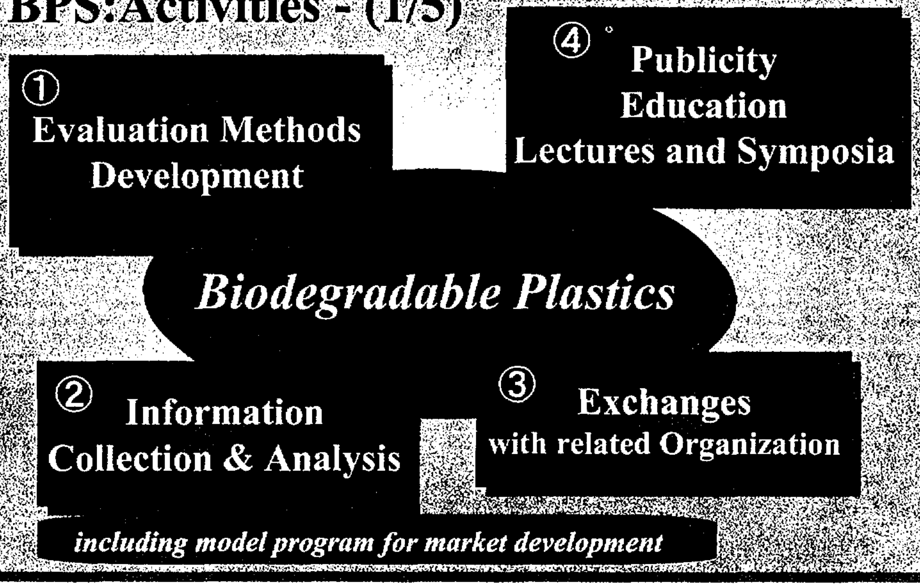
Research & Planning Committee

Technology Committee

Certification System Committee

from Jun.16th 2K

1. BPS:Activities - (1/5)



① Evaluation Methods Development

④ Publicity
Education
Lectures and Symposia

Biodegradable Plastics

② Information Collection & Analysis

③ Exchanges with related Organization

including model program for market development

1. BPS:Activities - (2/5)

① Evaluation Methods Development

Technology Committee

- Biodegradability Field Test, Nov.'95-Oct.'96
- Safety Evaluation Scheme, Plan & Do, Apr.'97-Mar.'00
- Simplified Evaluation Method of Biodegradability, Apr.'00-

Topics,1 = *Biodegradability* Field Tests =

Nov. '95 - Oct. '96

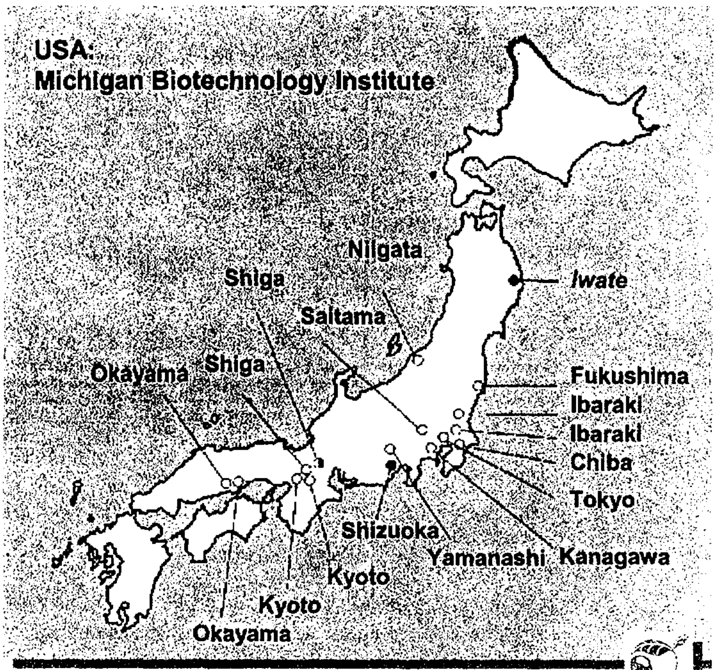
Soil : 17 *Places*
(20 *Points*)
Water: 3 *Places*

Testing Materials:

- Biopol
- Polycaprolactone
- Polylactide
- Polybuthylensuccinate
- Polybuthylensuccinate/adipate

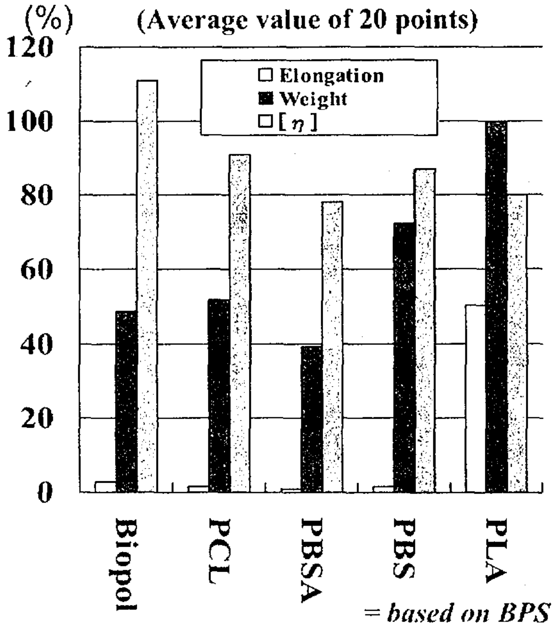
Evaluations:

Weight, TS, EL, [η],
molecular weight distribution

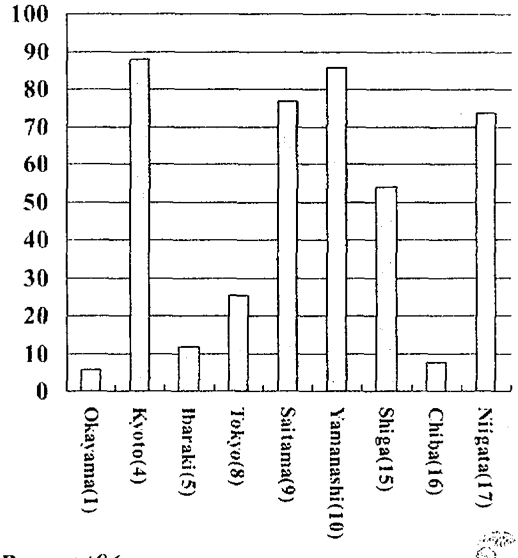


Results of Field Tests
- 12months -

Remain of Properties (%)
(Average value of 20 points)



Result in each point
(Biopol, weight remain(%))

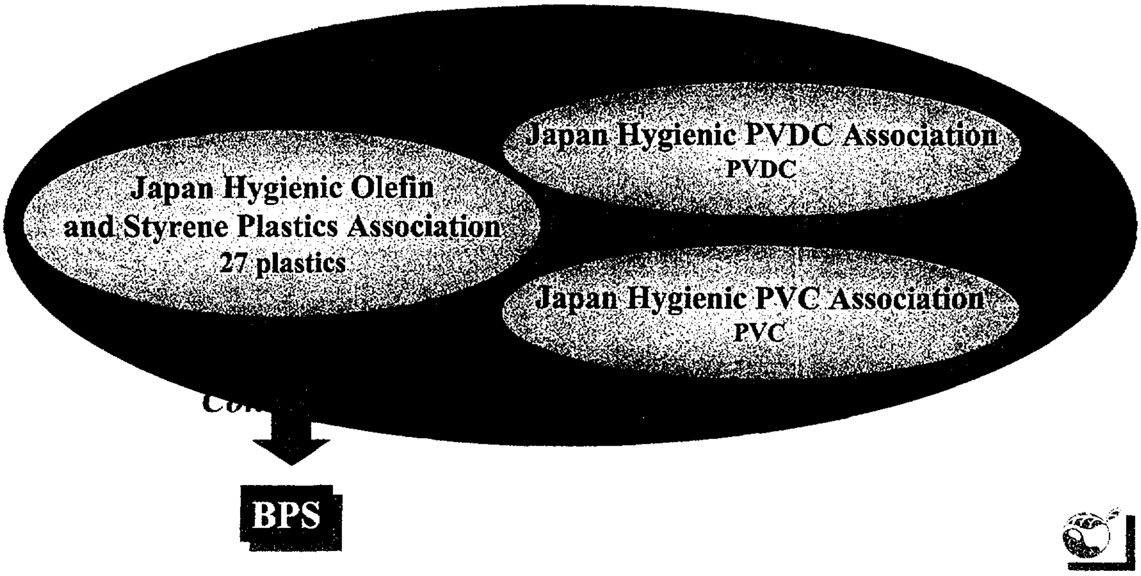


= based on BPS Report '96 =

Topics,2 Safety Evaluation Scheme and Self Regulation for *Food Packaging Use*

BPS

Ministry of Health & Welfare : Notification No.20



Japan Hygienic Olefin and Styrene Plastics Association
27 plastics

Japan Hygienic PVDC Association
PVDC

Japan Hygienic PVC Association
PVC

BPS

BPS

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Biodegradable Plastics Industry in Japan - Past, Present and Future -

1. BPS:Activities - (3/5)

- Model Program for commercial Use:
  - *Compost Bag* for Organic Waste Recycling, 1995
  - *Mulch Film*, 1999-2K
- Market Research:
  - Biodegradable Polymer Journal, 6 issues/year,
  - BPS Report, 6 issues/year

② Information Collection & Analysis

Research & Planning Committee

including model program for market development

Topics,3 Model Program : *Compost Bag* =

in 1995

BPS

MITI ⇢ **BPS** ⇢ **Resin Supplier**

Polylactide
Polybutylenesuccinate/adipate
Polycaprolactone
Starch/PVA
Polyethylensuccinate
Biopol

↓ *Compost Bag*

210 Households
4 Offices

Model [illegible]

↓ *Organic waste*

Hiroshima City
Fuchu City

Local Government

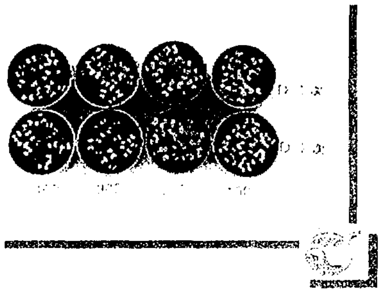
↓ *Collection*

450 kg x 93 days
=370 MT

Composting Plant

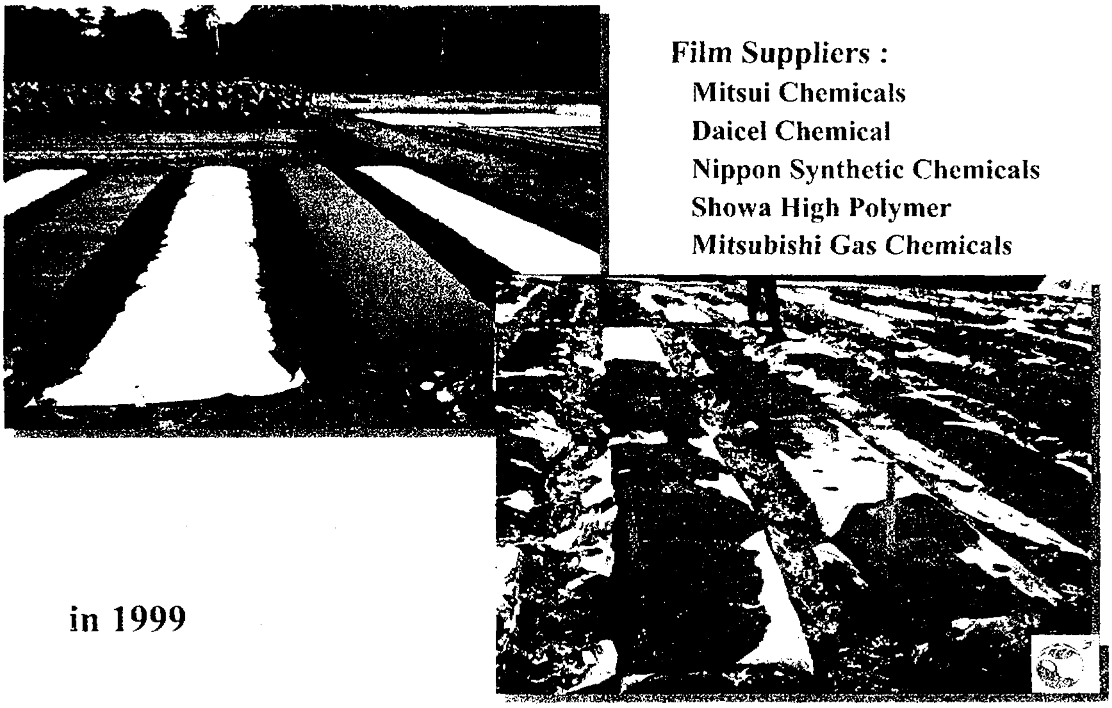
↓ *Compost*

- Ingredient Analysis
- Plant Growth Test



Topics,4 Model Program : *Mulch Film* =

BPS



Film Suppliers :
Mitsui Chemicals
Daicel Chemical
Nippon Synthetic Chemicals
Showa High Polymer
Mitsubishi Gas Chemicals

in 1999

1. BPS:Activities - (4/5)

- in Japan,
  - Japan Organic Resource Association (JORA)
  - Japan Bio-Industry Association (JBA)
  - Society of Polymer Science of Japan
- Biodegradable Products Institute (BPI, USA)
- Bio/Environmental Degradable Polymer Society (BEDPS)
- ORCA (EU)

③ **Exchanges**
with related Organization

Research & Planning Committee

---

1. BPS:Activities - (5/5)

Research & Planning Committee

④ **Publicity**
Education
Lectures and Symposia

- public Relations
- Lectures
- Symposia
-

Certification System Committee
new!

- Identification and Labeling of GreenPla Products

Topics,5 = GreenPla Certification System =

	EU	Germany Swiss	US.	Japan
Focus	Compostability	Compostability	Compostability	Biodegradability
Owner	-	IBAW	BPI	BPS
Manager	-	DIN-CERTCO	BPI	BPS
Supporter	-	-	USCC	-
	(Mandatory)	(Voluntary → Mandatory)	(Voluntary)	(Voluntary)
Norm	prEN13432 •Material characteristic •Biodegradability •Disintegration •Compost quality	DIN V54900	ASTM D6002 ASTM D6400	GreenPla *PL* Guideline •Material characteristic •Acute toxicity of additives •Biodegradability
Background	EU Packaging Directive EU Composting Directive EU Landfill Directive			Packaging Recycling Law Food-Waste Recycl

= Identification and Labeling of GreePla =

Purpose

1. Identification of Plastics Products made of biodegradable Plastics
2. Distinguish from non-degradable Plastics by Symbol Mark

System

GreenPla Product

applicant

- Application : (disclose all Ingredients)
- put a Mark

Identification Body

- check
- permit to use a Mark

- all Ingredients on "Positive List"
- organic Material > 50%
- heavy Metals < Criterion
- harmful Material = no

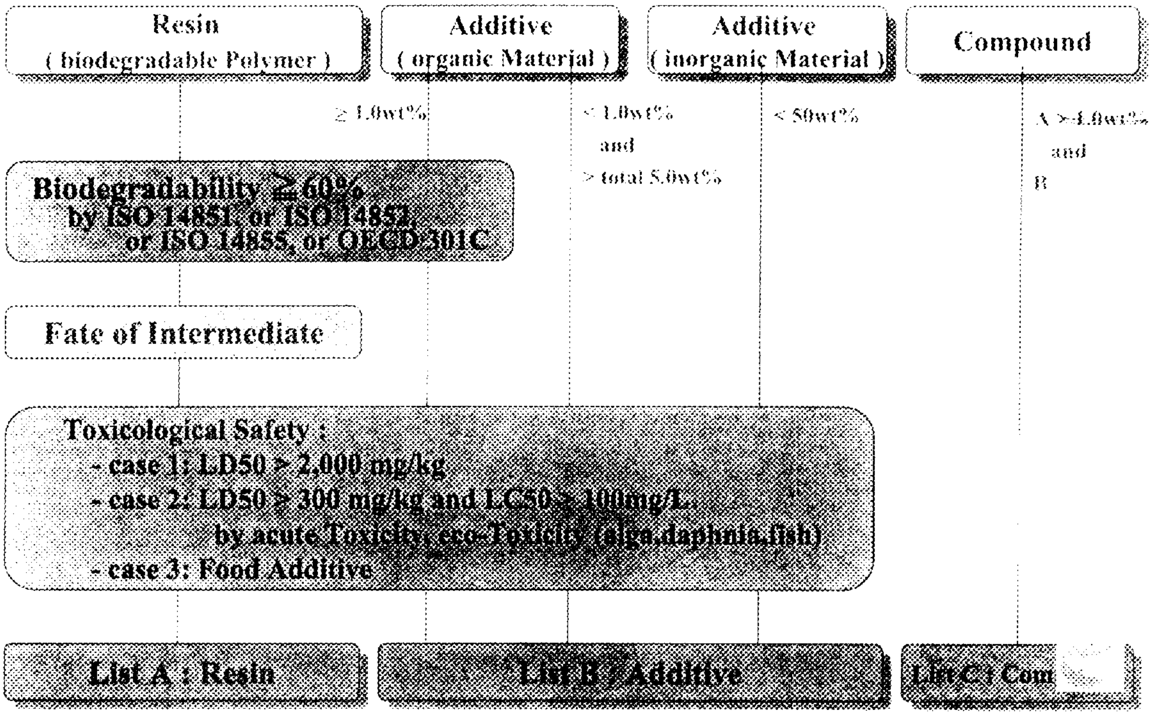
→ • judge

Symbol Mark

BPS

= *Greenpla Positive List* =

- Guideline / Criteria -



Resin
(biodegradable Polymer)

Additive
(organic Material)

Additive
(inorganic Material)

Compound

≥ 1.0wt%

< 1.0wt%
and
> total 5.0wt%

< 50wt%

A ≥ 1.0wt%
and
B

Biodegradability ≥ 60%
by ISO 14851, or ISO 14852,
or ISO 14855, or OECD 301C

Fate of Intermediate

Toxicological Safety :
- case 1: LD50 > 2,000 mg/kg
- case 2: LD50 ≥ 300 mg/kg and LC50 ≥ 100mg/L
by acute Toxicity, eco-Toxicity (alga,daphnia,fish)
- case 3: Food Additive

List A : Resin

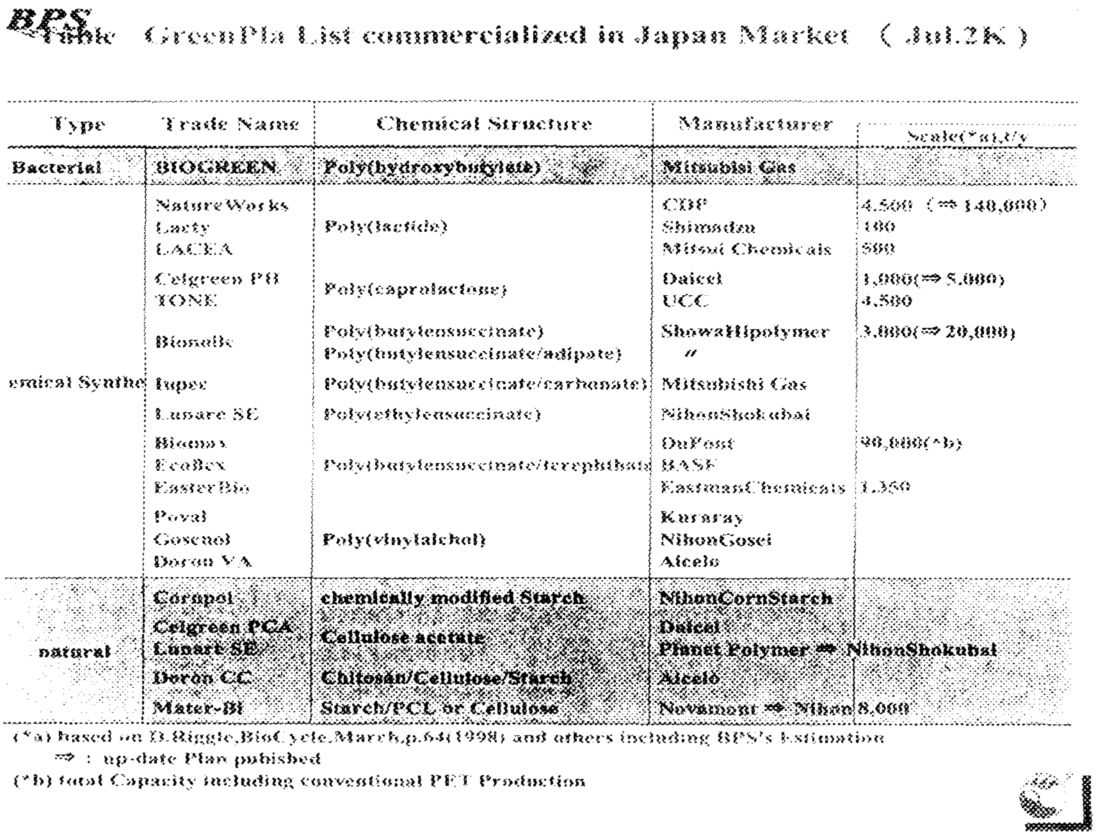
List B : Additive

List C : Com

BPS

2. Market Development in Japan

- Commercialized Materials
- Application Field
- Market Size : past, present, and future
- Background



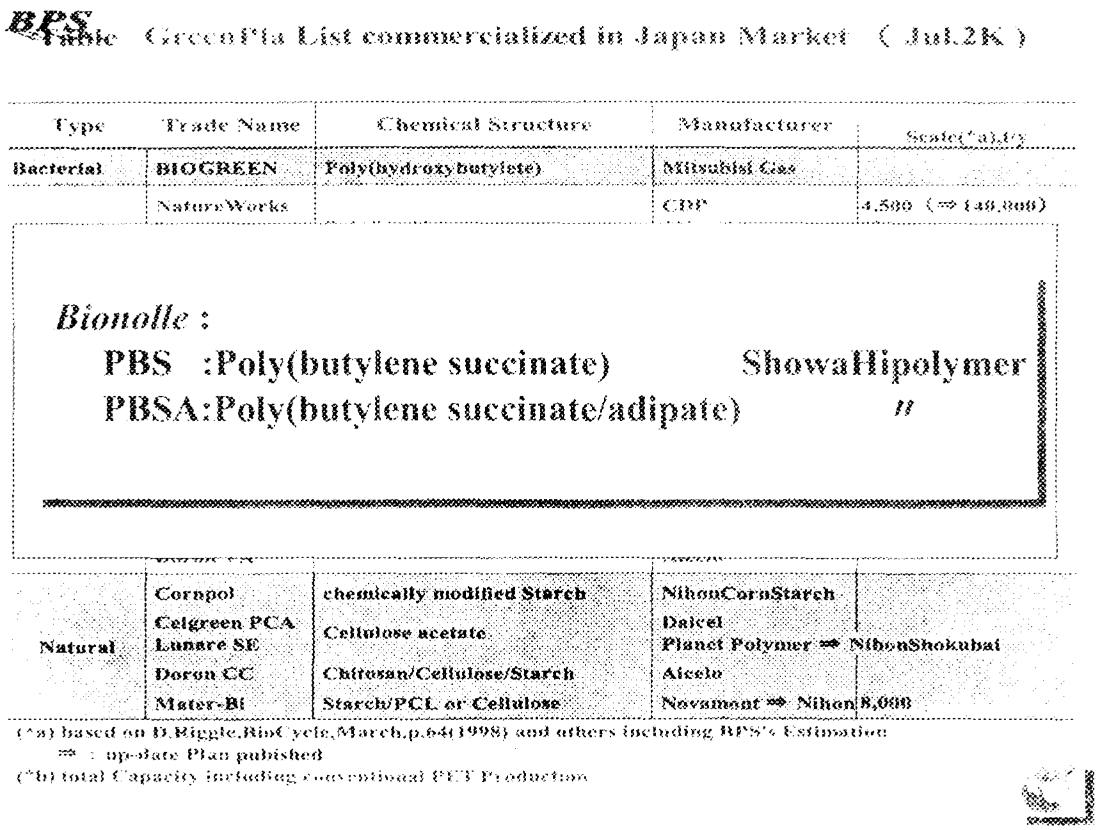
BPS Table GreenPla List commercialized in Japan Market (Jul.2K)

Type	Trade Name	Chemical Structure	Manufacturer	Scale(*a),t/y
Bacterial	BIOGREEN	Poly(hydroxybutylate)	Mitsubisi Gas	
emical Synthe	NatureWorks Lacty LACEA	Poly(lactide)	CDP Shimadzu Mitsui Chemicals	4,500 (⇒ 140,000) 100 500
	Celgreen PH TONE	Poly(caprolactone)	Daicel UCC	1,000(⇒ 5,000) 4,500
	Bionolle	Poly(butylensuccinate) Poly(butylensuccinate/adipate)	ShowaHipolymer 〃	3,000(⇒ 20,000)
	Iupec	Poly(butylensuccinate/carbonate)	Mitsubishi Gas	
	Lunare SE	Poly(ethylensuccinate)	NihonShokubai	
	Biomax Ecoflex EasterBio	Poly(butylensuccinate/terephthala	DuPont BASF EastmanChemicals	90,000(*b) 1,350
	Poval Gosenol Doron VA	Poly(vinylalchol)	Kuraray NihonGosei Aicelo	
natural	Cornpol Celgreen PCA Lunare SE Doron CC Mater-Bi	chemically modified Starch Cellulose acetate Chitosan/Cellulose/Starch Starch/PCL or Cellulose	NihonCornStarch Daicel Planet Polymer ⇒ NihonShokubai Aicelo Novamont ⇒ Nihon	 8,000

(*a) based on D.Riggle,BioCycle,March,p.64(1998) and others including BPS's Estimation

⇒ : up-date Plan pubished

(*b) total Capacity including conventional PET Production



BPS Table GreenPla List commercialized in Japan Market (Jul.2K)

Type	Trade Name	Chemical Structure	Manufacturer	Scale(*a),t/y
Bacterial	BIOGREEN	Poly(hydroxybutylate)	Mitsubisi Gas	
	NatureWorks		CDP	4,500 (⇒ 140,000)

Bionolle :

PBS :Poly(butylene succinate) ShowaHipolymer

PBSA:Poly(butylene succinate/adipate) 〃

Type	Trade Name	Chemical Structure	Manufacturer	Scale(*a),t/y
Natural	Cornpol Celgreen PCA Lunare SE Doron CC Mater-Bi	chemically modified Starch Cellulose acetate Chitosan/Cellulose/Starch Starch/PCL or Cellulose	NihonCornStarch Daicel Planet Polymer ⇒ NihonShokubai Aicelo Novamont ⇒ Nihon	 8,000

(*a) based on D.Riggle,BioCycle,March,p.64(1998) and others including BPS's Estimation

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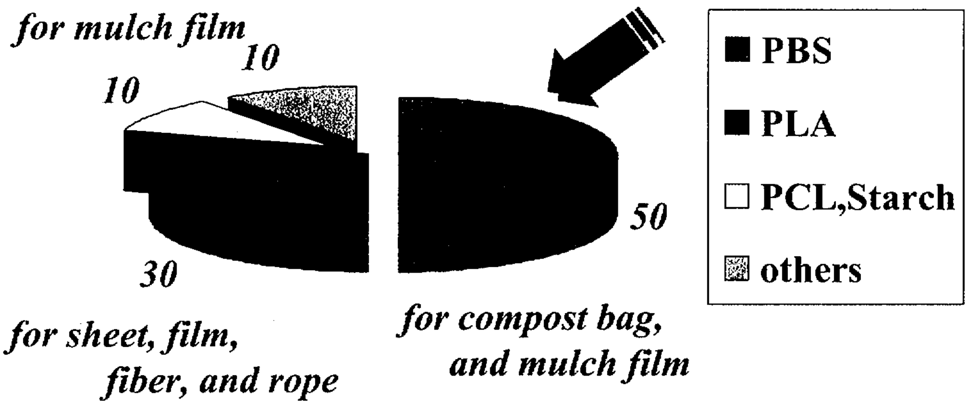
(*b) total Capacity including conventional PET Production

BPS



Market Structure of GreenPla in Japan (1999)

- total Size : about 1,600-2,000 t/1998, 2,500 t or more /1999

BPS

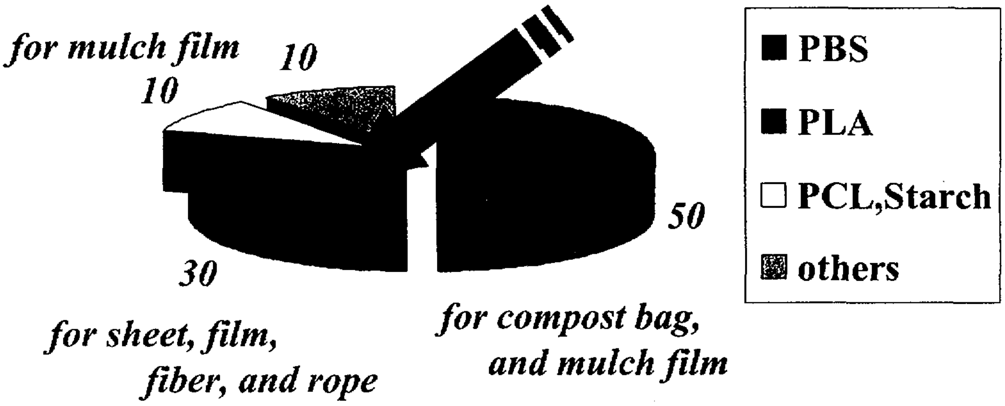
Table GreenPla List commercialized in Japan Market (Jul.2K)

Type	Trade Name	Chemical Structure	Manufacturer	Scale(*a),t/y
Bacterial	BIOGREEN	Poly(hydroxybutylete)	Mitsubisi Gas	
	NatureWorks		CDP	4,500 (⇒140,000)
Natural	Cornpol	chemically modified Starch	NihonCornStarch	
	Celgreen PCA	Cellulose acetate	Daicel	
	Lunare SE		Planet Polymer ⇒ NihonShokubai	
	Doron CC	Chitosan/Cellulose/Starch	Aicelo	
	Mater-Bi	Starch/PCL or Cellulose	Novamont ⇒ Nihon	8,000

PLA:Poly(Lactic Acid) :

NatureWorks	CDP
Lacty	Shimadzu
LACEA	Mitsui-Chemicals

(*a) based on D.Riggle,BioCycle,March,p.64(1998) and others including BPS's Estimation
⇒ : up-date Plan pubished
(*b) total Capacity including conventional PET Production



Market Structure of GreenPla in Japan (1999)

- total Size : about 1,600-2,000 t/1998, 2,500 t or more /1999

Table GreenPla List commercialized in Japan Market (Jul.2K)

Poly(caprolactone) :

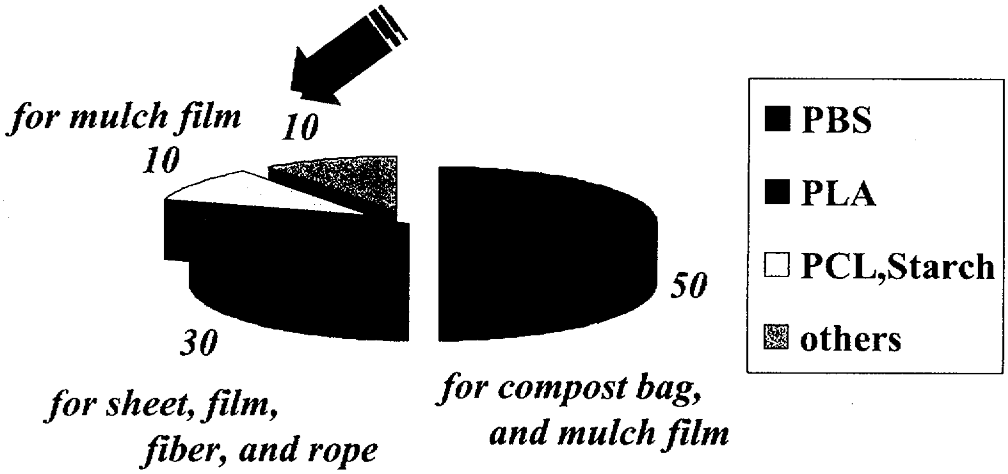
Celgreen PH	Daicel Chemicals
TONE	UCC

Starch-based :

Cornpol	Nihon Corn-Starch
Mater-Bi	Nihon Gosei *from* Novamont

	Doron CC	Chitosan/Cellulose/Starch	Aicelo	
	Mater-Bi	Starch/PCL or Cellulose	Novamont ⇒ Nihon	8,000

(*a) based on D.Riggle,BioCycle,March,p.64(1998) and others including BPS's Estimation
⇒ : up-date Plan pubished
(*b) total Capacity including conventional PET Production



Market Structure of GreenPla in Japan (1999)

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Natural	Cornpol	chemically modified Starch	NihonCornStarch	
	Celgreen PCA	Cellulose acetate	Daicel	
	Lunare SE		Planet Polymer ⇒ NihonShokubai	
	Doron CC	Chitosan/Cellulose/Starch	Aicelo	
	Mater-Bi	Starch/PCL or Cellulose	Novamont ⇒ Nihon	8,000

Poly(butylene succinate/terephthalate) :

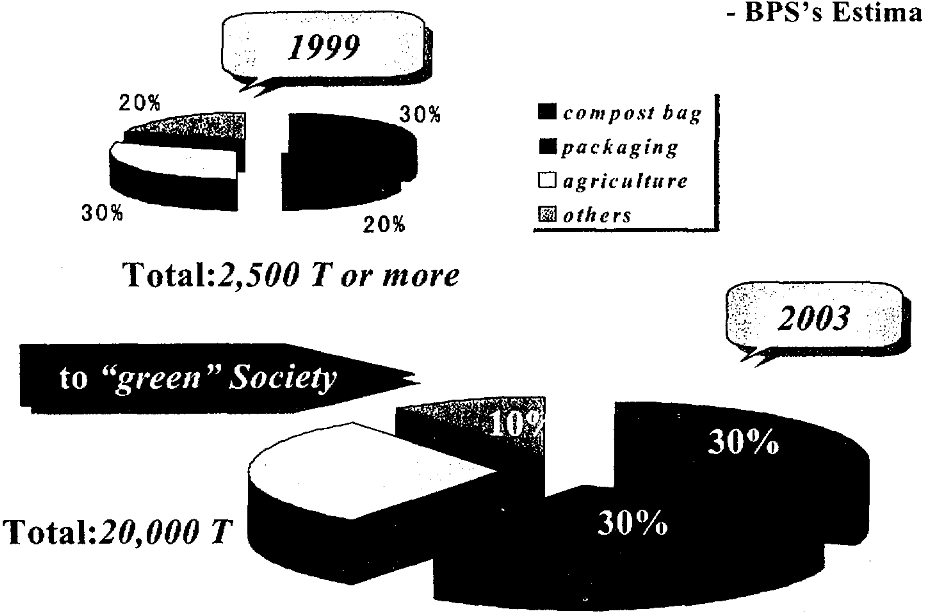
Biomax (*Tm*: ca. 200C, like "*PET*") **DuPont**

Ecoflex (*Tm*: ca. 100-110C, like "*LLDPE*") **BASF**

EasterBio (*Tm*: ca. 100-110C, like "*LLDPE*") **EastmanChemicals**

(*a) based on D.Riggle,BioCycle,March,p.64(1998) and others including BPS's Estimation
⇒ : up-date Plan pubished
(*b) total Capacity including conventional PET Production

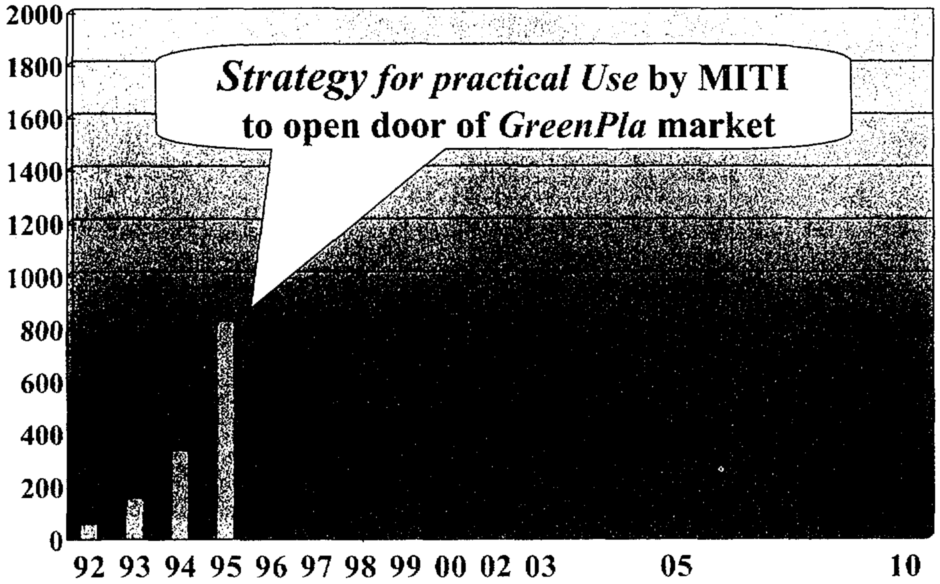
- BPS's Estimation



GreenPla's Market Size Trend in Japan
, when *bio (-material) recycle-based society is smoothly formed.*

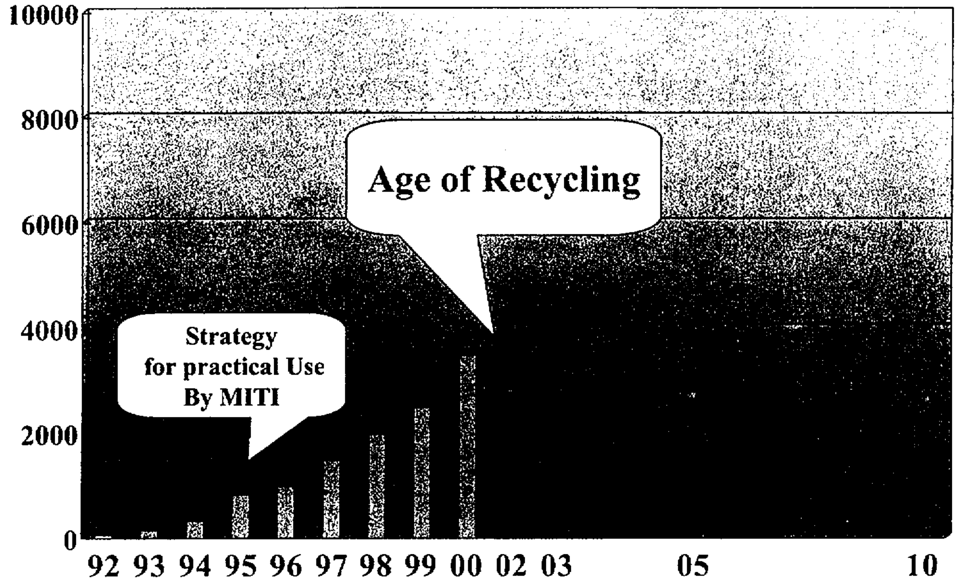
= *GreenPla's Market Estimation* =

(in Japan, from 1992 to 2010)



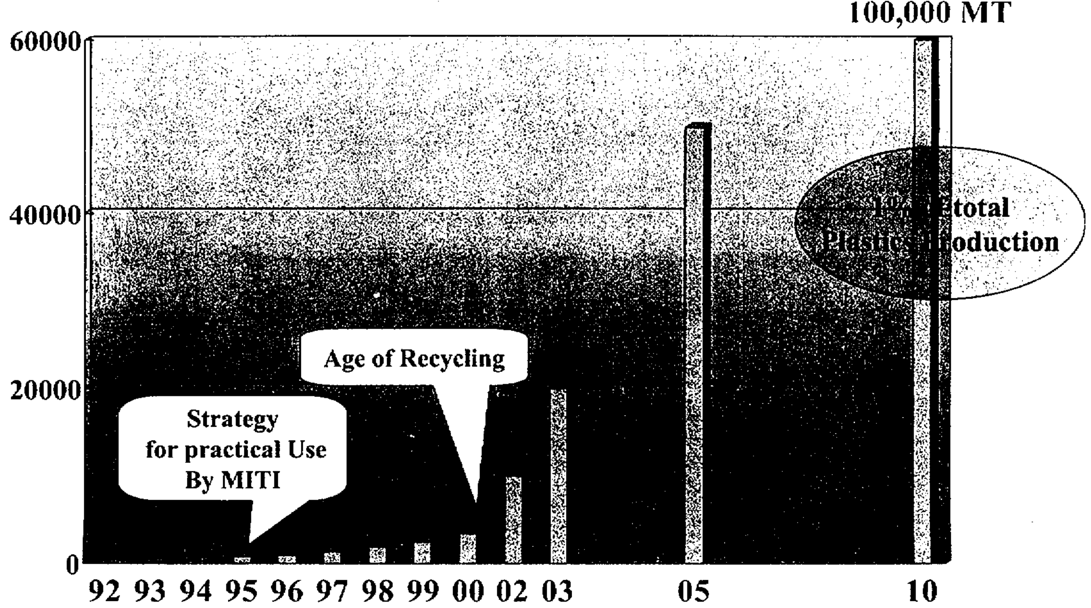
= based on BPS's Estimation('99) =

= GreenPla's Market Estimation =
(in Japan, from 1992 to 2010)



= based on BPS's Estimation('99) =

= GreenPla's Market Estimation =
(in Japan, from 1992 to 2010)



= based on BPS's Estimation('99) =

Legal and Regulatory Topics

- Waste Disposal and Clean-up Law (1997)
- Packaging Waste Recycling Law (2000)
- Recycling Society Establishing Law (2001)
- Food Waste Recycling Law (2002)

Regulations

- Basic Cyclic-Type Society Creation Promotion Law
  - Waste Disposal and Clean-up Law
  - Recycling Law
  - Food Waste Recycling Law
  - Construction Material Recycling Law
  - [illegible]
  - Packaging Waste Recycling Law
  - Home Appliance Recycling Law

25. Plastic Waste Treatments and EDP in Korea

Young Ha Kim and Soo Hyun Kim
Biomaterials Research Center, Korea Institute of Science and Technology, Korea
[E-mail: yhakim@kist.re.kr]

1. Waste treatment and plastic wastes in Korea

Development of environmentally degradable plastics (EDP)/compostable plastics is closely related with waste treatment systems and infrastructures, and should be supported by public to pay the extra fee due to the present high prices and inferior properties compared to conventional plastics.

In Korea for last 30 years the amount of wastes produced had been rapidly increased with the economical development and the expansion of consumption. Recently the industrial wastes are continuously increasing, but MSW (municipal solid waste) is rather reduced because charcoal briquettes was replaced rapidly. The MSW is further reduced since the introduction of "Volume Based Collection Fee (VCF) System" on Jan. 1995. The composition of MSW is changed much. The charcoal briquette ashes is decreased to a great extent, but papers and plastics are increasing. Food waste has the highest content. MSW is still mainly treated by landfill though recycling and incineration are increasing gradually. Composting is very in the initial stage to be carried out by test projects in some restaurants and apartment complexes. It is fortunate to increase the reprocessing food wastes into animal feeds since the Korean won devaluation on 1997. (Table 1, 2)

"VCF System" is to pay the waste treatment fee according to the volume of wastes discharged. All the waste should be disposed into the designated plastic bags of which prices include the waste treatment cost. All the recyclables such as papers, bottles, cans and plastic bottles should not be disposed into the designated bags, but separately collected to be recycled. Otherwise, ca. 1,000 US$ will be fined. VCF brought a tremendous effect to the whole production and consuming process. Amount of wastes is diminished 37% and the recyclables are increased about 40%.

In addition to the VCF system, "Deposit Refund System" for recyclable products and beverage containers and "Product Charge System" for non-recyclable and easily discharged products has been implemented since Jan. 1992.

Plastic wastes is gaining more and more concerns among public. Korea has the 5th largest petrochemical industry on the world. The present production of plastics is ca. 6 million T(MT), but the total domestic demand is ca. 4 MT (78 Kg consumption/capita).

Among them about 1 MT/y of plastic wastes, especially huge amounts of films and packages, is discharged to cause many problems in the environment and to treat them. Recycling of plastic waste is only 14.8%, much lower than those of 56.8% for papers, 55.3% for metals, 67.8% for glass and 48.9% for beverage cans.

Table 1. MSW treatments in Korea (unit: %)

treatments	1988	1990	1992	1994	1997
landfill	95.0	93.0	89.2	81.1	63.9
incineration	1.7	1.8	1.5	3.5	7.1
recycling	2.4	4.6	7.9	15.4	29.0
others	0.9	0.6	1.4	-	-

Therefore, the over-use or once-use of plastic goods and packages are increasingly limited by the government. EDP is very helpful to solve the problems, however their high prices and inferior properties have kept from the development of actual market.

Table 2. Composition and amount of municipal solid waste (unit: ton/day)

year	1988	1992	1994	1997
total amount	72,897	75,096	58,118	47,895
kg/day.capita	2.1	1.8	1.3	1.05
- charcoal ashes	28,994	17,750	5,534(9.5%)	1,245(2.6%)
- foods	17,055	21,807	18,055(31.1%)	13,075(27.3%)
- papers	7,756	13,125	12,468(21.5%)	6,035(12.6%)
- woods	2,476	3,077	2,443(4.2%)	1,916(4.0%)
- metal & ceramics	3,067	4,957	3,264(5.6%)	--
- recyclables (cans, bottles, clothes)	--	--	--	12,500(26.1%)
- plastics & rubbers	--	--	--	2,251(4.7%)
- others	13,549	14,380	16,354(28.1%)	10,872(22.7%)

2. R & D activities of EDP in Korea

Early in the late '80s starch filled bio-disintegrable (not biodegradable) or photodegradable plastics was introduced to the Korean market but not succeeded. From early '90s several companies have developed inherently biodegradable plastics based on starch or/and aliphatic polyesters to bring the samples to the market. Polyhydroxybutyrate (PHB) and its copolymer were the first biodegradable polymer introduced in Korea. However, the activity on PHB was declining due to the highest price. Then, PET fiber manufacturing companies followed by aliphatic polyesters based on diol (butanediol, ethylene glycol) and diacid (succinic acid, adipic acid). The polymers have shown relatively good mechanical properties and processibilities. Films, sheets, injected consumer products, and blown containers made of these plastics and starch based foam for loose-fill package were included. However, they have had difficulties in penetrating into the real market due to the high prices. The government has been hesitating to recommend them for eg. trash bags for the VCF system. The production and the polymerization of lactic acid has been also developed. Recently, most companies are concentrating to cut down the cost by developing starch based ones or by blending starch with aliphatic polyesters in addition to improve mechanical properties and processibilities.

Very recently, the government decided to apply EDP for trash bags used for VCF system. The trash bags will be bio-disintegrable ones made of LLDPE containing more than 30% of EDP to minimize the cost rise. They will replace the present HDPE trash bags and be expected to accelerate degradation and stabilization of household wastes even in the landfills. This is a good first example to establish a regular market for EDP on the world to expect further expansions in other areas.

Table 3. EDP developed in Korea

company	name of product	characteristics
SK Chemicals	SKYGREEN	PET manufacturer, Aliphatic polyester and/or its starch blend
Saehan Industries	ESLON GREEN	PET manufacturer, Aliphatic polyester and/or its starch blend
SK Corp.	GREENPOL	Oil and polyolefin manufacturer, Polycaprolactone/plasticized starch blend
Hanwha Chemical Corp.	ECO-PLAST	Polyolefin manufacturer, Modified starch containing aliphatic polyester
Daesang Corp.	BIONYL	Starch manufacturer, Modified starch containing aliphatic polyester
Ire Chemical	EnPol	Small company, Aliphatic/aromatic polyester

Plastic Waste Treatments and EDP in Korea

UNIDO-ICS Workshop Korea

2000.9

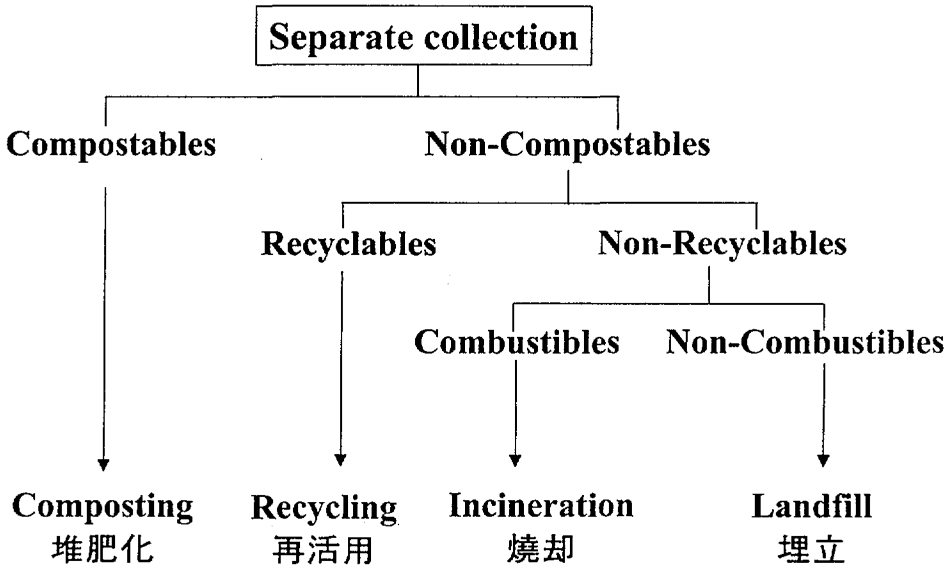
Young Ha KIM
KIST, Korea

Ⅰ. Waste treatments in Korea

Ⅱ. Plastic wastes and regulation

Ⅲ. R&D for EDP

Ultimate waste treatments



Separate collection

Compostables

Non-Compostables

Recyclables

Non-Recyclables

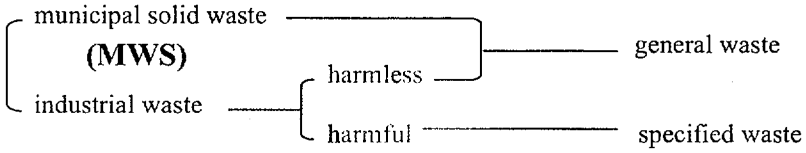
Combustibles

Non-Combustibles

	Composting 堆肥化	**Recycling** 再活用	**Incineration** 燒却	**Landfill** 埋立
Plastic Wastes	Δ	O	Δ	×

Ⅰ. Waste Treatment in Korea

o Classification of wastes



municipal solid waste (MWS)

industrial waste

harmless

harmful

general waste

specified waste

o Production of wastes

(unit: thousand ton/day)

year	'88	'92	'94	‘95	‘97
total	124.1	144.5	147.0	147.7	189.0
industrial	51.2	69.4	88.9	100.0	141.1
municipal	72.9	75.1	58.1	47.7	47.9

o Composition of MSW

(unit: thousand ton/day)

year	1988	1992	1994	1997
total amount	72.9	75.1	58.1	47.9
kg/day.capita	2.1	1.8	1.3	1.05
- charcoal ashes	29.0	17.8	5.5 (9.5%)	1.2 (2.6%)
- foods	17.1	21.8	18.1 (31.1%)	13.1 (27.3%)
- papers	7.8	13.1	12.5 (21.5%)	6.0 (12.6%)
- woods	2.5	3.1	2.4 (4.2%)	1.9 (4.0%)
- metal & eramics	3.1	5.0	3.3 (5.6%)	--
- recyclables(cans, bottles, clothes)	--	--	--	12.5 (26.1%)
- plastics & rubbers	--	--	--	2.3 (4.7%)
- others	13.5	14.3	16.4 (28.1%)	10.9 (22.7%)

o MSW treatment

(unit: %)

treatments	1988	1990	1992	1994	1997	2001 (plan)
landfill	95.0	93.0	89.2	81.1	63.9	45.0
incineration	1.7	1.8	1.5	3.5	7.1	20.0
recycling	2.4	4.6	7.9	15.4	29.0	35.0
others	0.9	0.6	1.4	-	-	-

Policy/Regulation of waste treatments

1961 **Law for Disposal of Garbage [Clean-up]**

1978 **Law for Environmental Protection**

1986 **Law for Waste Treatment [Prevention,Recycling]**

1992.1 **Deposit Refund System**

1993.7 **Production Charge System**

[Manufacturer's responsibility]

1993 **Integrated Solid Waste Treatment Plan**

[Reducing, Recycling, Proper Treatment]

[Pre-prevention, Indirect Regulation]

1995.1 **Volume based Collection Fee(VCF) System**

1994.4 **Limiting disposable goods and shopping bags**

1995.4 **Ban of plastic coated paper**

1995.5 **Diminishing PS foam packaging**

1999.2 **Ban of disposables in restaurants**

(waste from fast-food store 25% decreased)

Purchasing/Refunding plastic bags

(Plastic bags 60% diminished)

1999.9 **Biodisintegrable(EDP 30%) VCF trash bags**

Deposit refunds of products

product items		deposits (Korean won) * 1 US$=1200 won on 1999
containers for drugs, beverage, butane gas, detergents	- paper milk containers	
	below 250 ml/ea	0.3
	above 250 ml/ea	0.4
	- metal cans/ea	5
	- glass bottles	
	below 100 ml/ea	1.5
	below 350 ml/ea	2
	above 350 ml/ea	3
	- **PET bottles**	
	below 500 ml/ea	4
	below 1,500 ml/ea	5.5
	above 1,500 ml/ea	7
batteries	-mercury/ea	120
	-silver oxide/ea	75
tires	- for trucks/ea	450
	- for passenger cars/ea	130
	- for motorcycles/ea	50
lubricating oils/ℓ		25
electric appliances	- TV sets/kg	38
	- wash machines/kg	38
	- air conditioners	38
	- refrigerators	38

Product charges

product items		Charges (Korean won) * 1 US$=1200 won, 1999
1. containers for insecticides, harmful chemicals	- below 500 ml/ea	7(insect.)/ 6(chem)
	- above 500 ml/ea	6(insect.)/ 11(chem)
2. cosmetic containers	- glass : below 30 ml/ea	1
	below 100 ml/ea	3
	above 100 ml/ea	4.5
	- metal/ea	4-8
	- plastic/ea	**0.7**
3. containers for cookies/ea	composite made of 3 matl.	6
	of 4 matl.	12
4. batteries	lithium, nickel/cadmium/ea	2
5. antifreezing solution/ℓ		30
6. luminescent lamps/ea		6-8
7. gums		0.27% of the price
8. paper diapers/ea		1.2
9. plastics	**- polyethylene & other 13 kinds**	**0.7% of the price**
	- polyacetal	**0.35% of the price**
10. cigarettes/pack		4

Volume based Collection Fee(VCF) System

- o MSW should be discharged in the designated plastic bags usable only within each areas
  - -7 garbage bags : 5, 10, 20, 30, 50, 75, 100ℓ
- o Waste collection fee included in the bag prices
- o Recyclable materials(papers, cans, bottle etc) not disposed in the bags
- o Violation fine 800$

Effect of VCF System

- o Diminish of MSW → 31%
  - MSW 1.5kg/day.person → 1.1kg
- o Increase of recycled materials → 56%
- o Big effect on packaging & manufacturing of industries

Ⅱ. Plastic Wastes

Plastic production and demand in Korea

(unit: 1,000 M/T)

resin	'89 production	'94 production	'98			
			production	export	import	demand
LDPE/LLDPE	288	996	1,352	604	17	783
HDPE	345	1,309	1,539	868	9	678
PP	539	1,611	2,064	1,160	11	921
PVC	465	791	1,080	255	64	861
PS	445	801	939	477	22	475
ABS	172	384	566	333	7	246
total	2,255	5,892	7,540	3,697	130	3,964

source: Korea Petrochemical Industries Association

Manufacturing of plastic products (1994)

(unit: 1,000 M/T)

resin	LDPE	HDPE	PP	PVC	PS	ABS	total
1. **films**	403	133	216	47			799
-greenhouse, mulching	(120)	(20)					
-heavy duty for fertilizer	(25)						
-shopping bags	(10)	(50)					
-trash bags		(25)					
2. injection	46	138	270		184	134	972
3. extrusion	84	147	195				426
4. blow	23	139					162
5. pipes, hoses		106		224			330
6. cable coating	21			67			88
7. fibers, textiles			79	7			86
8. calendering				266			266
9. toy, stationery, container, furniture					104	13	117
10. construction	14				70		84
11. **packaging**					43		43
12. others	32	20	30	104	54	46	286
13. **PET bottles**							70
total	623	683	790	715	455	193	3,529

source : Korea Plastic Industry Association

Amount of plastic wastes

o MOE data('97) : 820 thousand ton/y
(4.7% of MSW, recycling is excluded)

o Korea Resources Recovery & Reutilization Corp. data('94) :
near to 1,800 thousand ton

(unit:thousand M/T)

Resin	'94 wasted	'94 recycled
LDPE	442	53
HDPE	490	46
PP	538	62
PVC	317	32
PS	184	14
ABS	46	
PET	63	3
Total	2,080	277

Recycling

o Recycled fractions

(unit :%)

	‘94	‘97
MSW	15.4	29.0
Ind.waste	60.0	61.2
Papers	40	56.8
Metals	70	55.3
Glass	35	67.8
Metalic cans	9	48.9
Plastics	9	14.8

From : ind. waste 28.1%
construction waste 16.0%
MSW 1.4%

o Labeling onto plastic products

o Forcing use of recycled materials

- Korea Resources Recovery & Reutilization Corp.
- Korea Plastic Recycling Ass.
- Korea EPS Recycling Ass.

Ⅲ. R&D on EDP in Korea

1991	Foreign Starch-filled(<8%) biodisintegrable and photodegradable plastics introduced
1992~	Starch filled (<8%) biodisintegrable plastics by Samyang Genex Co., SK Corp., Sewon Co.
1990~	PHB/PHA pilot plant by Kohap Ltd.
1992~1997	National Project on EDP (Leader Y.H.Kim, KIST, 1.5M$)
1993.6~	Aliphatic polyester EDP by SK Chemicals
1993.11~	Aliphatic polyester and starch-based EDP by Saehan Ind.
1995~	Starch foam for loose-fill by Samyang Genex Co.
1996~	Starch/PCL EDP by SK Corp.
1996 ~	Aliph. polyester/Starch EDP by Hanwha Petrochemical
1996 ~	Starch/Aliph. polyester EDP by Daesang Corp.
1997 ~	Aliph. polyester by Ire Co.

No actual market for EDP

1999.4 **Korea EDP Association**
Headed by Y.H.Kim(KIST) & S.S.Im(Hanyang Univ.)
1999.6 **Planning biodisintegrable trash bags for VCF**
30% EDP content
-Advantage : Rapid stabilization of MSW at landfill
Decrease of plastics buried
-Creation of actual market, 6,000t/y

Ⅲ-1. Commercial EDP in Korea

A. Aliphatic Polyesters

Co.	Trade mark	Characteristics
SK Chemicals	SKYGREEN	-PET, polyester adhesives producer -butanediol, succinic/adipic acid -film, extrusion, blow, injection grades -m.p. 80-118℃, 5$/kg
Saehan Ind.	ESLON GREEN	-PET manufacturer -similar to above
Ire Chemical Co.	EnPol	-former SK Chem. staff - similar to above
*Samyang Co.	TRISORB	-PET maker -Medical, PGA suture -cowork w. KIST
Samsung Color Ind. Co.	KOMAGREEN	- Polymer compounding co. - aliphatic/aromatic polyester, various grades - compounds & mater batch, m.p. 65-130°C -compostibility w. reasonable price

B. Starch-based

Co.	Trade mark	Characteristics
Samyang Genex	BIOFIL	-Starch producer -modified starch foam for loose fill -water soluble, but enough compression and resilience at 32℃, RH 70% - cowork w. Hanyang Univ. - withdarwn from market
Daesang	REGREEN	-Starch producer -modified starch foam for loose fill -water soluble, but enough compression and resilience similar to EPS foam

C. Starch/aliphatic polyester blend

Co.	Trade mark	Characteristics
SK Chemicals	SKYGREEN	-blend to lower cost
Saehan Ind.	ESLON GREEN	-starch-based plastics
SK Corp.	GREENPOL	-oil, naphtha, plastic maker -PCL/starch blend -film, injection grades -4$/kg
Hanwha Petrochemical	ECO-PLAST	- naphtha, plastic maker - starch/aliph. polyester blend
Daesang Corp.	BIONYL	-starch producer -starch/aliph. polyester blend

Ⅲ-2. In development

D. Microbial Polyester

Co.	Characteristics
Kohap Ltd.	-PET maker -PHB/PHA by fermentation -pilot plant
KAIST/ LG Chem.	-PHB/PHA fermentation by recombinant E.Coli -high productivity and polymer content

Ⅲ-3. Miscellenous

Co.	Characteristics
KIST/Kolon	-polylactide
Univ.	-aliphatic polyesters -starch -chitosan

26. R & D of Environmentally Degradable Polymers in China

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1. The Production and Consumption of Plastics in China

In China, the production and consumption of plastics has increased rapidly along with the economical development and the improvement of people's standard of living. During the past 10 years (1990-1999), the average annual growth rate is 15.32% in the production of synthetic resins and 18.95% in the manufacture products. Thus the total production of synthesis resins reached 6,756 kt in 1998, which made China the fifth largest production country after United States, Japan, Germany and Korea. The consumption of plastics has increased in concert with its production. Now plastics along with steel, wood and ceramics are the four pillar materials, playing an increasing important role in various national economies.

Still, there remain some problems in the manufacturing of plastics in China:

1). The product mix is inappropriate. Products are disproportionately more for general use than for special use. Most of these products are of low grade. For advanced plastic products that meet the requirements of special professions, we still rely on import, while products for general use have been overproduced and been piling up. Therefore, in 1998, the volume of the five major plastics (PE, PP, PS, PVC and ABS) imported reached 8,185 kt.

2). The production cost is high, the price system is inflexible and the ability for meeting market contingencies is poor.

3). The quality of some of the products lacks consistency.

2. Survey on plastic wastes and policy of its disposal in China

At present, the per capita production of municipal solid waste (MSW) in Chinese cities is about 440 kg/y. The total amount of MSW in urban areas in China was 110,000 kt in 1997 and has increased at an annual rate of about 8 %~10 % to 150,000 kt in the year 2000, adding industrial waste the last figure will be a tremendous 600,000 kt.

According to relevant statistics, the plastics used for packing purposes are about 4,000 kt in 1998; of this, 30% or 1,200 kt belong to the category "hard-to recycle". Two other sources add to the latter category, i.e. agricultural mulching film waste (400 kt) and daily and medical plastics waste (400 kt), making a total of around 2,000 kt. In Beijing, Shanghai and Tianjin, the plastics waste is about 3-7 wt% and 10-20 vol% in total MSW (municipal solid waste).

Because the disposal facilities of MSW in China are inadequate, and the formulation as well as the implementation of the relevant state laws and regulations are not strict, only 10% of waste plastics are recycled and reused, and only 25%~30% are incinerated or buried in depth. The remaining 60% are not treated safely, some are simply abandoned or stacked wantonly, some are even dumped in rivers, lakes or the sea. The details are as follows:

- Deep Burial (Landfill): Safe deep burial is considered to be an efficient wall of disposing waste plastics. However, whether or not it affects the environment is still unclear. It is commonly thought that waste plastics are not easy to degrade under the ground, so they do not produce any harmful percolate themselves. However, additives such as compounds of heavy metal used in processing of plastics, and organic substances such as food residues on the plastic packing will produce some percolate. If percolates are not properly collected, the ground water will be seriously polluted. Moreover, since general plastics are uncompressible and non-degradable, landfills take up lots of precious arable land.

- Incineration: Due to the fact that plastics and oil produce the same calorific value when they are burned, and the volume of the waste plastics is reduced by at least 90% after being burned, incinerating plastic wastes to generate electricity is considered as one of the best choices for waste plastics management. However, garbage incineration is only in a preliminary stage in China, though a few large incinerating factories are being built in big cities.

- Recycling, Regeneration and Reuse: Since natural resources and energy are scarce and exhaustive, recycling, regenerating and reusing of plastic wastes are exceedingly important. In addition, the amount of pollutant produced is much less in the recycling of existing material than in the original manufacture. Therefore, this method has been greatly encouraged in China. However, so far in China most of the enterprises involved in the regeneration of waste plastics are small or medium-sized village and township enterprises, lacking technical expertise and short in funds. Since these enterprises are large in number and scattered all around, it is not so easy to apply environmental control and management. It has to be admitted that they have brought about, to a certain degree, pollution to the rivers and harm to the health of employees.

- Wanton Stacking. The direct consequences of this irresponsible behavior is that: the total waste plastics and other domestic dust in China have been piled up to 600,000 kt, occupying over 500 km^2 of precious arable land, with almost 2/3 of the cities (more than 200 cities) being surrounded by garbage. This dose not only seriously pollute surface and ground waters, endanger the cities environment and people's living conditions, but also hinders further development of urban and rural areas.

Lately, problems of plastic wastes pollution (also called "white pollution", referring to harms to outlook or to natural landscape of cities and destruction to ecological environment caused by wanton disposal of plastics used in packing and agricultural films) have become extremely serious in China. For instance, the output of plastic production in Shanghai is about 600 kt/y, around 10% of the state's total. Daily consumption of plastic bags and non-reusable fast food containers are about 6 million and 600 thousand pieces, respectively, and daily generation of waste plastics is over 700 tons. In Beijing, it is estimated that there are 2.3 billion pieces of plastic bags (with a total weight of 18.7 kt) in household trash and 6.75 km^2 of used agricultural films (3.0 kt) in suburbs each year. This problem has drawn great public and government concerns. The relevant authorities at all levels in China have all listed this problem as one of priority. The Environmental Protection Bureau of China has worked out a basic principle for the resolution of white pollution. That is "to educate the public, to strengthen management, to promote recycling and reusing, and to produce degradable materials."

In many cities, white pollution mainly refers to wanton abandoning of plastic packing materials and foamed plastic boxes for fast food, which cause "visional pollution" and "potential harm". At the moment, the "visional pollution" has evoked strong repercussions in the public, while the "potential harm" has not yet drawn the attention of most people. Since 1995, dozens of local governments in China have issued local prohibition of foamed plastic fast food boxes. For example, recently, Shanghai municipal authorities issued a regulation of banning this type of plastic box with a series of practical measures. During the past five years, degradable plastics has been gradually introduced in many cities to replace the polystyrene-formed products. In Beijing, the authorities announced that the recycling of wasted plastic food boxes must reach 30%, 50% and 60% in 1998, 1999 and 2000, respectively.

Although the implementation of prohibition alleviated "white pollution" to some extent in certain areas, practice has shown that prohibition alone can not thoroughly solve this problem. Since most of the substitutions such as paper tableware or degradable tableware are not recyclable and have to be buried after use, it puts a heavy load on burial treatment. Secondly, the prices and durability of the substitute materials can not compete with general plastic products. Therefore there is a long way to go for reaching the goal of the prohibition

3. Current situation on research and manufacturing of environmental degradable plastics (EDPs) in China

3-1 Research and Production

Since photo-degradable plastics was developed in some of universities and research institutes in 1970s, the production of degradable plastics in China has undergone following development stages. From the 70s to the middle of 80s, additive-style photo-degradable plastics was developed by adding photo-sensitizing agents to ordinary PE; From the middle of 80s to the middle of 90s, the application of above-mentioned plastics was extended. From the end of 80s to 1995, a new technique of blending starch to ordinary PE to form biodegradable plastics was introduced and developed. Up to now, quality of various photo-degradable, biodegradable, photo-biodegradable plastics has been greatly improved and the costs relatively reduced. Meanwhile, mechanisms of chemical degradation such as thermal-oxidative degradation and other additives have been introduced to the research of above degradable plastics. Some universities and research institutes started to study artificial materials which are thoroughly biodegradable, such as polyhydroxyacid (Qinghua University, Beijing and The Institute of Microorganism, Chinese Academy of Science etc), polylactic acid (The College of Light Industry of Beijing, Chengdu Institute of Organic Chemistry, Chinese Academy Science etc) and polycaprolactone/polylactide copolymers (Beijing Institute of Chemistry, The Chinese Academy of Science) et al. Some research institutes have tried to use cellulose recovered from straw, wheat straw and bagasse as raw materials to develop degradable ground film and urethane foam. For example, lab work has also been done in Fudan University to extract tannin from bark of Arcacia Mearnsi and to use tannin and/or bark to synthesize biodegradable polyurethane foam. Since foamed polyurethane containing tannin can be decomposed by microbial, it has large potential applications to packing materials, thermal insulation materials etc. Fujian Normal University developed degradable plastics containing ultra-fine $CaCO_3$ particles, which were found to be able to promote biodegradability of the plastics and reduce the necessary amount of photo-sensitizer in the products.

In recent years, the production of degradable plastics has grown rapidly in China as over 100 raw material production lines have been installed producing starch blended plastics, photo-degradable plastics, and photo-biodegradable plastics etc. The total production capacity is about 100 kt, and the current production is near 30 kt. The applications field includes package, agriculture, daily and medical products etc. The principal corporations producing degradable plastics in China and their capacity (t/year) are as follows. Tianjin Dawnhalo Appliances Inc (30,000), Jilin Jinyin Industrial Co. (10,000), Nanjing Sushi Degradable Resin Co. (7,000), Ling Xia Huaxi Degradable Plastics Co. (2,000), Shengzhen Desiree group (China) Co. (1,000), Shenzhen Luwei Co. (1,000), Huizhou Huanmei Products of Degradable Resin Co. (1,000) and Hainan Tianren Products of Degradable Plastics Co. (1,000). Among the manufactures, Tianjin Dawnhalo Appliances INC, who produces "Starate" starch-base biodegradable series products, is one of the largest. In its products, the content of starch in packaging film is over 50 %, and in seeding pots and injection module reaches 60-80 %.

3-2 The society and its activities

The Chinese Society of Degradable Plastics attached to the Plastics Engineering Association of China was founded in July 1993. The activities of the society has focused on the follows:

1) To track R & D of degradable plastics both at home and abroad.

2) To organize conference and promote information exchange in the field of plastics at home and abroad. During 1992-1996, the society invited eight well-known foreign professors and experts in the field to attend the workshops of degradable plastics in China presenting lectures in China.

3) To edit and publish newsletters of the society.

4) To study the methods of test-evaluation and standard for degradable properties.

3-3 The related standards

The following four standards related to Biodegradable Plastics and its products have been issued in China.

GB/T 18006.1-1999	《The General Technical Conditions for One-Off Degradable Dinner Sets》
GB/T 18006.2-1999	《The Methods of Testing One-off Degradable Dinner Sets》
QB/T 2461-1999	《The Standard for Degradable PE Film for Packaging Purposes》
HJBZ 12-2000	《The Technique Demands for Degradable Packaging Products of Plastics》

4. Development Prospect of EDPs in China

Although various EDPs products have been developed in China after 20 years of research efforts, in terms of the production volume and application fields, the industry of EDPs as a whole is still in a delicate situation. However, it is encouraging to see that a new member of plastic family — EDPs has been used in trash bag, purchase bag, packing material and agricultural ground film et al. In spite of the fact that they can not degrade thoroughly in environment, EDPs, with the ability to decrease their weight and to compost, is still regarded by Chinese State Bureau of Environmental Protection and People as one of the environmental favorable products.

There has been an argument on the long-term effect of using polyolefine-based degradable (or more strictly 'disintegrable') mulching film on the soil quality. By having tracked the use of mulching films on a large scale in China, The Soil and Fertilizer Institute of Chinese Academy of Science, recently reported encouraging results about the long-term effect. The report says that in the fields where mulching film has been used for over ten years, no clear effects on the contents of the nutrition elements of N, P or K as well as the metal elements such as Cr, Cd, Co, Cu etc have been found. Besides, as long as the waste mulching film broke into cracks smaller than about 16 cm^2, the accumulated remnants in 20 years, have shown a little effect on the soil quality such as capacity, composition and water activity etc and consequently no harm effect on crop's growing.

To promote wide use of EDPs in China, following efforts should be done immediately by the government, research institutes and manufactories jointly. i). To work out reliable and feasible ways of characterization and appraisement of EDPs; ii). To put special sign on EDPs products to differentiate it from normal plastics; iii). To set up a complete set of methods of garbage treatment. For the best way to accelerate degradation of EDPs is to compost it with livelihood wastes and become resource again; iv). To upgrade technical level of EDPs and to reduce production cost.

There is a large demand for EDPs in China. For the time being, the annual per capita consumption of plastics is only about 5-6 kg, much less than that in the industrial countries (around 60 kg), and less than the world average 17.5 kg either. Particularly, the market for agricultural film, packing film and disposable tableware will be huge. The demand for agricultural film wills estimably reach 1,000 kt in the year of 2000. However, the total output value so far is only 400 kt each year. If EDPs can be used to bridge this gap or even substitute for a part of original agricultural film, there will be a tremendous need for EDPs. The consumption of plastic packing materials will increase to 5,000 kt in 2000. If 25% of them are disposable ones, the annual need will be 1,250 kt. If EDPs can be used instead, it will be much easier to solve the problem of pollution caused by random disposal of plastic bags that are difficult to recycle. In short, once the application fields are well developed, the market potential for EDPs in China is huge for sure.

27. Management of Plastic Waste in Taiwan

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Plastics waste has become the common problem worldwide since the industrial revolution. Consequently, the management of plastics waste becomes a critical issue in Taiwan like the rest of the global community.

According to the 1998 statistics, the annual plastics consumption in Taiwan is 3 million tons, equivalent to annual consumption of 135 kg per person. Bearing the characteristics of being non-degradable and not readily treated, the plastics waste not only pollutes the environment, it also consumes resources. Currently, one of the major solutions to the above problems is to recycle the plastics waste. According to the 1998 Taiwan EPA's statistics, the total treatment volume for the plastics waste containers is approximately 56,000 tons during the period of 1997.6.1 and 1998.8.31; with 80 companies in the recovery business and 16 companies in the reuse business; the materials involved include PET, PS foam, PS, PVC, PP/PE, etc.

For the purpose of better understanding the management strategy for the plastics waste recycling in Taiwan, this paper first examines the progress of the regulations and system for the recovery and treatment of the plastics waste. Next it studies the norms for the participants involving in the business of various kinds of plastics waste, especially for containers, under the current regulations. Then it analyzes the whole recycling mechanism, the future development, and the problems lying under the current recovery/treatment system for the various plastics waste containers. On the other hand, yet there are no mandatory promulgated regulations for degradable plastics waste. However, it has been officially included as an eco-labeling product, as the product from plastics recyclate has.

Management of Plastic Waste in Taiwan

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Background

•Landfills and incineration plan are strongly protested by local residents, the discharge volume of solid wastes is enormous, the burden of environment protection are getting serious.

•Plastics consumption: 3 million ton / year
Personal consumption : 135 kg/ person (Taiwan,1998)

•Source recycle and reuse can reduce burden of environment protection and cost of waste disposal.

•The management of plastic waste is critical issue and legislation should be a high priority.

Contents

- ➢Development of the Recycle Framework and its Regulations

- ➢Obligation for Community under Government Regulations

- ➢ Mechanism of Recycle Markets

- ➢Green Procurement and Green mark

Development of the Recycle Framework and its Regulations

1.Development of the Stages

❮Initiation Stage❯ System's formation

- ● Focus: to increase the items for recycling
  promulgating to recycle the PET bottle (January, 1989)

❮Integration stage❯ Integration

- ● Focus: integration of recycling methods and organizations

  Promulgation the act for recycle, clearance, and treatment for general waste containers (April, 1994)

❮Confirmation Stage❯ Four- in- One integration

- ● Focus: Confirmation of the recycle framework

  Promoting EPA's "Four- in- One Project" (March, 1997)

Development of the Recycle Framework and its Regulations

2. Progress of the **Four-in-One regulations**

1998.1.8 Promulgation: recycle rate and fee rate for recycle, clearance, and treatment for general articles and containers

1997.12.26 Promulgation:Define Businesses and Products that need to be recycled, cleared, and treated

1997.8.6 Promulgation :Acts for recycling, clearance, and treatment for general articles and containers

1997.3.11
- Waste Disposal Act Draft were amended
- "Four-in-One Project" Started

Regulations

Development of the Recycle Framework and its Regulations

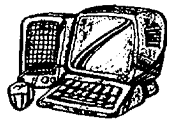
3."Four- in- One Project"

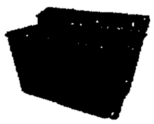
Local government clean up teams)

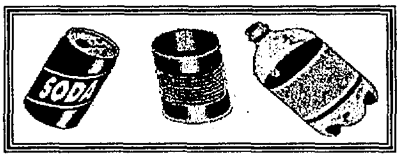
Houses, communities

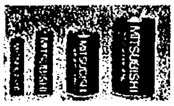
Civilian organizations for resource recycling

Foundation Board Committee









providing incentives and designed for all citizen's participation

“Four- in- One Project”

❮Essence❯

- Government provides incentives, rewards and other feedback for waste sorting and recycling in communities
- Government promotes resource recovery in association with local government clean up team, civilian organizations for resource recycling, and Foundation Board Committee

❮Operational module❯

- Foundation Board Committee acts as a commandment center to introduce economic incentives into market’s mechanism, such as charge rate, subsidy, recycle reward fee, etc.
- Integrate manufacturing system and resource recovery system to open the closed collection channels in the past

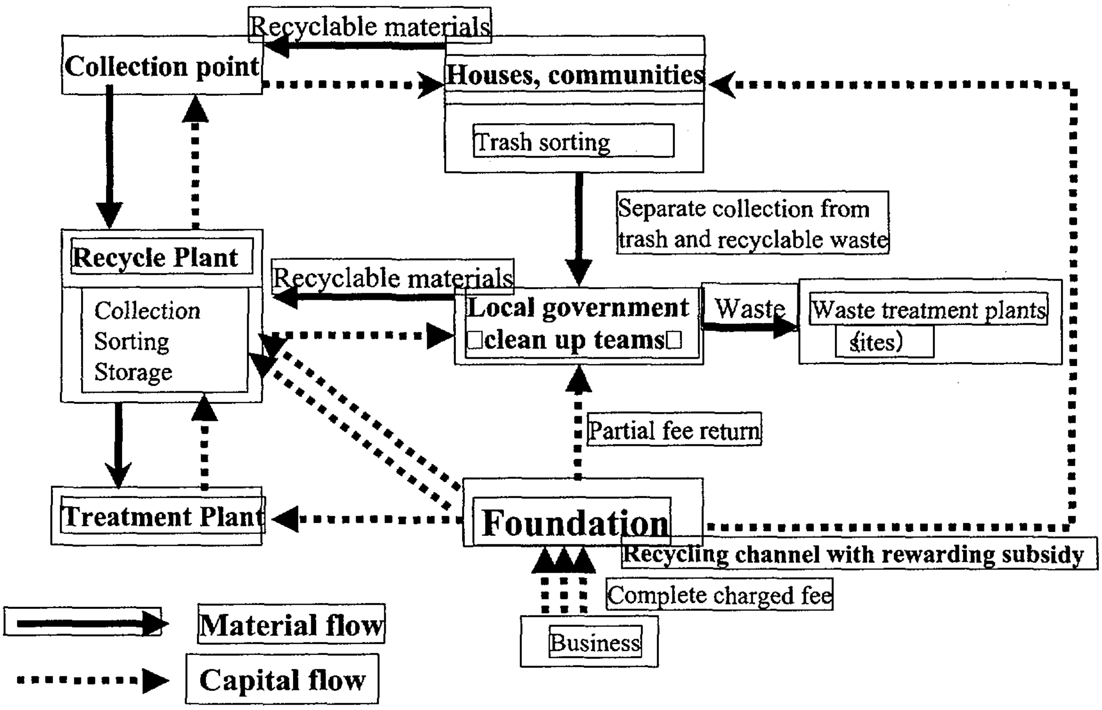
“Four- in- One Project”

❮Objectives❯

- **The announced businesses of containers are to pay the fee for recycle, clearance, and treatment disregard the targeted recycle rate**
- **All legal applicants can apply for subsidy according to the certified amount of waste containers without limitation from targeted recycle rate and contracted resource recovery organization**
- **In the collecting process, the executive units follow waste categorization regulations and eventually to separate resource materials from waste completely**

Development of the Recycle Framework and its Regulations

4.Flow chart of Four-in-One Project



Obligation for Community under Government Regulations

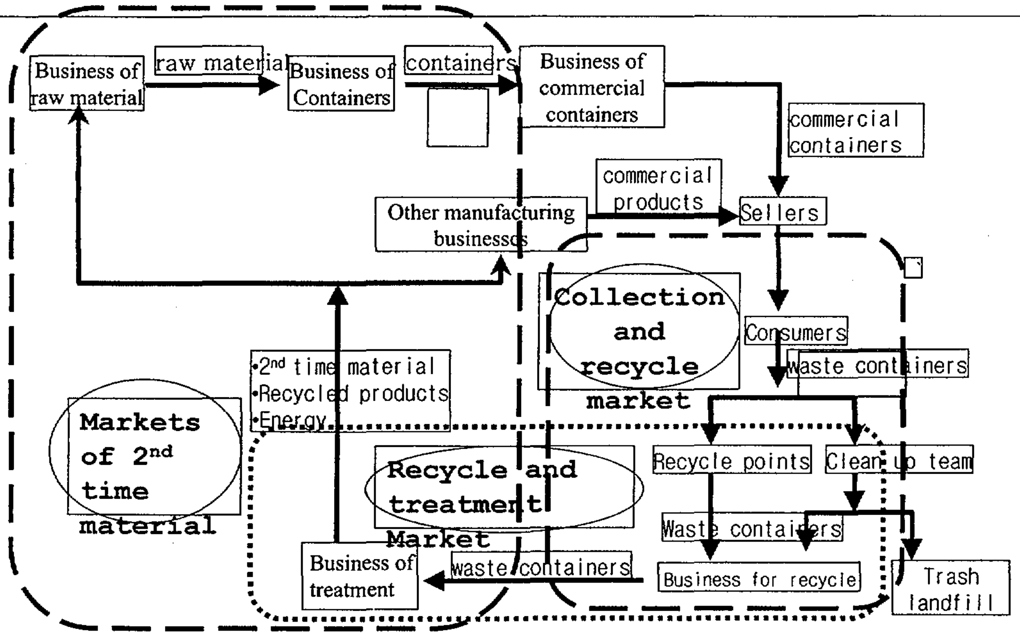
Community	Obligations
Raw material business	No regulations yey
Manufacturers, importers, and Containers users	•Force businesses to include the cost for recycling in the production process consideration •Use less and more recyclable material during in the design •Mark recycle number.
Sellers	•Setting up related recycle facilities
Resource recycle organizations	•Setting up recycle points •Treatment the recyclable materials

Obligation for Community under Government Regulations

Community	Obligations
Local government (clean up team)	•Were asked to separate resources from waste in the collecting process.
Foundation Board Committee	•Decide the fee rate or subsidy •Report the recycle, clearance, and treatment fees and audit the payments •Plan and promote the recycle, clearing and treatment system of waste containers
Auditing and certifying office	•auditing and certifying to ensure a right management of the recycle of waste containers
Consumers	•No regulations so far •Encouragement to recycle

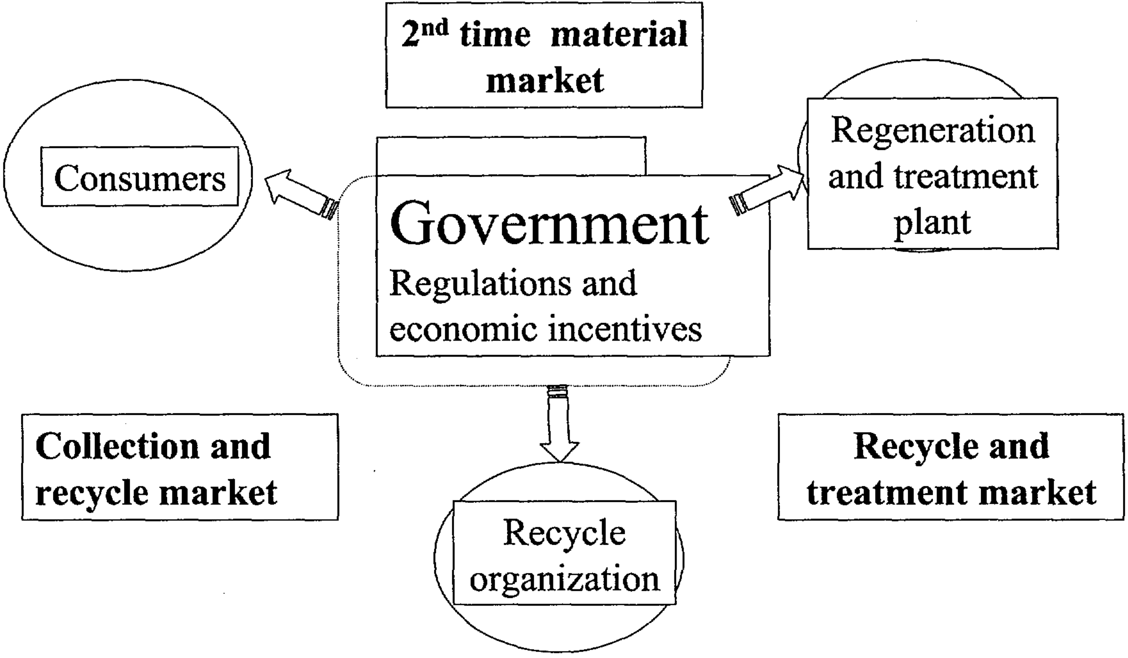
Mechanism of Recycle Markets

1. Life Cycle of the Production, Consumption, Recycle and Disposal



Mechanism of Recycle Markets

2. Relationship among the three markets

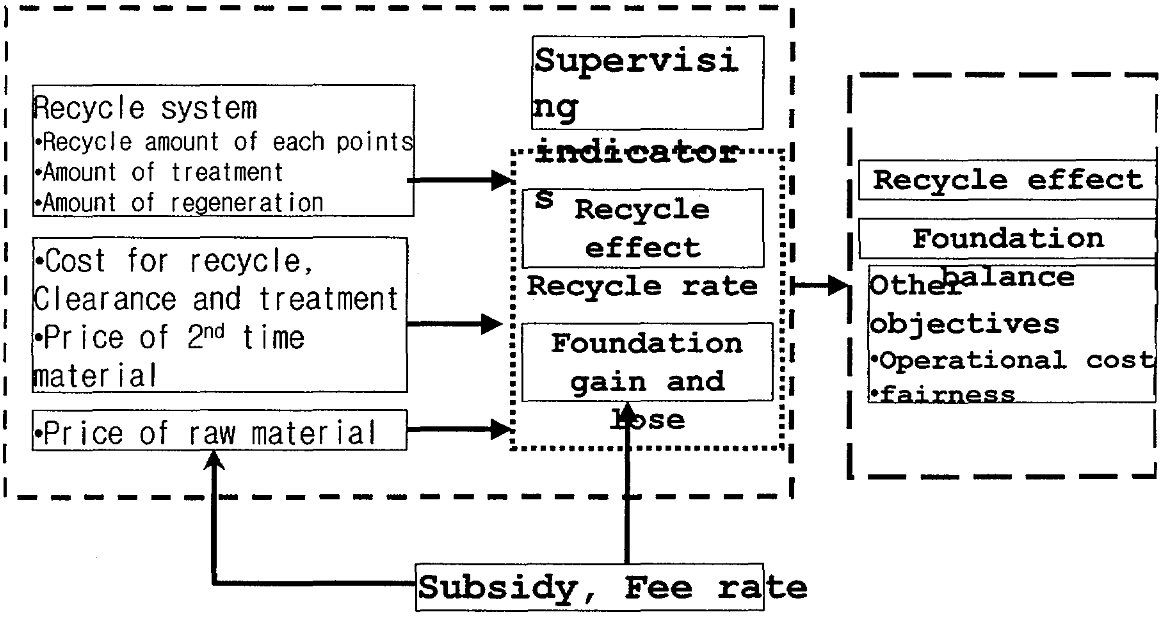


Mechanism of Recycle Markets

3. Fee rate and subsidy-- Construction of recycle market mechanism

	Fee rate	Subsidy
Object/Rate	Payers and amount of the fee rate	•Consumers, recycle business, treatment plant, 2nd time material market •Subsidy rate
Possible problems	Fake reporting or avoid reporting	•Ineffective management • Can not obtain practical operation data •High cost
Subsidiary manners	•Honest reporting •Setting up auditing system •Punishment mechanism	•Bidding, honest reporting, •Evaluation of the system for recycle, clearance and treatment

Mechanism of Recycle Markets
4. Supervising indicators and adjusting mechanism



Recycle system
- Recycle amount of each points
- Amount of treatment
- Amount of regeneration

- Cost for recycle, Clearance and treatment
- Price of 2nd time material

- Price of raw material

Supervising indicators

Recycle effect

Recycle rate

Foundation gain and lose

Recycle effect

Foundation balance

Other objectives
- Operational cost
- fairness

Subsidy, Fee rate

Mechanism of Recycle Markets
5.Long term strategy

❮policy objectives❯

- Waste minimization
- Regeneration (material, chemistry, and energy)
- Compatible with environment
- Improved technology and low operational cost

❮Suggestions ❯

- Levying tax from the original material sources
- Moral obligation(package based on LCA design)

Mechanism of Recycle Markets

6. Fee rate of recycle, clearance, and treatment of plastic container

items	*fee rate*
PET	(1) 13.01[$NT/Kg] (2)Body of the bottle with multiple materials 14.01[$NT/Kg] * recycle reward fee 0.7 $NT / bottle
PVC	(1)19.55 [$NT/Kg] * recycle reward fee 0.7 $NT / bottle
PP/PE	(1)9.39 [$NT/Kg] (2) Body of the bottle with multiple materials 10.39 [$NT/Kg]
Other plastics	(1)9.39[$NT/Kg] (2) Body of the bottle with multiple materials 10.39 [$NT/Kg]
PS	Body of the bottle with multiple materials,9.39[$NT/Kg]
Foaming PS	37.29 [$NT/Kg]

recycle reward fee 0.7 $NT per unit bottle
1 $NT per unit bottle, calculated based on 70% of real selling amount

Mechanism of Recycle Markets

7. Subsidy of recycle, clearance, and treatment of plastic containers

Unit: [$NT/Kg]including tax)

Subsidize to Materials		Recycle and clearance organization	Recycle plant
Waste plastic containers (PET)	beverage	10.11+18.40(RRF)	----
	Mineral water (large)	11.55+21.02(RRF)	----
	Mineral water (small)	18.79+34.19(RRF)	----
	Soy sauce	9.46+17.22(RRF)	----
	Others	13.00	----
Waste plastic containers (PVC)	Mineral water (large)	15.00+16.69(RRF)	----
	Mineral water (small)	19.39+31.29(RRF)	----
	Others	10.00	4.00
Waste plastic containers (PP/PE)		10.00	----
PS containers Without foaming		----	12.00
Other plastic containers		----	10.00
Waste PS foaming containers	remote areas	38.00	7.00
	Other areas	35.00	

Mechanism of Recycle Markets

8. Number of recycle and treatment companies and total recycle amount

Materials		No. of recycle companies (1998)	No. of treatment companies (1998)	Total amount (Kg) (1997.07~1999.01)
Plastics	**PET**	74	16	42,214,203
	Foaming PS	37		3,336,917
	Non Foaming PS	33		100,677
	PVC	72		4,652,574
	PP/PE	72		5,880,918

Green Procurement and Green Mark

1. Green Mark- Taiwan's Eco-labeling

Governmental institutes are requested to priority purchase products with green marks

- Products with green mark are applicable to "Act of prior procurement of environmental friendly products"
- These products possess 10% price difference

Green mark

- with recyclable materials,
- can be regenerated
- low pollution
- energy saving

Green Procurement and Green mark
2.Degradable plastics

Domestic regulations

- No regulation is enacted for compulsory use
- Government promotes degradable plastic as items for environmental protection reward

Test standards

- ISO 14851
- ISO 14852
- ISO 14855

Green Procurement and Green mark
3. Degradable plastics in Taiwan

- **EYA-GE Inc.-Developed light degradable plastics in 1992.** Due to unstable demand, its manufacture is now based on customers' requests
- **Hing-Li BioTechInc. □former Ze-Sen Inc.□**

  — starch thermoplastics as major materials

  one pilot production line only, the second line is under construction, six line in total are scheduled in the early developmental stage, total production can reach 9,000 tons.
- **Swen-Ghu Inc, subsidiary of Tai-GE Inc, produces light degradable plastics**

  plastic bag and film based on customers' requests. Raw materials are developed and supplied by Tai-GE

Conclusion

☞“Four-in- One” Action (1997.7~1999.1)
Total treatment volume of plastic container: ~57,000ton
Recovery business : 80 companies
Reuse business: 16 companies
Recycle plastic material: PET, PE/PP, PVC, PS, PS Foam

☞The problems in “Four-in- One” project, need all parties to participate with honesty and responsibility to create a win-win opportunity for industry and environmental protection

☞Green procurement regulation- Degradable plastics and plastic recycled are eco-labeling product,with high priority purchase by governmental institutes.

28. Environmentally Degradable Polymers and the Potential for its Application in Singapore

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Abstract

First-generation environmentally degradable polymers (EDPs), which were commercialized in the 1980s, did not satisfy the public and scientific communities' view of complete degradation. Subsequently, new natural and petrochemically based plastics have been introduced and promoted as completely biodegradable by research and industrial concerns in the 1990s. These new polymers, however, were much higher priced than the commodity polymers typically used. Today, continued development of these biodegradalble polymers has been towards bringing down manufacturing costs by increasing production capacity, improving the processing technology, and using low-cost feed-stocks. Legislations and tax incentives favoring "environmentally friendly materials" such as degradable plastics are being increasingly introduced into North America, Japan, and Europe. Industrial motivation has originated from consumer products industries, which in recognizing the growing public awareness of environmental issues has also lead to a high demand for "environmentally friendly" products. Although, incineration and landfilling continues to be a primary means of waste management for countries such as China, and South Korea, environmental accountability associated with these methods has shown EDPs to be a very desirable option for the future. Singapore has the potential within the international framework of the United Nations Industrial Development Organization to include EDPs in their current solid waste management strategies.

Introduction

Realization is growing, that the use of long-lasting polymers for short-lived applications is not entirely justified, especially when there is greater concern for the preservation of living systems on earth. The elimination of waste plastics is therefore of a great interest for a number of industries, such as packaging, agricultural, fishing, medical, hygiene and cosmetics, food etc. (Colvin 1995). Environmentally degradable polymers (EDP's) represent a potential solution for managing problems concerning the global environment and solid waste administration (Swift 1993, Abbey 1996). Polymers lose their physical properties over time either via a chemical process, e.g. hydrolysis and oxidation, or by the action of microorganisms and enzymes, or a combination of both. Biodegradable, by definition, means that the targeted polymer loses its properties in an environment with microorganisms (cells, bacteria, etc.) and that the macromolecules are broken down to a molecular level (Albertson 1994). The biologically driven degradation process for polymers of a natural or synthetic origin is a function of the chemical, biochemical, physical and biological factors listed in Table 1. The degradation of polymeric materials has been defined by Vert et al (1992): "Polymers undergo changes, which are the result of chemical, physical, and biological interactions between active living environment and the material". In the terrestrial and aquatic environments, the properties of the soil and water play a key role in the biochemical activity of microorganisms; and therefore in the environmental biodegradation process of natural and synthetic macromolecules. Over the last two decades a great number of petrochemically-based polymers with a wide variety of chemical and physical properties have been synthesized, guided by the need to substitute products made of natural macromolecules. A number of excellent books (Vert et al 1992, Ching et al 1993, Griffin 1994, Doi and Fukuda 1994,) and reviews (Jane 1995, Swift 1997) have reported on the ongoing research of biodegradable polymers for biotechnological applications. It is the aim of this paper to give the reader a general overview of EDBs made from petrochemical (synthetic) or renewable (natural) sources. The second part will discuss the resources and infrastructure of Singapore to implement EDPs in its current solid waste management scheme.

Polymers of a Synthetic Origin

Poly (vinyl alcohol), obtained by the hydrolysis of poly (vinyl acetate) is the only synthetic carbon chain polymer accepted as being fully biodegradable. However, poly (vinyl acetate) hydrolyzed to less than 70% is non-biodegradable under conditions similar to polymers that biodegrade when fully hydrolyzed (Matsumura et al 1988, 1998). The biodegradation mechanism has been defined as a random chain cleavage of 1,3 diketones formed by an enzyme catalyzed oxidation of the secondary alcohol functional groups in the polymer backbone. Yamamoto (1966) first observed biodegradation as a reduction in the aqueous viscosity of a polymer in the presence of soil bacteria. At present a great number of bacterial strains (*Pseudomonas*, *Flavobacterium*, *Acinetobacter* (Fukunaga, 1977)), as well as fungi, moulds and yeast are identified to have the ability to break down poly (vinyl alcohol) to a molecular level. Studies by Casey (1976) and Wheatley and Baines (1976) conclude that over 90% of poly(vinyl alcohol) entering wastewater treatment plants are removed. Hence, environmental pollution by this polymer group is not likely.

Lester et al (1988) reviewed the application of poly (carboxylic acids), which are commonly used in detergents. However, only carbon chain oligomers are likely to be biodegradable, regardless of functionality (Potts et al 1973, Suzuki et al 1978, and Kawai 1993). Hence, all efforts to synthesize degradable poly (acrylic acid) and co-poly (acrylic/malice acids) failed. Biodegradable carboxylated polymers have been based on combining low molecular weight oligomers through degradable linkages and by introducing weak links into the polymer backbone (Baur et al1993, Irie 1993). Also scientific proof of total degradability of these polymers has yet to be published.

Table 1 Factors determining the biodegradation of polymers from petrochemical and renewable sources

Polymers of Natural and Synthetic Origin	Environment (Soil, Water, Air)	*Microorganism*
• Chemical structure • Molecular weight and molecular weight distribution (polydispersity), • Presence of low molecular weight components (monomers, oligomers, solvents, softeners, etc.) • Hydrophilicity versus hydrophobicity • Presence of ionic groups and of side group defects • Manufacturing procedures and their process parameters, • Morphology (amorphous versus semi-crystalline, presence of microstructures and stress within the polymer parts, surface area • Tempering, • Storage	• System stability and kinetics • Pressure • Energy transfer (temperature, light, etc.) • Gas concentration (oxygen, carbon dioxide, etc.) • Moisture • Salts and metals (type and concentration) nutrients • pH	• Organism/cell type: aerobic, anaerobic, facultative, specific versus non-specific metabolisation process, metabolisation inhibitors versus inducers • Enzymes: type, location (intra- versus extra cellular), concentration, kinetics

The chemical linkages of polymers with a heteratom chain backbone, such as polyesters, polyamides, polyethers, and polyacetals are copied from natural polymers papers (Kaplan 1993). Consequently, polymers of this chemical structure are truly biodegradable. Medical grade aliphatic polyesters have been used for the design and fabrication of sutures and medical devices for more then three decades (Hutmacher 1996). The application of polyesters for commodity products has been delayed until now due to their high cost. With cheap lactic acid becoming available from the fermentation of waste agricultural products (derived from plants such as corn, wheat, beets and rice), there has been a surge of activity to develop new polymerization methods and to find biotechnological applications for this polymer group (Suzuki and Tokiwa 1977, Kim 1994). Though still more expensive than common commodity polymers, the introduction of products for niche markets such as agricultural films and mulch has been advocated by the biodegradable polymer society for many years.

There are many patents being issued for the synthesis and processing of homo- and copolymers, principally from a few corporate players, Cargill (Benson, 1992, 1993), Dupont (Ford, 1992, 1993), Mitsui Toatsu (Kitamura et al, 1992, 1993), and Battelle Memorial Laboratories (Sinclair et al, 1992). Other companies/organizations with noted activity in this area include Shimadzu and Argonne National Laboratories.

Recently, the joint venture company of Cargill and Dupont, namely Cargill Dow Polymers LLC, has been the first enterprise, to successfully commercialize aliphatic polyester for environmental applications. Cargill Dow Polymers LLC uses their patented NatureWorks™ technology to produce poly (L-lactid) (PLA). Natural sugars (derived from corn) are fermented to manufacture lactic acid, a common food additive. Through a special condensation process, a cyclic intermediate dimer, referred to as a lactide, is formed. The monomeric lactide is purified through vacuum distillation. Ring opening polymerization of the lactide is accomplished with a solvent-free melt process. A wide range of PLA materials that vary in molecular weight and crystallinity can be produced. At present, films, foams, fibers and textile products are produced in a market development facility. In 1999, Cargill Dow Polymers LLC started building a manufacturing plant in Nebraska, which has a maximum output of 250,000 tons/year and will be fully operational in 2003.

The potential applications of aliphatic-aromatic copolyesters as EDPs have been studied only for a number of years (Witt 2000). This copolyester group offers to synthesize EDPs with different biodegradation kinetics and mechanical properties based on the aromatic component content. BASF has developed and characterized a group of EDPs with a chemistry based linking of statistical copolyester units such as 1,4-butanediol and the dicarbonic acids, adipic acid and terephthalic acid (Witt 2000). The polymers are commercialized under the trade name ECOFLEX.

A polymer group (Takiyama and Fujimaka, 1994; Taniguchi et al 1993) at Showa High Polymer has developed a new type of aliphatic polyester marketed under the name BIONOLLE®. Studying the literature and patents it can be concluded that BIONOLLE® is synthesized from aliphatic dicarboxylic acids and glycols via polycondensation. Coupling with a polyisocyanate is used to increase the molecular weight. Yokota et al (1994) concludes that the skeletal structure of BIONOLLE® is similar to that of PHB/V or PCL. Nishioka et al (1994) characterized the biodegradation properties of four different grades of BIONOLLE® in sludge's, soils and compost. Today, the polymer is used in films, foams, and other products by several Japanese commodity companies (Table 2).

Polymers of Natural Origin

Natural polymers are synthesized by a living organism. The most widespread natural polymers are the polysaccharides, such as cellulose and starch. Other important groups of natural polymers are polyesters such as polyhydroxyalkanoates, protein based such as silk and poly (glutamic acid), and hydrocarbons such as natural rubber. Bryom (1991) edited a recommendable book in which different international authors report and discuss the state of the art of natural polymer properties and applications. Another excellent and detailed information source is a review on biodegradable polymers by Lenz (1993). At present, a great number of natural polymers are not suitable for biotechnological applications, either because they lack the property requirements or are too expensive for anything other than specialty high value niche markets such as medical applications, which are discussed by the author in other chapter of this book.

Polysaccharides

Polysaccharides are largely limited to starch and cellulose derivatives for biotechnological applications, either in thermoplastic or as water-soluble polymers (Buchanan 1993). High molecular weight starch as well as cellulose is composed of thousands of D-glycopyranside repeat units. However, the difference in structure of cellulose and starch determines their chemical and physical properties (Jane 1995). Microbial synthesized carbohydrates such as xanthan; curdlan, pullulan, hyaluronic acid, alginates, carageenan, and guar are used in the food and cosmetics industry, where more costly raw materials can be justified. For example, xanthan is used in the food industry and as thickener in many industrial applications; more than 14,000 tons of it is produced annually.

Green plants use starch as their main form of carbohydrate storage. Hence, starch is the second largest biomass produced on earth. Natural polymers are made up of six-member-ring glucose units, are semicrystalline and have molecular weights ranging from 10^4 to 10^7 daltons. The -1-4-linked glucose units have a random-coil conformation. Depending on its botanical origin (pigweed, canna, potato, maize, oats, rice, etc.) and genetic background, starch has different chemical structures and functional groups, which make the natural polymer useful for different applications. The modification of granulated crystalline starch to an amorphous phase is defined as gelatinization (treatment and processing in hot water, organic solvents, and aqueous alkaline or salt solutions). Starch is made thermoplastic at elevated temperatures in the presence of water as a plasticizer, allowing melt processing alone or in blends with other thermoplastics (Zobel, 1984, Sogren 1993, Stenhouse 1993, Koenig 1995). Thermoplastic polymer processing (injection molding, extrusion, etc.) can be done well below the decomposition/degradation temperature by using water, which lowers the melt transition temperature of amylose, the crystalline component of starch (Loomis 1993).

The most important commercial application has been the blending of polyethylene with starch in the presence or absence of other additives to promote compatibility. Ohtake et al 1994 reviewed starch blends in detail from the perspective of structure and material compatibility. Interest in this approach goes back to Griffin (1994) in the seventies and there is continuing activity with commercial products from several companies, including Agritech, Henkel, Novamont, Solvay, and Warner Lambert. The major deficiencies of starch blends based on the above-described chemistry is: incomplete biodegradation due to the non-degradable synthetic polymer component and water sensitivity of the manufactured products. Starch-based products are difficult to market in countries, which have a high content of wet solid waste. Mater-Bi, available from Novamont, is manufactured primarily from corn or potato starch, along with smaller amounts of food-grade additives (not intended for human consumption). This EDP is suitable for manufacturing injection-molded pieces; films (for bags) and a starched based loose fill packaging material. Starch-based EDP's degrade in an active biological environment like PLA. However, unlike PLA they can require a year or more to degrade. Current sole production capacity is in Italy and imported into the United States. Prices range from $2.25 USD to $2.90 USD per pound. Commercial scale production is available at this time. Novon International also produces Novon, a starch-based resin that contains performance-enhancing additives, such as synthetic linear polymers, plasticizers, and compounds that trigger or accelerate degradability. Novon is intended to be mixed with synthetic polymers to create a plastic product, while making the product more degradable than traditional synthetic plastics. A typical product would contain about 43 % starch, 50 % synthetic polymer, and 7 percent proprietary ingredients. Typical application is for agricultural mulch films. Current pricing for Novon is about US$1.60~$1.70 per pound. Currently, the sole production capacity is in New Jersey, with commercial scale production being available at this time. A number of Asian-based companies have entered their local and regional markets

(Table 3). This market segment is projected to become more competitive in countries, which produce a high amount of dry solid waste.

Protein based Polymers

The structure of proteins is an extended chain of amino acids joined through amide linkages, which are degraded by enzymes, specifically proteins. Proteins do not have a wide range of commercial applications because they are expensive, difficult to process, not fusible without decomposition, and insoluble in non-toxic solvents. In general, they are difficult to modify and have to be used in their natural state. Collagen in its gelatin form is applied as an encapsulate in the pharmaceutical and food industries. Silk and wool fibers are used mainly in the textile industry.

Several types of bacteria store polyesters as intracellular material to be used as food sources during times of environmental stress (Timmins 1993). These polymers have been under intensive investigation over the last three decades (Doi and Fukuda 1994) because they are enzymatically degradable, can be processed like a thermoplastic material, and are produced from renewable resources in different chemical compositions. These polyesters are 100% optically pure and are 100% isotactic. Theoretically, polyesters of bacterial origin can be produced for biotechnological use with properties ranging from soft elastomers to rigid brittle materials, depending on the structure of the pendant side-chain of the polymer.

Poly-β-hydroxybutyrate (PHB) is highly crystalline with a melting point of 180°C and a glass transition temperature, Tg, of 5°C (Marchessault et al 1988). Due to the combination of a high Tg and high crystallinity, polymer films and plastics are very brittle and plasticization is necessary for processing and to improve properties. This was accomplished in the formerly commercially available BIOPOL from Monsanto/Zeneca (formally ICI) by using bacteria, to produce a copolymer containing β-hydroxyvalerate. By feeding the bacteria, *Alcaligenes eutrophus*, mixed feed of propionic acid and glucose (Cox 1992), a random copolymer is synthesized. Biopol is stable when stored in air and is quite stable when stored even in humid conditions. Degradation to carbon dioxide and water will occur only when they expose the polymer to microorganisms found naturally in soil, sewage, river bottoms, and other similar environments. The rate of degradation is dependent on the material thickness and the amount of bacteria present. Landfill simulations over a 19-week period revealed test bottles experiencing a weight loss ranging from 30% with oxygen present to 80% with no oxygen present. The fact that Biopol decomposes more rapidly without oxygen present is significant because oxygen is generally not present in modern landfills. The PHB/PHVcopolymers have better mechanical properties and were produced by ICI/Zeneca and Monsanto on a relatively large scale by applying a newly developed fermentation technology (yielding a few hundred tones per year). For more then a decade, PHB either alone or as a co-polymer or blend was a promising candidate for the development of a biodegradable commodity plastic (Gilmore 1992, Bourque 1992, Kemmish 1993, Tsuchikura 1994, Takagi 1994, Abbey 1996). Unfortunately, the commercial expectations were never matched by PHB because its price never came close to the synthetic commodity polymers.

Plastic Industry and Solid Waste Management in Singapore

Since its independence in 1965, Singapore has achieved rapid industrialization and economic growth. From modest beginnings of factories implementing pineapple canning and rubber processing, and the manufacturing of soap, biscuits, cooking oil, soya sauce and soft drinks in the 1960s, Singapore today has a very competitive and technically advanced chemical as well as electronics industry. There are approximately 200 to 250 chemical companies, representing one of the major pillars of the Singaporean economy. Today, 150 large and medium-sized companies are registered under the Chemical Industry Council (SCIC). Approximately 50 companies are manufacturing plastics and resins. Table 3 shows the estimated figures for polymer production of the main players in Singapore.

As experienced in other industrialized countries, Singapore's annual waste generation rate has also experienced a sharp increase. The annual waste increased 278% from 1974 to 1998. The daily waste output increased from 1260 tones in 1970 to 7800 tones in 1998, a growth that has kept pace with the trends in economic development and national income. In 1998 2.84 million tones of solid waste (about

Table 2 Manufacturers of EDBs of synthetic and natural origin

Company	Polymers	Trade name	Industrial Applications
Air Products and Chemicals, Inc.	Polyvinylalcohol	Airvol	Adhesives, Ceramics, Paper and Paperboard, Textiles
Sigma-Alderich	Polycaprolactone	-	Pharmaceutical
BASF	Copolyester	Ecoflex	Packaging
BAYER	Polyesteramide	BAK	Packaging
Biotec	Starch, Starch Blends	Bioplast	Packaging, Food
Cargill Dow Chemicals LCC	Polylactide	Nature Works	Packaging (bottles, films, foams) Textiles, Emulsions
Daicel Chemical Ind. Ltd	Cellulose Acetate, Polycaprolactone	Celgreen	Packaging (bottles, films, foams)
Eastman Chemical Co.	Cellulose	Tenite	Automotive, Toys, Packaging, Containers
EPI Environmental Products Inc.	Degradable Polyoefins	-	Packaging (bottles, films, foams)
Hoechst AG	Cellulose Acetate	Celanese	Packaging
Ire Chemical	Aliphatic Polyester, Aromatic/Aliphatic Polyester	EnPol	Packaging, Containers
Kuraray Co.	Polyvinylalcohol	Poval resin	Adhesives, Ceramics, Paper and Paperboard
Mazzucchelli	Cellulose Acetate	Bioceta	Packaging
Mitsui Chemical	Polylactide	Lacea	Packaging (bottles, films, foams)
Monsanto Co.	poly(hydroxybutyrate-co-hydroxy-valerate)	Biopol	Packaging, Textiles
National Starch and Chemical Co. (member of ICI Group)	Starch	Eco-Foam	Packaging
Novamont S.P.A.	Starch-Ethylen-vinylalcohols	Materi-Bi	Packaging, Food
Planet Polymer Technologies, Inc.	Polyvinylalcohol EnviroPlasticZ	Aquadro Cellulose	Packaging Packaging
Showa High Polymer Co LTD	Polyester	BIONILLE	Automotive, Toys, Packaging, Construction
Solvay	Polycaprolactone	CAPA	Automotive, Electrical boards, Packaging, Shoe, Orthopedics
Tianjin Danhai Co. Ltd	Starch-Blends	Starate	Packaging, foams, non-woven-cloth
Union Carbide	Cellulose Polyethylenglycols Polycaprolactone	Cellosize Carbowax Tone Polymer	Painting, Textiles, Household, Pharmaceutical, Ceramics

7,800t/d) were produced (Yang 2000). It is estimated, that similar to other industrialized countries (according to a study by the U.S. Environmental Protection Agency (EPA), plastics alone account for roughly 21% (by volume) of the nearly 200 million tons of municipal waste generated each year in the USA.) 15-20% of Singapore's solid waste is composed of plastics.

Land filling of waste was the only way to dispose of Singapore's waste in the 1970s. Today, the landfills in mainland Singapore have all closed and land suitable for landfill is no longer available. Hence, the government decided to build an offshore landfill. However, the construction and operation costs of an offshore landfill are very expensive. It cost $610 million to build the first phase of the offshore landfill at Pulau Semakau. Having to transport the waste offshore by barge, the operating costs are estimated at $30 millions dollars per year. To reduce the quantity of waste to be landfilled in land scarce Singapore, four incineration plants have been built since 1979 with a total capacity of processing 8,200 tonnes of waste per day.

Singapore still faces great waste disposal challenges in the 21st century while it continues to strive for higher economic performance. Over the past 20 years, our total solid waste grew at an average annual rate of 6.4%. If this trend continues, it is projected that the industries and consumers will generate at least 10,000 tonnes of waste per day or 3.65 million tonnes per year in 2005 (Yang 2000). The construction and operating costs for incineration plants are skyrocketing. In 1997 and 1998, the total operational cost of Singapore's three incernation plants was around $50 million per year. With more incineration plants in the future, this yearly cost could be doubled. The first Singaporean incineration plant costs S$130 million dollars. At present a state of the art incineration plant would cost S$1 billion dollars to build.

Table 3 Main Manufacturers of Plastics in Singapore

Company	**Product**	**Production in tons per annum**
TPC	PP	250,000
	LLDPE	150,000
	LDPE	250,000
PHILIPS PETRO	HDPE	400,000
TEIJIN	PC	60,000
DUPONT	NYLON 66	26,000
	NYLON 66 COMP	9,000
	POM	20,000
SEKISUI	EPS	22,000
GE/PLAS	ENGINEERING PLAS	30,000
EXXON MOBIL	LDPE PP	480,000
	Total	**315,000**

The Potential to Apply Environmentally Degradable Polymers in Singapore

Plastic materials are globally accepted due of their economic viability and ease of processing to produce a large variety of goods that improves the quality of life in developed and industrialized countries. The global issues of environmentally friendly and economically viable plastic waste management has promoted the development and application of EDPs to minimize the negative impact of the increasing consumption of plastics in a great number of nations. Unfortunately, EDPs were represented over the last two decades only in a niche markets because of their poor physical properties and processing difficulties, as well as non-competitive pricing structures in bench marking against conventional commodity plastics. The demand for commodity and specialty plastics in the 21st century are forecasted to triple over the next ten years due to an increased application of polymer-based products, mainly in the developed countries. Public awareness and education of environmental issues have raised serious concerns about the problems related to the disposal of plastic waste.

The International Center for Science and High Technology (ICS), which is an Institution within the legal framework of the United Nations Industrial Development Organization (UNIDO) plans to implement a transfer of know-how and technology from industrialized to developing countries. ICS-UNIDO has focused on the topic of EDPs as one major branch of its activity to support countries to tackle the global issue of plastic waste. The outcomes of the ICS-UNIDO International Workshop 2000 in Seoul justifies the statement, that beside mechanical and chemical recycling, new technological developments in EDB research and manufacturing can contribute significantly in tackling environmental issue related to plastic use in the industrial and consumer sector in the 21st century. A number of companies (see Table 3) have now the economics of scale or developed a new generation of EDPs, which exhibit good physical properties and ease of processing as well as being economically competitive. For example, in 1994 PLA and PHB sold for more than US$25.00 per pound. Today, PLA, depending on quantities, is between $1.50 USD and US$3.00 per pound and PHB, in large quantities is near US$4.00 per pound. In Asia; China, Japan, and South Korea are implementing programs, which actively support the application, and commercialization of EDPs to minimize the environmental impact of increasing production and consumption of plastic materials. Significant growth is expected for degradable plastics used for make compost bags, trash bags, golf tees, stationery, and thermoforms (Frost& Sullivan 1998). Legislation favoring such "environmentally friendly materials" as degradable plastics is increasing in North America, Japan, and Europe. Degradable plastic product already is a US$50 million/year market in the U.S. and Japan alone. The market reports suggest that global sales "will grow tremendously" in the years ahead, as new "environmentally friendly" end-use products are developed.

Singapore's Ministry of Environment has established a Waste Minimization Unit (budget in 1998 was S$652,000) to promote waste prevention, reuse and recycling since 1991. However, the exponential increase of plastic consumption could not be influenced significantly because of limited resources and manpower. Singapore has a highly educated society and a well-organized infrastructure. With the support of the ICS-UNIDO, Singapore has a great potential to introduce EDPs to help augment the current waste minimization program. ICS-UNIDO offers the service to educate officials, politicians and any individuals involved in creating policies within the state and federal governments of the new technology, which can be used towards reducing the serious problems currently facing plastic waste disposal. The Singapore government could for example, introduce tax incentives, grants, and low-interest loans to encourage industry and consumers to develop and use EDP based products.

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29. Status of Plastics Waste Treatment and R & D Activity on EDP in Thailand

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The total waste of the country is about 14 million tons, of which 10-12% is plastics waste. However, only 2-3% of the whole plastic waste is recycled, the rest being treated by landfilling. The principle reason for the relatively small quantity of plastics waste being recycled is the inefficiency of plastics waste collection and sorting. At present, return of used plastics products to recycling plants is carried out manually by human labor. Systematic collections of plastics waste as practiced in many countries in North America, Europe or Japan have not been developed in Thailand. Neither has legislation been passed which requires public involvement in recycling of used plastics products or imparts financial responsibility to companies which manufacture plastics products or supply plastics products. Such practice, however, is being considered. Efforts to create public awareness of the waste problems and the benefit of waste recycling, on the other hand, are increasing by the government agencies responsible, NGO or private sectors. A few small pilot projects that encourage public participation in collection and return of plastics waste for recycling have also been established.

Returned plastics waste is processed by hundreds of small converters employing the usual extrusion technology. The qualities of the recycled plastics resins still, however, vary and are not yet standardized. Recycled plastics are converted into low priced plastics household products. R&D on plastics waste technology converting into valuable products is lacking except for laboratory work carried out in universities for academic interests.

R&D on environmentally degradable polymers (EDP) in Thailand are still at the beginning. The EDP that may be of particular interest in Thailand is cassava starch. Food tray produced from cassava starch foam has been experimented at Kasetsart University. Blends of cassava starch with polycaprolactone (PCL) were also studied at the same University. Microbial polyesters are being studied at Chulalongkorn University. A rather more extensive R&D on synthetic polyesters are being carried out at Chiangmai University for biomedical applications. A work on environmental degradation of natural rubber is being carried at Mahidol University. None of these works have, however, produced substantial impact. On the positive side, funding for R&D on EDP does exist, mainly from the National Metal and Materials Technology Center (MTEC).

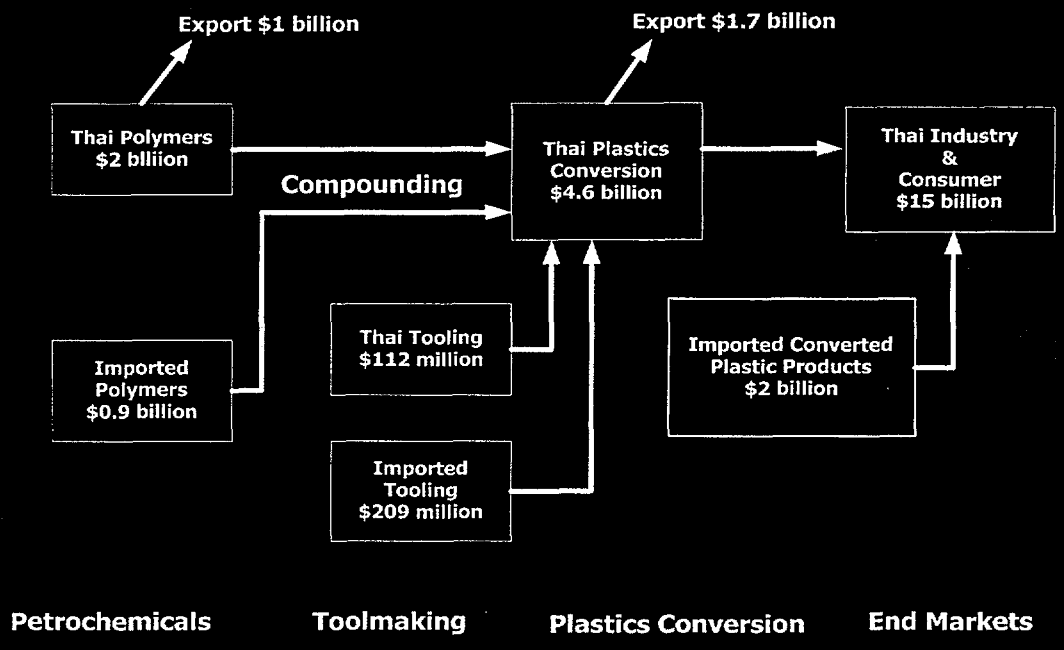
STATUS OF PLASTICS WASTE TREATMENT AND R&D ACTIVITIES ON ENVIRONMENTALLY DEGRADABLE PLASTICS IN THAILAND

KRISDA SUCHIVA

NATIONAL METAL AND MATERIALS TECHNOLOGY CENTER
NATIONAL SCIENCE AND TECHNOLOGY DEVELOPMENT AGENCY
MINISTRY OF SCIENCE, TECHNOLOGY AND ENVIRONMENT
BANGKOK, THAILAND

OVERVIEW OF THE THAI PLASTICS INDUSTRY

PLASTICS AND PLASTICS RELATED INDUSTRY IN THAILAND



Export $1 billion

Export $1.7 billion

Thai Polymers
$2 blliion

Compounding

Thai Plastics
Conversion
$4.6 billion

Thai Industry
&
Consumer
$15 billion

Imported
Polymers
$0.9 billion

Thai Tooling
$112 million

Imported Converted
Plastic Products
$2 billion

Imported
Tooling
$209 million

Petrochemicals

Toolmaking

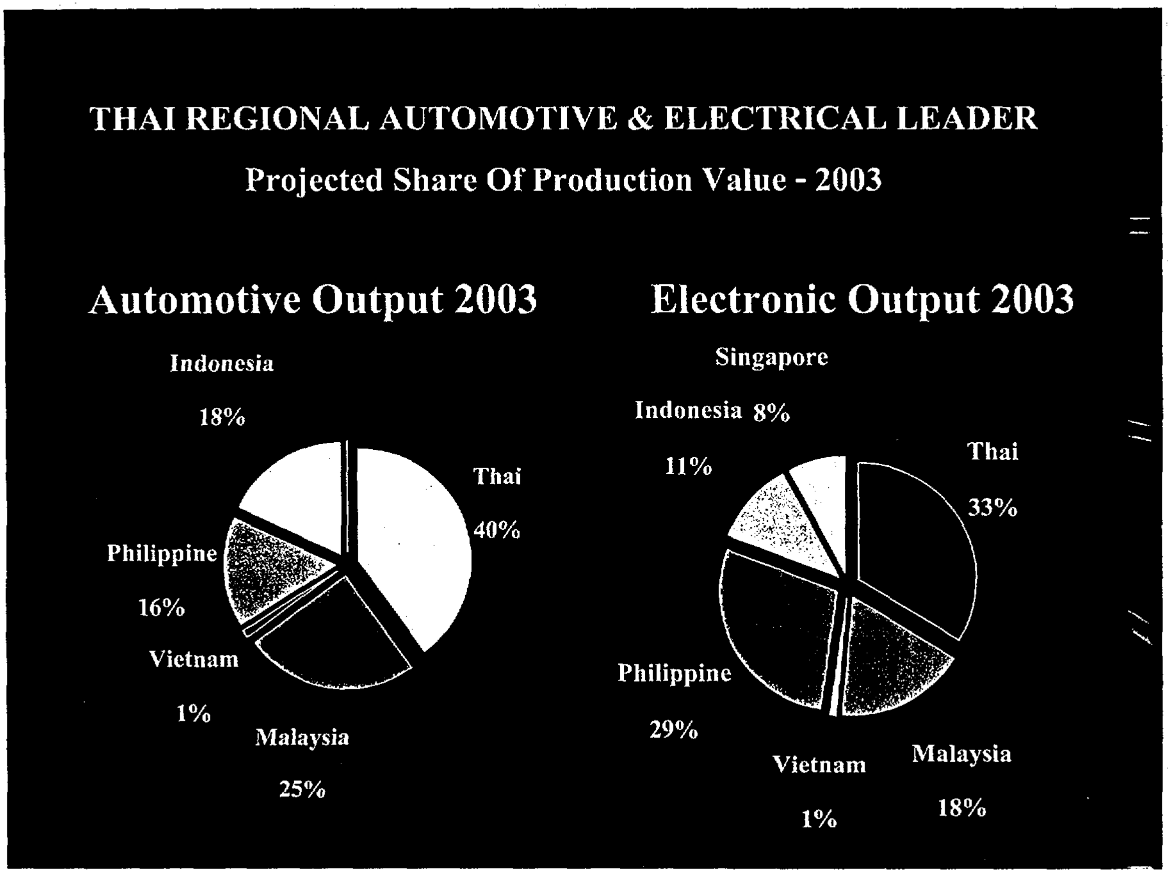
Plastics Conversion

End Markets

PLASTICS CONSUMPTION IN THAILAND

- **END USES**

– PACKAGING	33.2	Billion baht
– FIBRE & TEXTILES	24.0	
– CONSTRUCTION	16.5	
– ELECTRICAL & ELECTRONICS	14.3	
– HOUSEWARE	6.0	
– FURNITURE & BEDDING	4.7	
– LEISURE PRODUCTS	4.7	
– TRANSPORT	4.5	
– FOOTWEAR	2.1	
– OTHERS	7.9	
TOTAL CONSUMPTION	2,400,000	TONNES



THAI REGIONAL AUTOMOTIVE & ELECTRICAL LEADER

Projected Share Of Production Value - 2003

Automotive Output 2003

Electronic Output 2003

PLASTICS WASTE AND WASTE TREAMENT IN THAILAND

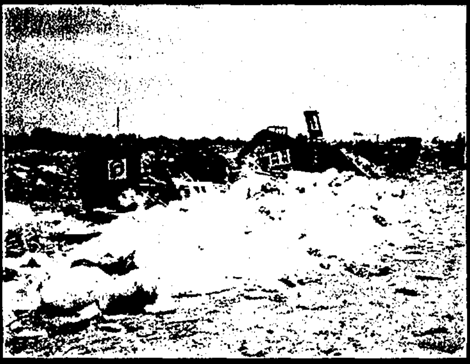
- TOTAL WASTE IN THAILAND 14 Million Tonnes
- APPROXIMATELY 12% IS PLASTICS WASTE
- RECYCLABLE WASTE (~45% OF TOTAL)

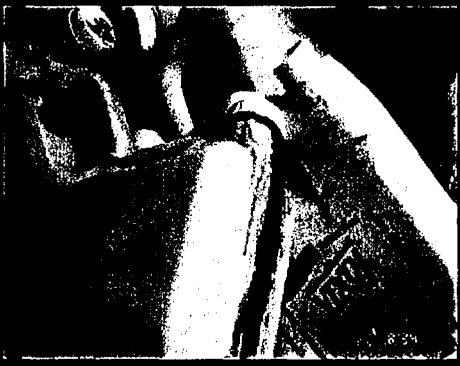
– PLASTICS	1.93 Million Tonnes
– PAPER	1.60
– GLASS	0.56
– METAL	0.54
– WOOD, CLOTH, LEATHER, RUBBER	1.49

- ONLY 2-3% OF WHOLE PLASTICS WASTE ARE RECYCLED
- THE REST ARE TREATED BY
  - LAND FILLING
  - INCINERATION

PLASTICS WASTE TREATMENT

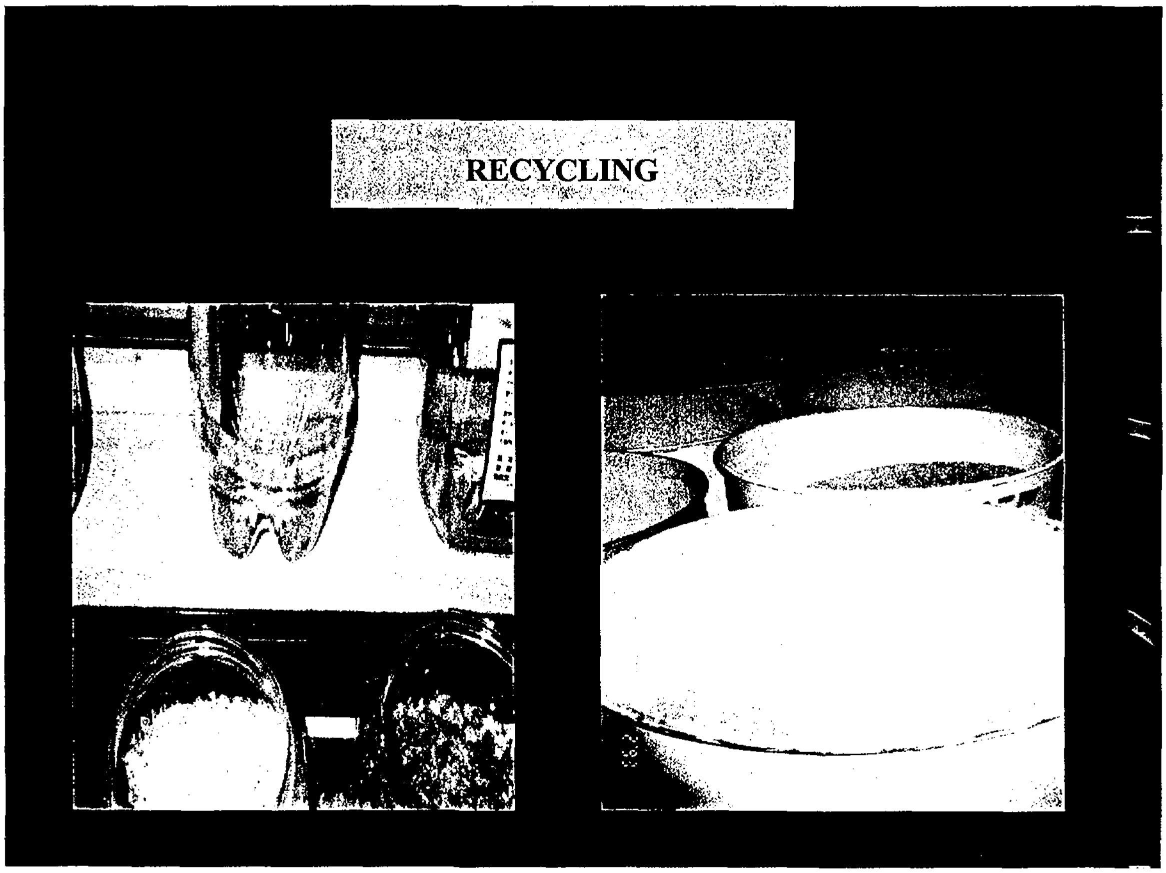
COLLECTION





SEPARATION

RECYCLING



RECYCLING

RECENT INTEREST IN PLASTICS RECYCLING

POLY (ETHYLENE TEREPHTHALATE) - PET

e.g. PET ---> CARPET

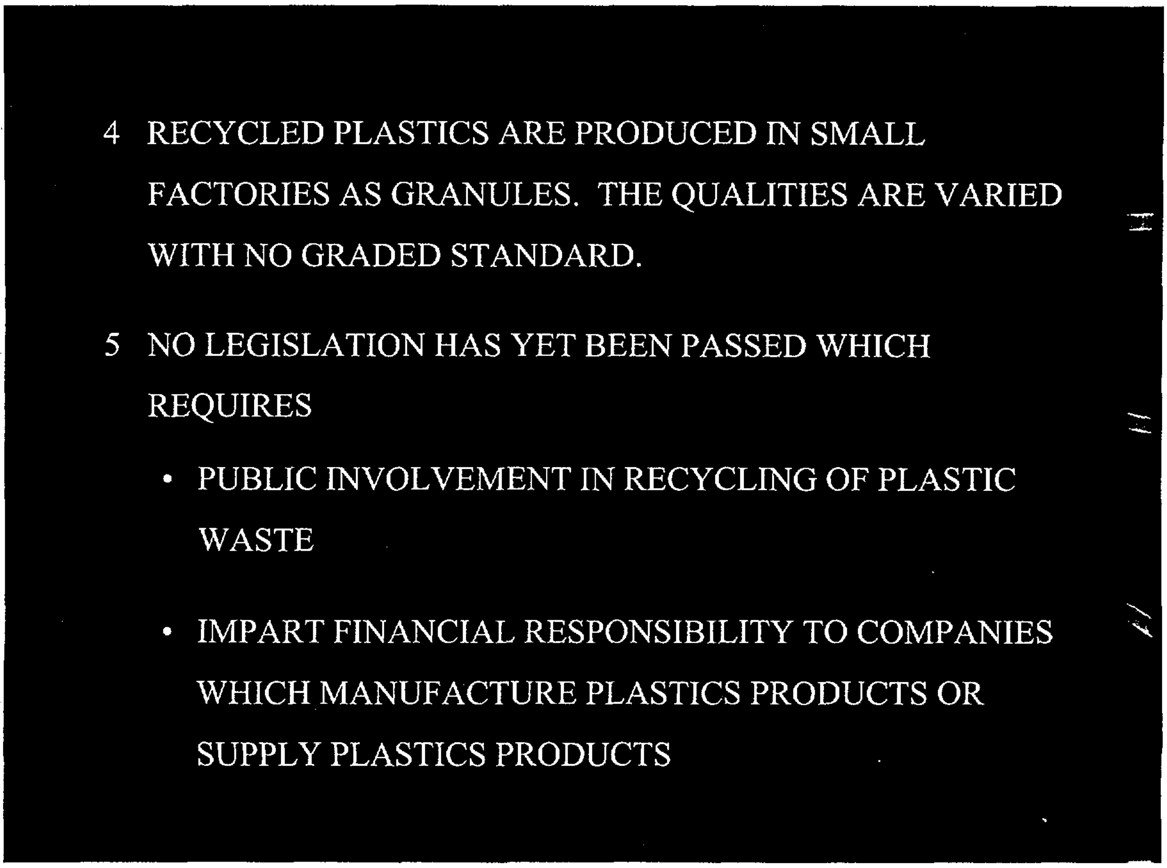
SUMMARY OF PLASTICS WASTE TREATMENT IN THAILAND

1 THERE IS NO ORGANISED COLLECTION SYSTEM AS OPERATED IN U.S.A. OR SOME EUROPEAN COUNTRIES

eg. : KERB SIDE COLLECTION
BRING SYSTEM

2 COLLECTION AND SORTING ARE DONE BY HUMAN LABOUR

3 THERE IS NO WASTE SORTING AND PROCESSING PLANT (AUTOMATIC OR OTHERWISE)



4 RECYCLED PLASTICS ARE PRODUCED IN SMALL FACTORIES AS GRANULES. THE QUALITIES ARE VARIED WITH NO GRADED STANDARD.

5 NO LEGISLATION HAS YET BEEN PASSED WHICH REQUIRES

- PUBLIC INVOLVEMENT IN RECYCLING OF PLASTIC WASTE
- IMPART FINANCIAL RESPONSIBILITY TO COMPANIES WHICH MANUFACTURE PLASTICS PRODUCTS OR SUPPLY PLASTICS PRODUCTS

PRESENT ACTIVITIES

1 PROMOTION OF PUBLIC AWARENESS OF THE WASTE PROBLEMS AND THE NEED TO REDUCE WASTE AND RECYCLE USED MATERIALS, INCLUDING PLASTICS

2 SMALL TRIAL PROJECTS ON SYSTEMATIC COLLECTION OF PLASTICS WASTE eg. IN SCHOOLS, VILLAGES (PART OF EDUCATING THE PUBLIC)

PRESENT ACTIVITIES

3 NATIONAL MASTER PLAN FOR WASTE MANAGEMENT INCLUDING THAT OF PLASTICS WASTE, ARE BEING MADE, COMPRISES MEASURES SIMILAR TO THOSE ALREADY PRACTISED IN THE WEST

eg. - LEGISLATION
- POLLUTER PAYS PRINCIPLE (PPP)

4 PLAN TO SET UP PILOT PLANT FOR PLASTICS WASTE TREATMENT

PLAYERS IN PLASTICS WASTE TREATMENT ACTIVITIES IN THAILAND

- STATE AGENCY
  - MINISTRY OF SCIENCE, TECHNOLOGY AND ENVIRONMENT
    - Department of Environmental Quality Promotion
    - Department of Pollution Control
  - BANGKOK METROPOLITAN ADMINISTRATION
- PRIVATE SECTOR
  - FEDERAL OF THAI PLASTICS INDUSTRY
  - RESIN PRODUCERS
- NGOs

R&D ON PLASTICS WASTE TREATMENT TECHNOLOGY

- ONLY LIMIT TO ACADEMIC INTERESTS IN UNIVERSITIES eg. POLYMER BLENDS
- MINIMAL PARTICIPATION FROM PLASTICS AND PLASTICS PRODUCT MANUFACTURERS
- NO COMMERCIALISABLE PLASTICS WASTE TREATMENT TECHNOLOGY PRODUCED

RESEARCH AND DEVELOPMENT ACTIVITIES ON ENVIRONMENTALLY DEGRADABLE POLYMERS

R&D ON EDP IN THAILAND ARE ONLY AT THE BEGINNING

PRESENT ACTIVITIES

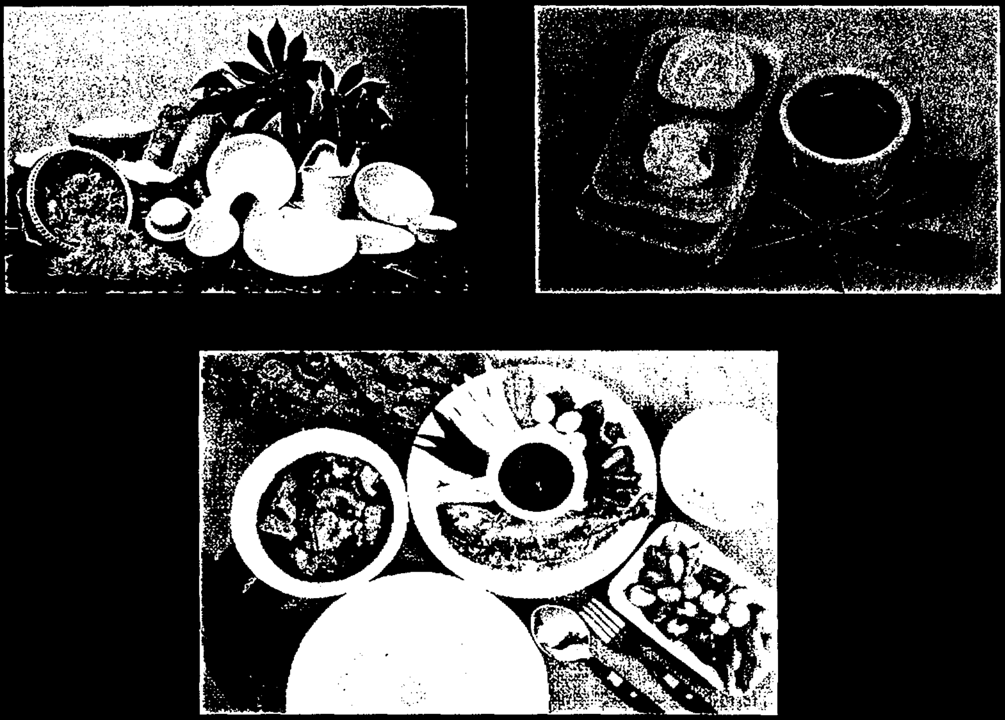
1 R&D IN UNIVERSITIES

2 INITIATIVES IN PILOT PROJECTS

R&D IN UNIVERSITIES

1 EDP BASED ON CASSAVA STARCH

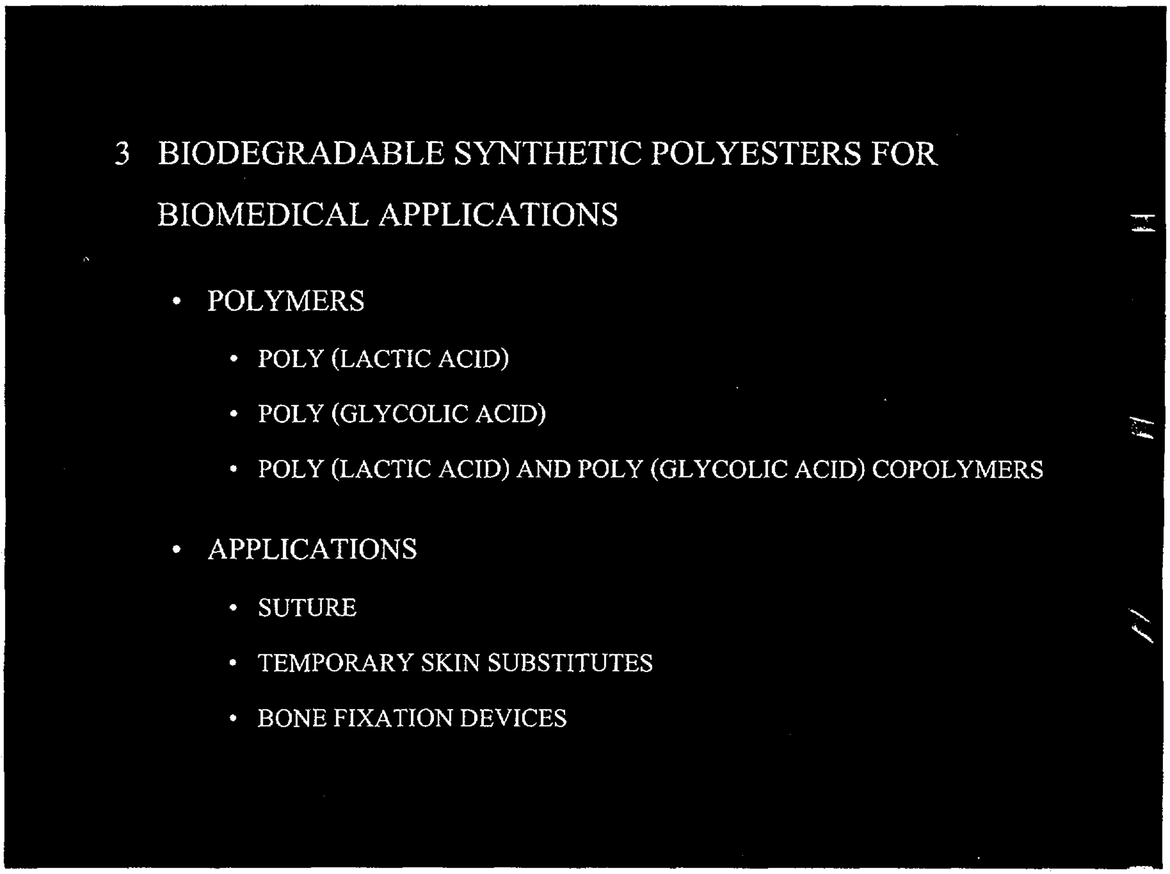
- FOOD TRAY FROM CASSAVA STARCH FOAM
  (KASETSART UNIVERSITY)
- BLENDS OF CASSAVA STARCH WITH POLY CAPROLACTONE
  (KASETSART UNIVERSITY)



2 MICROBIAL POLYESTERS

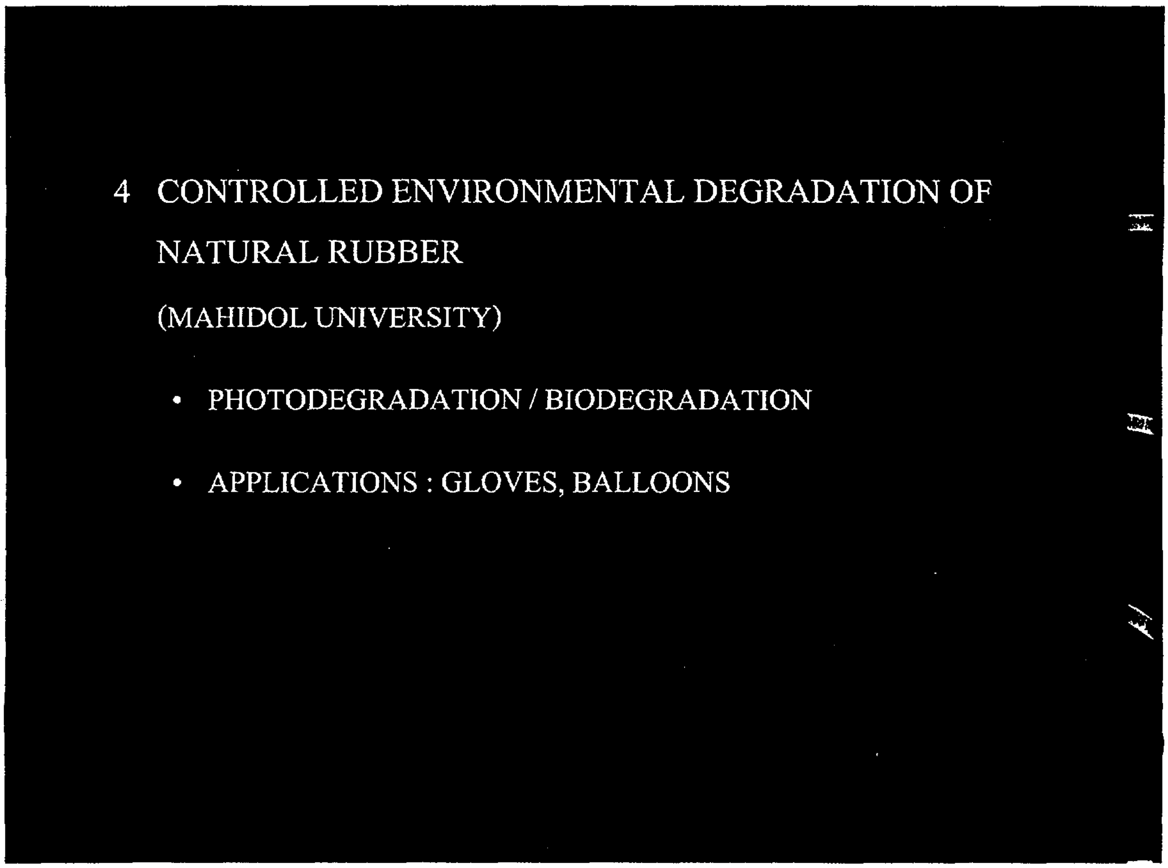
- PRODUCTION AND CHARACTERISATION OF MICROBIAL POLYESTERS

  (CHULALONGKORN UNIVERSITY)



3 BIODEGRADABLE SYNTHETIC POLYESTERS FOR BIOMEDICAL APPLICATIONS

- POLYMERS
  - POLY (LACTIC ACID)
  - POLY (GLYCOLIC ACID)
  - POLY (LACTIC ACID) AND POLY (GLYCOLIC ACID) COPOLYMERS
- APPLICATIONS
  - SUTURE
  - TEMPORARY SKIN SUBSTITUTES
  - BONE FIXATION DEVICES



4 CONTROLLED ENVIRONMENTAL DEGRADATION OF NATURAL RUBBER

(MAHIDOL UNIVERSITY)

- PHOTODEGRADATION / BIODEGRADATION
- APPLICATIONS : GLOVES, BALLOONS

MARCH 1997

- THAILAND INVITED TO COSPONSOR THE DEVELOPMENT OF BIODEGRADABLE PLASTICS
- INVITED BY MINISTRY OF INTERNATIONAL TRADE AND INDUSTRY (MITI), JAPAN

  (Agency of Industrial Science and Technology)
- THAI HOST : THAI TAPIOCA DEVELOPMENT INSTITUTE
  NATION BIOTECHNOLOGY CENTER
  KASETSART UNIVERSITY

DECEMBER 1996

- ATTEMPT TO SET UP PILOT PROJECT ON BIODEGRADABLE PLASTICS WITH TECHNOLOGY FROM MICHIGAN BIOTECHNOLOGY INSTITUTE THROUGH BIOPLASTICS CO.

  (Based on cassava starch blends with PCL)
- THAI HOSTS : NATIONAL PETROCHEMICAL CO.
  PETROLEUM AUTHORITY OF THAILAND

SUMMARY ON R&D ACTIVITIES

- NO SUBSTANTIAL IMPACT HAS BEEN MADE
- R&D ON EDP WILL CONTINUE
    - WITH FINANCIAL SUPPORT FROM THE NATIONAL METAL AND MATERIALS TECHNOLOGY CENTER (MTEC)

30. Trends in Plastics Production, Consumption and Associated Waste Management in Malaysia

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Introduction

Plastics industry in Malaysia started in 1950 and it has registered a 15% average annual growth over the last 10 years due to increased applications, robust economy and increased demand. There were only 68 plastics producing companies in operation in 1968 and the products were simple household and consumer products. The number of companies increased to 230 in 1973 and it was 400 in the late 1970s. The development of multi-national electrical and electronic industries created a demand for plastic parts and components for electrical and electronics products. Three petrochemicals companies were established in 1972 to produce polyvinyl chloride (PVC) and polystyrene (PS) raw materials. This saw the production of materials like pipes, artificial leathers etc. from PVC and household wares from PS. In 1989, there were about 800 plastics processing companies, which employed 50,000 workers and generated RM 1.2 billion worth of plastics products. The paid-up capital then was only RM 5 million and the industry were dominated by Malaysian-owned small and medium sized companies. The industry was very much dependent on foreign technology from Hong Kong, Japan, Taiwan and Europe. By 1997, the countries per capita consumption of plastics reached 50 kg, which is high by the standard of developing country.

Production and utilization of plastics

It is estimated that currently there are about 1200 companies involved in the manufacture of plastics products of which 70 percent are small and medium sized industries (SMIs), providing job opportunities to some 85,000 workers. Production reduced by about 3 to 4 percent in 1998 and 1999 due to economic slowdown but there was no decline in exports during the same period. Turnover in 1999 was about RM 7.0 billion, when the exports amounted to RM 2.98 billion and the plastics industry contributed an 8% share to the country's GDP. The exports for 2000 is estimated at RM 3.2 billion. By 2003, the turnover is expected to reach RM 10 billion, when the export is projected to be about RM 4.3 billion. In 1998, the plastics industry achieved a record turnover of about RM 6.3 billion and contributed to 2.5 percent of the country's GDP. The total contribution of the manufacturing industry to the Malaysian economy was 34 percent in which the plastics industry contributes to about 8 percent of the total goods manufactured. It is estimated that by the year 2003, there will be 1400 plastics manufactures with an aggregate investment of RM 4.5 billion (1 US = RM 3.80).

Resin consumption has been increasing steadily from 300,000 metric tonnes in 1989 to about 1.1 million metric tonnes in 1998. Recession caused a gradual decline in resin consumption in 1999 and is postulated to increase again to reach 1.4 million metric tonnes in the year 2003. Similarly the per capita consumption of plastics increased from 20 kg in 1989 to about 55 kg in 1997 after which, a decline of 5 percent was observed during the economic crisis in 1998. Plastics consumption is expected to reach 60 kg per capita in 2003, which is not far from the per capita consumption of 80 to 100 kg in the developed nations.

Thirty five per cent of the plastics products manufacturing is by film extrusion process, while injection molding generates 30 percent. Pipes and profile extrusion and blow molding produced 10% each, while composite fabrication, foam molding and other processes accounted for 5 percent production each. Other processes include lamination, calendering, yarn extrusion, rotational molding and sheet extrusion.

In Malaysia, packaging consumes 30 percent of the plastics materials produced, with a close 28 percent for electrical and electronic industry. The third largest consumption is for household products and containers (15%) while automation manufacture uses 10 percent, construction uses 7 %, agriculture 5% and other uses account for another 5 percent.

Production and treatment of plastics waste

Almost half a million (516,000) tonnes of plastic materials which could be recycled was thrown away annually nationwide. This represents 50% of the resins used. Daily, 11.5% of 12,5000 tonnes of municipal waste consist of plastic materials and are disposed into almost 200 landfills in Malaysia. These non-biodegradable plastics clog-up landfills and causes numerous problems. The bulk of the plastic materials discarded are plastic bags and household containers. Some industrial, non-hazardous and non-toxic containers are also disposed into the landfills. There is no authoritative information on plastic recycling in Malaysia but based on unconfirmed data the amount of plastic recycled is 2-5% of the amount of plastic waste generated. The bulk of the recycling is done by scavengers at the landfills. However it must be emphasised that some selected industries do recycle their plastic waste very efficiently.

Regulations against plastic waste

Currently there are no specific regulations controlling the disposal of plastic waste in Malaysia although SIRIM is in the process of developing one. So long as it is non-hazardous, it can be disposed into sanitary landfills. Municipal Solid waste disposal regulations which also encompass the disposal of plastic waste are as follows:

i. Local Government Act, 1976
ii. Anti-litter By-Laws, 1983
iii. Refuse Collection, Removal and Disposal By-Laws, 1983.

R&D activity related to EDP

EDP has been introduced into the Malaysian market recently but its use is very sluggish. The prohibitive costs are delaying the widespread use of EDP. EDP cost 5 times more compared to thermoplastics. Research on EDP is almost negligible and R&D on plastics is currently focused on the biotechnological aspects of polymer production using various agro-industrial and agricultural wastes. Universiti Sains Malaysia has initiated a multi-disciplinary approach to develop biodegradable plastics using locally available resources.

Recently some innovative R&D programs on degradable polyolefin (PE & PP) packaging products were carried out by Environmental Products Inc.(EPI) (Malaysia) in cooperation with a few Malaysian plastics processors. These programs were based on Total Degradable Plastics Additives (TDPA™) Technology which comprises Degradable and Compostable Plastics (DCP™) and Agri-Plastics (AGP™) additives. These additives were incorporated into polyolefin end products (PE & PP) used mainly in packaging, composting and MSW disposal. The degradation of the material is by oxidative degradation but in landfills, under anaerobic conditions, the high temperatures (35-60°C) also caused satisfactory degradation. The degradation is molecular meaning the ensuing degradation results in molecular weight reduction of the polyolefin main chain with evidence of physical disintegration of the products into minute fragments. Trials in Malaysia (and USA) using shopping bags incorporated with 3% (by weight) of EPI® TDPA™ additives, have successfully demonstrated the photo and thermal degradation properties of the material. Under Malaysian conditions, the bags disintegrated within 4 months while control bags without EPI® TDPA™ did not degrade and remained intact. EPI® TDPA™ polyolefin products made in Malaysia include refuse sacks (mainly made of HDPE, LDPE and LLDPE) and are used commonly to contain household/office/industrial rubbish, to be disposed at landfills. Chemical analysis of the degraded film residue composition also confirmed non-toxicity. These bags are confirmed to have physical and product performance attributes such as tensile strength, load bearing and puncture resistance properties meeting all the standard needs and requirements. Hence it is gradually replacing paper bags in most light duty packaging uses.

OVERVIEW

- Industry began in 1950s
- 15% average annual growth achieved
- 68 companies in 1950s, has grown to 1 200 currently
- Electrical & electronic industry was one of the main reasons for rapid expansion
- 70% are small and medium sized
- Employs 85,000 workers

PRODUCTION

- Currently there are 1 200 companies
- 70% are SMIs
- Employs 85,000 people
- Aggregate investment RM 3.5b (US$ 0.92b)

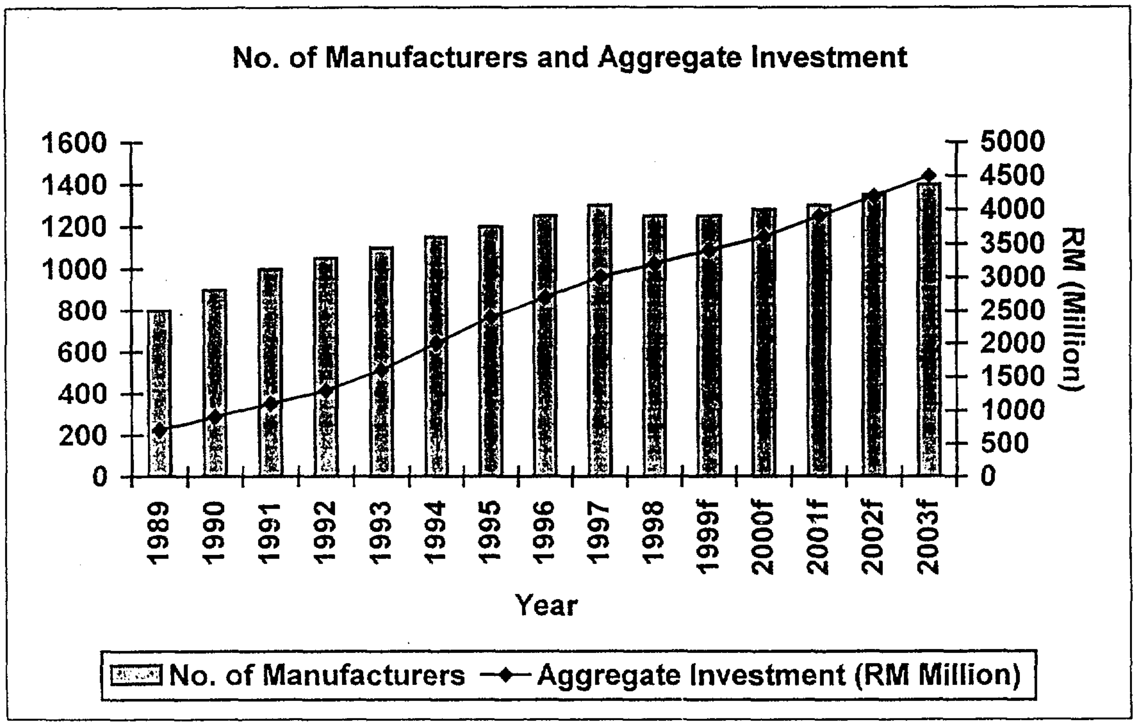

Figure 1: Number of manufacturers and aggregate investment

- Turnover in 1999 RM 7.0b (US$ 1.8b)
- Exports RM 2.98b (US$ 0.78b)
- 8% share of GDP
- Exports for year 2000 expected: RM 3.2b (US$ 0.84b) and by 2003 production will reach RM 10b (US$ 0.47b) with an export of RM 4.3b (US$ 1.13b).

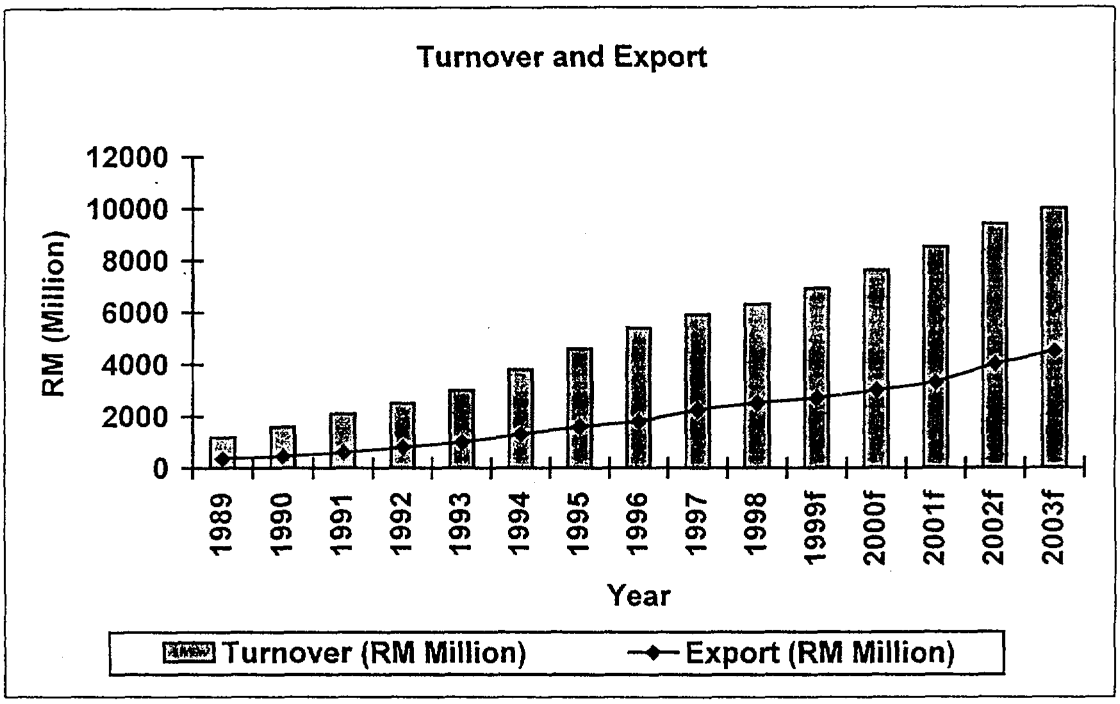

Figure 2: Turnover and export

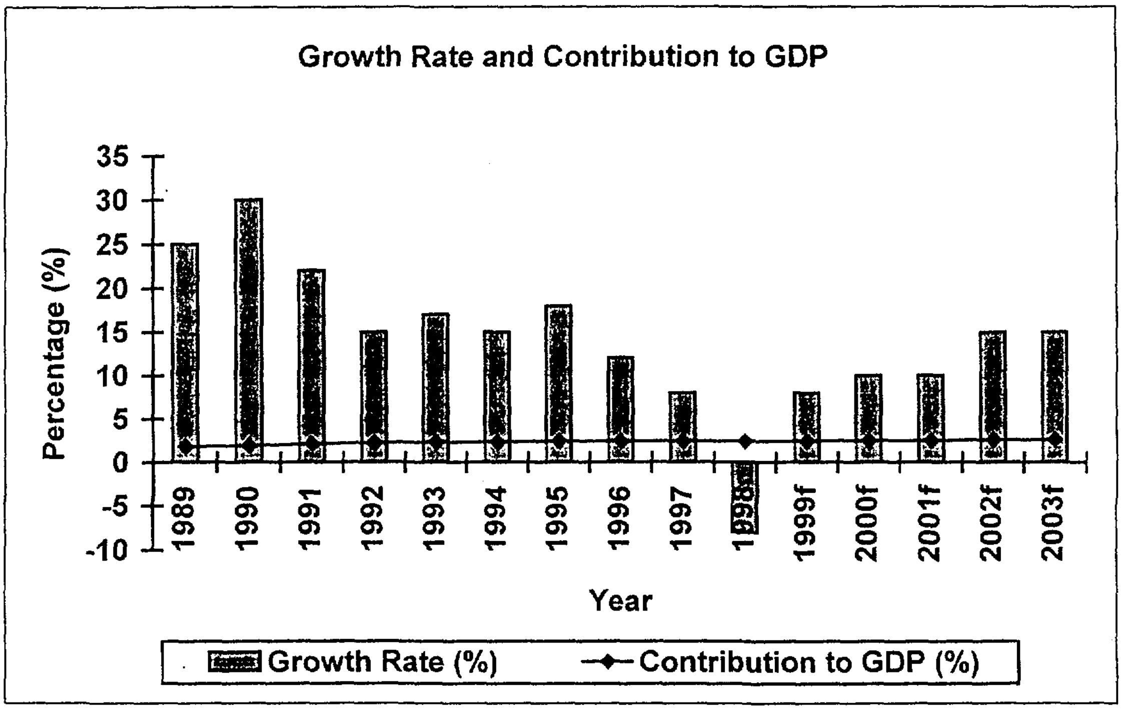

Figure 3: Growth rate and GDP

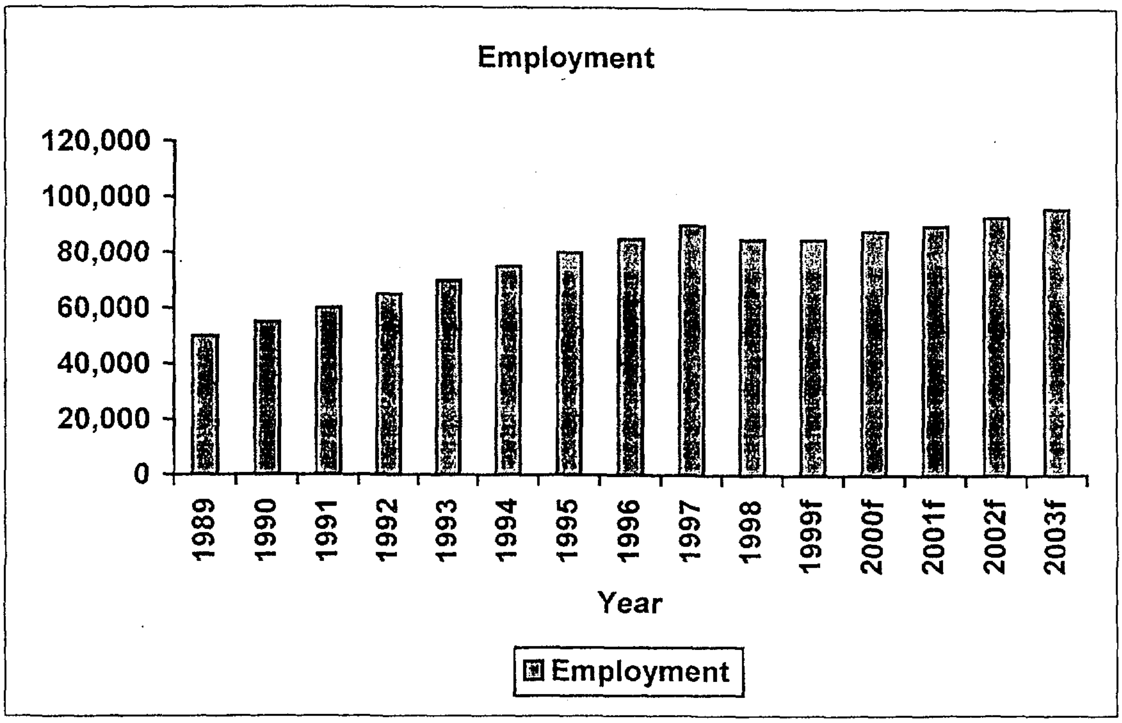

Figure 4: Employment

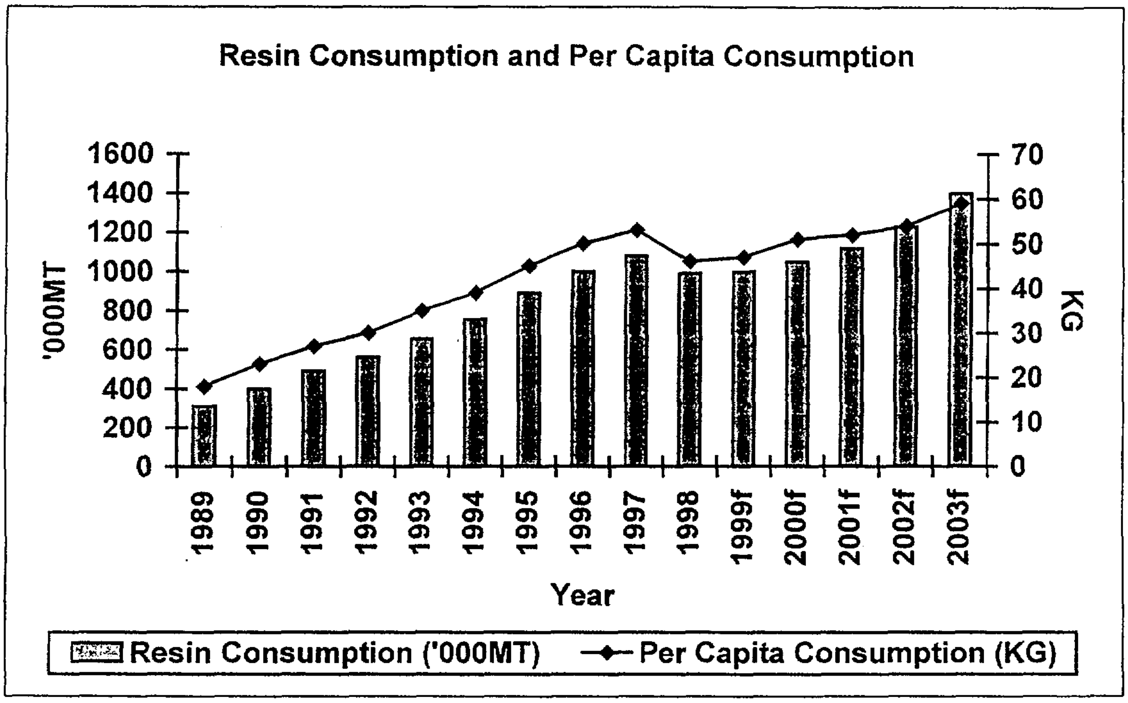

Figure 5: Resin consumption and per capita consumption

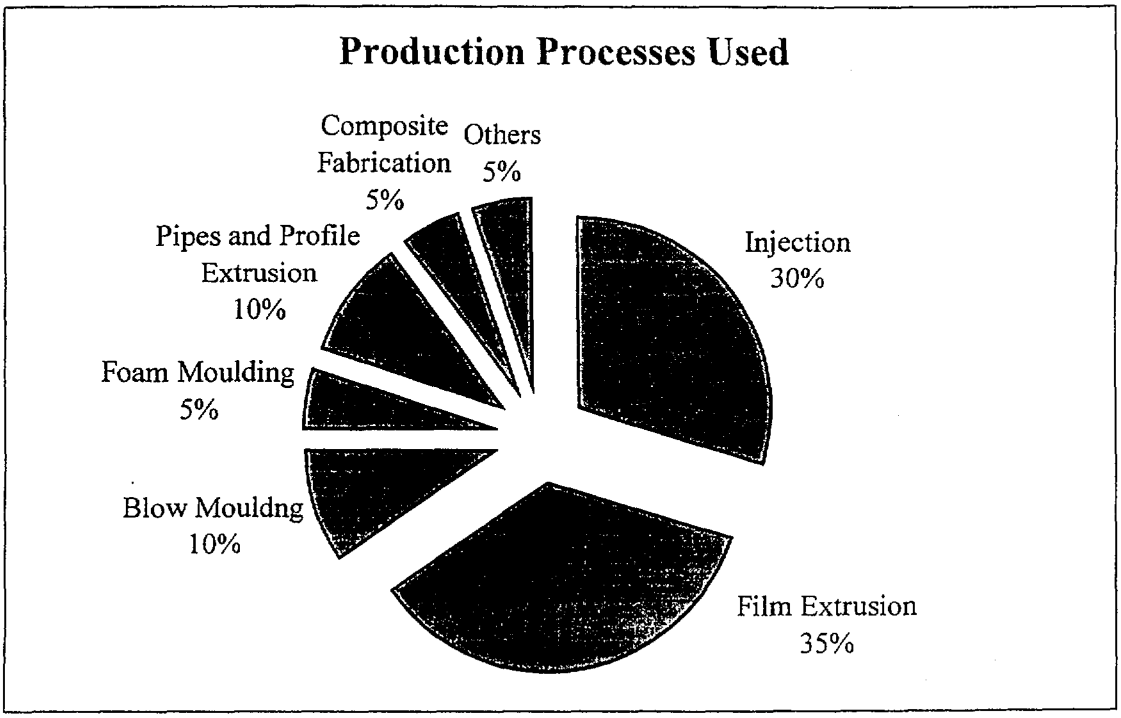

Figure 6: Major production processes

Table 1: Common production processes used by the Malaysian plastics industry

Process	Product	Market
Injection moulding	Parts and components for electrical appliances, casings and parts for computer and telecommunication equipment, compact discs, diskettes, automotive parts, plates, bowls, brooms, brushes, cutlery, pails, basins, food containers, tables, chairs, stools.	Electrical, electronics, automotive, housewares, tablewares and kitchenwares, toys, stationery and furniture.
Film extrusion	Films, shrinkable films, multi-layer films, labels, bags, sacks (garbage, carrier, zip-lock, envelopes).	Food packaging, consumer packaging, agriculture, fishery, medical and pharmaceutical.
Blow moulding	Bottles, containers.	Food and beverages industries, chemical, cosmetic and oil.
Pipes and profile extrusion	Pipes and fittings, soft hoses.	Construction, agriculture, household.
Sheet extrusion	Sheets, sun roofings.	Construction, premium products.
Foam moulding	Foam packaging products, fishery boxes, disposable cups and bowls.	Electrical, household, agriculture.
Calendering	Artificial leather, wall papers	Furniture, construction.
Lamination	Laminated films	Food packaging
Yarn extrusion	Woven bags, tarpaulin.	Food packaging, leisure products, household.
Rotational moulding	Water tanks, containers, drums.	Construction, chemical.

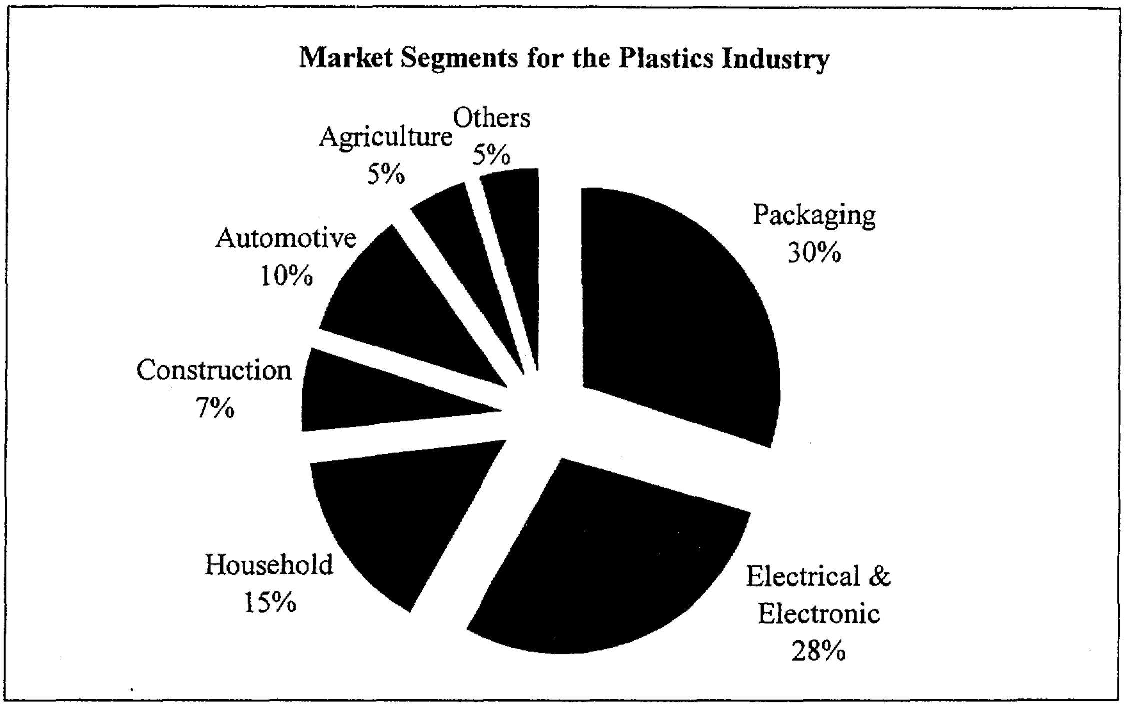

Figure 7: Market segment

PRODUCTION AND TREATMENT OF PLASTIC WASTE

- In 1999, about 560,000 tonnes of plastic waste was generated
- Represents about 50% of resin used
- Daily 12% of the 12 750 tonnes MSW (1 530 tonnes) consists of plastic
- Disposed into 200 landfills
- Hazardous ones disposed at sanitary landfills
- Mainly plastic bags and household items
- Recycled estimated at 2-5%

REGULATIONS

No specific regulations for disposal of plastic

SIRIM is developing a standard/regulations

MSW disposal controlled by

(i) Local Government Act, 1976
(ii) Anti-Litter By-Laws, 1983
(iii) Refuse Collection, Removal and Disposal By-Laws, 1983

R&D ACTIVITY

- EDP used in Malaysia very sluggish
- Cost 5X more than thermoplastics
- Research is focused on the biotechnological aspects of polymer production using various agro-industrial and agricultural wastes
- USM has initiated one multi-disciplinary approach to develop biodegradable plastics using locally available resources

BIODEGRADABILITY STUDIES

- Investigations using polyolefins (PE&PP) using Total Degradable Plastics Additives (TDPA^{TM}) additives
- Comprises Degradable and Compostable plastics (DCP^{TM}) and Agri-Plastics (AGP^{TM}) additives
- Breakdown by Oxidative Degradation or in landfills by thermal
- Molecular degradation observed
- 3% (by weight) TDPA^{TM} additives (in shopping bags) gave successful photo and thermal degradation
- Under Malaysian conditions, the bags degraded within 4 months
- TDPA^{TM} polyolefins products made in Malaysia include refuse bags and used to dispose household/office/industrial rubbish
- Degraded materials were non-toxic with positive performance attributes.

31. Plastics Development and Recycling in Indonesia

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Abstract

Plastics in Indonesia right now have been widely used due to their properties such as durability and resistance to natural degradation and enable to conserve more resources during a product's life when compared to other materials. Currently, the number of plastic industries in Indonesia is nearly 800 companies. Increasing demand for plastic could result from the unique capability of plastics themselves that can provide the things consumers want and need. Therefore, the industrial prospect of plastics in Indonesia supported by the abundant availability of raw materials is promisingly.

Since economic crises especially during the period of 1998-1999 plastic production in Indonesia decreased 10%-50%, while the decrease for export and consumption of plastics at that period were accounted for 21% and 40%, respectively. The turning point for this bad condition of plastic has begun since 1999 signed by the increase of plastic production that reached 14% to 33%. Meanwhile, the increase of export for the period of January – December 1999 has reached 101.87%, and for domestic consumption has increased 61%.

The properties of plastics such as durability and resistance to natural degradation have made them undesirable if disposed of improperly and will enhance the degradation of environmental quality. Since the use of plastics was increasing, the amount of plastic waste was also increasing.

In order to minimize some negative impacts of plastic wastes to the environment, it requires some efforts such as recycling programs that can change the plastic wastes into new plastic products. These efforts have been carried out in Indonesia and created new businesses and job opportunities. Yet, only certain kind of plastic waste that can be recycled.

In addition, advanced recycling such as chemical recycling might be another important way to conserve resources. It processes and yields the building blocks from which plastics are made. It can produce monomers or a petroleum product that can be made into monomers or a number of other petroleum-based products. This activity in Indonesia that uses supercritical water for polymer decomposition is still being researched.

1. Introduction

The Indonesian archipelago consists of more than 17,000 islands extending 2,900 miles along the equator between mainland Southeast Asia and Australia. Almost half of which are inhabited and about 60 percent of the population is found on Java islands that make up just 8 percent of the total land area.

Indonesia has been positioned on the fourth most populous country in the world after China, India, and the United States. In the mid of 2000 its population has reached 212 millions and the overall population density is about 289 per sq. mi.. Existing and projected population for the year of 2025 and 2050 for some countries and other demographic data are presented in table-1

Table-1: Demographic Data for Some Countries

Country	Population mid-200 (millions)	Projected Population (millions)		GNP Per Capita, 1998 (US$)	Area of Countries (square miles)	Population per square mile
		2025	2050			
Indonesia	212.2	273.4	311.9	640	735,355	289
Malaysia	23.3	37.0	48.2	3,670	127,317	183
Philippines	80.3	117.3	139.6	1,050	115,830	693
Singapore	4.0	8.0	10.4	30,170	239	16,714
Japan	126.9	120.9	100.5	32,350	145,869	870
North Korea	21.7	25.7	26.4	-	46,541	466
South Korea	47.3	53.3	51.1	8,600	38,324	1,234

Source: Population Reference Bureau, 2000.

The climate of Indonesia is tropical, with two monsoon seasons – a wet season from November to March and a dry season from June to October. The yearly average humidity is about 80 percent and the average daily temperature range is about 23^{0} to 30^{0} C or 74^{0} to 86^{0}F. Rainfall in the lowlands averages about 1780 to 3175 mm or about 70 to 125 in. annually and in some mountain regions it reaches about 6100 mm or about 240 in.

2. Development of Plastics in Indonesia

Plastics in Indonesia right now have been widely used in various segment of daily life. They have played an important part in everyday life and grown in use in consumer products because plastics can provide the things what people need. They are durable and can be formed into a variety of shapes.

The increase demand of plastics product has stimulated the growth of plastic industries. Currently, there are about 800 manufactures in Indonesia that involve in the production of plastic materials. And the domestic demand for plastic this year has reached 1.5 millions tons or about 7 kg/capita. It is reasonable that investors are interested in this sector of the industry because of the availability of potentially large market and raw materials in Indonesia.

In the domestic markets in Indonesia some plastic basic materials which have high in demand include polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and polyester. Such materials including alkyd resin, polyol, melamine resin, unsaturated polyester resin and polyester chips have been produced domestically while other materials have to be provided through imports. Table-2 shows the value of export and import for plastics basic material in 1998 and 1999.

Table-2: Export and Import of Plastics' Raw Materials during 1998-1999 (Tons)

No	Commodities	1998		1999	
		Export	Import	Export	Import
1	Ethylene	74,400	205,307	18,840	434,506
2	Propylene	19,900	98,000	0	139,000
3	Polyol	9,566	6,723	10,699	8,873
4	Melamine	21,788	6,048	19,537	6,828
5	VCM	113,954	23,659	37,158	31,647
6	Polyethylene	172,000	141,984	189,000	146,000
7	Polypropylene	127,000	162,000	46,000	96,000

8	Acrylonitride Butadiene Styrene	3,628	10,481	7,665	6,806
9	Ethylene Glycol	11,015	329,458	7,203	350,508
10	PVC – Resin	193,000	2,000	230,000	2,000
11	Polystyrene	20,336	22,478	23,967	4,788

Source: Department of Trade and Industry

Plastic productions in Indonesia from 1996 to 1999 are illustrated in Table-3 while the value of export and import for plastic products during the period of 1998-1999 are shown in Table-4. There have been decreased for toothbrush, photographic film, and magnetic tape export. Similar changes have been seen on the import side. Import of plastic pipe and fitting, formica, toothbrush, button, magnetic tape, and imitation leather are down.

Table-3: Plastics production in Indonesia for the period of 1996-1999

No.	Commodities	Unit	Years			
			1996	1997	1998	1999
1	PVC pipe	Ton	170,000	204,000	126,800	118,200
2	Plastic Bag	Sheet	245,200	269,680	1,239,000	1,740,250
3	Disposable Syringe	Unit	86,800	91,100	88,259	114,920
4	Plastic Sack	Sheet	1,626,406	2,310,301	2,200,716	2,475,116
5	OPP Film	Ton	58,386	64,874	5,172	9,025
6	Cassette Tape	Box	239,520	251,216	148,240	148,239
7	Video Tape	Box	6,017	6,861	4,250	4,251
8	Plastic for Industry	Ton	40	19	49	92
9	Safety Hat	Unit	3,520	3,552	1,478	1,879
10	V-belt	Unit	6.992,148	7,691,362	3,851,062	4,500,000
11	Imitation Leather	Ton	19,100	25,541	17,878	18,971

Source: Department of Trade and Industry

Table-4: Export and Import of Plastics Products in thousands US $

No	Commodities	Export		Import	
		1998	1999	1998	1999
1	Plastic pipe & fitting	1,060.17	10,431.48	14,933.46	11,688.36
2	Formica	4,244.94	6,974.51	261.90	237.32
3	Plastic Bags	7,692.08	21,888.52	3,905.20	4.842.74
4	Disposable Syringe	469.86	587.01	2,888.59	5,555.98
5	Plastic Sack	13,365.16	56,912.10	2,638.42	3,247.60
6	Toothbrush	1,821.15	1,663.70	596,90	318,82
7	Button	968,57	1,781.73	5.777,36	4,167.79
8	Fishing net	9,946.18	13,379.88	635,08	1,011.43
9	Other Plastic products	138,872.45	280,927.75	124,397.21	131,006.67
10	Photographic Paper and Film	6,105.39	4,460.52	40,372.22	56,939.17
11	Chemicals for Photography	1,524.59	1,671.80	9,556.74	10,422.15
12	Recorded Tape	123,00	689,77	102,55	434,17
13	Magnetic Tape	24,995.27	23,867.20	4,611.72	4,167.33
14	Imitation Leather	1,513.16	4,147.26	66,795.12	64,522.15
	Total	**212,701.96**	**429,383.23**	**277,472.46**	**298,561.68**

Source: Department of Trade and Industry

The economic recession, the unstable exchange value of the Indonesian currency, and the drop of oil price in the past had contributed to the decline of plastic production. During the period of 1998-1999 the production decreased 10-50 percent, while the decrease for export and consumption of plastics at that period were accounted for 21 percent and 40 percent, respectively. But, since 1999 such unexpected conditions have been recovered where the production can increasingly reach around the value of 14 percent to 33 percent.

Meanwhile, the increase of export for the period of January to December 1999 was 101.87 percent or US$ 429,383,230 and of domestic consumption was about 61 percent.

Subsequent progress from this sector came from trade balance during the period of January-December 1999. At this period Indonesia had consistently had positive trade balance that stood at an estimated US $ 130.82 million or 43.82 percent.

3. Polymer related activities in Indonesia.

The activities of polymer in Indonesia involve three bodies i.e. industries, governmental research institution, and universities. Polymer industries include resin producers, plastic goods manufacturers, plastic processing machine manufacturers, and mould makers.

In Indonesia resin producers are usually big companies and conduct some research for product quality control and development. They also make some modifications of resin through blending with various additives. Cooperation with the licensers is sometimes conducted in R&D.

Some universities also carry out basic research on polymeric material for educational purposes. While research activities for governmental institutions always depend on R&D budget available. Sometimes several research institutions make joint research in order to eliminate duplicating research topics. Yet, solid cooperation among three bodies has not been realized.

4. R&D of EDP in Indonesia

There are six research institutions and three universities that are interested in the topic of biodegradable polymer. Some of them are concerned with natural polymers such as cellulose, rubber, cotton and other natural fibers.

A governmental research institution, BPPT, right now is developing biodegradable plastic by using starchy materials extracted from renewable resources in Indonesia. The research has been started with grafting methyl acrylate on tapioca starch where ceric ammonium nitrate (CAN) is used as an initiator. Biodegradation test was carried out by using *Aspergillus niger sp.* as microorganism. The additive agent such as irganox and organox was added to the synthesis product as heat stabilizer while stearic acid was used as a lubricant. This research is still need to be further developed in order to find the appropriate additive agent.

Another research activities on EDP in BPPT is blending of starches such as tapioca and sago with poly (ϵ -caprolacton)/PCL where glycerin is used to inhibit starch retrogradation. The results show that blends of PCL/sago and PCL/tapioca gave good physical properties and biodegradability.

Department of Chemistry of Bandung Institute of Technology (ITB) in Bandung, West Java has made a polyethylene-starch blend. This research uses two types of polyethylene i.e. HDPE and HDPE with additive; and three kinds of surfactants i.e. Hyamine; N-cetyl-N, N, N trimethyl ammonium bromide (CTB); and N-cetyl pyridium chloride (CPC) with the ratio of HDPE, starch and surfactant is 1:1:10%, respectively. They also investigated photodegradation of HDPE-starch polyblend. They use three types of HDPE i.e. pure HDPE, HDPE with additive, and HDPE activated by chromic acid and nitric acid.

Gajah Mada University in Yogyakarta, Central Java, through its Department of Chemical Engineering in cooperation with the Institute for R&D of Leather, Rubber, and Plastics Industries (BBKKP), has prepared polyethylene-starch polyblend. They use HDPE and tapioca starch with three kinds of cationic surfactants i.e. N-cetyl pyridium chloride monohidrate (CPC); N-cetyl, N, N, N, trimethyl ammonium bromide (CTAB); and Hyamine 622; and an anionic surfactant of stearic acid.

Indonesian Institute of Science (LIPI) in Bandung through its Center for Applied Physics has blended LDPE and corn starch with the addition of urea and oleic acid. This institute also made grafting maleic anhydride (MAH) on LDPE with dicumyl peroxide (DCP) as its initiator.

National Atomic Energy Agency (BATAN) has developed biodegradable plastic by changing molecular structure of miscellaneous plastic waste material with gamma- or beta ray radiation. The new structure of radiated plastics produced has shorter molecular chain and can be degraded by microorganism within three to six months.

Another institutions and universities who involve in the R&D activities on EDP are presented in the attachment-1.

5. Plastic Waste Recycling

In the past time, municipal waste containing plastics in Indonesia were discarded in open dumping, littering, combustion, and landfill. Today, increasing quantities of these wastes are collected and processed to recover their plastics content.

Municipal solid wastes (MSW) in Indonesia which include all community wastes with the exception of industrial process wastes and agricultural wastes has been estimated approximately 2-3 liters per day for each person with the density of 200-250 kgs/m^3. The percentage distribution values for the components in this MSW actually vary with location, economic condition and many other factors. On the average plastic waste contents in MSW is about 12-13 percent of total MSW by weight with the compositions as the following:

- Polyethylene (PE)	30%
- Polypropylene (PP)	25%
- Polyvinyl chloride (PVC)	20%
- Polystyrene (PS)	15%
- Others	10%

Source: Indonesian Recycling Plastic Industry Association (AIDUPI)

Each of the plastics in those wastes can not be treated in the same way once they are disposed. And not all types of plastics can be recycled in the same place because companies involved in the activity of plastic recycling in Indonesia are relatively young and small. Some recycling firms therefore have varying standards for the plastics they accept. A small plastic recycling firm in West Jakarta, Sumber Rejeki Plastik for instance requires that the plastics be sorted by type such as PET, PP, and PE. The firm receives post consumer plastic material from *Lapak* or Waste Receiver varying in weight from 800 kgs. to 1000 kgs. per day. Plastic wastes received are turned into small flakes by a granulator, washed by detergents and then dried with hot air to reduce moisture content.

The activities of plastic recovery and recycling in Indonesia generally consist of the following components:

1. ***Perangkas*** or **Collector** who work independently without any employee and sell their collection to the receivers/*lapak*. They got some capital from Receiver or without any capital at all. There are three types of scavenger's residence; they are, on the open space such as in front of the shops, in the waste dumping location and in the receivers' place. They experience being confiscated and rehabilitated, but they prefer to return to be scavengers.
2. ***Lapak*** or **Receiver** is the one who buys the collection from the scavengers and he works independently or is assisted by his relatives or employees. The receiver has his own capital, certain residence, and afford to buy motorcycle. Small receiver usually organizes scavengers and sells the collection to larger receiver, and large receiver owns wide location, organizes scavengers and small receivers, and can sell the collection directly to the processors.
3. **Supplier/Agent** is the trading organization who receives the collection from receiver/*lapak* and submit it to the processors.
4. **Processors** who buy plastic waste from the receivers or suppliers and process the wastes into saleable materials such as a flake or pellet.
5. **Recycling Industry** who buys plastic waste material (flake, pellet) from the Processor and produce new product from recycled plastics

   The interactions involved among them are shown in Figure 1.

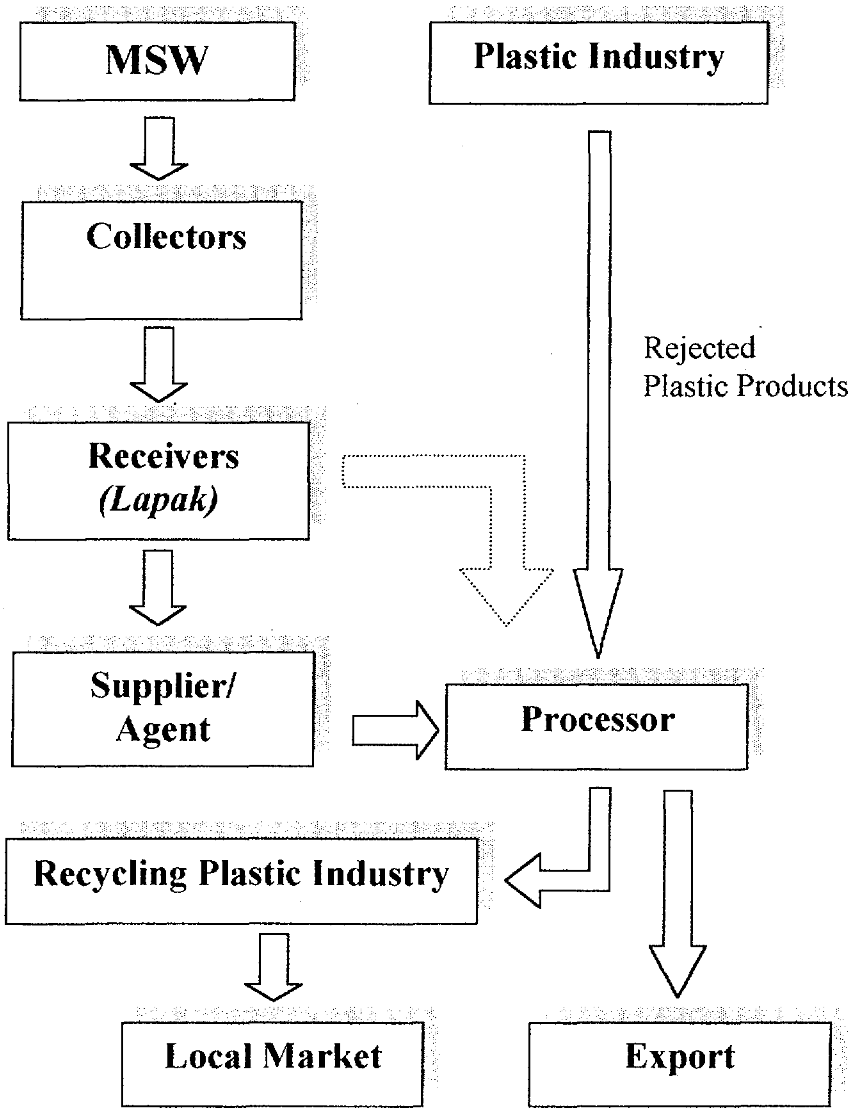

Figure-1: Diagram of Plastic Recycling Activities in Indonesia

In addition, advanced recycling such as chemical recycling of plastic wastes might be another important way to conserve resources. It can process and yield the building blocks from which plastics are made and further produce monomers or a petroleum product that can be made into monomers or a number of other petroleum-based products. This activity in Indonesia that uses supercritical water for plastic decomposition is still being researched.

6. Laws and Regulations

Until recently there are no special laws and regulations related to plastic and plastic waste in Indonesia except those who are listed in the attachment of "Hazardous Waste from Specific Source" of the Government Regulation No. 19/1994 concerning Hazardous Waste Management. This regulation was then revised by the Government Regulation No. 12/1995. The examples of materials listed in such attachment are unreacted monomer and used catalyst from polymer industries such as PVC, PVA, etc.

Similarly, regulations concerning solid wastes containing plastic have not been issued nationally. However, each local authority in Indonesia issues its solid waste regulations to implement and control solid waste management functions.

7. Conclusions

The increase demand of plastics product has stimulated the growth of plastic industries and the demand of polymer as their raw materials. This increase will also increase the amount of plastic waste generation. It tends to increase year by year with the increase of population growth. And if the waste is disposed of improperly it will enhance the degradation of environmental quality because of plastics' properties themselves such as durability and resistance to natural degradation.

In order to minimize such negative impacts of plastic wastes to the environment, it requires some efforts such as recycling programs for plastic wastes, modification or substituting plastic raw materials with another environmentally friendly materials such as biodegradable plastics, etc. Otherwise, non-biodegradable plastic wastes will create difficult problem at the final disposal sites.

Degradable plastic products which use renewable resources as their raw materials are necessary to be developed in order to save fuel (naphtha) consumption and minimize the degradation of environmental quality. However, these new invention products are still costly and have not been widely accepted by the consumers. But, through the enforcement of environmental laws and regulations and the improvement of polymer technology, biodegradable plastics may substitute some of non-degradable ones.

8. References

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ATTACHEMENT 1

Topics of Polymer R&D in Indonesia

CODE. NO	INSTITUTION GOVERNMENT RESEARCH INSTITUTION	1	2	3	4	5	6	7	8	9	10
LP- 01	Agency for the Assessmentt & Application	•	•	•		•				•	
	Of Technology (BPP Teknologi)										
LP- 02	Sub. Div. Of Petrochemical Quality Control	•	•	•			•	•			
	Pertamina										
LP- 03	Ministry of Mine & Energy, R & D Center	•	•			•					
	Oil and Gas Tech. (LEMIGAS)										
LP- 04	Indonesian Institute of Science, R & D Center										
	For Applied Physics (P3FT- LIPI)	•	•				•			•	
LP- 05	Indonesian Institute of Science, R & D Center										
	For Applied Chemistry (P3KT – LIPI)		•	•		•	•		•	•	
LP- 06	Ministry of Trade and Industry, Institute for										
	R&D of Cellulose Industries (BBS)	•	•	•	•	•	•		•	•	•
LP- 07	Ministry of Trade and Industry, Institute for										
	R & D of Chemical Industries (BBIK)	•			•						
LP- 08	Ministry of Trade and Industry										
	Institute for R & D Leather, Rubber, &	•	•		•	•	•			•	•
	Plastics Industries (BBKKP)										
LP- 09	Ministry of Trade and Industry	•	•		•	•	•				
	Institute for R & D of Textile Industries (BBIT)										
LP- 10	Ministry of Agriculture, Indonesian	•	•		•					•	•
	Rubber Research Institution (BPTK)										
LP- 11	National Aeronautics & Aerospace Institute										
	Propellant Div. Adv. Propulsion Div. (LAPAN)	•		•							
LP- 12	National Atomic Energy Agency (BATAN)										
	Center of Application of Isotopes & Radiation	•	•				•		•		
LP-13	National Atomic Energy Agency (BATAN)										
	Material Science Research Center (PPSM)	•	•	•		•	•			•	
	UNIVERSITIES										
PT- 01	Airlangga Univ. Surabaya (UNAIR)	•	•								
	Fac. Of Math. & Natural Science										
PT- 02	ATMI Solo							•			
PT- 03	Bandung Institute of Technology, Bandung										
	Department of Chemistry	•	•			•	•		•	•	
PT- 04	Bandung Institute of Technology, Bandung										
	Dep. Of Chemical Engineering	•	•	•	•	•			•		
PT- 05	Bandung Institute of Technologi, Bandung										
	Department of Physics	•	•	•							
PT- 06	Bandung Institute of Technology, Bandung										
	Program Study of Material Science & Eng.	•	•								
PT- 07	Bandung Polytechnic for Manufacturing (POLMAN)				•			•			
PT- 08	Gajah Mada University (UGM), Yogyakarta			•			•			•	•
	Department of Chemical Engineering										

ATTACHEMENT 1

Topics of Polymer R&D in Indonesia

CODE. NO	INSTITUTION GOVERNMENT RESEARCH INSTITUTION	1	2	3	4	5	6	7	8	9	10
PT- 09	Hasanudin University (UNHAS), Ujung Pandang	•	•	•		•			•		•
PT- 10	Indonesian Institute of Technology (ITI), Jakarta										
	Department of Chemical Engineering	•		•		•			•	•	•
PT- 11	ITB Polytechnic For Manufacturing, Bandung	•		•							
PT- 12	North Sumatra University (USU), Medan	•	•	•		•	•			•	
	Fac. Of Math. & Natural Science										
PT- 13	Surabaya Institute of Tech. (ITS) Surabaya										
	Department of Chemistry			•							
PT- 14	Surabaya Institute of Tech. (ITS) , Surabaya										
	Department of Chemical Engineering			•					•		
PT- 15	University of Sebelas Maret, Solo										
	Fact. Math & Natural Science			•	•	•					
PT- 16	University of Indonesia , Jakarta										
	Department of Chemistry		•	•		•			•		
PT- 17	Univeresity of Indonesia, Jakarta										
	Department of Gas Technology										
PT- 18	University of Indonesia, Jakarta										
	Department of Metalllurgy	•				•					
	INDUSTRIES										
NI- 01	PT. Abadi Adimulia										
NI- 02	PT. Audio Sumitomo Techno				•			•			•
NI- 03	PT. Bakrie Kasei Coporation			•							
NI- 04	Chandra Asri Petrochemical Centre	•	•	•	•	•	•				
Ni- 05	PT. Eternal Buana Chemical Industries			•							
NI- 06	PT. Federal Motor				•			•			•
NI- 07	PT. Gajah Mesin										
NI- 08	PT. Intilon Sagita				•			•			
NI- 09	PT. Jaya Fibrindo Karsa Pratama	•	•		•						
NI- 10	PT. Maspion	•			•			•			
NI- 11	Risyad Brasali Industries	•	•	•	•	•					
NI- 12	PT. Supratik Suryamas				•			•			•
NI- 13	PT. Tomoko Daya Mas							•			
NI- 14	PT. Tripolyta Indonesia		•	•				•			
NI- 15	PT. Unilever Indonesia	•	•		•						
	ASSOCIATION & PROF. SOCIETIES										
AS- 01	Indonesan Federation of Plastics Industries										
	(FIPLASIN)										
AS- 02	Indonesian Plastic Center										
	Sentra Plastik Indonesia (SPI)										
AS- 03	Indonesian Plastics Manufactirers										
	Asociation (APINDO)										
AS- 04	Indonesian Plastic Recycling Industies										
	Association (AIDUPI)										•

ATTACHEMENT 1

Topics of Polymer R&D in Indonesia

CODE. NO	INSTITUTION GOVERNMENT RESEARCH INSTITUTION	1	2	3	4	5	6	7	8	9	10
AS- 05	Indonesian Polymer Association (HPI)										
AS- 06	Indonesian Producers of Basic Plastic Mat.										
	(A.B. Plastik)										
AS- 07	Indonesian Woven Polyolefine Manufacturers										
	Association (GIATPI)										
AS- 08	Plastic Pipe Producers Association (AP3)										
	NOTE										
1	Polymer blend & composites										
2	Polymer Characterization										
3	Polymer Synthesis & Reaction										
4	Polymer development										
5	Polymer structure & properties										
6	Polymer degradation										
7	Plastic Processing										
8	Membranes										
9	Biodegradable polymers										
10	Polymer recycling										

32. Plastic Production in the Philippines

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I. INTRODUCTION

The worldwide industrialization, the advent of new technologies, and the changing lifestyle of the people, one of the considered versatile products used in industrial, commercial, and household is plastic. Plastic is the product of science and technology research introduced in the 20th Century. It has become extensively used as consumer products packaging, industrial processes, research laboratory supplies and even in the construction and engineering.

Commercial production of plastic in the Philippines began in the 1960s. In 1987, the plastic processing sector in the Philippines has grown to about six hundred (600) companies compared to early 80's that is about 200 companies. These companies ranged from relatively large to small, one-machine operations.[3] Of the 600 companies, 300 are classified as fabricators while the others are cutting, assemble, glue or machine semi-finished products. Casting of polyester resin into fiber glass is another operation these local industries are doing.

The plastic industry in the Philippines are divided or classified according to the processes employed and the products produced as shown in Table 1. It is noticed that plastics do not require sophisticated processes to produce the desired products which are merely by extrusion, molding and

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[3] Report presented by Mr. Antonio Dy Ching Bing, President Philippine Plastic Industrial Association, Philippine Country Report on the Plastic Industry, 3rd ASEAN Federation of Plastic Industries Conference, 12-14 January 1989, Manila, Philippines

additives that requires application of heat at a desired temperature. Due to its low boiling point, plastics could easily be processed into useful products however, its environmental impacts based on its biodegradability is still at present a pressing environmental issue or concern. Further, disposal of plastics is one of the major concerns of environmentalist due to its non-biodegradability and potential source of toxic gases like dioxin and furans when burned at low level temperature. Another concern is flooding especially in the Metro Manila area wherein improper management and disposal of these plastic wastes is experienced.

Table 1: Processes involved in the manufacture of plastic products

PROCESS(ES)	PRODUCT(S)
Extrusion process	Film bag, nets and ropes, pelletized or recycled plastic products, pipes, profiles, sheets, wires and cables, woven sacks, etc.
Molding process	Housewares, industrial parts or products (e.g. crates), packaging containers (e.g. bottles), personal care products, toys and novelties, wearables.
Specialty process	Adhesive tapes, calendered products, castings, dip coated products, laminated or coated or metallized products, office and school supplie(s), printed plastic products, vacumm formed products.

II. PLASTIC PRODUCTION

Plastic and polymer production in the Philippines is composed of the manufacturers of polyvinyl chloride (PVC) resins, polystyrene resins, biaxially oriented polypropylene film and polyester film. At present, there are two (2) PVC resin and four (4) polystyrene resin manufacturers in the Philippines.

Since there is no petrochemical facility in the Philippines, most of the raw materials of these manufacturers are imported.

The petrochemical (synthetic resin) industry includes a wide range of products. These products are mainly used by packaging, construction, textile and transportation industries. Some of the plastic products commonly manufactured, produced or used in the Philippines are polyvinyl chloride (PVC), polyethylene (PE), polypropylene (PP) and polystyrene (PS) plastics. Table 2 shows the estimated size of the domestic market or industry that uses these petrochemical (synthetic) products. On the other hand, Table 3 presents the three (3)-consecutive years of consumption of plastic products and its growth rate as well as the estimated per capita consumption and its growth rate including the projected consumption for the year 2000.

Table 2. Size of Domestic Market of Petrochemical (Plastic) Products

Synthetic Resin used in Manufacturing Product	Estimated Size of Domestic Market (MT)	Total (%)
Polyethylene, PE	85,400	50
Polypropylene, PP	51,000	30
Polyvinyl Chloride, PVC	27,000	16
Polystyrene, PS	7,000	4

The estimated synthetic resin consumption was derived from the importation of plastic processors that also includes the local production of the synthetic resin manufacturers. From this, the major products produced for the local market include film bags (for consumer products packaging), calendered products, housewares (mostly food containers), woven sacks, industrial products and packaging containers.

Table 3. Estimated domestic consumption of plastic products.

Year	Estimated Consumption (MT)	Growth rate,%	Estimated per Capita Consumption (kg)	Growth rate, %
1990	227,000	8.0	3.69	5.7
1991	244,000	7.5	3.88	5.1
1992	263,000	7.8	4.09	5.4
2000	466,000	9.6	6.04	6

The domestic consumption of the four (4) major synthetic resins is estimated in 1992 to be 263,000 metric tons (MT) and by the year 2000, a total of 466,000 MT is estimated to be consumed. The projection is based on a regression equation that correlated the historical values of the gross national product (GNP) in constant 1972 prices and the consumption or importation of the synthetic resins. In the absence of a petrochemical in the Phillippines, all the raw materials for the plastic industry are imported.

Plastic products containing PVC or products made from PVC resins constitute seventy-seven percent (77%) of the total export of the 4 major synthetic resins in 1986. Other products made of polypropylene shared twenty-one percent (21%) of the export while PE and PS plastic products were minimal. Data from the Foreign Trade Statistics of the Philippines' National Census and Statistics Office (NCSO) showed that for the seven-year (7) period [1980-1986], export of plastic products made from the four (4) major resins considered fluctuating (Table 4).

Table 4. Philippine Plastic Product Export

YEAR	QUANITY MT)	%INCREASE (DECREASE)	FOR VALUE US $'000
1980	6,340	135	5,712
1981	14,921	(59)	14,344
1982	6,092	0	7,365
1983	6,091	(24)	6,728
1984	4,638	86	5,681
1985	8,623	10	10,537
1986	9,446		13,461

III RECYCLING, TREATMENT AND DISPOSAL OF PLASTICS

Generation of plastic wastes has increased substantially from the household, commercial, and industrial activities and has become a major problem in the country. With the advancement of alternative technologies in the plastic industry sector as well as the government's effort in promoting pollution prevention and waste minimization towards achieving the goal of sustainable development, treatment and/or recycling facilities has emerged in the Philippines.

At present, there are three (3) industrial facilities that are into treatment or recycling of scrap plastic. Some of these scrap materials are being recycled into new products mainly as an alternative to using virgin plastic products in the construction industry as well as sanitation. According to these facilities, locally collected or sourced plastics are insufficient to sustain their production requirements. Thus, these facilities have resorted to importation of scrap plastic materials. Scrap plastics came mostly from Germany, Japan, Korea, Taiwan, the Netherlands and the USA.

Table 5: Importation of Scrap Plastics

YEAR	VOLUME (MT)
1994	6,760
1995	13,450
1996	16,017
1997	59,082.5
1998	61,430

Most of the products produced from the recovered or recycled plastics are pipes and fittings for sanitation and electrical installations in the construction of buildings and offices. Some good and better quality plastics, due to its homogenous segregation, are used in the manufacture of some housewares and industrial products packaging (heavy duty like drums, crates, carbouys and bottles). The most common process used is extrusion and molding.

With the promotion of life cycle analysis (LCA), closing the loop in the plastic industry is now a step ahead in the other industrial sectors. Some of the synthetic resin manufacturers are putting their effort and time in conducting research with the goal of upgrading their products into an environment-friendly as well as human health friendly.

IV. NATIONAL ENVIRONMENTAL LEGISLATION IN THE PHILIPPINES

In 1990, the Philippine Senate and Congress enacted Republic Act No. 6969 ***the "Toxic Substances and Hazardous and Nuclear Waste Control Act of 1990"***. This environmental legislation provides for the regulation of the use of toxic substances and the disposal of wastes classified as hazardous that has impact to the environment and to human health. The use of plastics in the manufacture of children's toys i.e. teethers and feeding bottles, housewares and plastic bags had been an issue.

In 1994, issue of the importation of hazardous wastes has emerged and to address this issue, the DENR-EMB issued the DENR Administrative Order No. 28, Series of 1994 (DAO 94-28) entitled ***"Interim Guidelines for the Importation of Recyclable Materials Containing Hazardous Substances".*** DAO 94-28 regulates the importation of scrap plastics, electronics scraps, scrap metals and lead acid batteries among others. Importation guidelines require the approved notification procedures of the Basel Convention on the Control of the Transboundary Movement of Hazardous Wastes and Their Disposal.

V. ISSUES AND CONCERNS ON PLASTIC PRODUCTION AND MANAGEMENT OF ITS WASTE PRODUCTS

The improvement of plastic production, distribution, consumption and management of waste products is the major issue/concern of the plastic industry. To address this issue research and development efforts should be done. The promotion of upgrading the plastic processing facilities and inclusion of modernization activities in the plastic processing industry should be encouraged. The establishment of a Plastic Research and Development Center which will provide technical support to the plastic industry should be looked into.

33 . Production and Consumption of Plastics and the Treatment of Plastic Waste in Vietnam

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1. Introduction:

Like many other low-income developing countries, Vietnam is currently facing critical problems because of the degradation of its natural resources and the decline in its environmental quality. After 30 years of devastating war, the Vietnamese people and the Government have made efforts to develop the economy while at the same time conserving resources and protecting the environment. The ongoing transition from a centralized planned economy to a market-oriented one, accelerated economic growth, the liberation of agricultural and industrial production, as well as the development of the service sector, the opening of the country for foreign investment, and the promotion of exports and participation in regional and international trade are all of great benefit to the people of Vietnam, as they mean relatively rapid economic growth, but at the same time, Vietnam is being confronted with a number of very real trade-offs in its development objectives between growth and the environment. Among the serious environmental problems such as deforestation, the degradation of land resources, the inefficient conservation of fresh water, and fresh water shortage, the overexploitation of biological resources, threats to ecosystems, the depletion of genetic resources and rise of environmental pollution, the yearly fast increasing amount of nondegradable plastic waste becomes one of the most serious one.

2. Production of plastics:

The first factory of PVC production is Viet Tri Chemical factory, founded in 1960. It produced yearly 150 tons PVC. But because of the war, the factory had to stop producing it in 1967.

The recent years (90-99) the plastic processing develops with increasing rate, average yearly 28%.

Most plastic materials in Vietnam now are imported from abroad. The total amount imported plastics (PE, PP, PVC, PS... and plasticizer (DOP) in 1995 was 230,000 tons, in 1996 was 283,000 tons, in 1997 was 350,000 tons.

3. The consumption of plastics:

The consumption of plastic in Vietnam is increasing:

- In 1990 - Plastic consumption 0.5kg/person.
- In 1996: It reaches 5.7kg/person.
- In 2000 it expects 11kg/person.

The consumption of plastics is expected:
In 2000: 800,000 tons.
In 2005: 1,300,000 tons.
In 2010: 2,100,000 tons.
Thus, the average will be 15 kg/person in 2005.
and 23kg/person in 2010.

It is expected that the consumption of plastics in the industrial branches increases about 25-30% in 2010.

4.The demand of PVC:

In the year 2000 it demands: 100,000 tons.
In 2005: 200,000 tons.
In 2010: 400,000 tons.

The demand of PE is about 150,000 - 250,000 tons per year.

The demand of PP is about 75,000 - 100,000 tons per year.

5.Industry of plastic processing:

It focuses on 4 main groups of the products, as it is shown in the following table:

Year / Material	In 2000, (%)	In 2010, (%)
Bag	30	30
For construction	30	25
Household appliances	15	20
For Industry	15	25

The demand of plastics for industry is increasing (about 30% in 2010).

6.Production of plastics in Vietnam:

At present there are 2 joint venture factories:
- A factory for production of plasticizer (dioctylphtalate) 30,000 tons/year.
- A factory for PVC production in DONGNAI, South Vietnam making about 80,000 tons/year.

Besides, there are 45 factories for plastic processing.

7. Solid waste:

The consumption of plastics is increasing year by year. This implies that the amount of solid waste should be also increasing.

For example, in Hanoi:

- In 1995 the amount of solid waste was of 245,348 tons (about 589,790 m^3), among them, plastic bags: 1.7%.
- In 1996: the amount of it was 200,633 tons (about 689,638 m^3), among them, plastic bags: 3.2%.
- In 1997: the amount of it was 322,376 tons (about 744,942 m^3), among them, plastic bags: 5.7%.

8. Degradable plastics:

8.1. Situation:

At present the degradable plastics has not been produced anywhere in Vietnam. The Institute of Industrial Chemistry (I I C) only started investigating in this field in 1998, the I I C continues now this research with the aim that in 2003 it can make the plastics with degradability of 75- 90%.

8.2. Application:

- To replace the nondegradable plastic shopping bags.
- To produce the pots for cultivate seedlings for Ministry of Forestry.

9. Domestic need of plastics:

It estimates that in the year 2000 -2003 the need of plastics is about 800,000 - 1000,000 tons/year.

Thus, if it spends 10% for the plastic bag production, so it needs about 80,000 - 100,000 tons degradable plastics per year.

According to the orientation plan of plastic industry, the percentage of the consumption for the plastic bag production is increasing 3 times (240,000 - 300,000 tons per year).

Besides, the Forestry needs about 400 - 600 tons degradable plastics for soil protective membrane and plastic pots for cultivate seedling.

10. Approach of solving the environmental problem caused by plastic waste:

There are two solutions for solving the environmental problem caused by the plastic waste:

a, Recycling of the used plastics.

At present in Vietnam there has not yet any factory or enterprise of the Government where the waste plastics is reused. But there are the small private enterprises that are using the recycling plastics to make various products. So, there are the people who are collecting the old already used plastics to provide those enterprises. Although this is a spontaneous process, only by this way about 30-40% of total plastic waste are collected.

b, Production of the new degradable plastics or modification of polyethylene, polypropylene... to obtain the degradable membranes.

Besides the I[C, as mentioned above, there are some other institutions in Vietnam now, that involve also in solving this environmental problem caused by the plastic waste. For example: National Centre for Sciences and Technology, Hanoi University of Technology, HoChiMinh University...)

The research directions they are dealing with are as the following:

a: Production of degradable plastic membranes based on polycarprolactones and their derivatives.

b: Production of plastics filled with the natural fibers.

c: Modification of PE, PP... with polysaccharides and starch... to obtain the degradable membranes.

11. Development of Environmental Management

The Vietnamese Government has made efforts to protect the environment. A National Conservation strategy was prepared in 1985 and since then a National Action Plan for the Environment and sustainable development has been developed and partly implemented. On the base of this National plan, various activities are being carried out in the country relating to environmental legislation, management, education, research and experimentation.

In December 1993, the National Assembly of the Socialist Republic of Vietnam passed the Law on environmental protection. This is the country basic environmental Law, which includes an introduction and 5 chapters on:

(1) general provision, containing 9 articles.

(2) protection and abatement of pollution and environmental quality degradation, containing 20 articles.

(3) solving the problem of the environmental pollution and environmental risk, containing 9 articles.

(4) environmental management containing 9 articles.

(5) international cooperation in environmental protection, containing 4 articles.

(6) environmental inspection and procedures for violation of the law, containing 8 articles, and

(7) law on implementation, containing 2 articles.

The central government and the local people's committee, on the provincial, municipal, district and village levels, which are the executive bodies, are responsible for enforcing the law. The Ministry of Science, Technology and Environment and its affiliated offices at the corresponding levels are the agencies responsible for the technical aspect of its enforcement.

In order to promote environmental management at all levels, many training courses in environmental engineering, environmental economics, environmental management and impact assessment have been organised by MOSTE and different universities and colleges. Through these training activities, there are now many hundreds of people in Vietnam with a basic knowledge of environmental science , EIA and environmental management involves in practical environmental activities.

The Vietnamese people and Government are currently receiving support of various kinds for resource conservation and environmental protection from developed countries including Sweden, Australia, Denmark, France and Germany. Vietnam also cooperates with and receives technical aid from developing countries in the region, as well financial and technical aid from many international organisations and funding agencies. Internal efforts combined with this external assistance are creating favorable conditions for the implementation of sustainable development in Vietnam.

12. Conclusions:

The ongoing transition from a centralized planned economy to a market-oriented one accelerated economic growth, the Liberation of agricultural and industrial production, as well as the development of the service sector, the opening of the country for foreign investment, and the promotion of exports and participation in regional and international trade are all of great benefit to the Vietnamese people, as mean relatively rapid economic growth, but at the same time, Vietnam is being confronted with a number of very real trade-offs in its development objectives particularly between growth and the environment.

The solid plastic waste is one of the serious environmental problem, that has to be solved.

The Vietnamese Government has made efforts to protect the environment.

A National Conservation strategy was prepared in 1985 and since then a National Action Plan for the Environment and sustainable development has been developed and partly implemented.

We believe that the environmental problem in general and problem of plastic waste in particular in Vietnam are being gradually solved.