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SELECTED PAPERS FROM

International Workshop on ENVIRONMENTALLY DEGRADABLE POLYMERS: POLYMERIC MATERIALS AND THE ENVIRONMENT

Doha - Qatar, March 21-25 1999

Editors: Ziad F. Said
Emo Chiellini

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ENVIRONMENTALLY DEGRADABLE POLYMERS

Selected papers from ICS – UNIDO International workshop on Environmentally Degradable Polymers:

Polymeric Materials and the Environment

Organized by

United Nations Industrial Development Organization :
The International Centre for Science and High Technology (ICS)

and

Scientific and Applied Research Centre (SARC)
University of Qatar
Doha – Qatar, March 21 – 25, 1999

Edited by :

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FOREWARD

This publication is the outcome of an international workshop organized, jointly, by the International Centre for Science and High Technology (ICS) and the Scientific and Applied Research Centre (SARC) - University of Qatar held in Doha on March 21-25, 1999.

The workshop was attended by 50 experts and participants from many disciplines in 19 countries participants' affiliations included Universities and Polytechnics, R & D, industrial and environmental institutions.

The main objectives of the workshop are as follows:

1. To provide participants from developing countries with updated knowledge and information on recently introduced and evolving technologies concerned with environmentally related problems in polymer producing, processing and end of life disposal industries.
2. Update the scientific and technological knowledge of the participants in terms of the waste management of polymeric materials and to stimulate planning for the minimization of waste generation.
3. To raise industrial, academic and public perceptions on the issues of environmental effects of plastics, and to emphasize the positive contributions that manufacturing industries can make including the increased utilization of environmentally degradable polymers (EDPs).
4. To stimulate international research and technology transfer and enhance international cooperation through possible, joint or follow-up projects and feasibility studies which could be coordinated by ICS-UNIDO.

A total of forty-three papers were presented. These were classified into four categories as : general lectures, case studies, research papers and country reports.

For this publication, twenty-four papers were selected which cover the main topics and satisfy the general objectives of the workshop. Some of them were reviewed and edited to become consistent with the general textural form of the book.

We regret that some participants have failed to send full texts of their contributions. Few papers were also excluded for being irrelevant to the main topics of the workshop. Nevertheless, the present contributions cover the major and most important topics related to EDPs and plastic waste management.

We gratefully acknowledge the financial contributions to the workshop from Qatar Petrochemical Company (QAPCO) and Qatar Industrial Manufacturing Company (QIMCO).

We also acknowledge the efforts of other members in the organizing committee, the administrative and secretarial staff at SARC and University of Qatar for their collaboration and efforts that helped in making the workshop a success.

This book would not have been possible without the work of Mr. Soman who typed the major part of the manuscript and Mr. K. Shanmughan who typed the final corrections, and finally Eng. M. Manadilli who designed the cover and worked out some computer manipulations.

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Introduction to the ICS-UNIDO Programmes and Activities in the Area of Pure and Applied Chemistry, with Special Focus on the Sub-programme of Environmentally Degradable Plastics

PREFACE

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 first event of 1999 in the Subprogramme on EDPs is the Workshop on "Environmentally Degradable Polymers: Polymers and the Environment", scheduled for 21-25 March; Qatar was selected as the hosting country of this event, due to the importance of the Gulf region in the exploitation of raw materials for plastic production as well as for plastic production itself. The relevant development of environmentally degradable plastics in this region has therefore a great potential for economies and environmental issues at a global level.

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January 2000

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Environmentally Degradable Plastics. 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 appeared on EDPs and related issues (9-13).

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

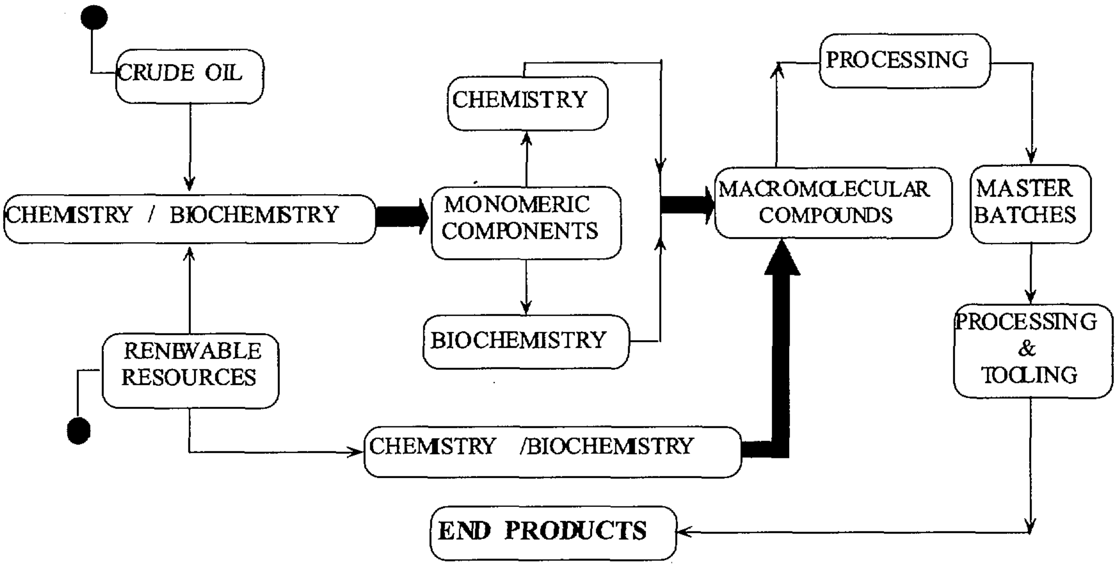
1. ***Petrochemical polymers*** (raw material crude-oil, and multistep processes for their production). They are better known as *synthetic polymers*.
2. ***Natural polymers*** of organic and inorganic origin that are used without any major chemical modification (cotton, juta, wool, silk, microbial polyesters, 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 M Tons including agrifood, mines and sludge: 1,564 M Tons (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

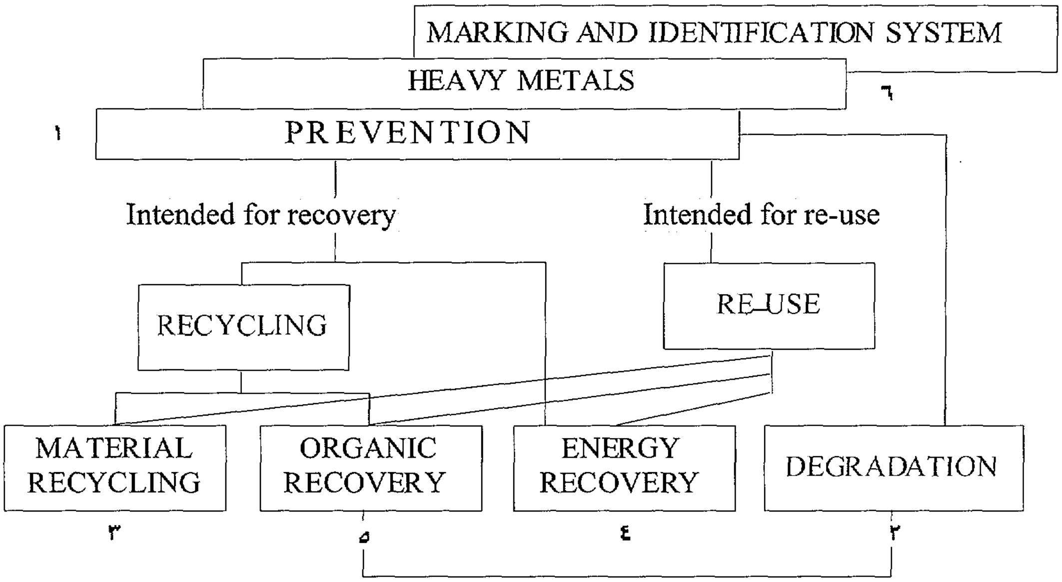
- ***Municipal solid waste***
  Waste coming from households, offices, retailers and small industries.
- ***Distribution***
  Waste generated by the distribution activity. It is mainly packaging. These waste are collected by private collectors.
- ***Large industry***
  Waste generated by large industries. 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 ١٩٩٧(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.

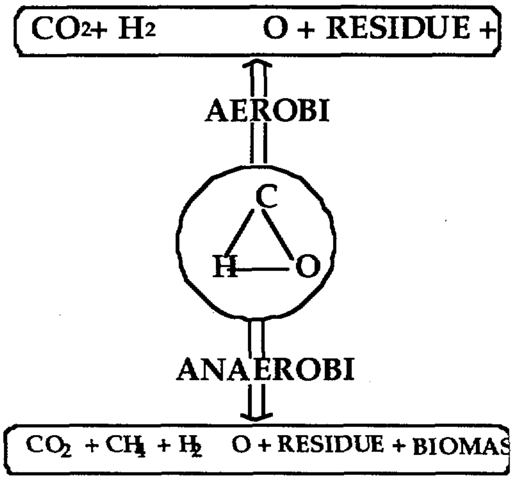
Chart 9: Potential Factors Impacting Polymer Degradation

○ **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.

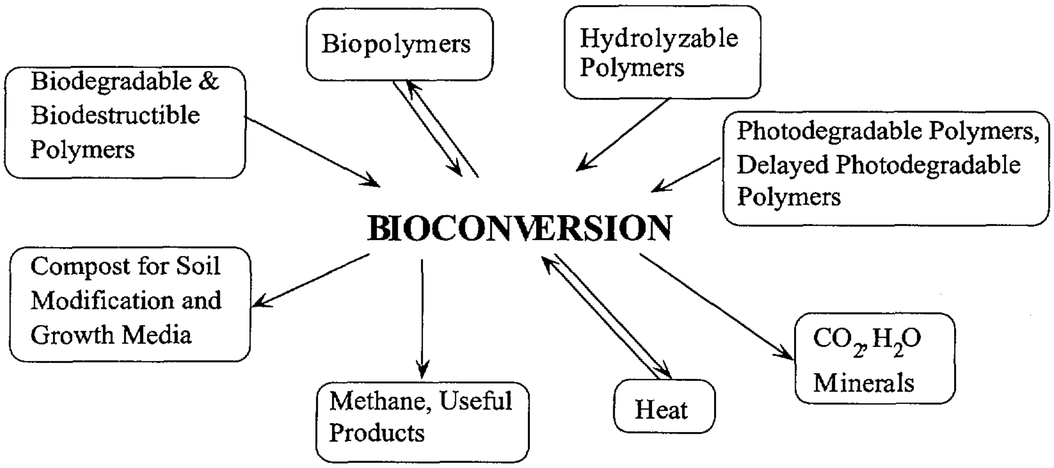
Chart 10: Biodegradation of materials containing C, H, O



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

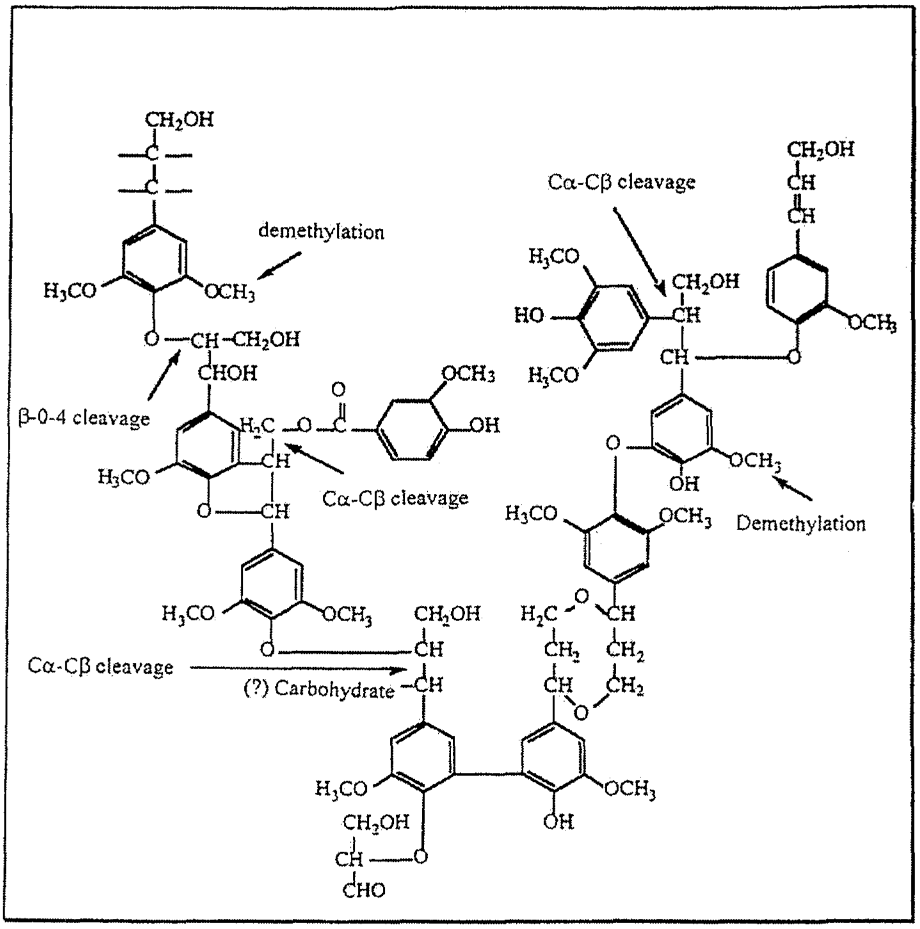


Chart 15 : Lignin degradation by phanerochaete

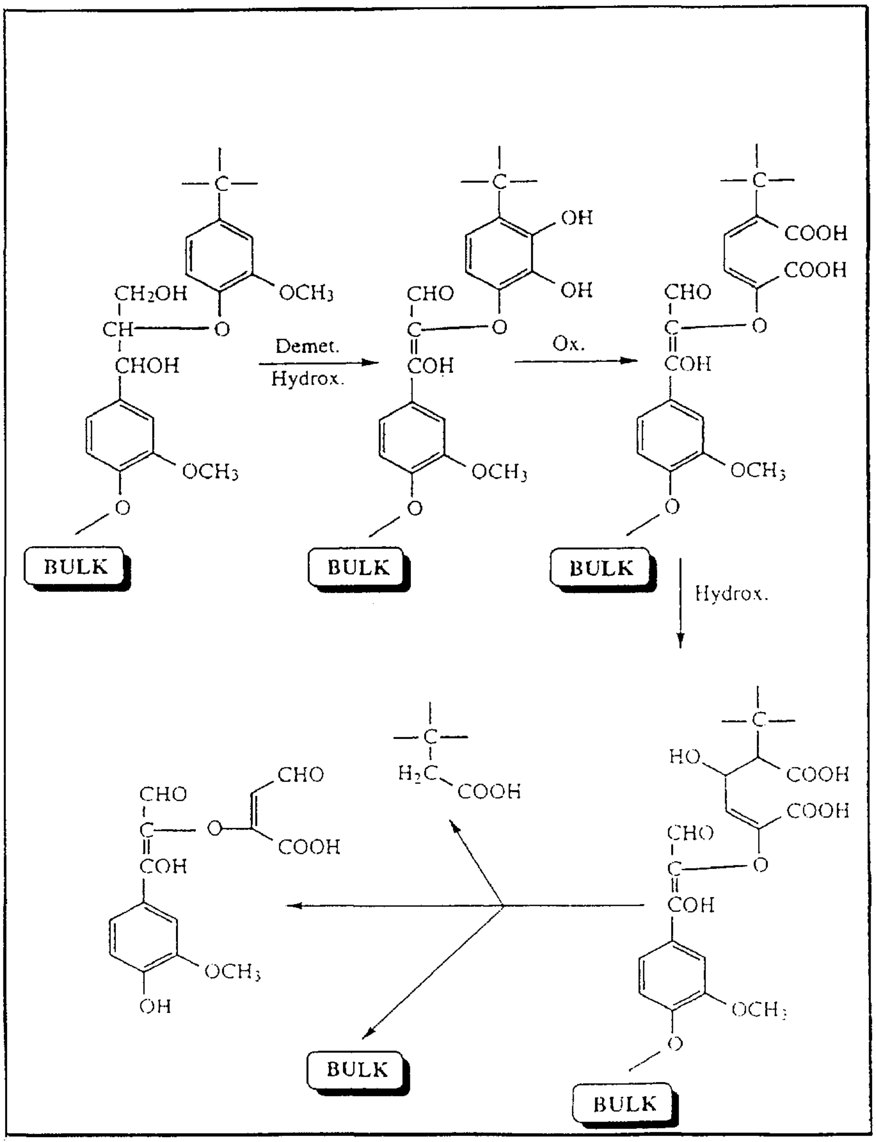


Chart 16: LMW fragments identified in lignin degradation by *white-rot* fungi

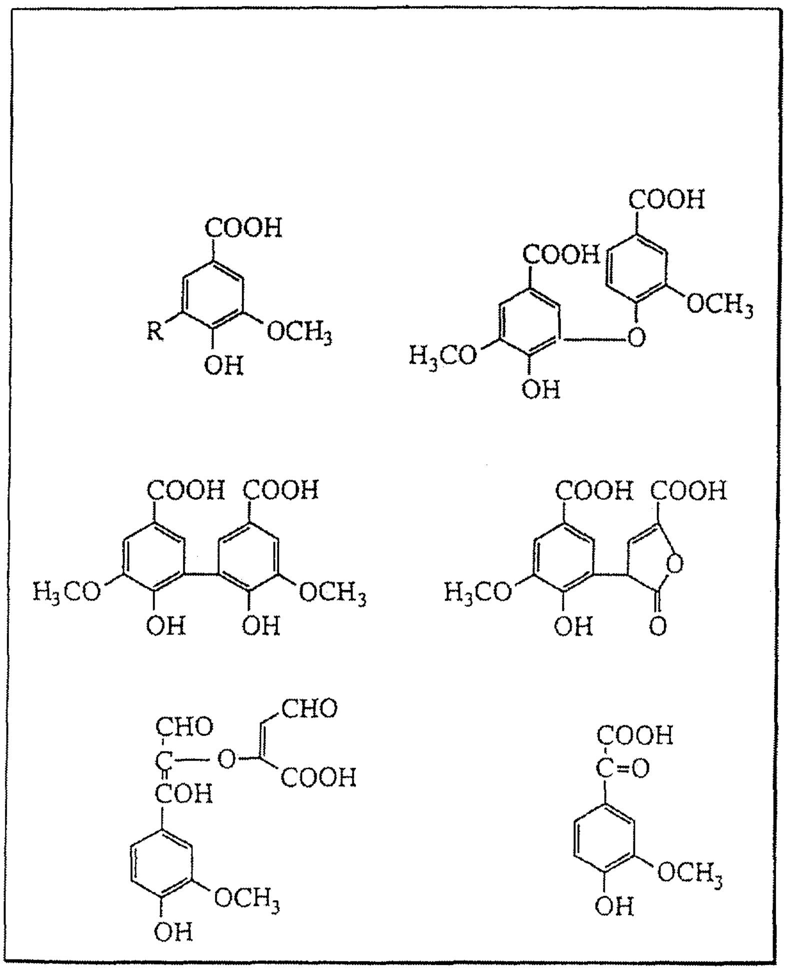
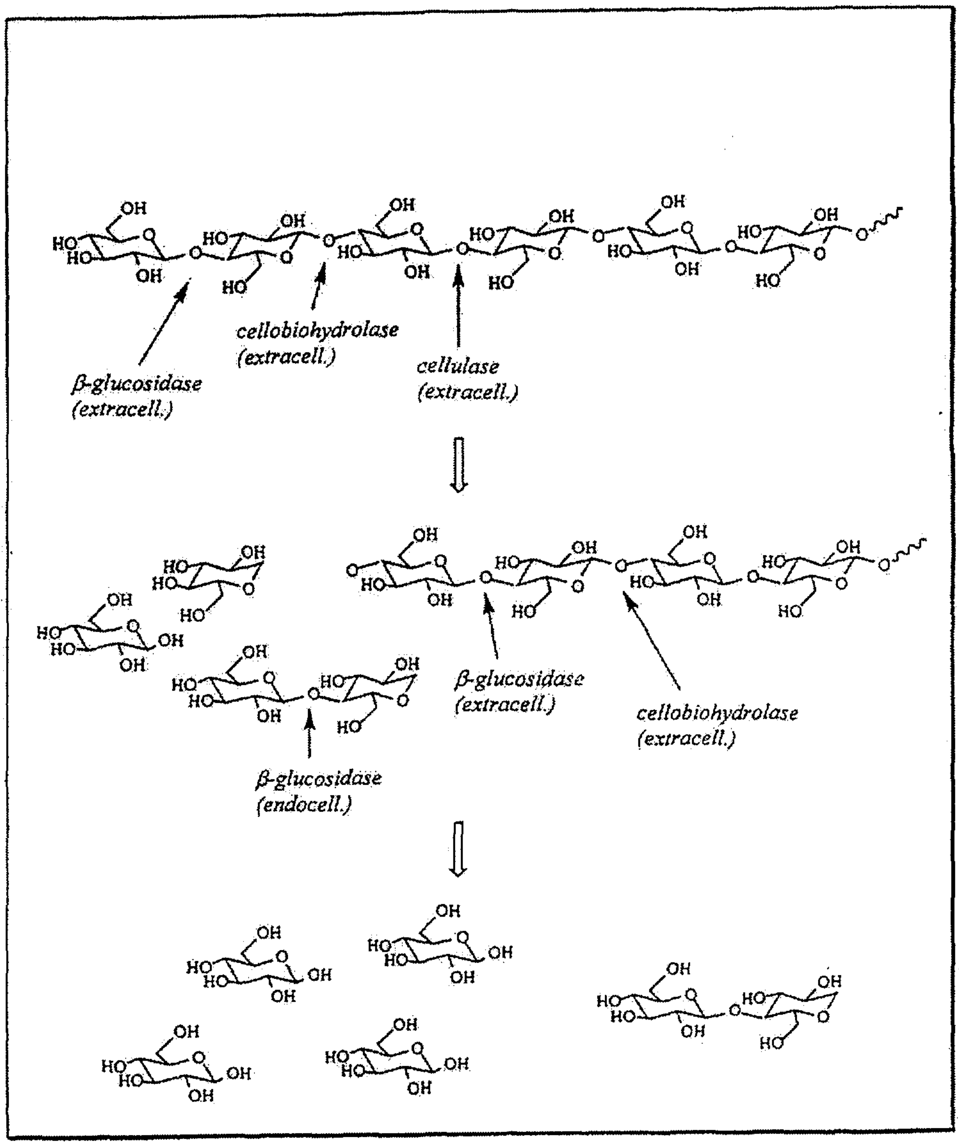


Chart 17: Cellulose biodegradation



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.

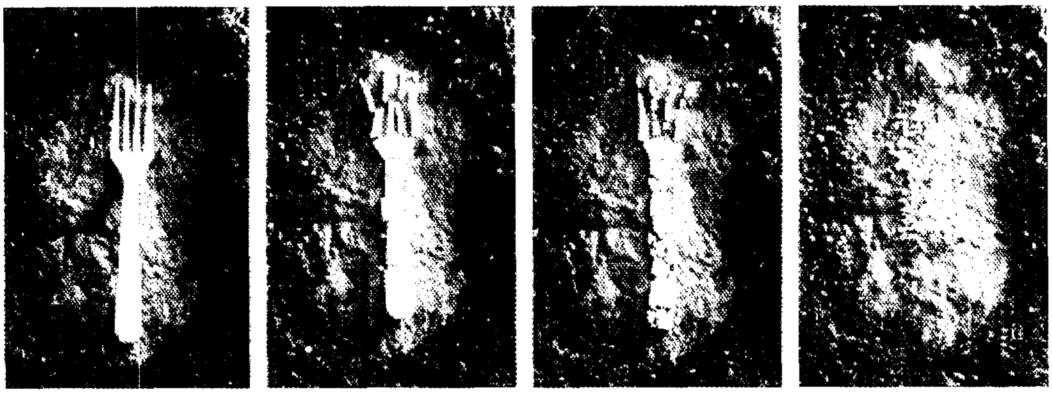
Chart 18: Environmentally Degradable Polymeric Materials From Renewable Resources

ADVANTAGES	DRAWBACKS	REMEDIES
◆ Ample Structural Variety Combined with High Versatility	◆ Limits Imposed by Production Costs	◆ Incentives for the Develop-ment 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 accompanied 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$_{TM}$ - 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

complete degradation to carbon dioxide, water and soil nutrients after 60days

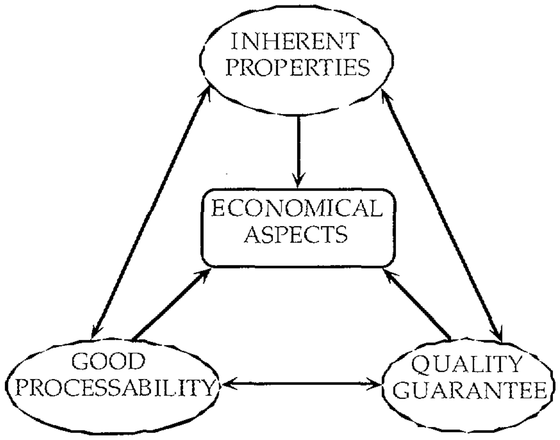
In the ecobalance, the life-cycle assessment of the plastic manufact plays indeed a key role. The main parameters to beta ken into account are reported in Chart 20. A correct analysis of the impact of all them on the cost/effectiveness ratio should be taken into serious account by decisionmakers.

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 (Chart21).

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

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	
AmericanExcelsior	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

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* Materials soluble in water media

Chart 25: *(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

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* 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

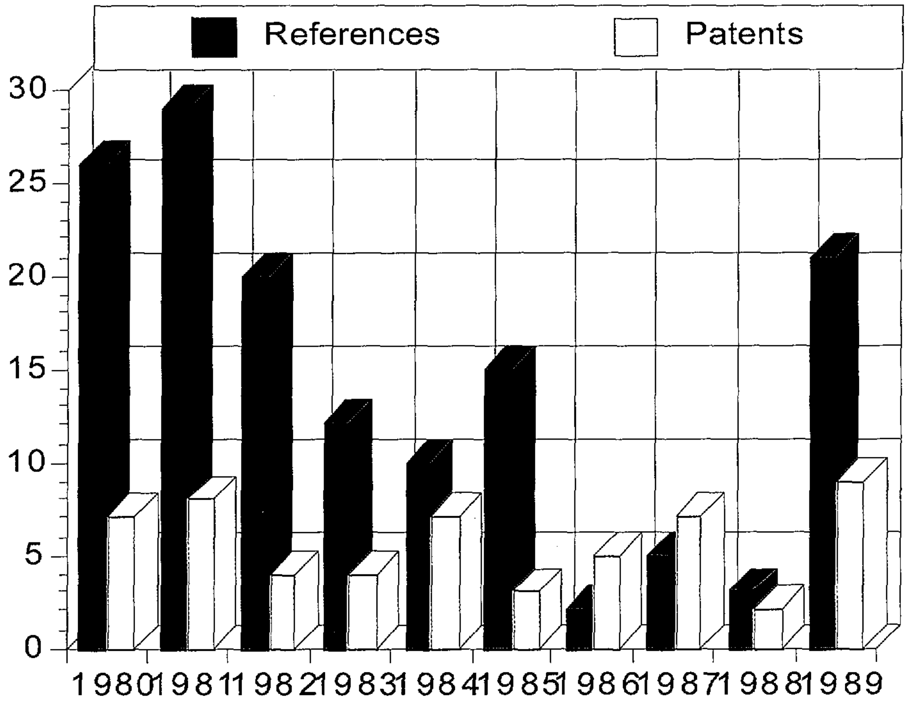
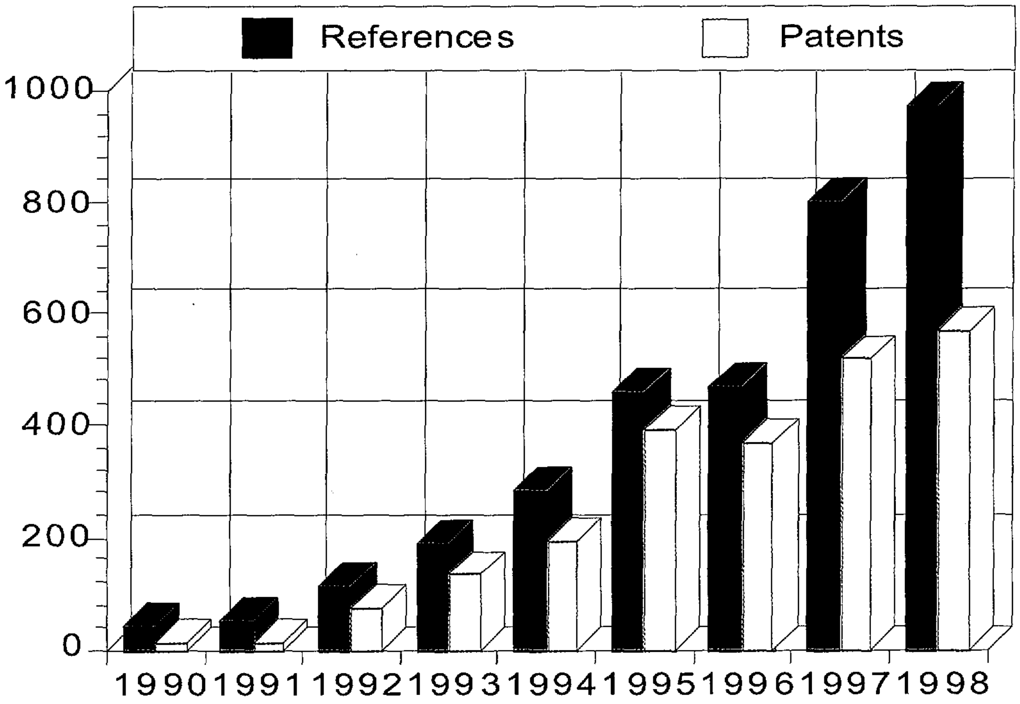


Chart 27: Total References & Patents on Biodegradables in the 90_s



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Rationale, Drivers and Standards for Biodegradable Plastics

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Abstract

New environmental regulations, societal concerns, and a growing environmental awareness throughout the world have triggered the search for new products and processes that are compatible with the environment. 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 have 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 criteria. This has opened up new market opportunities for developing biodegradable products.

Currently, most products are designed with limited consideration of its ultimate disposability. Of particular concern are plastics used in single-use disposable packaging. Designing these materials to be biodegradable and ensuring that they end up in an appropriate disposal system is environmentally and ecologically sound. For example, by composting our biodegradable plastic and paper waste along with other "organic" compostable materials like yard, food, and agricultural wastes, we can generate much-needed carbon-rich compost (humic material). Compost amended soil has beneficial effects by increasing soil organic carbon, increasing water and nutrient retention, reducing chemical inputs, and suppressing plant disease. Composting infrastructures, so important for the use and disposal of biodegradable plastics, are growing in the U.S. and are in part being regulatory driven on the state level.

As industry began implementing approaches to design environmentally benign products, questions about the practicality, efficacy, and the effects of such products on the environment were raised. The U.S. Federal Trade Commission (FTC), a group of State Attorney General's, State legislatures, and the U.S. Congress became very concerned about the various degradability and environmental claims being made, especially as it related to existing waste management practices. Verification of degradability claims and environmental fate and effects of the new degradable products using acceptable well-defined testing protocols were lacking.

It was in this confused, contentious, vexing, and regulatory action climate that ASTM Committee D20 on Plastics undertook the development of Standards in the area of "Degradable Plastics". ASTM's proven, century old, voluntary, consensus process involving a balanced participation of government, industry, and academe was well suited to bring order and understanding in this new area.

ASTM has, to-date, 26 approved Standards on the books. These Standards cover various photo and bio environments that plastics may be exposed to, and methods to quantify the degradability. Definitions for degradable, biodegradable, and compostable plastics were crafted by the subcommittee. The International Standards Organization (ISO), CEN (European) and DIN (German) committees have or are developing Standards for biodegrabale/compostable plastics. A successful effort has been made to ensure harmony between the evolving Standards in the various organizations.

The majority of the Standards address the composting disposal environment, given the importance of composting as an important, ecologically sound, disposal method that generates useful soil amendment product, important for sustainable agricultural practices.

INTRODUCTION

New environmental regulations, societal concerns, and a growing environmental awareness throughout the world have triggered the search for new products and processes that are compatible with the environment. 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 have to be factored into the design of the product. The use of annually renewable resources and the biodegradability or recyclability of the product are becoming important design criteria. This has opened up new market opportunities for developing biodegradable products.

Currently, most products are designed with limited consideration of its ultimate disposability. Of particular concern are plastics used in single-use disposable packaging. Designing these materials to be biodegradable and ensuring that they end up in an appropriate disposal system is environmentally and ecologically sound. For example, by composting our biodegradable plastic and paper waste along with other "organic" compostable materials like yard, food, and agricultural wastes, we can generate much-needed carbon-rich compost (humic material). Compost amended soil has beneficial effects by increasing soil organic carbon, increasing water and nutrient retention, reducing chemical inputs, and suppressing plant disease. Composting infrastructures, so important for the use and disposal of biodegradable plastics, are growing in the U.S. and are in part being regulatory driven on the state level.

Polymers have been designed in the past to resist degradation. The challenge is to design polymers that have the necessary functionality during use, but destruct under the stimulus of an environmental trigger after use. The trigger could be microbial, hydrolytic or oxidation susceptible linkages built into the backbone of the polymer, or additives that catalyze breakdown of the polymer chains in specific environments. More importantly, the breakdown products should not be toxic or persist in the environment, and should be completely utilized by soil microorganisms. In order to ensure market acceptance of biodegradable products, the ultimate biodegradability of these materials in the appropriate waste management infrastructures needs to be demonstrated beyond doubt.

As industry began implementing approaches to design environmentally benign products, questions about the practicality, efficacy, and the effects of such products on the environment were raised. The U.S. Federal Trade Commission (FTC), a group of State Attorney General's, State legislatures, and the U.S. Congress became very concerned about the various degradability and environmental claims being made, especially as it related to existing waste management practices. Verification of degradability claims and environmental fate and effects of the new degradable products using acceptable well-defined testing protocols were lacking.

The U.S biodegradable's industry fumbled at the beginning by introducing starch filled (6-15%) polyolefins as true biodegradable materials. These at best were only biodisintegrable and not completely biodegradable. Data showed that only the surface starch biodegraded, leaving behind a recalcitrant polyethylene material. Starch entrapped within the PE matrix did not appear to be degraded.

This resulted in a number of regulatory actions. Eleven States enacted environmental marketing claim laws. A task force of several State Attorney General's issued recommendations (Green Report I & II) on advertising related to products and environmental attributes. Between October 1990 and June 1992, 48 separate actions were taken for misleading or deceitful environmental advertising. The highest numbers of actions were on claims of biodegradable plastics, and the use of the terms biodegradable, recyclable, ozone friendly.

The initial Green Report I was very restrictive, basically prohibiting the use of terms such as biodegradable and compostable. However, Green Report II was more accommodating and allowed for the development and introduction of true biodegradable materials. For claims relating to biodegradability, Green Report II states:

"It may be appropriate to make claims about the "biodegradability" of a product when that product is disposed of in a waste management facility that is designed to take advantage of biodegradability and the product at issue will safely break down at a sufficiently rapid rate and with enough completeness when disposed of in that system to meet the standards set by any existent state or federal regulations."

Therefore, in order to ensure environmental, regulatory, and market acceptance of biodegradable plastics, the ultimate biodegradability of these materials needs to be demonstrated in appropriate waste management infrastructures (like composting or sewage treatment facilities or soil where biodegradation can occur). More importantly, the breakdown products of the biodegradation process should be non-toxic, and should not build up in the environment at a rate faster than it is being utilized by the microorganisms.

The U.S. Federal Trade Commission (FTC) guidelines states :

"Unqualified degradability claims should be substantiated by evidence that the product will completely break down and return to nature, that is decompose into elements found in nature within a reasonably short period of time after consumers dispose of it in the customary way ...."

With regards to compostability claims, the FTC guidelines state:

"........ substantiated by evidence that all the materials in the product or package will break down into, or otherwise become part of, usable compost (e.g., soil-conditioning material in a safe or timely manner in an appropriate composting program or facility , or in a home compost pile or device ....")

Thus it became increasingly clear that Standards were sorely needed in this area. Standard test methods and protocols were needed to establish and quantify biodegradability of the plastics, and to confirm the benign nature of the breakdown products. It is also clear that claiming biodegradability for a product without linking it with the waste management infrastructure that the product can be sent to, does not make environmental sense and is unacceptable.

STANDARDS FOR ENVIRONMENTALLY DEGRADABLE PLASTICS

It was in this confused, contentious, vexing, and regulatory action climate that ASTM Committee D20 on Plastics undertook the development of Standards in the area of "Degradable Plastics". ASTM's proven, century old, voluntary, consensus process involving a balanced participation of government, industry, and academe was well suited to bring order and understanding in this new area.

ASTM Technical Committee on Plastics (D20) formed a subcommittee D20.96 on "Environmentally Degradable Plastics" to address the issue of standards for degradable polymers. The scope of the subcommittee was the promotion of knowledge, and the development of standards (classification, guide, practice, test method, terminology, and specification)for plastics *which* are *intended to environmentally degrade.* One hundred and seventy plus members representing a broad spectrum of interests ranging from producers, converters, users, consumers, and general interest joined the subcommittee. Industry, government, academia, and national laboratories were represented on the subcommittee.

Recognizing the complexity and diversity of the standards development activity in this area, a modular standards development protocol was adopted. This is exemplified in Figure 1, and addresses:

- the environment that plastic will be exposed to (simulating a real world disposal system or environment)
- the test method to measure degradability (mechanical, and chemical property loss) and biodegradability (microbial assimilation/degradation)
- the fate and effects of the degraded products
- classification based on intended application

Using the protocol described in Figure 1, the subcommittee has, to-date, 26 approved Standards on the books. These Standards cover various photo and bio environments that plastics may be exposed to, and methods to quantify the degradability.. Table 1 lists the definitions crafted by the subcommittee. These definitions are now ISO (International Standards Organization) Standards as well. Table 2 lists the developed Standards The Standards measure biodegradability under different environmental/disposal conditions including composting, soil, marine, wastewater treatment, and anaerobic digestion. The original Standards activity was started in ASTM with CEN (European), DIN (German) and ISO Standards closely following the ASTM Standards with only minor variations. The majority of the Standards address the composting disposal environment, given the importance of composting as an important, ecologically sound, disposal method that generates useful soil amendment product, important for sustainable agricultural practices.

INTERNATIONAL STANDARDS ORGANIZATION (ISO) STANDARDS

ISO/TC 61 is the International Committee responsible for Plastics standards. Under this committee biodegradability standards are being developed as International Standards IN Subcommittee 5, Working Group 22. These Standards are in harmony with the ASTM, CEN

(European), and DIN (German) Standards. The Standards are expected to issue in 1999. They are:

- ISO/FDIS 14851 (Work item 619/639 combined)
  Plastics-Evaluation of the ultimate aerobic biodegradability of plastic materials in an aqueous medium-Method by determining the oxygen demand in a closed respirometer (TC61/SC5 N 798)

- ISO/FDIS 14852 (Work item 636)
  Plastics-Evaluation of the ultimate aerobic biodegradability of plastic materials in an aqueous medium-Method by analysis of released carbon dioxide (TC61/SC5 N 799)

- ISO/FDIS 14855 (Work item 641)
  Plastics-Evaluation of the ultimate aerobic biodegradability and disintegration of plastics under controlled composting conditions-Method by analysis of released carbon dioxide (TC61/SC5 N 800)

- ISO/CD 15985 (Work item 701) Plastics-Evaluation of the ultimate anaerobic biodegradability and disintegration of plastics under high solids anaerobic digestion conditions-Method by analysis of released biogas (TC61/SC5 N 861).

- This is based on ASTM Standard "Standard test method for determining anaerobic biodegradation of plastic materials under high-solids anaerobic digestion conditions [D5511-94]

- ISO/CD 14853 (Work item 637) "Plastics-Evaluation of the ultimate anaerobic biodegradation of plastics in an aqueous system-Method by analysis of carbon conversion to carbon dioxide and methane (TC61/SC5 N 831)".

- This is based on ASTM Standard "Standard test method for determining the anaerobic biodegradation of plastic materials in the presence of municipal sewage sludge [D 5210-91]". The project leader for this is Bruno DeWilde (Belgium) who was the ASTM project leader for this Standard.

- ISO/CD 15986 (Work item 702). "Plastics-Evaluation of the compostability-Test scheme for final acceptance (TC61/SC5 N 862)". This is based on ASTM Standard "Standard Guide to assess the compostability of environmentally degradable plastics [D6002-96]".

- ISO Work item 718. "Plastics-Determination of the ultimate aerobic biodegradability in soil by measuring the oxygen demand in a closed respirometer or the amount of carbon dioxide released". The ISO committee noted that the content of the existing similar ASTM D5988 method will be consider in preparing the draft.

European Standards (CEN, DIN)

The European Commission (EC) has mandated the development of Standards for Biodegradable Packaging Materials. This is under the jurisdiction of CEN TC 261(packaging)/SC4(packaging & environment)/WG2(degradability & compostability). The

Standard under development is very similar to the ASTM D6002, except that it has pass/fail specifications built into it. The key specification is the requirement of >90% biodegradability for blends, copolymers etc., and >60% biodegradability for homopolymers as measured by ISO 14855 (controlled composting) test method.

In Germany for biodegradable plastics to be accepted in compost operations and satisfy the DSD requirement, the plastic will have to pass the DIN V 54900. This is similar to the CEN standard and is a three tiered testing protocol (like the ASTM D6002). It has the same strict pass/fail requirements of the CEN Standard – requiring complete biodegradability and disintegration to become a integral part of the compost. A product certification from DIN-CERTO (an affiliate of the DIN Standards Organization) would be needed – third part validation.

Table 1: ASTM & ISO Definitions on Environmentally Degradable Plastics

degradable plastic, n -- A plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and the application in a period of time that determines its classification.

biodegradable plastic, n -- A degradable plastic in which the degradation results from the action of naturally-occurring micro-organisms such as bacteria, fungi and algae.

photodegradable plastic, n -- A degradable plastic in which the degradation results from the action of natural daylight.

oxidatively degradable plastic, n -- A degradable plastic in which the degradation results from oxidation.

hydrolytically degradable plastic, n -- A degradable plastic in which the degradation results from hydrolysis.

Compostable plastic, n -- a plastic that undergoes degradation by biological processes during composting to yield carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with other known, compostable materials and leaves no visually distinguishable or toxic residue.

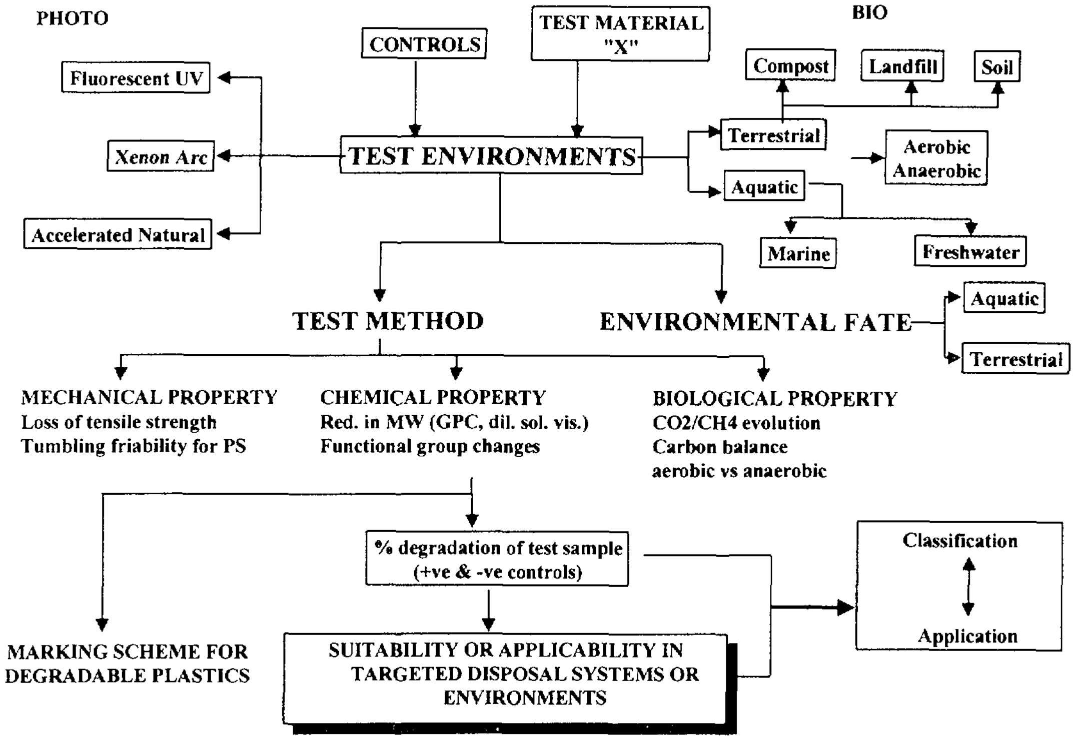

Figure 1: ASTM D20.96 Standards Development Protocol

Table 2: List of Environmentally Degradable Plastics Standards (ASTM)

Composting Environment

1. Standard test method for determining the aerobic biodegradation of plastic materials in the presence of municipal sewage sludge [D 5209-91].
2. Standard test method for determining the aerobic biodegradation of plastic materials under controlled composting conditions [D5338-93].
3. Standard practice for exposing plastics to a simulated compost environment [D5509-94]
4. Standard practice for exposing plastics to a simulated compost environmnet using an externally heated reactor [D5512-94]
5. Standard test method for determining weight loss from plastic materials exposted to a simulated municipal solid waste (MSW) aerobic compost environment [D6003-96]
6. Standard test method for determining the aerobic biodegradation in soil of plastic materials or residual plastic materials after composting [D5988-96]
7. Guide to assess the compostability of environmentally degradable plastics [D6002-96] – ISR program
8. Standard test method for determining weight loss from plastic materials exposed to a simulated municipal solid-waste (MSW) aerobic compost environment [D6003-96]
9. Standard test for determining Aerobic biodegradation of Radiolabeled Plastic materials in compost environment [New Standard, in committee ballot] – ISR program
10. Standard Test Method for Determining aerobic Degradation of Plastic Materials in a Full Scale Composting Environment [New Standard, in committee ballot] – ISR program
11. Specifications for Compostable Plastics [New Standard, in process] – ISR program

12. Standard practice for preparing residual solids obtained after biodegradability standard methods for toxicity and compost quality testing [D5951-96] – **Fate & Effect testing**
13. Standard Practice for water extraction of residual solids from degraded plastics for toxicity testing [D5152-91] – **Fate & Effect testing**

Anaerobic digestion/processes

14. Standard test method method for determining the aerobic biodegradation of plastic materials or residual plastic materials after composting in contact with soil [D5988-96]
15. Standard test method for assessing the aerobic biodegradation of plastic materials in an activated-sludge-wastewater-treatment system [D5271-92]
16. Standard test method for determining the anaerobic biodegradation of plastic materials in the presence of municipal sewage sludge [D 5210-91]
17. Standard test method for determining anaerobic biodegradation of plastic materials under high-solids anaerobic digestion conditions [D5511-94]
18. Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under Accelerated Landfill Conditions [D5526-94]
19. Standard Practice for Exposing Plastics to a Simulated Landfill Environment [D5525-94A]

Other.

20. Standard Practice for Weathering of Plastics Under Marine Floating Exposure [D 5437-93]
21. Standard test method for determining the aerobic biodegradability of degradable plastics by specific microorganisms [D 5247-92]
22. Standard practice for heat aging of oxidatively degradable plastics [D5510-94]
23. Standard test method for determining hydrolytic degradation of plastic materials in an aqueous solution [D6118]

Photodegradation environment

24. Practice for Determining Degradation End point in Degradable polyolefins using a tensile test [D3826-98]
25. Practice for operating Xenon arc-type exposure apparatus with water for exposure of photodegradable plastics [D5071-91]
26. Practice for operating flurorescent UV and condensation apparatus for exposure of photodegradable plastics [D5208-91]

Some Chemical and Environmental Aspects of Polymer Degradation and Recycling

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Abstract

The constant increase in global consumption of plastic waste is being accompanied by an increasing quantity of used plastics dumped with domestic and industrial wastes, raising the level of solid waste pollution due to their slow degradability. More over, most commercial polymers contain stabilizers incorporated to protect them against photodegradation. This had raised the need to have available procedures allowing cheap polymer decomposition for the non-returnable plastics which allow reasonable time for their use before being dumped as waste. In addition dumping makes no use of either the material value or the high energy content of plastic.

As landfill space shrinks, plastic recycling continues to ride a wave of strong public support. In addition to its main advantage in reducing the size of dumped waste, the process can be done on any scale. Recycling, however, is not always worthwhile due to the cost of the process, the various technical problems related to the deterioration of some mechanical properties; and also due to toxicity of some additives which might leach during recycling making recycled plastics non-suitable for use in food packaging. However, new technologies for sorting and reprocessing plastics are improved, the cost will be reduced and recycling is gaining ground; the amount of recycled plastics in the industrialized world has tripled in 5 years.

In this presentation some of these topics are discussed with a comparison between the environmental impacts of different options applied in plastic waste management.

INTRODUCTION

The global consumption of plastics has increased steadily from 85million tons in 1988 to 100million tons in 1990, reached 130 millions in 1995(1,2), and expected to exceed 180 million tons by the year 2000(3,4).The demand is in a constant growth due to their unique properties which include durability, ease of processing, low density, resistance to corrosion, low cost and the tremendous technological flexibility which enabled them to supersede and replace metals in the construction of many household tools and comodities; and in all branches of industry. They also possess low energy cost per unit volume of production (table - 1) (5). However, the increase in consumption is also accompanied by an increasing quantity of used plastics dumped with domestic and industrial wastes, raising the level of solid waste pollution due to their slow degradability; although plastics still account for only 8% by weight of solid waste in the world's landfills.

Table 1: Energy requirements for the manufacture of glass & plastic containers(5)

Container	Glass		Plastic	
	mass, g	Energy, kJ	mass, g	Energy, kJ
Milk bottle (1L)	370	3850	(PE) 20	1600
Cooking oil bottle (1L)	390	4050	(PVC) 28	1770
Yogurt container (180g)	112	1160	(PS) 7.5	630

PLASTIC WASTE

The patterns of solid waste disposal vary significantly from region to another, in USA for example, in 1990, about 85% of the total solid waste went into landfills and only 5% was incinerated. For plastics these figures were 96% and 3% respectively. In Japan 70% of the solid waste was incinerated, while in western Europe 50% of the solid waste was dumped and 35% incinerated(1). The patterns have changed since then; in USA for instance, in1993 the amount of solid plastics waste incinerated was about19% while that dumped declined to 73%(5) which indicates that incineration has become a serious option. Contributions from individual plastics to the total waste differ also from region to another. Table (2) shows the pattern in the three major industrialized communities.

Table 2: % Contributions of individual plastics in total plastic wastes (1)

Type of plastic	EC	USA	Japan
Polyolefins	65	80	70
Polystyrene	15	9	15
PVC	10	4	10
PET	5	6.5	0
Others	5	0.5	5

The numerous applications of plastics have revealed the necessity for a sensible disposal procedure for scrap materials. Non-returnable packaging materials are often disposed of carelessly in parks, beaches, and resorts which results in a conspicuous litter problem. This problem is more serious in the country side of many developing countries, where there is a little concern about pollution; in addition to their notorious look, these wastes become very hazardous especially for cattle and sheep. In a report published by a daily newspaper in Jordan(6), litters of plastic bags and coffee cups are responsible for the death of nearly 20% of the total deaths among the sheep in the kingdom.

Efforts are being made to minimize polymer wastes or to provide suitable means of disposal or re-use. Among these efforts are those legal measures and laws decreed by municipalities and governments. As examples, the use of PVC packaging is banned in some countries like Denmark, Austria, and Switzerland; in USA restrictions or bans on polystyrene have been introduced in eight states. In Florida, a law bans plastic bags which do not degrade within 120 days(1).

Due to these environmental pressures and scrutiny from, some environmental lobbies, the demand, and consequently the prices, for PVC decreased by 20% during the last months of 1995. Thus in Germany, prices for PVC piping fell to below 1DM/ kg at the start of 1996, from 1.7DM/kg in mid 1995(3).The use of the more environmentally friendly plastics such as polypropylene(PP) has contributed to this decline in PVC(7) especially after the new developments in PP technology, specifically the introduction of a zirconium- metallocene catalyst (an organometallic compound of zirconium) which allows the synthesis of this polymer with any required degree of elasticity(8).

Waste economy programs usually center around three objectives:

i- reduction of waste levels by producer and consumer
ii- increased recycling in manufacturing and processing and
iii- the safe disposal of wastes.

RECYCLING

The object of recycling is to reduce the amount of waste by recirculation of raw materials and to improve material utilization. Methods for recycling of plastics include incineration(combustion) for energy recycling, pyrolysis, and some chemical processes.

As landfill space shrinks, plastic recycling continues to ride a wave of strong public support. Technology is available to take polymer back to monomer or even to crude oil. In addition to its main advantage in reducing the size of dumped waste, the process can be done on any scale.

Recycling, however, is not always worthwhile; for instance the cost of recycled material is about $60 per barrel of oil(9); the reuse of plastics by adding them to virgin polymers encounter various technical problems mainly because the degradation occurs in all stages of recycling causing the deterioration of some mechanical properties, and, mostly, a color shift although it is usually possible to complete four to five full cycles without the need to add new materials(8). Many recycling processes require that plastics be separated from the waste stream, and sorted by type which adds to cost. Also not all recycled plastics are efficient for use in food packaging (10).

Table 3: European Postconsumer Plastics Recycling Market(9)
(Thousands of metric tons)

Type of Plastic	1991	1993	1996
LDPE	560	917	1,335
HDPE	152	263	447
PP	75	136	245
PET	21	29	40
PS	70	106	163
PVC	35	73	1,112
ABS	0	3	6
Others	1	3	14
Total	**914**	**1,530**	**3,362**

As new technology, for sorting and reprocessing plastics is improved, the cost will come down and recycling is gaining ground in most industrial and developing countries. Table -3 shows the growth in plastics recycling market in Western Europe. As shown from the table, the amount recycled has tripled in 5 years with similar pattern in USA and Japan (9). However, there are still many plants recycle in a cheap way by remelting the plastic and reforming it into low value products. The technique is known as down-cycling, because each successive cycle further degrades the material .

SORTING: ELIMINATING THE DIRTY WORK

Although manual sorting remains the rule, systems based on X-rays, near infrared (NIR) spectroscopy, and floatation are being improved. Commercial units are already using these technologies to sort up to 3 bottles and to separate PVC, PP, PE, PS and PET fractions. Some non-commercial devices use mass Spectrometry.

- X-ray Fluorescence is used mainly for PVC identification. Low level X-rays pass through the plastic and onto scintillation material on a receiver board, where PVC is detected by detecting chlorine. Sorting rates of more than 99.8% are claimed for systems used to separate PVC from PET.

- NIR Spectroscopy uses the light absorption characteristics of different plastics to sort bottles of PVC, PET, PP, PE and PS. The technique can also identify polycarbonate and ABS. A near infrared beam is focused on the surface of each bottle and the transmission or reflection spectrum measured and analyzed. Sampling typically required 0.5 millisecond, and the NIR system can be combined with strobe lights for colour identification.

- Floation is used to separate the polyolefin fraction of shredded plastic waste from the other plastics. Plastics with similar densities, such as PS and PVC, are separated by adding flocculating agents. Hydrocyclones can separate materials of similar densities, without chemicals.

- Mass Spectrometry can identify even painted, dirty or filled plastics.

INCINERATION

Incineration is favored by many plastics manufacturer, mainly for being cheap and easy but the public resistance on environmental ground is strong. PVC for instance, which is being used with an average of 15kg per person a year, has gained a notorious reputation for generating dioxins and furan during incineration.

However, the use of some modern, but elaborate and expensive, flue-gas washing facilities makes it possible to reduce the level of these harmful substances to the legal allowed limits(11). But there are more subtle difficulties, heavy metal additives (used as stabilizers or fire retardants) such as the compounds of barium, nickel, arsenic, and chromium, end up in the air, or as toxic ash during incineration. Cadmium and lead are more serious culprits as they have greater tendency to leach in landfills. As a result of these problems, such additives are disappearing from use and being replaced by less harmful systems.

Further problem is the incomplete burning of most polymers even those composed only of carbon, hydrogen, and possibly oxygen. Instead they give off significant amounts of smoke and leave behind a solid residue of char. Also the halogen containing polymers have high limiting oxygen index (LOI) when compared with other polymers (12) which make it difficult to burn smoothly.

(LOI is the minimum % of oxygen in an oxygen-nitrogen mixture that will just allow flaming combustion to continue for at least three minutes). Table-4, shows the LOI values of the most common polymers.

Table 4: Limiting Oxygen Index of some Polymers(12)

Polymer	LOI%
Poly(methyl metacrylate)	17.3
Polypropylene	17.4
Polyethylene	17.4
Polystyrene	18.1
Poly(vinyl alcohol)	22.5
PVC	45.0
Poly(vinylidene chloride)	60.0
PTFE	95.0

Incineration might gain wider acceptance if it is connected to energy recovery. The energy content (caloric value) of plastics is higher than that of most other materials(1,2,5). The caloric value of 1 kg of plastic waste is roughly that of 1L of fuel oil and higher than that of coal. Table -5 compares the calorific value of polymers with fuels. As can be seen from the table, the value of all polymers are higher than coal and wood and very close to natural gas. Therefore under circumstances where recycling is not a feasible option, the use of plastics in waste-derived fuels may be an acceptable conservation measure if effective combustion procedure is available which can keep the level of the above mentioned notorious pollutants at minimum.

Table 5: Calorific values of plastics and fuels (14)

Polymer	Calorific Value (kJ/ kg)
Poly ethylene	43,000
Polystyrene	40,000
Polypropylene	43,000
Natural gas	45,000
Bituminous coal	30,000
Wood	17,000
Oil	44,000

In USA, 15.6% of plastic waste was incinerated in 1993 with energy recovery, compared with 3.7% without energy recovery(5), whilst in 1990 only 3% of the total plastics waste was incinerated with only 1% for energy recovery(1) which, as mentioned earlier, is an indication of increasing concerns about the necessity of energy recycling which was more notable in Europe and Japan.

Dumping and Degradation

In most countries, waste material is generally dumped; large quantities of plastic waste are dumped with household garbage. In USA about 16.5 Mt.(or 73%) of plastic waste went to dumping in 1993, and nearly half that amount in Europe. The plastic waste is unlikely to decompose under dump site conditions, and will persist over a long time. Because of the low density of polymers, this plastic waste takes up a large volume for relatively little mass. As an example, the polymer waste in USA, in 1991, represented 7.3% by weight but 16.3% by volume of the total solid waste and it is predicted to grow to 31.4% in the year 2000(12).

The difficulty facing the use of municipal landfills is that space is dwindling. For this reason and because of the highly visible litter problem caused by e.g., plastic bags, bottles and containers, it is often demanded that plastics should be degradable. Degradation of plastics, to give materials of lower molecular mass, can be affected by heat, light, and both chemical and biological processes. However, the degradation products may have a greater adverse impact on the environment than the plastics in their original form. Thus, some of these degradation products may penetrate in to the under ground water creating another pollution problem(2).

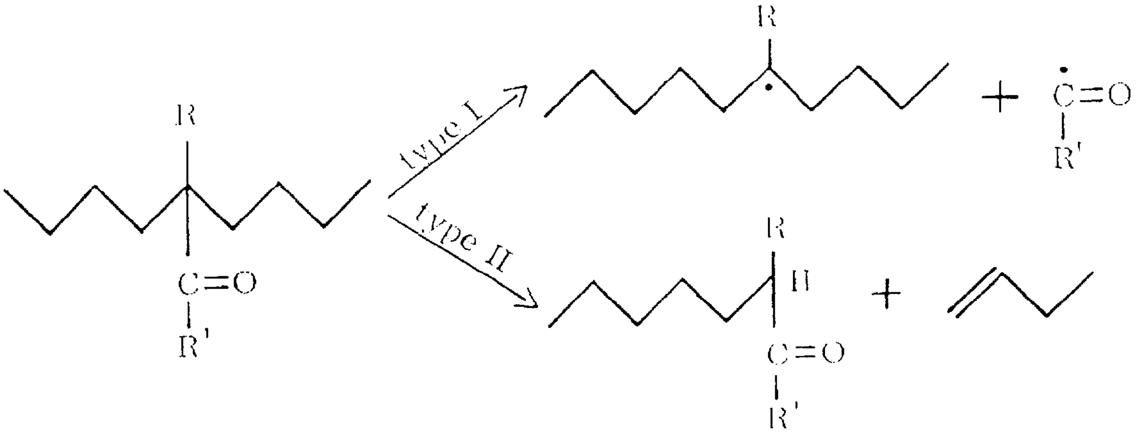
Dumping makes no use of either the material value or the energy content of plastics produced from, high energy content, hydrocarbons. Therefore, recovery and reuse of synthetic polymers seems to be the most acceptable way of dealing with the problem of waste(12).

Photodegradation

Most commercial organic polymers undergo chemical reactions upon irradi tion with UV light because they possess chromophoric groups, either as regular constituents, or as impurities. Therefore, stabilizers are usually added to plastics to protect them against the effect of light. But the concern about the environment raised the need to have available procedures allowing cheap polymer decomposition, for the non-returnable plastic materials, which allow reasonable time for their use before being dumped as waste. Photodegradation by sun light would be the most convenient, and this may be achieved by either of two methods:

(a)- *Incorporation of carbonyl-containing materials*

The light absorbed by carbonyl-containing compounds can induce bond scission by either Norrish type I or type II processes(13). Scheme-1 shows the reaction mechanisms of both types.



Type I process gives two radicals which needs oxygen to break the chain. Type II process is the major photochemical decomposition that causes chain breaking especially at ambient temperature. Examples of industrial application of these reactions include the copolymerization of ethylene with carbon monoxide, and the copolymerization of styrene with phenylvinyl ketone.

(b)- *Addition of photosensitizers*

The term sensitization refers to processes involving energy transfer (from additives) which is subsequently followed by a chemical reaction or a physical process such as luminescence. These additives are capable of, effectively, absorbing UV light at $\lambda > 300$nm. The reactions can be summarized as follows:

$$S + h\nu \longrightarrow S^*$$

$$S^* + P \longrightarrow S + P^*$$

$$P^* \longrightarrow \begin{cases} \xrightarrow{\text{chemical reaction}} & p_1^{\bullet} + p_2^{\bullet} \\ \xrightarrow{\text{physical deactivation}} & P + h\nu \end{cases}$$

S is the additive, P is the polymer molecule, $p_1^{\bullet}$ and $p_2^{\bullet}$ are polymer radicals. Chemical reaction of a radical, usually, involves hydrogen abstraction, thus:

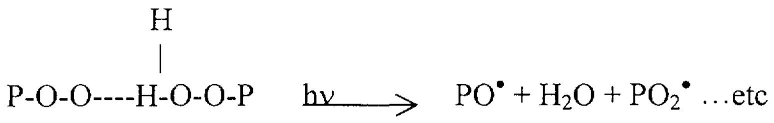
$$\begin{aligned} S^* &+ PH \longrightarrow RH + P^\bullet \\ S^* &+ RH \longrightarrow HS^\bullet + R^\bullet \end{aligned}$$

PH and RH are macromolecules and low molecular weight molecules, respectively, capable of acting as hydrogen donor. The free radicals produced might subsequently attack the polymer

$$R^\bullet + PH \longrightarrow RH + P^\bullet$$

In the presence of oxygen, the macroradical will, most probably, be converted to peroxy radicals and thus autoxidation reactions proceed; these peroxy radicals can initiate a series of radical chain reactions(13):

$$\begin{aligned} P^\bullet &+ O2 \longrightarrow POO^\bullet \\ POO^\bullet &+ PH \longrightarrow POOH + P^\bullet \end{aligned}$$



$$\overset{\overset{\text{H}}{|}}{\text{P-O-O}}\text{----H-O-O-P} \xrightarrow{h\nu} PO^\bullet + H_2O + PO_2^\bullet \ldots\text{etc}$$

Examples of organic photosensitizers are benzophenone, ketones, p-quinone, 1,4,-naphthoquinone, diketone, and carboxyaldehyde derivatives(2,13).

Inorganic compounds include some salts of iron, cobalt, copper, and more recently titanium dioxide(15). An example of using inorganic salt is the significant acceleration of the rate of main-chain scission in poly(methyl methacrylate) and polycarbonate caused by anhydrous $FeCl_3$ (16). It is assumed that, after the light has been absorbed by $Fe^{3+}Cl^-$ ion pairs, distributed in the polymer matrix, chlorine atoms are subsequently formed as free radicals which attack the polymer chains:

$$Fe^{3+}Cl^- + h\nu \rightarrow [Fe^{2+}Cl] \rightarrow Fe^{2+} + Cl^\bullet$$

Titanium dioxide is the most widely used white pigment for both polymer and paints. It is believed now that it may contribute to polymer degradation via some photochemical events (15, 17, 18) which involve an electron-hole generation:

$$TiO2 \xrightarrow{h\nu} e^- + \text{positive hole } (h^+)$$

$$(e^- \text{-} h^+) + Ti^{+4} \longrightarrow Ti^{2+} + h^+$$

Although many of the photogenerated e^-- h^+ pairs, simply, recombine, a fraction escape to the TiO_2 surface and then react with oxygen or hydroxyl group invariably present at oxide surface:

$$\begin{aligned} O_2 + e^- &\longrightarrow O_2^- \\ O_2^- + \text{positive hole} &\longrightarrow \text{singlet } O_2 \text{ or } 2O^\bullet \end{aligned}$$

These reactions have been applied to degrade some organic pollutants and toxic metals(18) and may very soon, with similar photochemical reactions, become widely utilized in processes for abatement of environmental pollution.

SUMMING UP

- Plastics have improved the quality of life, they provide a wide range of economical products, they help to conserve natural resources and the environment. But we need to use and dispose of them in responsible manner.
- The substitution by alternative materials of all synthetic polymers with their excellent properties is impossible.
- EDPs will constitute a key option among those available for the management of plastic waste, competition will intensify although all technologies may coexist with an appreciable decrease of landfilling.
- EDPs will replace conventional commodity plastics in those segments where recycling is difficult and heavily penalized.

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The Impact of Polymer Stability on the Environment

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Abstract

Polymer stability is regarded as an extremely important issue to the producers. The polymer requires protection during manufacturing, storage, processing and end use stages. Protecting the polymer properties against the influence of weathering conditions is a common problem in hot climate regions including the GCC region. To stabilize polymers during their life cycle, additives are used during the manufacturing process to protect the properties of the polymers from any deterioration. The polymers may undergo a degradation process that leads to changes in the mechanical, physical and rheological properties. Degradation of polymer occurs as a result of radical formation due to the combined effects of heat, stress and catalyst. In addition, the presence of oxygen induces the production of peroxide radicals that could be transformed into hydroperoxides. These radicals lead to chain scission or cross-linking processes. To interrupt this degradation process, antioxidants such as hindered phenols are used to deactivate the peroxide radicals while the use of secondary antioxidants such as phosphates or phosphonites to eliminate the hydroperoxide groups.

Degradation of polymers can be detected by using various techniques such as DSC, TGA, GPC, FTIR and others.

Another important aspect related to polymer stability is the environment. Recovering the polymer waste is a concerned issue to the environment. However many methods are adopted to dispose of polymers waste including recycling, dumping (landfilling) and incineration. The degradation of polymers has an impact on the environmental management in many ways, for example, the degraded polymer could have a considerable effect on the properties of the recycled polymer. The above mentioned aspects will be highlighted in details in this paper.

INTRODUCTION

The polymer properties require protection from any deterioration during the polymer life cycle. This can be achieved by incorporation of additives during processing. The type and level of additives used depend on the end product application including the weathering condition requirement.

Antioxidants, UV stabilizer and others are important ingredients to the stability of polymer. The role of antioxidants is to protect the polymer during processing from possible thermal degradation while UV stabilizer acts as a barrier to UV radiation, which may cause photo-oxidative degradation.

The impact of degradation not only changes polymer properties, but its effect extends to the environment.

However, the polymer producers aim to extend the life cycle of the polymer to the highest level, while from the environmental point of view they are concerned with the type and level of certain additives incorporated with the product that could complicate the plastic waste management program.

A compromise is essential to achieve customer satisfaction in the finished product and on the other hand to minimize the impact of such product on the environment.

PLASTIC CONSUMPTION IN GCC REGION

The production of polymers in the GCC region has increased sharply over the last two decades. Many petrochemical plants were established due to the advantage of many factors such as the local availability of feedstock, cheap labours, the increasing demand for various plastic products in the local market and the strategic position of this region to the Asian markets.

The plastic production in the GCC region has increased in the first decade between 1975-1985 from 64,630 MT/Y to 167,640 MT/Y respectively. While in the second decade 1985-1996, the production of plastic materials has increased sharply to 888,240 MT/Y in 1996.

The consumption of thermoplastic products in the GCC region is shown in Table 1.

Table 1: Thermoplastic products consumption in GCC (1)

Country	Apparent Consumption (MT)	Per Capita (Kg)
KSA	679,070	35.0
UAE	178,470	72.3
Kuwait	62,080	37.8
Oman	50,150	22.6
Qatar	28,350	49.9
Bahrain	13,320	22.4
Total	**1,011,440**	**37.6**

The global consumption of thermoplastic products in comparison to GCC region is given in Table 2.

Table 2: The global consumption of thermoplastic products (2)

Region	Consumption (MT) (X1000)		
	1994	**1996**	**2000**
GCC	749	1,011	1,853
North America	36,201	39,092	45,586
Latin America	4,959	5,629	7,251
W. Europe	31,743	33,934	38,780
E. Europe	6,897	7,375	8,434
Africa & Middle East	3,362	3,532	3,671
Asia	33,514	37,030	45,207

The per capita consumption in the GCC region has accordingly increased from 5.5 kg in 1975 to 37.6 kg in 1996 and expected to increase to 60.0 kg in year 2000 which is self evident of the considerable development in the infrastructure of plastic industry during this period as shown in Figure 1

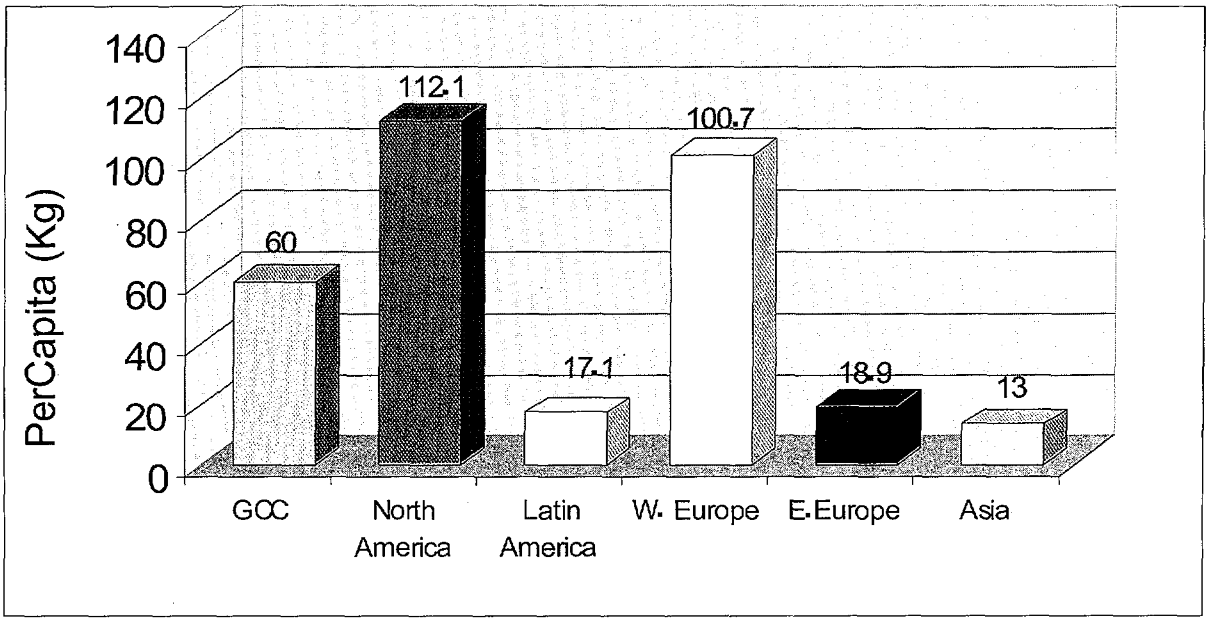

Figure 1: Global Per Capita Consumption (kg) in Year 2000

This increasing trend in plastic consumption has ultimately resulted in higher volume of plastic waste.

However, the volume of used plastic material in Municipal Solid Waste(MSW) is below the size of paper and glass waste in most cases.

DEGRADATION MECHANISM

Degradation process is a chemical reaction that polymer undergoes as a result of.free radical formation. This process could lead to chain scission of the polymer (bond scission in the backbone of the macromolecule) or crosslinking of the polymer (molecular weight enlargement). The polymer producer uses antioxidants as primary and secondary to interrupt the degradation processes as follows;

- The primary antioxidants such as hindered phenols react rapidly with the peroxide radicals (radical scavengers) and causes chain termination.

- The secondary antioxidants such as phosphates or phosphonites react with hydroperoxides and result in decomposition of these hydroperoxides that yield non-radical products (3).

A schematic drawing of the antioxidants role in interrupting the degradation process is shown in Figure 2.

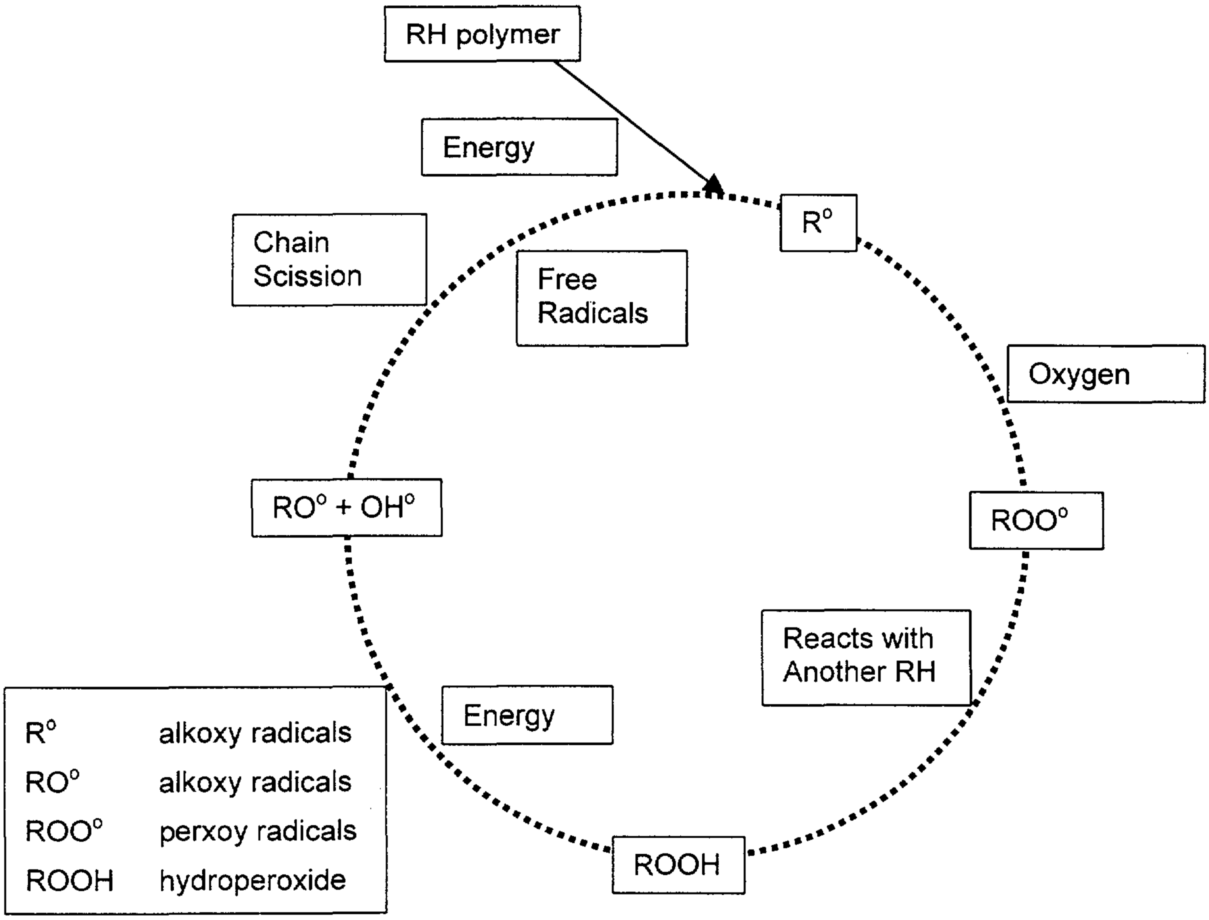

Figure 2: The role of antioxidants during degradation process

The effectiveness of antioxidants used can be assessed by conducting multiple extrusion tests and determine the changes in the melt flow index (MFI) and colour of the extruded material. The effect of antioxidants concentration on the processing stability of Polyethylene resin is demonstrated in Figure 3.

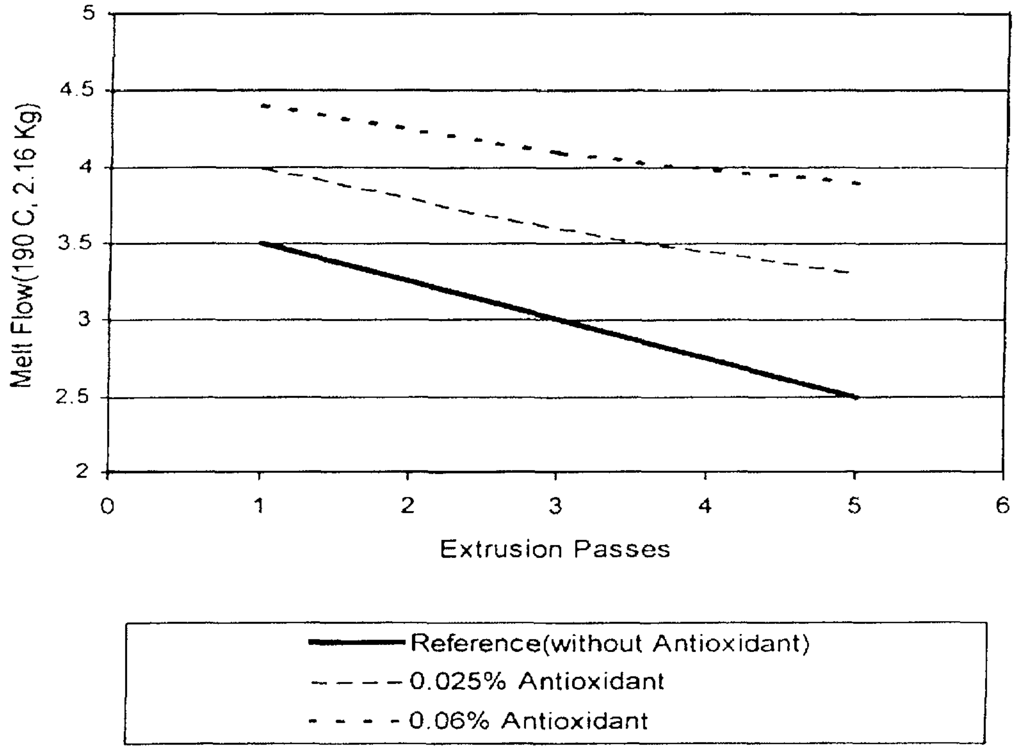

Figure 3: Processing Stability of Polyethylene

TYPES OF DEGRADATION

Polymers may undergo various types of degradation process as follows:

1. Thermal: Thermal degradation is initiated when the polymer is exposed to high temperature during processing.

2. Mechanical: Mechanical degradation is initiated when the polymer is subjected to mechanical stress.

3. Photo oxidative: This process is initiated when the polymer is exposed to UV light. The material can be protected by the addition of UV stabilizer which deactivates photochemical stimulated molecules and intercept the free radical formed.

   Polymer oxidation is a concern problem in the GCC region due to the extreme weathering conditions in this area. Hence handling the material during storage requires more precaution by the user.

4. High energy: High-energy degradation is initiated when the polymer exposes to radiation such as gamma radiation. The polymer may undergo cross-linking process depending on the type and level of radiation.

5. Chemical: Chemical degradation is caused by chemical reaction. This process is useful in certain applications such as wire and cable industry whereby peroxide agent is added to polyethylene resin in order to cross-link the product prior to processing into finished products.

EFFECT OF DEGRADATION PROCESS ON POLYMER PROPERTIES

Degradation process causes changes in the molecular weight of polymer that lead to loss of physical, mechanical and optical properties.

The mechanical properties including elongation, tensile strength and impact resistance is reduced when polymer undergoes degradation.

The physical properties are also affected by degradation process such as density, colour and appearance.

The polymer crystallinity increases during degradation and hence the optical properties such as haze, gloss and clarity decrease.

Degradation also reduces the polymer melt strength and affects other rheological Properties such as melt flow index (MFI). Depending on type of degradation process that the polymer may undergo, the MFI could be increased as a result of chain scission process or decreased due to cross-linking process.

The deterioration in polymer properties, due to degradation, can be detected through various techniques; examples of some of these methods are:

1. Thermal Gravametric Analyzer (TGA) technique measures the loss in weight of polymer during heating.

2. Fourier Transfer Infra Red (FTIR) technique detects changes in polymer structure "finger print".

3. Gel Permeation Chromatography (GPC) technique determines the molecular weight(MW) and molecular weight distribution(MWD).

4. Differential Scanning Calorimetry (DSC) technique determines the melting point and crystallinity.

5. Melt Indexer technique measures the MFI of the material.

6. Rheometer technique determines the melt strength of the material and the viscosity changes at various shear rate.

7. The mechanical properties such as the tensile strength, elongation and impact resistance of the material.

8. The optical properties such as haze, gloss and clarity, and material discoloration.

PLASTIC WASTE MANAGEMENT

The integrated plastic waste management solution consists of the following routes:

1. Source reduction - Identify and minimize the source of waste.
2. Re-use - Use the waste back into the process.
3. Material recycling - Collecting and sorting of mixed plastics.
4. Feed stock recycling (chemical recycling) - Recover the plastic from their monomers through various chemical processes.
5. Incineration with energy recovery.
6. Dumping into landfills.

The industrialized countries are using various approaches to manage the plastic waste. In Canada and Germany legislations are introduced to encourage recycling of plastic packaging and hard goods. While in Japan incineration method is adopted to most plastic wastes due to shortage of landfill space. In the US and most Europe a combination of landfilling, incineration and recycling methods are used with a trend to increase recycling.

The disposing of solid waste in the GCC countries is mainly conducted through landfilling; however small incineration units are used for handling medical waste.

Generally, plastic waste represent a small portion of the total solid waste as shown in the breakdown of domestic waste in Qatar in Table 3.

Table 3: Domestic waste in Qatar (4)

Constituent	Percentage
Vegetable & Putrescible	54
Paper & Cardboard	13
Plastics	16
Bottles & Glass	7
Tins & Metals	4
Textiles	4
Miscellaneous	2

In certain markets legislations are imposed on the recycled materials whereby the recycled resins in food and beverage containers must be put into different applications because of concerns over food contact. These regulations restrict the use of recycled polyethylene in some markets.

The most plastic recycled is originated from packaging application, and polyethylene resin represents the main material used in packaging manufacture.

Improving the quality of recycled plastic can be achieved through various technical and physical/chemical methods. Technical methods such as washing, separation, compounding and melt filtration of the recycled plastic. Physical/chemical methods include blending with various types of additives such as compatibilizers, polymer modifiers, fillers and stabilizers (5).

There is a trend in some markets to implement quality programs such as registration under international standards of ISO-9000 series. This approach is increasingly encouraged by polymer producers and users as a requirement of doing business, particularly in specialty markets (6).

THE IMPACT OF DEGRADATION ON ENVIRONMENT

Degradation process has considerable effects on the method adopted to manage the plastic waste whether it is recycling, landfilling or incineration methods. Degradation causes changes in polymer properties and that in turn affects the properties of the recycled polymer. Hence, further complications are added in managing the degraded plastic waste using recycling method. On the other hand, managing the degraded polymer through landfilling also raises many difficulties, such as the emission of gases from degraded plasticizers and the long period of polymer degradation. However, various additives could be used to extend the stabilization period of the dumped material against degradation effect, but this approach could raise further complications to the management of plastic waste.

Incineration method is an alternative approach to manage the solid waste, it is considered as an expensive option compared to other approaches. This method could also harm the environment if the gases released from the incineration process are not restrictedly controlled.

Selecting the type of disposal method depends on economical, environmental and other factors. Incineration with the generation of power, results in rather higher net cost than landfill for most plastic waste products. The net cost of recycling as predominantly single polymer depends on the quantity and quality of the waste which can be recovered. With recovery efficiencies used here, recycling incurs a significantly higher net cost than landfill in most cases. The net economic cost of recycling as a mixed plastic appears more expensive than other disposal options in all cases (7).

Environmental impact of the disposal route varies. Incineration is generally energy effective but results in net increases in the emissions of some atmospheric pollutants over landfill. It is also an effective method for reducing the quantity of final solid wastes. Recycling to conventional end uses is not always as beneficial in terms of energy as incineration (8).

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Environmentally Degradable Polymers in Waste Management

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Summary

The fate of polymers when they become wastes is determined by the type of material used. Personal hygene products frequently end up in sewage systems and have to biodegrade rapidly. Hydro-biodegradable polymers (e.g. polyesters and carbohydrate-based polymers have the ideal properties for this type of application. Plastics used in packaging or in agriculture by contrast must be able to resist the effects of biotic environments for a controllable length of time before beginning to biodegrade. The hydrocarbon polymers are most suitable for this purpose. Since they degrade initially by peroxidation, this process can be controlled by antioxidants containing transition metal ions designed to 'invert' in the outdoor environment to give prooxidants. Physical disintegration must be rapid, for example as litter or in compost but, as in the case of nature's litter, the primary objective should be the production of useful biomass rather than 'greenhouse'gases.

SOURCES OF POLYMER WASTES

Most post-consumer plastics waste is generated by households as discarded packaging and constitutes about 8% of total waste (Table 1). At the other end of the spectrum, a relatively small proportion of recovered waste comes from agricultural sources because most of the hay-wrap and feed packaging is left in the farm yards or in the fields where it is blown by the wind and appears as unsightly litter on river banks or caught against fences and hedges to the detriment of the environment (1).

In the past, landfill has been the preferred method of disposing of collected waste and in many countries this is still the repository for waste plastics. However, the environmental disadvantages of landfill have become very evident in recent years and this is now being discouraged by Governments. The most important arguments against landfill are increasing costs and the energy wastage in transporting bulky wastes to available sites. The generation of environmentally polluting greenhouse gases, particularly methane is ecologically unacceptable. In addition methane can cause explosion and subsidence may occur when the recovered land is re-used for building (1). Landfilling will be discouraged by increasing levies and local authorities are now being encouraged to view waste as a resource to be re-used.

Table 1: Generation of Post-User Plastics Waste by End-Use in 1995 (1)
(Source: Association of Plastics Manufacturers in Europe, APME)

End-Use	kT	Percentage by Weight	Percentage of Plastics in Total Waste
Households	10,139	63.2	7.9
Distribution	2,409	15.0	1.0
Automotive	888	5.5	7.0
Building	841	5.2	0.29
Electrical and Electronic	812	5.1	15.4
Agriculture	293	1.8	0.03
Total	16,056		

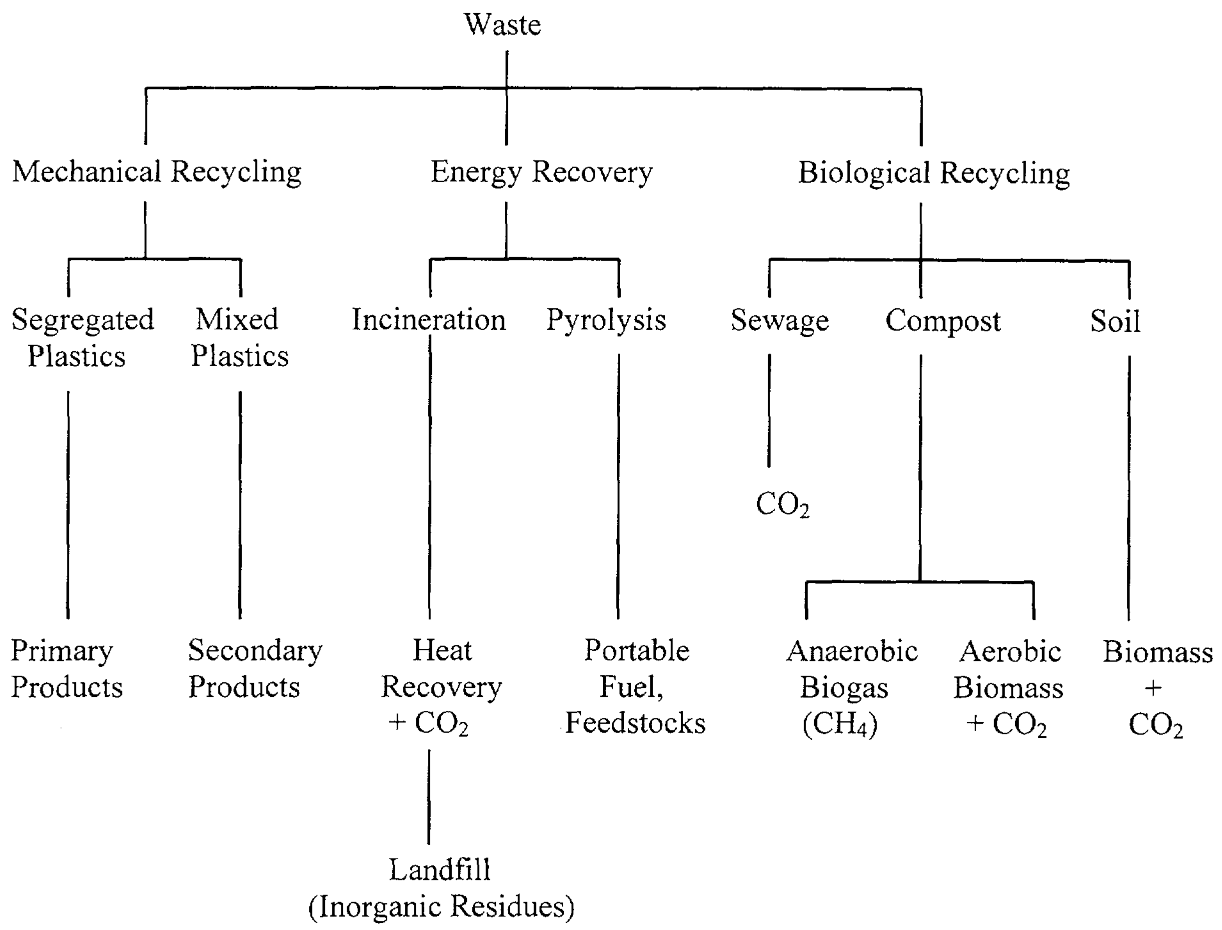
DISPOSAL OPTIONS

Scheme 1 shows the three main ways of utilizing polymer wastes to the benefit of the environment (2). It should be emphasized that these represent the ideal to be aimed at rather than the present position and in principle, landfill should be the last resort for waste that has no further value.

Mechanical Recycling

In-house reprocessing of clean plastics waste has been practised for many years and for this reason, reprocessing of post-user waste was thought to be the preferred alternative to landfill for all polymer wastes. It is certainly true that some items of clean plastics recovered from the waste stream can be collected in bulk (e.g. industrial shrink-wrap, battery case, crates and car bumpers) and blended into the primary application in a ‘closed-loop’ with clear ecological gain in terms of energy utilization (1.3). However, the situation is very different in the case of domestic wastes. Materials recycling of household wastes is particularly difficult when they are contaminated with biological residues or, as is usually the case, when they are a mixture of different kinds of plastics (1,3). A great deal of entrepreneurial effort has gone into the development of special processing equipment to convert mixed plastics wastes to secondary products such as wood or concrete substitutes for use as fence posts, benches, boat docks, etc (1) but the ecological benefits of doing this have not been demonstrated. It has been shown in a recent study of the Duales Deutschland System (DSD) that to compete with conventional materials such as wood and concrete, the recycled products would have to last 3.3 times as long as the materials they replace (4). However, practical experience shows that reprocessing of mixed contaminated plastics produces materials that are inferior mechanically and lacking in durability compared with those produced from virgin polymers (2,5,6). Some limited success has been achieved in the manufacture of concrete replacements for underground chambers where the weather has no significant effect (1) but this could never utilize more than a small fraction of the mixed waste available. The use of ‘compatibilizers’ to improve the mechanical performance of polyblends of mixed plastics is in general expensive and energy intensive.

Scheme 1: Polymer Waste Management Options (2)



Energy Recovery

Energy recycling by incineration of plastics waste with heat recovery is now accepted in principle as a viable use for waste polymers since it replaces fossil fuels and thus reduces the CO_2 burden on the environment. The calorific value of polyethylene is similar to that of fuel oil (Table 2) and the energy produced by incineration of polyethylene is of the same order as that used in its manufacture (Table 3).

Table 2: Calorific Values of plastics compared with Conventional Fuels (1)

Fuel	**Calorific Value MJ/kg**
Methane	53
Gasoline	46
Fuel Oil	43
Coal	30
Polyethylene	~43
Mixed Plastics	30-40
Municipal Solid Waste	~10

Table 3: Energy Balance in the Manufacture and Incineration of Polyethylene
(adapted from Ref. 7)

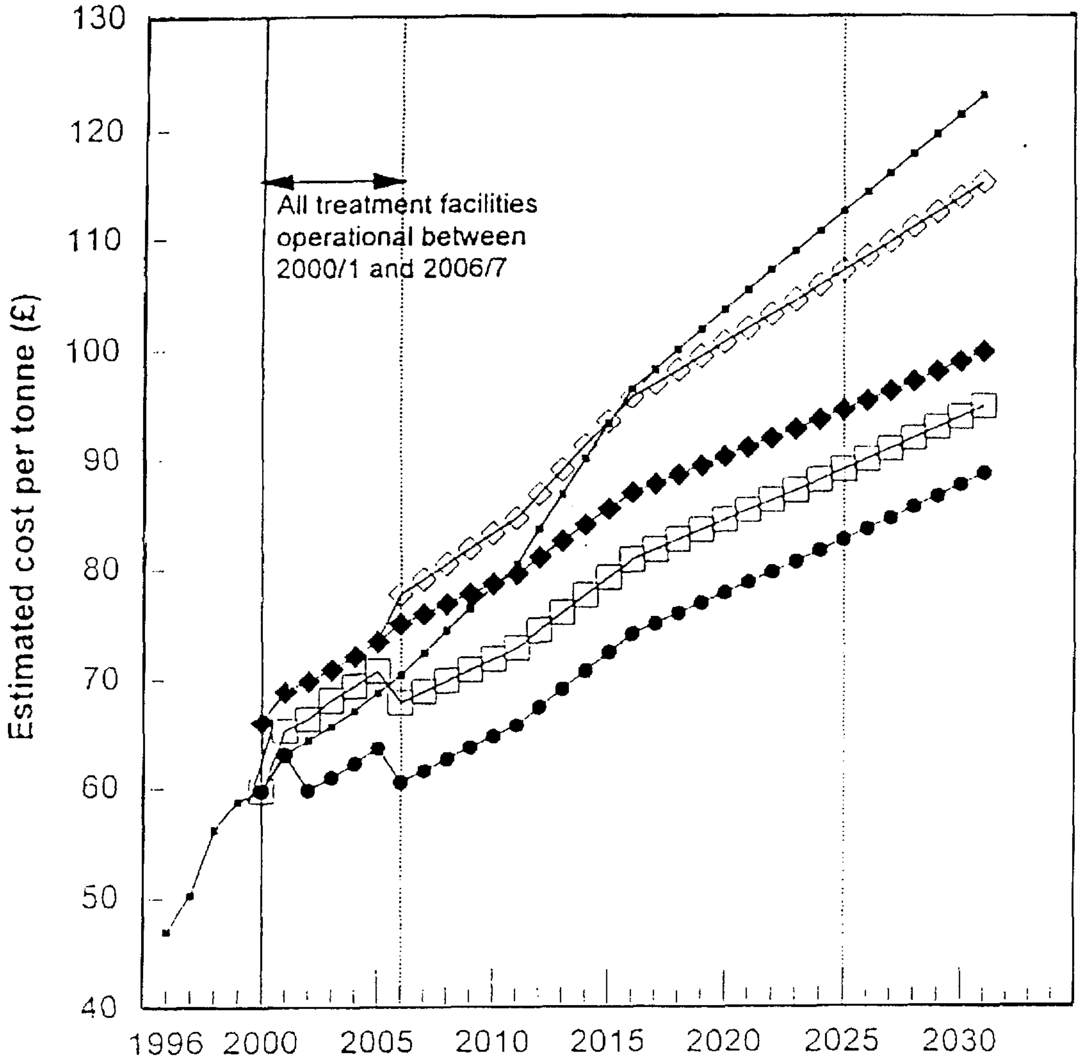
Energy utilized during Manufacture	%
Crude oil to naphtha	9
Naphtha to ethylene	21
Ethylene to polyethylene	10
Polyethylene to finished product	17
Total energy used	57
Energy produced by incineration of the product	43

Incineration is the preferred energy recovery option of local authorities because they can benefit economically by selling plastics waste as fuel (1) (see Fig. 1). However, in most developed countries there is a deep public distrust of incineration due to the possibility of generating toxic gases and in particular the chlorine-containing dioxins. There is some evidence from studies in Japan, where waste incineration was pioneered, that populations down-wind from incinerators have a higher incidence of child-birth defects than the rest of the population (1). However, it should be noted that polyolefins can produce only carbon dioxide and water and is consequently a very 'clean' fuel. The most ecologically acceptable incineration process at present available is in the firing of furnaces and cement kilns (4).

An alternative to direct incineration is to convert polymer wastes by pyrolysis (thermolysis) or by hydrogenation to low molecular weight hydrocarbons for use either as portable fuels or as polymer feedstocks (1). This option is preferred by the polymer manufacturers and is a potentially important outlet for recovered polymers.

Biological Recycling

Nature's waste is returned to the natural carbon cycle by biodegradation which is often preceded by abiotic peroxidation. The primary product is biomass which acts as a seed-bed for new growth (8). Biomass formation is beneficial to the environment since it 'ties up' the carbon for a more extended period compared with incineration. The importance of making use of this natural process by controlled composting of organic wastes has been recognised by waste disposal authorities and it can be seen from Fig. 1 that all the preferred alternatives to landfill involve composting. If man-made polymers are to be incorporated into this system then they must be ultimately biodegradable in compost and as litter. The present range of commodity packaging polymers are not biodegradable within the time scale envisaged but can be made so by controlled peroxidation. The principle involved is that the polymers remain stable during manufacture and use but break down rapidly after discard with conversion to biomass in an acceptable time (9-17). The time to ultimate mineralisation of polymers in compost or as litter is much less important than the time taken to fragment with the subsequent formation of biomass. The polyolefins are particularly useful in this process since abiotic peroxidation can be controlled accurately by the use of antioxidants which 'invert' under the influence of light and/or heat with the formation of transition metal prooxidants (9, 12-14, 16, 17). Post-user polymer wastes that end up in sewage, by contrast, require a much shorter time-scale than either compost or litter (Fig. 2) since it is essential that they are substantially mineralised within the time scale of sewage treatment.



¦ Current position (landfill); ¦ maximised mechanical recycling with energy recovery for remaining combustible waste; ? lowest cost waste to energy incineration with mechanical recycling and composting at no extra cost; ? balanced cost mechanical recycling and composting with energy recovery; ? maximed mechanical recycling and composting with energy recovery.

(Reproduced with permission from G. Scott, Polymers and the Environment, Royal Society of Chemistry, p. 90)

Figure 1: Projected Local Authority Costs of Alternative Waste Management Procedures compared with Present Practice

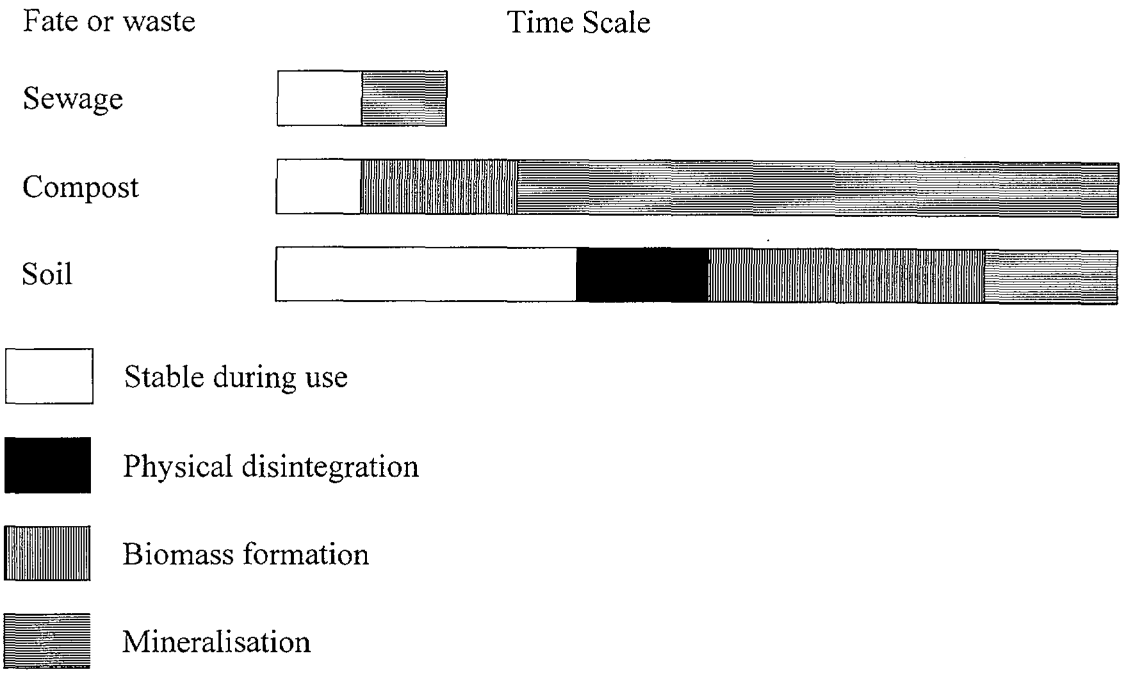


Figure 2: Relative Time-Scale for Bioassimilation in different Environments (2)

The aliphatic polyesters and polymers derived from natural products (e.g. starch and cellulose derivitives) are particularly suitable for biodegradation in sewage since they normally require only a minimal durability in use and then mineralise rapidly when exposed to microorganisms (9).

At present only about 25% of plastics waste is recovered for the recycling processes discussed above and in Europe about 65% of this is incinerated, the remainder being recycled to secondary products or to feedstocks (1). Thus 75% goes to landfill or ends up as litter.

THE ROLE OF BIODEGRADATION IN THE ECOLOGICAL UTILISATION OF POLYMER WASTES

Two categories of biodegradable polymers have to be recognised. The first is used in applications where biodegradability is part of the function of the product. For example in temporary sutures in the body or in controlled release of drugs. In agriculture, time-controlled biodegradable polyethylene is used to ensure earlier cropping and to increase crop yields, to reduce water and fertilizer utilization (16, 19) without the need to collect and dispose of the waste after the crop has been harvested. Substantial economic benefits accrue to the farmer from these procedures (Table 4) which more than justifies any increase in expenditure due to the use of biodegradable plastics.

Table 4: Ratio of Increased Income to Cost of Mulching Film (18)

Crop	Increased Income / Cost
Melons	13.0
Vegetables	5.0
Peanuts	3.9
Sugar Cane	3.6
Cotton	3.0
Maize	2.5

Another agricultural application of biodegradable plastics which brings considerable environmental benefits is in controlled fertilizer release (20) with reduction in eutrophication of rivers and lakes.

By contrast, degradability had no functional value in packaging and public opinion still has to convince packaging manufacturers of the ecological benefits of biodegradable plastics. It is evident from Fig.1 that all the preferred alternative strategies to landfill involve composting as a contributory technique for obtaining benefit from recovered organic wastes. But in addition to collected waste substantial quantities of very obtrusive plastic litter appears in the countryside and on the seashore. Agricultural litter appears in the form of feed packaging, hay and silage stretchwrap and twines (9) whereas coastal detritus consists mainly of fishing nets, ropes and crates together with packaging discarded from ships (21). It seems inevitable then that environmentally biodegradable plastics will play an increasing part in the 21st century in the management of waste and litter.

LIFE-CYCLE ASSESSMENT

In spite of the above, it should not be assumed that biodegradability is the only and sufficient criterion of ecological acceptability. The complete life-cycle of the product from raw materials to ultimate disposal has to be considered. Life-cycle assessment (LCA) estimates the ecological significance of four major parameters (1).

Energy Consumption

Includes electrical, thermal and traction power used in extraction, transformation and transportation of raw materials and in the treatment of waste to make it safe in the environment.

Air Pollution

The volume of air that must be added to gas emissions to conform to existing regulations. This includes all gas emissions from raw materials, extraction, production of electrical and thermal energy and in transportation at all stages in the history of the product.

Water Pollution

The volume of water that should be used to dilute liquid emissions produced over the whole life cycle of the product.

Waste Production

The total volume of wastes produced in each stage in the manufacture, use and disposal of the material.

This idealised procedure can be used to compare the ecological acceptability of different raw materials, processes and end products and in general there is a correlation between ecological acceptability and cost which is of primary concern to the manufacturer of polymer products. According to the 'polluter pays' principle this should include ultimate safe disposal (1). It is often claimed by 'green' enthusiasts that natural products are more ecologically acceptable than petrochemical-based products, but when the above criteria are applied, this generally turns out not to be the case. The vinyl polymers are preferred to paper and most other bio-based materials because they are produced on a very large scale with minimal energy and land utilization. Consequently they are cheap but they also cause less pollution and waste during manufacture (18). LCA is particularly valuable when applied to recycling procedures. In particular it does not always show the environmental benefits predicted by 'green' campaigners for mechanical recycling. It can be seen from Table 2 that almost one third of the energy used in the manufacture of polyethylene products from mineral oil is in the processing operation. When this is added to the energy expended in transportation and cleansing and in the manufacture of additives used to provide a product as serviceable as that made from the virgin polymer, then incineration with energy recovery becomes the most ecologically favorable disposal technique (1).

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Overview and Case Studies of Biodegradable Plastic Technologies

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Abstract

Biodegradable plastic technologies can be classified under three broad categories and several subcategories:

1. Aliphatic polyester based
    - petrochemical feedstock
    - agricultural feedstock
    - microbial synthesis
2. Natural polymer based
    - starch & starch derivatives (starch esters)
    - cellulose and cellulose esters
    - proteins, other polysaccharides, & amino acids
3. Blends, alloys and graft copolymers of natural polymers and polyesters.

With a better understanding of the rationale for biodegradable plastics, and with standards in place to evaluate biodegradability, technologies are under development that meets the biodegradability/compostability criteria.

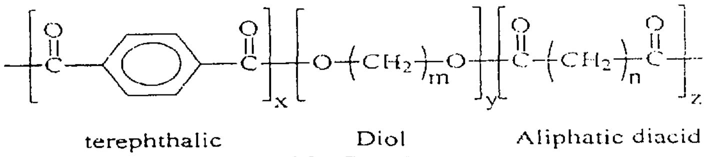
Several technologies based on aliphatic polyesters and copolyesters have emerged spearheaded by Eastman Chemical, DuPont, BASF, Mitsui Chemicals, Showa High Polymer. The following figure shows the general copolyester structure.

Aliphatic polyesters like poly (ε-caprolactone) and poly(lactic acid) are also viable biodegradable polyesters that are being marketed.

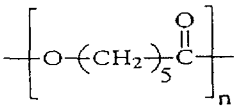
Several companies are commercializing starch based thermoplastic technologies using water or other polyhydric alcohol's. These have found applications as loose-fill packaging material and in arts and crafts and toys.

Starch esters, and thermoplastic starch-polyester blends are also being commercialized.

These technologies will be reviewed including our work in this area.

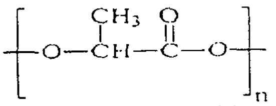


Biodegradable Copolyester



$$-\left[O-(CH_2)_5-\overset{O}{\overset{\|}{C}}\right]_n-$$

Poly(ε-caprolactone)



$$-\left[O-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O\right]_n-$$

Poly(lactic acid)

INTRODUCTION

Biodegradable plastic technologies can be classified under three broad categories and several subcategories:

1. Aliphatic polyester based
   - petrochemical feedstock
   - agricultural feedstock
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2. Natural polymer based
   - starch & starch derivatives (starch esters)
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3. Blends, alloys and graft copolymers of natural polymers and polyesters.

With a better understanding of the rationale for biodegradable plastics, and with standards in place to evaluate biodegradability, technologies are under development that meets the biodegradability/compostability criteria.

ALIPHATIC POLYESTER BASED BIODEGRADABLES

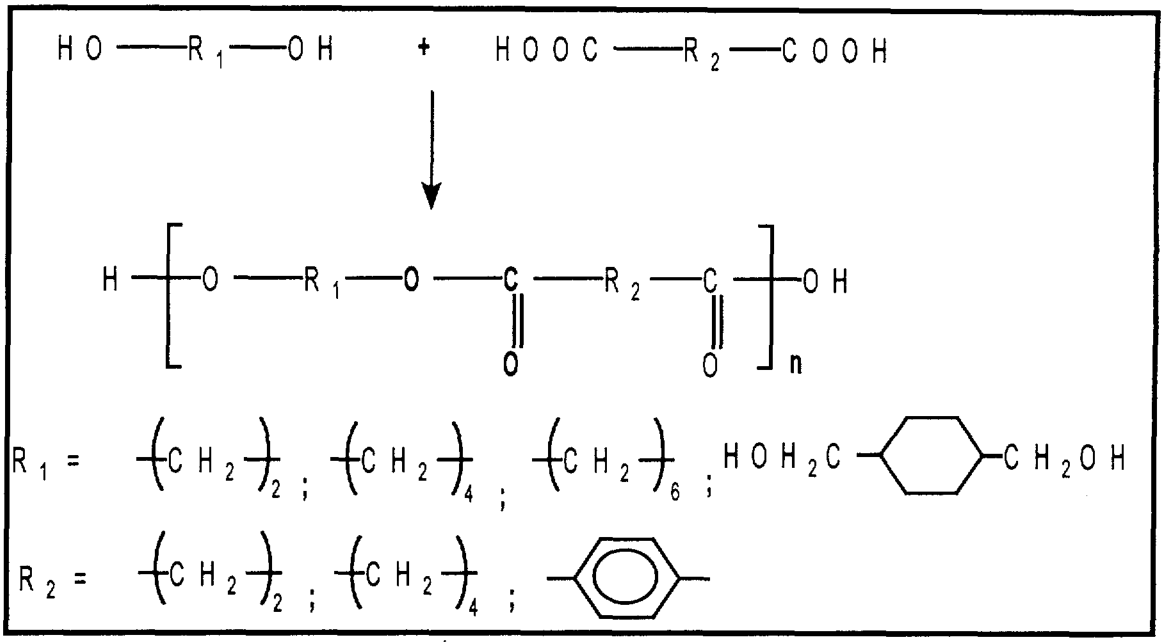
Incorporation of an ester group on the backbone of the polymer opens up the polymer to attack by nonspecific esterase secreted by soil microorganisms and water (hydrolytic attack). In all probability both enzymatic and hydrolytic mechanisms operate in varying degrees during the biodegradation process. Ultimately the polymer chains are broken down into smaller molecules which are readily assimilated by soil microorganisms.

Polyesters are prepared by step polymerization involving condensation of a hydroxy carboxylic acid monomer or a diol with a dicarboxylic acid. Ring opening polymerization of a lactone yield polyester as well. Aromatic polyesters like polyethylene terephthalate (PET) have achieved commercial success. However, the presence of aromatic groups on the backbone chain completely inhibits biodegradation. Aliphatic polyesters are susceptible to biodegradation directly through action of non-specific enzymes like esterases secreted by microorganisms or undergo hydrolysis to the monomer which undergoes subsequent biodegradation (polylactic acid). Aliphatic polyesters have been studied since the 1920's by Carothers. However, high molecular weight polymer were difficult to achieve by direct condensation polymerization did not find utility in plastics applications.

Interest in biodegradable plastics, especially for film applications, has rekindled interest in aliphatic polyesters. The monomers used in preparing aliphatic polyesters can be obtained from petrochemical feedstocks or agricultural feedstocks. Aliphatic polyesters can also be prepared by microbial synthesis.

Aliphatic polyesters derived from petrochemical feedstocks

Several technologies have emerged in this area. The basic composition involves a polyester prepared by using idols like ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,4-cyclohexanedimethanol and dicarboxylic acids like succinic, sebacic, and adipic acid. In some cases a few mole percent terephthalic acid has been used along with adipic acid to generate copolyesters to obtain suitable properties for plastic applications. The following figure shows the general synthetic scheme.

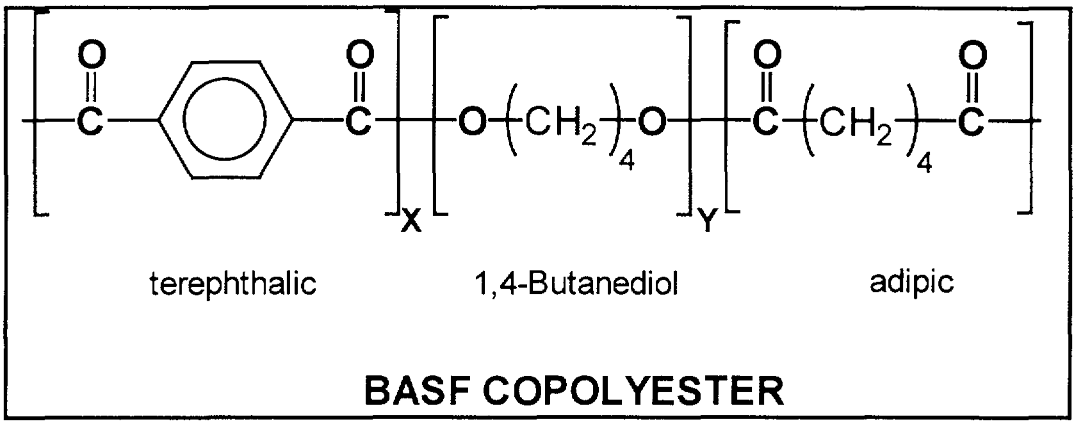


Showa High Polymer (Japan) has prepared polyesters/copolyesters using the diols, and dicarboxylic acids listed above. The problem of low molecular weight was solved by chain extension using isocyanates like isophorone diisocyanate and 2,4-tolyldiisocyanate to give polyester-urethanes. There are two issues with this approach. The first pertains to biodegradability—a high percentage of urethane linkages may reduce and even eliminate biodegradability. The second relates to the use of isocyanates—these require caution and care during handling and storage and are listed in the EPA's Toxic Chemicals Inventory List.

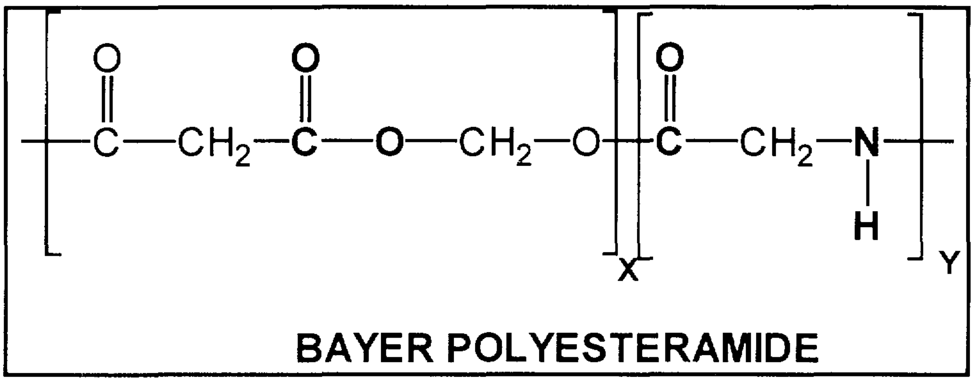
Mitsui Toatsu (Japan) have prepared high molecular weight aliphatic polyesters by direct condensation polymerization of the diol and the diacid using a suitable catalyst and a high boiling solvent like diphenyl ether. They report preparation and properties of polyethylene, polybutylene, and polycyclohexanedimethanoyl succinate (see earlier polyester synthetic scheme).

Eastman Chemical has developed aliphatic copolyesters for film applications that may contain some aromatic units on the backbone. However, they report complete biodegradability.

BASF (Germany) have developed a random copolyester incorporating adipic acid, terephthalic acid and 1,4-butane diol. The T_m of the polymer is around 110 ^{0}C. The projected selling price of the resin is \$ 2.40/lb. They claim that incorporation of a low mole percent aromatic carboxylic unit in the polyester backbone permits the polyester to maintain biodegradability. It has been clearly documented that long aromatic blocks in a polyester chain completely retard biodegradation. BASF also report the preparation of thermoplastic starch-polyester blends with enhanced biodegradability and lower cost. As will be discussed later, the starch forms the dispersed phase in the continuous matrix of the polyester phase.



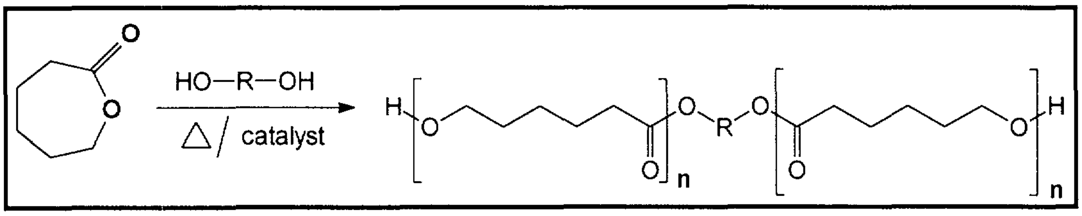
Bayer recently announced the introduction of a new biodegradable polyester amide thermoplastic, that is fully biodegradable/compostable. The polymer possess an interesting structure and has a T_m of 125 ^{0}C. The reported selling price for the resin is around $ 2.60/lb.



The Korean company Sunkyong has introduced polybutylenesuccinate/adipate polyester for biodegradable plastics applications. It is a semi-crystalline polymer with T_m of 118 ^{0}C, and a price of $ 3.30/lb.

DuPont recently advertised a new biodegradable polyester (Biomax) that incorporates up to three proprietary aliphatic monomers into the chain. The technology is based on DuPont's PET technology. No details are available at present.

Poly(ε–caprolactone) (PCL) is sold under the trade name of Tone polymers by Union Carbide. PCL is prepared by the ring opening polymerization of ε–caprolactone using Sn-octonate as a catalyst.

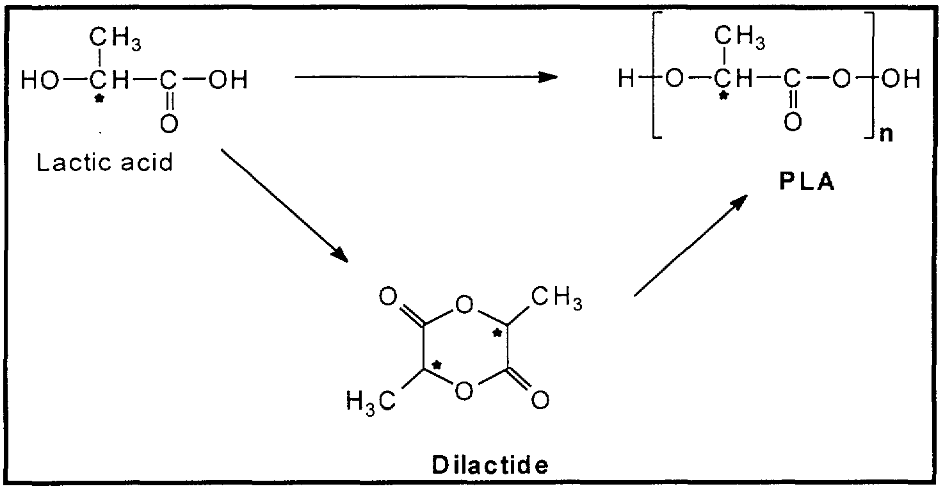


Grades of PCL have been commercially available since 1975 and used in coatings and elastomers. More recently film extrusion of PCL resins have been reported. Blends of PCL with linear low-density polyethylene (LLDPE) have excellent film forming capabilities. However, the issue of biodegradability of the PE segment remains unknown. Clendinning et al. describe degradable transplanter containers that are a blend of PCL and PE containing a polyvalent transition metal salt with a auto-oxidizable additive. The container disintegrates in soil, but the degradability of the PE component is unknown. The biodegradability of PCL is well documented. The major problem with PCL is its low melting point of 60 ^{0}C which puts a restriction on its use to low temperature application. Additionally, the dart and tear strength of PCL film is poor. More recently blends, alloys and graft copolymers of PCL with starch have been reported in the patent literature and commercial compost bags (film) based on starch-PCL are being sold in Europe. These are discussed in detail in the section dealing with starch polymer systems.

Polyesters derived from agricultral feedstocks—Poly(Lactic acid) (PLA) polymers

Hydrolysis of corn starch or cellulosic materials yields simple sugars that can be readily fermented into lactic acid. L-Lactic acid is produced by the bacterial fermentation of corn sugar (D-glucose): $C_6H_{12}O_6 = 2C_3H_6O_3$, ΔGo(25oC) = -136kJ/mol. Purac Biochem BV (division of CSM) currently produces an estimated 80% of the worlds lactic acid. Cargill and Purac recently announced (5/96) a 50-50 joint venture to build and operate a 70 million lb/yr lactic acid facility in the US (startup in 1998); the current US consumption of lactic acid is 55 million lb/yr.

There is considerable commercial and R&D activity in the field of biodegradable plastics based on lactic acid polymers. The basic chemistry involves step polymerization (condensation polymerization) of lactic acid (α-hydroxy acid). However, the degree of polymerization achieved by direct condensation was found to be insufficient to achieve mechanical properties required in plastic applications. The reason for this low degree of polymerization is the low equilibrium constant of lactic acid esterification and the difficulty of water removal in the increasingly viscous reaction mixture. Mitsui Toatsu (Japan) have successfully resolved this issue and report preparation of high molecular weight poly(lactic acid) polymer by the direct condensation route. They have achieved this by conducting the reaction in a high boiling solvent using Sn compounds or protoic acids as catalysts. Molecular weights ranging from 100,000 to 300,000 have been reported. The conventional route to high molecular weight PLA is through the dilactone of lactic acid. The following reaction scheme illustrates the two approaches.



Lactic acid has a chiral center and can exist in two stereiomeric forms, (S) L-lactic acid, and ®D-lactic acid. The repeat units are either added as dimer (lactide units) or as lactic monomer units. Both involve acyl cleavage of the ester bond with retention of chirality. The dilactide monomer has two chiral centers and can exist in three stereisomeric forms -- (SS) L-lactide, (RR) D-lactide, and (RS) meso lactide. The molecular architecture of the PLA is determined by the stereochemical makeup, and depending upon the isomer composition, the polylactides can either be semi-crystalline or amorphous. Interestingly, the properties of PLA prepared by the direct process are similar to those of the lactide process. The exception being the melting point, poly(L-lactic acid) (163 ^{0}C) is lower than the poly(L-lactide) (178 ^{0}C). If the starting lactic acid feedstock is a racemic mixture, then one obtains an amorphous poly(D,L-lactic acid/lactide).The presence of a few percent meso isomer in the predominantly poly(L-lactide) polymer will render the polymer amorphous. Essentially all of the PLA literature involves L, & D,L-lactide copolymers.

The first commercial applications of PLA were in the biomedical field—biodegradable sutures, prosthetic devices, and controlled drug release applications. However, there has recently been an explosion of activity in this area. Since 1966 there have been 2525 PLA publications -- 1540 journal articles, and 985 patents. The period between 1990 -1996 accounts for nearly 70% of these PLA publications. There are five major companies aggressively developing PLA polymers for biodegradable plastics applications, and several smaller ones in Japan. The following table illustrates the activity in the area.

Table 1 : Companies Developing Polylactides

company feedstock	company size[a] (billion USD/yr)	PLA production[b] capacity (million lb/yr)	patent[c]	Integrated through activity
Cargill (US)	51.0 (1995)	10	10	yes, corn
Mitsui Toatsu (Japan)	4.3 (1993)	2-20 planned (1995)	97	no
Neste OY (Europe)	na	na	1	na
Shimadzu (Japan)	1.3 (1992)	0.2 (1995)	22	na
Chronopol (US)	na	2 planned (1996)	56[d]	yes, corn

[a] Japan sales values from *Biodegradable Polymers and Plastics in Japan: Research, Development, and Applications*, Lenz, R.W., Loyola College, NTIS Report # PB95-199071, distributed by the US Dept. of Commerce and NTIS.

[b] production capacity values based on published news report.

[c] patent activity based on Chemical Abstracts Search (5/96), ACS. Includes both granted and applied for patents as normally published by the 23 patent offices followed by Chemical Abstracts including: US Pat Office, Eur. Pat Office, Japan Patent Office, World Intellectual Property Org.

[d] Chronopol patents include those assigned to Battelle, Ecochem, Ecopol, and DuPont.

Cargill, Inc. currently operates the largest PLA facility. With over 50 billion in annual sales, Cargill is the largest privately held company in the US. To our knowledge, Cargill is the only PLA company that is back-integrated through feedstock, corn. Cargill is well known for building and operating safe, low cost plants and has considerable separations expertise. The synergistic alliance of Purac and Cargill links the worlds lactic acid experts with one of the worlds largest corn wet milling biotechnology companies. Cargill is confident that their EcoPLA resins will sell for less than or equal to $1/lb at large scale.

Mitsui Toatsu produces polypropylene, polystyrene, and poly(vinyl chloride) and manufactures poly(glycolic acid) and glycolic-lactic acid copolymers for medical applications. They plan to become a raw material supplier for biodegradable plastics and are building a new poly(lactic acid) pilot plant. Mitsui Toatsu has clearly been the most aggressive PLA company in patent applications.

Neste OY is a Finnish company that is known to be developing PLA applications. Very little has been published on their plans.

Shimadzu of Japan has been producing PLA in a 100 ton/yr pilot plant and has plans for future scale-up. They have developed a lactic acid fermentation process and have plans to be a PLA resin supplier. They are collaborating with Mitsubishi Plastics to develop PLA.

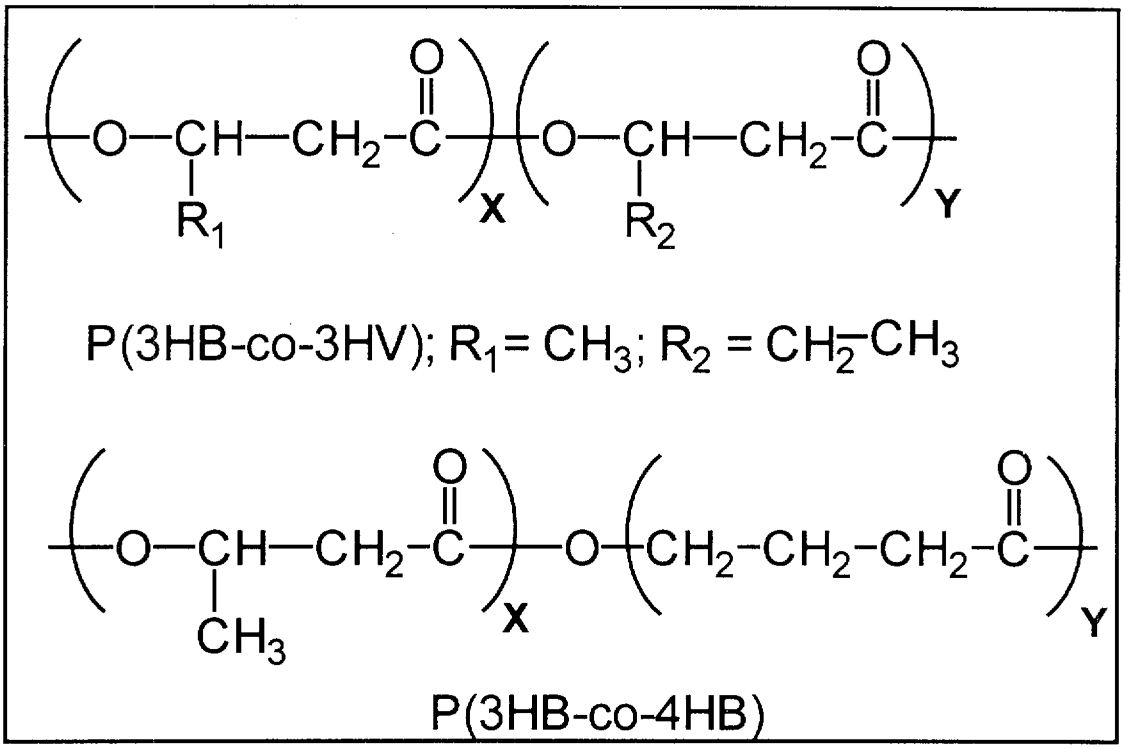
Chronopol is a subsidiary of Golden Technologies which is the R&D division of ACX Technologies, a spin-off company of Adolph Coors.17 Chronopol and Ecochem entered a 50-50 joint venture in 1995 named EcoPol. Ecochem is in turn a joint venture between DuPont and ConAgra. Ecochem had a short-lived (7/92 to fall/94)21 lactic acid business using technology developed by ConAgra and the University of Wisconsin. The business dissolved as a result of technical difficulties and falling lactic acid prices. Chronopol has since shut down operations.

Other companies that have expressed interest in developing polylactides include Dai Nippon (Japan) and Hycail (Netherlands, relationship with the University of Groningen). Hycail has considerable polylactide modification technology as evidenced by their journal articles on the subject (e.g., Gripjma et al.)

Although there have been no public announcements, major US corn wet millers such as Archer Daniels Midland Co (ADM) and A.E. Staley (subsidiary of Tate & Lyle PLC) should be considered potential PLA resin suppliers. ADM has numerous biotechnology businesses based on corn, including a 10-15 million lb/yr lactic acid business that it plans to double by the end of this year.22 A.E. Staley has announced (5/96) that they will be entering the lactic acid market in early 1997.

Microbial polyesters—Polyhydroxyalkanoates

Poly(hydroxybutyrate) (PHB), and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) are novel thermoplastic polyesters that are prepared by a bacterial fermentation process using a variety of feed stocks including glucose and acetic acid . PHB is a brittle polymer. However, the introduction of hydroxyvalerate groups in the polymer backbone (0-30%) reduces the crystallinity, and the resultant material is much more ductile and flexible. A good balance of properties can be achieved by varying the comonomer content to yield polymers for specific applications.



$$\left(-O-\underset{R_1}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-\right)_X\left(-O-\underset{R_2}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-\right)_Y$$

P(3HB-co-3HV); $R_1 = CH_3$; $R_2 = CH_2\text{-}CH_3$

$$\left(-O-\underset{CH_3}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-\right)_X-O-\left(CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-\right)_Y$$

P(3HB-co-4HB)

PHBV is in commercial use for blow molded shampoo bottles in the U.S., Japan, and Germany. It is also being used in razor handles in Japan. There is a considerable body of literature in this field and the reader is referred to papers by Holmes and Galvin and the references cited in them. There is significant R&D activity in the field of bacterial polyesters under the general name of polyhydroxyalkanoates and they are the subject of yearly International Symposia. The different polyhydroxy alknoates arise from differing side chain R groups. Bacterial polyesters carrying long side chain R groups like C-6 and C-8 are being investigated for its elastomeric properties. Zeneca was the major commercial developer of this resin. The technology has recently been acquired by Monsanto. Monsanto has considerable expertise and strength in plant biotechnology. Their goal is to genetically engineer plants like soybean and canola to produce PHB, thereby dramatically reducing cost of the polymer which is currently \$4-10/lb. However, because of recent merger failures, this technology development has been shelved.

Natural Polymer Based Biodegradables

Naturally occurring biopolymers like starch and cellulose are readily biodegradable. Several companies are commercializing starch based thermoplastic technologies. Basically, these technologies involve thermoplasticization of the starch using water and heat under pressure. The starch is heated above the glass transition and melting temperature of its components. This results in disruption of the molecular structure resulting in a "destructurized starch" that has thermoplastic properties. A number of polymer compositions containing destructurized starch for different applications have been described. However, products based solely on starch are extremely water sensitive and of limited utility. However, 90 to 99% starch, or very low ds (0.5, degree of substitution) hydroxy propylated starch, have found applications as loose-fill packaging material. They are offerred as a biodegradable, water soluble, anti-static, environmentally friendly alternatives to expanded polystyrene(peanut packaging). The entire operation is carried out in a twin-screw extruder specially designed to hold the water (which functions as the plasticizer, and blowing agent). Additives such as poly(vinyl alcohol) (PVOH) and other similar compounds are added to the starch to improve processability. The resultant foam has the compressibility and resilience of polystyrene foam products. National

Starch (through American Excelsior), Empak (a DuPont-Conagra joint venture), Novamont (Italy), Clean Green Packaging (Minnesota) are marketing loose-fill packaging products.

This year, a Michigan based small business, ***KTM***Industries, has cleverly exploited the light-weight, non-toxic, water wetable adhesive property of extrusion foamed starch to produce a new family of products for children. The first product is a multi-colored foamed building block that is marketed under the brand name "**Wet N' Set Magic Nuudles**". Within the next three months, this product will be marketed in approximately 500 stores in all 50 States, and in Europe, (visit web site www.wetnset.com). This is expected to expand to 1200 stores within a year.

Starch esters

Modification of the starch -OH groups by esterification chemistry to form starch esters of appropriate degree of substitution (1.5 to 3.0 ds) imparts thermoplasticity. Unmodified starch shows no thermal transitions except the onset of thermal degradation at around 260 ^{0}C. Starch acetate of ds 1.5 shows a sharp glass transition at 155 ^{0}C and starch propionate of same ds had a Tg of 128 ^{0}C. Plasticizers like glycerol triacetate and diethyl succinate are completely miscible with starch esters and can be used to improve processability. Water resistance of the starch esters is greatly improved over the unmodified starch.

EverCorn Inc., is commercializing biodegradable plastics based on starch esters and blends of starch esters with aliphatic polyesters. Appropriately formulated starch esters with plasticizers and other additives provide resin compositions that can be used to make injection molded products and for direct lamination onto Kraft paper. Starch acetates up to ds=2.5 undergo complete and rapid biodegradation. In the case of starch triacetates, 70% of the carbon is converted to CO_2 at 58^{0}C in 45 days.

Blends, alloys, & graft copolymers of polyester and natural polymers

Starch-polyester blends are being evaluated for commercial applications. Starch can be incorporated in several ways:

- as a filled composite
- graft copolymerization
- plasticized starch phase in which the granular structure of starch has been disrupted.

In all these cases, the starch can either be in its native form or be physically or chemically modified.

Starch-Poly(e-caprolactone) (PCL) alloy—BioPlastics Inc., technology - "ENVAR" -- This technology involves reactive extrusion processing of plasticized starch with modified PCL in a twin screw co-rotating extruder with modified screw elements. By controlling the rheology in the extruder, one can obtain a morphology in which the plastic starch is dispersed in a continuous PCL matrix phase. Good adhesion and compatibilization is promoted between the plastic-starch phase and the modified PCL phase to obtain enhanced mechanical properties.

Two other companies, Novamont, and Milleta (Biotech Division), are manufacturing and selling starch-PCL blends for film applications (compost bags, trash bags). Starch is plasticized using water or hydroxy solvents and blended with TONE 787 polymer from Union Carbide.

Improved Performance of Environmentally Friendly Materials via Modification of Thermoplastics

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Summary

Environmentally friendly materials should have minimal negative impact on environment. Considering the commodity plastics, the main problem arises is the waste disposal. Besides incineration and deposition in landfills, either recycling or biodegradable materials are the most promoted ways of plastic waste disposal.

Biodegradable polymers are in many cases a suitable solution for the decrease of the impact of plastic waste on environment. Nevertheless, the properties of many biodegradable polymers are not suitable for application as flexible foils for packaging. A substantial improvement of flexibility of polyhydroxy butyrate was achieved by a physical modification by cold roll milling. The effect of the presence of plasticizers on long - term storing was also investigated. Broad range in properties can be achieved by mixing the PHB with poly(vinyl alcohol).

Considering the improvement of plastic waste recycling several ideas have been investigated. A process of an in situ formation of compatibilizers via reactive processing can be applied for mixtures of waste plastics. The properties of an in situ compatibilized blend of LDPE and PP in different ratios is shown as an example.

Another example of utilizing reactive processing in two-phase materials is LDPE filled with organic fillers. An improvement of properties was observed for LDPE filled with various amounts of sawdust, recycled paper or rubber crumb produced by milling the old tires.

INTRODUCTION

The share of plastics in total amount of waste is increasing, as a result of the extensive increase in the production and consumption. Therefore, plastic waste management is becoming to be more and more important from point of view of sustainable development.

A substantial decrease in the amount of plastic waste would be the most effective way for dealing with the problem. However, this requirement is absolutely unrealistic at present, on the contrary, the decisions must be done to be able to deal with the increase of plastic waste all over the world.

Four main procedures are generally used for a waste disposal, namely deposition in landfills, incineration, recycling, and fast and safe decomposition in the environment. Apparently, landfills are the least favourable, although highly preferred in most countries, because of relatively low costs and easy application. Incineration is reasonable, especially if a part of energy can be utilized for heating. Nevertheless, this is a rare case at present. Recycling seems to be the most favoured in industrially developed countries. The waste is used as a raw material for production of goods. However, in many cases the process is economically dubious and technically complicated. Environmentally degradable materials present a great potential of dealing with plastic waste in many cases, especially for products with short lifetime such as packaging.

Environmentally degradable polymers

When talking about plastic waste management, it would be advantageous if certain products with short lifetime would dissappear after the service time expires. This goal might be reached by using biodegradable or more generally environmetally degradable plastics. Commonly considered fully environmentally degradable materials are polyhydroxyalkanoates. These polymers, which are produced by bacteria, possess high strength and Young's modulus. However, the most common plastics, namely polyhydroxy butyrate (PHB), is quite brittle and it is not suitable for production of foils for packaging.

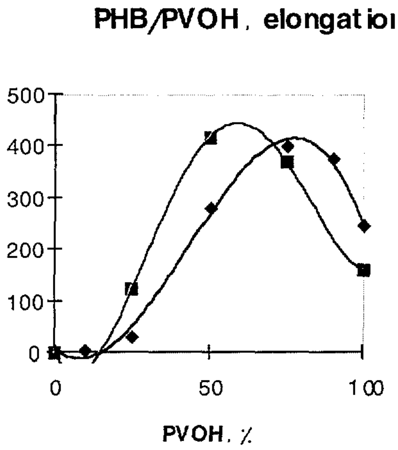
In many cases an addition of a plasticizer is quite suitable option for the increase in ductility of the foils. Several types of plasticizers have been tested, such as glycerol tricetate (triacetin), dibutyl phthalate (DBPh) and oligomeric polylactic acid. The effect of the two low molecular plasticizers is the same if mechanical properties are compared. Generally, a decrease in tensile strength and Young's modulus was observed with the increased plasticizer concentration while elongation at break increased. Nevertheless, the increase in elongation was not large enough to obtain the material with sufficient ductility. The highest elongation was achieved with 20 % of the plasticizer, while further increase in the concentration resulted in a reverse trend indicating low cohesion forces in the material.

An addition of an oligomeric plasticizer resulted in better results, especially since the concentration of plasticizer could be increased. Even in this case the elongation did not exceed 20 %, which is the value on the threshold of yield strain. Thus, no plastic deformation was observed in these materials. Further, the well known phenomenon, i.e. extreme influence of ageing (changing the properties during storing) was not eliminated by the modification. The effect consists in a gradual increase in Young's modulus accompanied by a decrease in strain at break during several days which continues up to three months. The deformation decrease ends up with values as low as 1.5 % which is typical for extremely brittle plastics, especially regarding the glass transition temperature which is around 25 °C.

As a next step, a physical modification was examined. Simple cold rolling of PHB slabs proved to be quite useful modification of the PHB foils. By this procedure the thickness of the slab is decreased about three or four times and rather ductile foil can be prepared. It is interesting that Tg of the polymer increases by several centigrades as a result of cold rolling and at the same time the area under the tg δ peak, measured by DMTA, is decreasing, which indicates lower portion of mobile phase. It is proposed that some defects in the materials are healed by the cold rolling process leading to an increased resistance towards a formation of catastrophic crack at early stage of deformation. Nevertheless, even in this case the modification did not suppress the ageing effect of the material and no sufficient increase in the deformability was observed after storing for 14 or more days. Better results regarding the deformability increase and diminishing the effect of storing was achieved by a cold rolling of material containing a plasticizer.

Although each of the above mentioned modification resulted in certain positive effect, no such an improvement of the deformability was achieved which might be of interest for the desired application. Therefore the effect of blending with polyvinyl alcohol (PVOH) was investigated. PVOH is rather brittle material which is difficult to process. Therefore an addition of a plasticizer is necesssary. After addition of few percent of plasticizer, PVOH is quite ductile and suitable for production of foils. Glycerol was used in our experiments as a plasticizer. Several concentrations were examined, however, in all experiments described in this paper 20 wt % of glycerol was used, calculated on the polymer content (PHB + PVOH). It was found that the addition of PVOH leads to a dramatic increase in elongation at break and substantial decrease in Young's modulus as seen in Figs 1 and 3. The data of tensile strength are similar for PHB and for PVOH (both with the glycerol content). Again, it has to be admitted that the reason for high strength of PVOH, in spite of low modulus, consists in rather high deformation, i.e. some kind of orientational strengthening occurs. From this point of view it is worth to note that an extreme at about 75 % of PHB content is observed for all the mechanical properties in dependence on the blend composition. It is suggested that phase inversion occurs at this composition and PVOH behaves as the continuous phase when its content is higher than 25%.

In Figures 1 - 3 the data for the blend modified by an addition of modified collagene (MCol) are also given. It is seen that both strength and modulus values are lower compared to the blends without the collagene while elongation maximum is shifted to lower PHB content. It is worth to note that the addition of MCol to virgin PHB without another polymer nor plasticizer resulted in a substantial decrease in viscosity of the melt during processing and was possible only up to 7 wt %. PHB containing 10 % of MCol was of very low viscosity and after cooling down the material was too brittle to allow to cut the testing specimens for tensile tests. It was suggested that the presence of MCol results in an extensive PHB degradation which is detrimental for the material itself but can be beneficial for the PHB / PVOH blend. Although the mechanism of this degradation is not discussed here, it is expected that carboxyl or amine moieties in MCol are the species responsible for the PHB degradation.



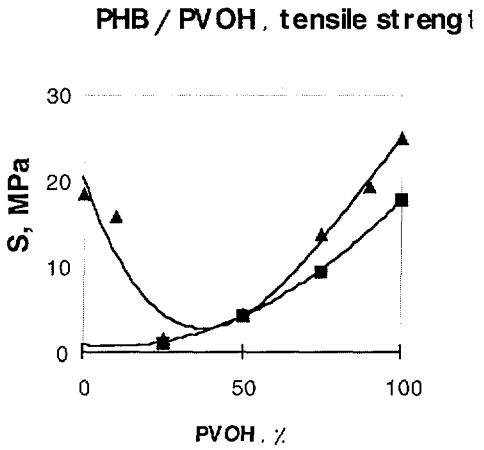


Figure 1: The effect of the addition of hydrolyzed collagene on the elongation at break of PHB / polyvinyl alcohol blends (diamonds - no collagene, squares - 10 wt % collagene)

Figure 2: The effect of the addition of hydrolyzed collagene on the tensile strength at break of PHB / polyvinyl alcohol blends (triangles - no collagene, squares - 10 wt % collagene)

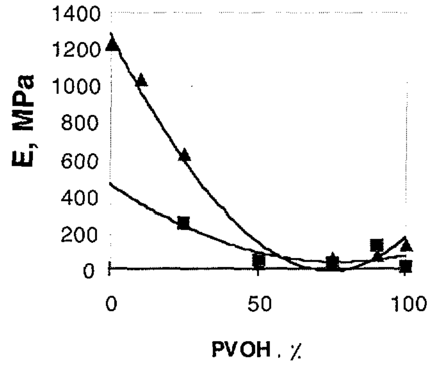


Figure 3: The effect of the addition of hydrolyzed collagene on the Young's modulus of PHB / polyvinyl alcohol blends (triangles - no collagene, squares - 10 wt % collagene)

RECYCLING

Recycling is considered as the most effective way for plastic waste disposal. For a laymen it seems to be really the most desirable process since apparently the used goods are transformed into new ones in one simple process saving raw materials and energy. Recycling of industrial waste plastic usually brings little problems since the materials are well characterized and of rather uniform quality. Different situation occurs when dealing with the plastic waste from household, e.g. from separated collection since a mixture of various materials has to be processed which differ in a broad range of compositions. The main components of household plastic waste are represented by high and low density polyethylene, polypropylene, PVC and polystyrene. The processing of the mixtures requires an application of efficient compatibilizers, usually the block or graft copolymers. We investigated an alternative way, consisting of the formation of an in situ compatibilizer via peroxide - initiated cocrosslinking on the phase boundaries. As an example the blend of LDPE and PP was chosen.

Compatibilization of LDPE / PP blends

Crosslinking of LDPE / PP blends is complicated by the presence of polypropylene. If the process is initiated by thermal decomposition of organic peroxide in the absence of a coagent of PP crosslinking, PE part is only crosslinked as indicated by a linear decrease of crosslinked portion with the increased PP content in the blend [1]. In the presence of hydroquinone as the coagent, the gel content (related to the crosslinked insoluble portion of the material) is constant in the whole range of the component concentration.

When investigating mechanical properties, an extreme increase in elongation at break is the most important phenomenon observed [2]. Young's modulus data are lower for crosslinked blends because of a lower crystallinity due to defects introduced by crosslinking into the crystalline structure, similar to crosslinking of individual polymers. Tensile strength at break of crosslinked blends is higher than that for the uncrosslinked ones mainly because substantial orientation strengthening occurs during drawing at high deformation after complete development of the neck.

The effect similar to crosslinking by compression moulding can be reached also by dynamic crosslinking during mixing in a chamber of Brabeder Plasticorder. The mechanical properties of the blend LDPE / PP in a ratio 50:50 are shown in Table 1. The effect of various coagents is compared.

Table 1: Mechanical properties (tensile strength at break σ, elongation at break ε, Young's modulus E) and gel content g for the blend LDPE / PP 50 : 50 crosslinked by 3 wt % of peroxide in the presence of various coagents (hydroquinone HQ, Santonox R SX, bisphenol A BP, triallyl cyanurate TAC, oligomeric polybutadiene hydrogen terminated PBH and hydroxyl terminated PBOH). The properties at the optimal concentration of coagent are given.

additive	c	σ	ε	E	g
HQ	0.5	26.6	515	500	43
SX	1.5	27.0	586	480	48
BP	1.0	25.7	626	460	39
TAC	1.0	18.8	391	250	25
PBH	1.0	20.4	408	340	37
	10.0	21.6	212	510	67
PBOH	3.0	21.6	303	320	61

Note : Santonox R is a phenolic antioxidant

It is seen that the crosslinking with different coagents results in different properties, although the peroxidic part of the crosslinking system is the same in all the cases. The lowest mechanical properties have been obtained with triallyl cyanurate as a coagent. Hydroquinone is similar to the other two phenolic coagents while with oligomeric polybutadienes lower tensile strength was observed. In any case, it is interesting to note that very good properties can be reached via dynamic crosslinking. In that case the material is processable even after crosslinking. In that case, obviously, thermal resistance is not reached, i.e. the material flows if heated above the melting temperature of polypropylene.

An important practical consequence of higher deformation consists in a high impact resistance [3]. A presence of polypropylene in LDPE results in inferior impact behaviour which is improved tremendously by crosslinking so that even 25 % of LDPE in PP leads to the impact resistance comparable to a virgin LDPE.

The above mentioned processes can be used for improvement of the material properties of various mixtures. Thus, it is possible to use this concept for design of materials based on polymeric waste consisting of a mixture of several commodity plastics.

Crosslinked composites of LDPE with organic fillers

Peroxide initiated crosslinking was examined also as a method for the improvement of properties of mixtures of LDPE with organic fillers. Several waste materials have been used as fillers, such as milled grass, recycled paper, and starch. The results obtained for wood flour are presented here and they are representative for behaviour of the other fillers, although certain differences exist. A tremendous increase of both tensile strength at break and Young's modulus was found as a result of crosslinking. At high crosslinking degree the composite with the organic filler is superior even compared to the LDPE filled with silica (Table 2), although silica with high surface area is considered to be a reinforcing filler, while wood flour should be incompatible due to higher polarity of the filler surface preventing the wetting of the surface by polymer melt during mixing.

Table 2: The effect of peroxidic crosslinking on the mechanical properties (tensile strength at break σ, elongation at break ε, Young's modulus E) of LDPE filled with silica or wood particles.

peroxide wt %	σ MPa		ε %		E, MPa	
	silica	wood	silica	wood	silica	wood
0	12.0	3.2	50	4	1400	330
0.2	12.1	4.3	240	6	1150	200
0.5	12.3	10.7	260	6	910	590
1.0	12.7	13.1	260	6	650	620
1.5	13.2	14.4	270	6	550	720

An explanation for the observed behaviour is based on a hypothesis that oxy radicals formed by peroxide decomposition can abstract hydrogen atom from both polyethylene chains and from the filler surface. The radicals formed by such a way can recombine, similar to the recombination of polyethylene and polypropylene macroradicals in LDPE / PP blends. Grafting of LDPE chains can occur leading to the increase of adhesion on the interface.

It is worth to note that similar effect consisting in an improvement of properties via crosslinking can be obtained also for mixtures of LDPE with rubber crumb produced by milling of old tyres. By such a way the recycled material can be utilized to produce a product with higher added value compared to currently used applications of rubber crumb.

CONCLUSIONS

A modification of polyhydroxybutyrate by the addition of plasticizer was found to be of little practical effect. On the other hand, by a cold rolling of the PHB foils with quite intersting properties can be prepared, especially if PHB with the admixtures of an oligomeric palsticizer is used. Interesting materials can be prepared by mixing PHB with polyvinyl alcohol. The properties of the blend can be further modified by addition of modified collagene causing a degradation of PHB in situ during processing of the blend.

Several ideas have been outlined which can be used in plastic waste recycling. It was shown that peroxide initiated cocrosslinking on LDPE / PP blends can result in a formation of very efficient compatibilizers. The process is suggested to be applied for a mixture of crosslinkable polymers of unknown portions of the components.

Similar process of peroxide - initiated crosslinking can be used for improved properties of polyethylene filled with organic fillers such as wood flour, aspen fibres or recycled paper. The same process can be used for preparation of mixtures of polyethylene with rubber crumb obtained by milling the old tyres. The resulting blend possess the properties which are superior compared to uncrosslinked material with the same proportion of components.

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Production and Use of Polyhydroxyalkanoates from Renewable and Non Renewable Resources

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INTRODUCTION

Polyhydroxyalkanoates (PHAs), a general formula is given in figure 1, are polyesters formed by many prokaryotic microorganisms when unbalanced nutritional conditions are chosen for the producing cells (1-3). Up to more than 90% of the cell dry weight can be accounted for as polymer (4). Beside the homopolyester poly-R-3-hydroxybutanoate, consisting of 3-Hydroxybutanoate (3HB) only, two main types of copolyesters can be formed by different microorganisms (5). 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 (6), double bonds (7), epoxides (8), and aromatic structures (9) can be introduced into the side chain. Furthermore copolyesters containing ω-chloroalkanoates (F, Cl, Br) can be produced (10-12). 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).

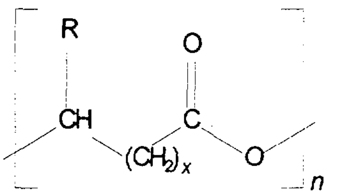


Figure 1: General formula of PHAs

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 (back-bone 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):

$$[1] \qquad \frac{Pr_{CSTR}}{Pr_{DSTR}} = \ln \frac{X_e}{X_i} + t_0\,\mu_{max}$$

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

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

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 τ_{CSTR}, during which X_i is converted to X_e, is therefore simply

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

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

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

Here again, τ 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 τ_{PFTR} and τ_{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 τ_{CSTR}/τ_{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 $\pi_{P3HB,\, max}$ can reach 0.50 h^{-1} during growth on sucrose, whereas a $\pi_{P3HB,\, max}$ 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 $q_P = 1/X\ dP/dt$.

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

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 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 (Figure 2), 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 can be seen from Figure 2, methanol must be oxidized to formaldehyde (via a methanol dehydogenase) before the C_1

compound enters the cycle, and due to a CO_2 fixation, 1mol of acetyl-CoA can be generated by the cycle.

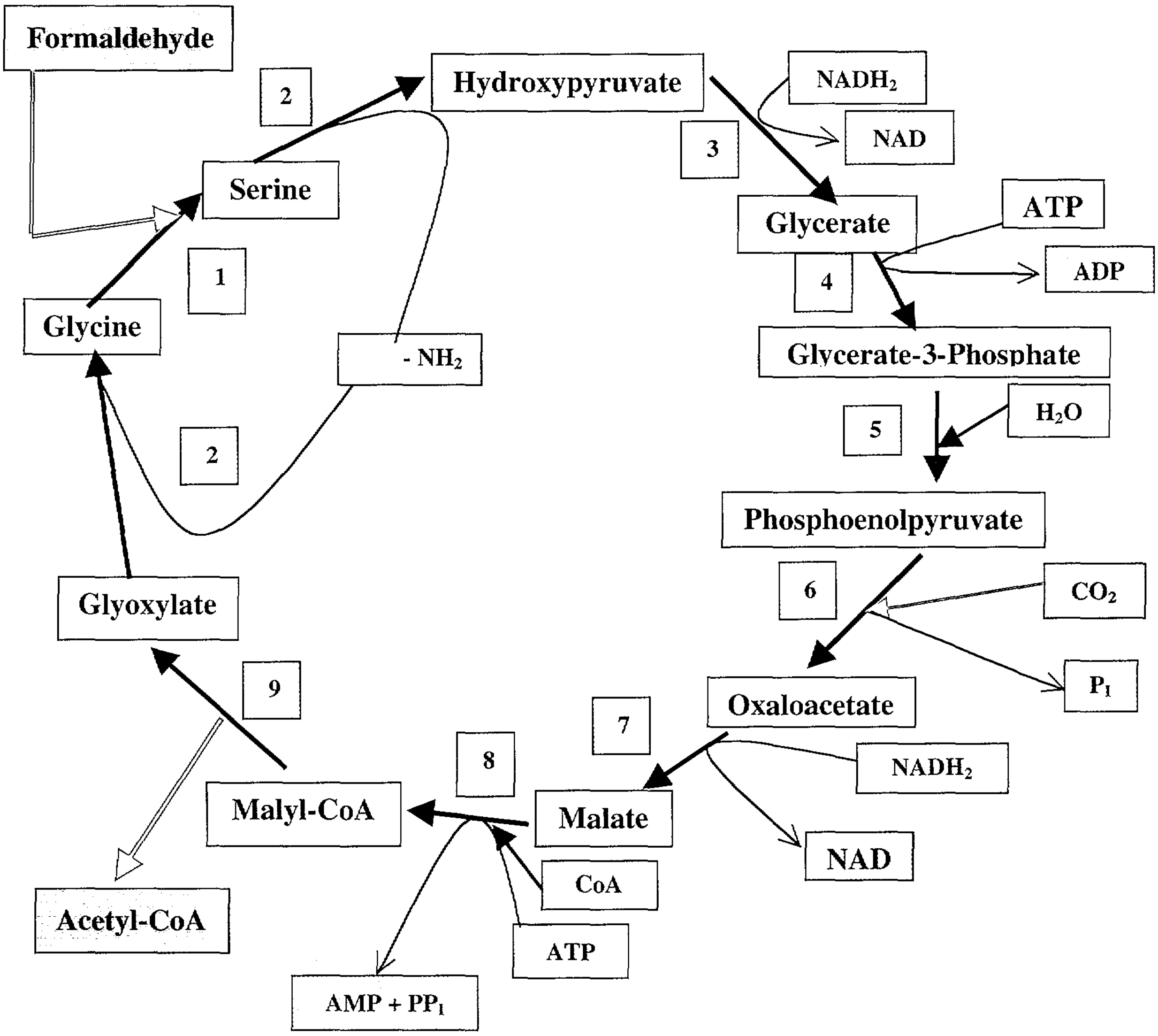
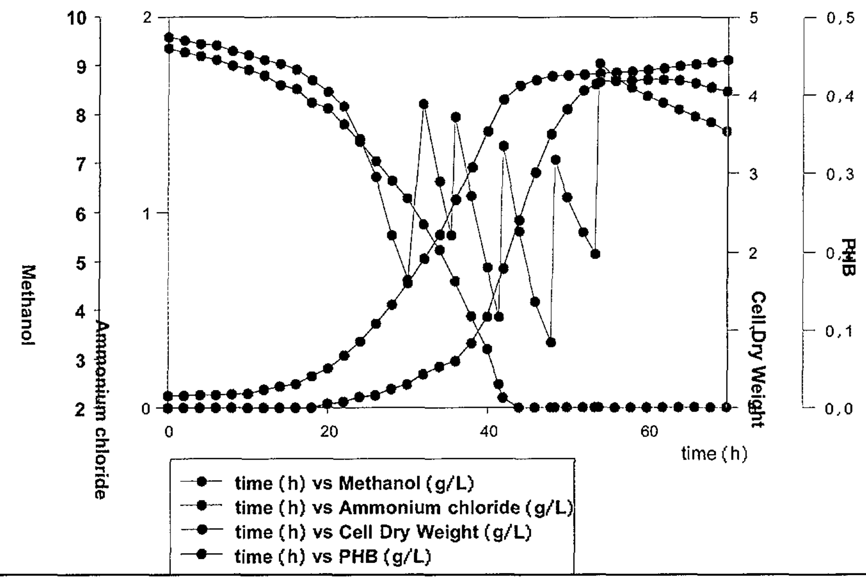


Figure 2: Methanol utilization via the Serine Cycle. Enzymes involved:

1 serine hydroxymethylase, 2 transaminase converting serine into hydroxy-pyruvate and glyoxylate into glycine, 3 hydroxypyruvate reductase, 4 glycerate kinase, 5 phosphoglycerate mutase and enolase, 6 phosphoenolpyruvate carboxylase, 7 malate dehydrogenase 8 malyl-CoA synthetase, 9 Malyl-CoA lyase.

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 byMycoplana 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 concentrationssuboptimal for growth (0,05 _ 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.

Mycoplana rubra: Production of PHB from Methanol under Ammonium limiting conditions



Mycoplana rubra: Production of PHB from Methanol under Phosphate limiting conditions

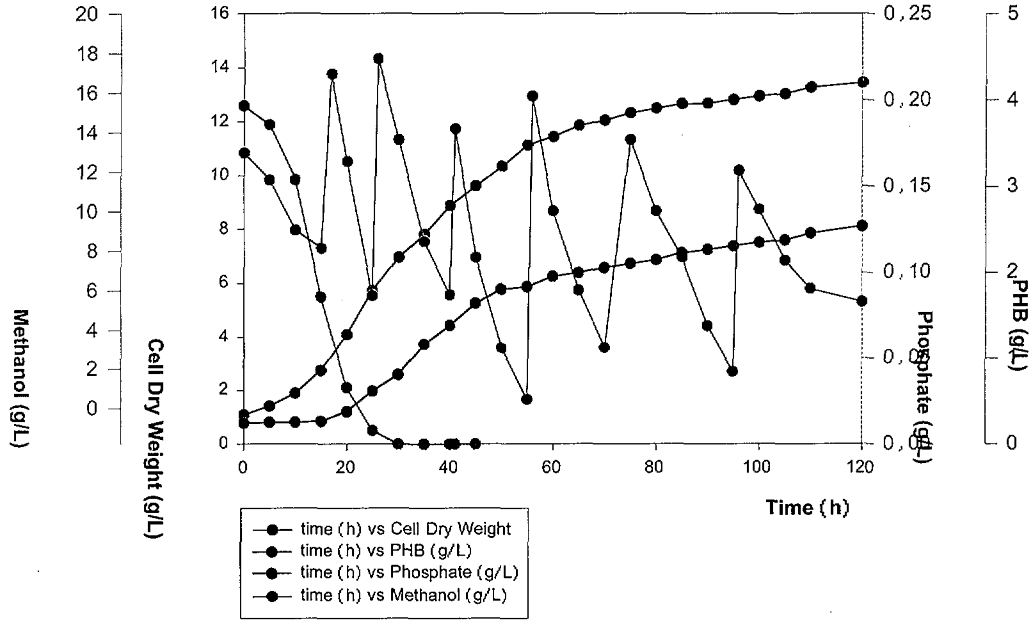


Figure 3 : Production of PHB with Mycoplanarubra with Ammonium or Phosphate as a growth limiting substrate.

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 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 3 and 4.

Table 3: 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

Investigations by Huijberts et al. (28) with *P. putida* revealed the synthesis by this microorganism 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 (Lee et al., 1995a) 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 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							

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. (9) 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.

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 (10, 11, 33), poly(3-hydroxyalkanoate) copolymers containing brominated repeating units have been produced. Kim et al. (12) 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 (34).

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The Effect of Thermal-Mechanical Stress on Polypropylene and Phosphite Additive Degradation

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Abstract

Thermal-mechanical stress, as it occurs under polymer recycling and processing has a detrimental effect on the properties of polypropylene. The addition of processing stabilizers can suppress this negative side effect to a certain degree. However, data about the optimum additive concentration and combination required for a certain processing condition and a certain product are rarely available. The effect of multiple extrusions at different temperatures and with different levels of two common antioxidants (phenolic Ciba Geigy Irganox-1010 and phosphite Irgafos-168 on key properties of polypropylene is examined. Design of Experiment (DOE) technique was used as the tool of choice for obtaining the data in this study. It can be shown that for a certain product requirement very narrow additive concentrations must be selected. Particularly highly stressed polypropylene, which simulates the recycling case, needs unconventional high levels of phosphite addition and relatively low phenol addition in order to meet the standards for yellowness and melt-flow within an acceptable range. Partial oxidation of the additive during sample preparation can be completely avoided. Phosphite additive degradation after multiple extrusion at elevated temperatures can be generally correlated to an increased melt-flow and a decrease in oxidation induction time. Yellowness was found mainly due to phenolic oxidation during stress and could be inhibited by the phosphite additive.

INTRODUCTION

Polymer resins are usually compounded with different additives in order to modify certain properties or to stabilize the material against harmful environmental effect. Most polymers are subject to attack by oxygen from air. Therefore, they require the addition of antioxidants to minimize degradation during processing, storage and service [1]. Degradation occurs during polymer manufacturing, processing, pelletizing, compounding, storage, end-user application and particularly during the recycling process [2].

The reaction of organic compounds with molecular oxygen is called autoxidation, because such reaction proceeds by itself [3]. Frequently, the presence of small amounts of impurities, particularly metals, e.g. from residual catalysts have an accelerating effect on the oxidation. There are mainly the initiation reactions (1)-(2), generating free radicals, the propagation and chain-branching reactions (4)-(9), yielding oxidation products and the termination reactions (10)-(13) eliminating free radicals from the system.

Scheme 1: General Degradation Mechanism of Polymers During Processing

Chain initiation:

$RH \xrightarrow{\Delta} R\cdot + H\cdot$ (1)

$RH + O_2 \xrightarrow{\Delta} R\cdot + HO_2\cdot$ (2)

Chain propagation:

$R\cdot + O_2 \longrightarrow RO_2\cdot$ (3)

$RO_2\cdot + PH \longrightarrow ROOH + R\cdot$ (4)

Chain branching:

$ROOH \xrightarrow{\Delta} RO\cdot + O\cdot H$ (5,a)

$ROOH + RH \xrightarrow{\Delta} RO\cdot + R\cdot + H_2O$ (5,b)

$2ROOH \xrightarrow{\Delta} RO\cdot + RO_2\cdot + H_2O$ (6)

$RO\cdot + RH \longrightarrow ROH + R\cdot$ (7)

$O\cdot H + RH \longrightarrow H_2O + R\cdot$ (8)

Chain termination:

$RO_2\cdot + RO_2\cdot \longrightarrow ROOR + O_2$ (9,a)

$RO_2\cdot + RO_2\cdot \longrightarrow RO\cdot + RO\cdot + O_2$ (9,b)

$RO_2\cdot + RO_2\cdot \longrightarrow \text{inactive products} + O_2$ (10)

$R\cdot + RO_2\cdot \longrightarrow ROOR$ (11)

$R\cdot + R\cdot \longrightarrow R{-}R$ (12)

During polymer processing and recycling, mechanical stress and/or heat leads to the formation of macro alkyl radicals through homolysis of carbon-hydrogen or carbon-carbon bonds. The direct interaction of the polymer with molecular oxygen (2) may also contribute to the formation of free radicals. However the primary initiation step, in the presence of O_2, the reaction of the radicals formed, yield hydroperoxides. These groups are rather sensitive towards heat or the combined action of heat and traces of transition metals. Thus it is very likely, that once the radicals are formed, they are of paramount importance for the oxidative degradation of polypropylene.

The chain propagation, chain-branching and chain termination steps are rather straight forward [5]. The chemical changes accompanying thermal oxidation of polypropylene consist mainly in the formation of aldehydes, ketones, carboxylic acid, esters and γ-lactones [6]. The physical changes resulting from the thermal oxidation of polypropylene are essentially the consequence of the main chain scissions. As a matter of fact, the latter lead to a decrease in polypropylene molecular weight, resulting an increase in melt flow index, due to the lowered viscosity.

The autoxidation scheme shows clearly the detrimental degradation reactions with the polymer. These are initiation and chain-branching on the one hand, propagation on the other hand. The role of an antioxidant additive must be consequently to interrupt the autoxidation process at an early stage. The most important antioxidants, the chain-breaking or primary antioxidants, interfere with the chain propagation step (reaction 5 in scheme 1). The preventive or secondary antioxidants destroy hydroperoxide groups, which are responsible for chain initiation and chain-branching (scheme 2).

Scheme 2: Mechanism of Antioxidants: R (Polymer), AH (Primary antioxidants), $P(OR)_3$ (Secondary antioxidants)

Primary antioxidants mechanism

$R\cdot + AH \longrightarrow A\cdot + RH$

$RO\cdot + AH \longrightarrow A\cdot + ROH$

$HO\cdot + AH \longrightarrow A\cdot + HOH$

Secondary antioxidants mechanism

$ROO\cdot + P(OR)_3 \longrightarrow RO\cdot + O=P(OR)_3$

$RO\cdot + P(OR)_3 \longrightarrow R\cdot + O=P(OR)_3$

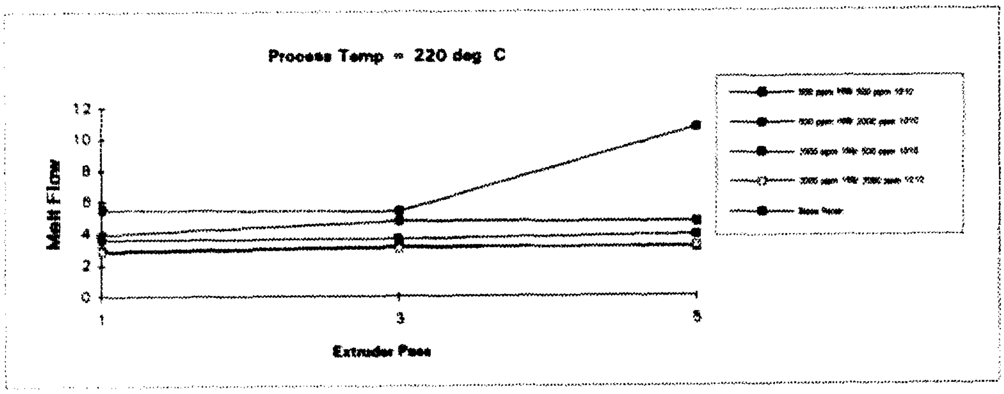
EXPERIMENTAL

Base resin for the experiments was SABIC polypropylene grade HB-30, obtained from Ibn Zahar plant. The study of the thermal-mechanical stress on PP has been carried out with a Brabender 19/25D extruder in air and at temperatures between 220°C and 300°C. In order to minimize the number of experiments, a 2-level factorial scheme in 4 factors, which are the level of Irganox-1010, the level of Irgafos-168, the temperature, and the extrusion pass number, has been designed.

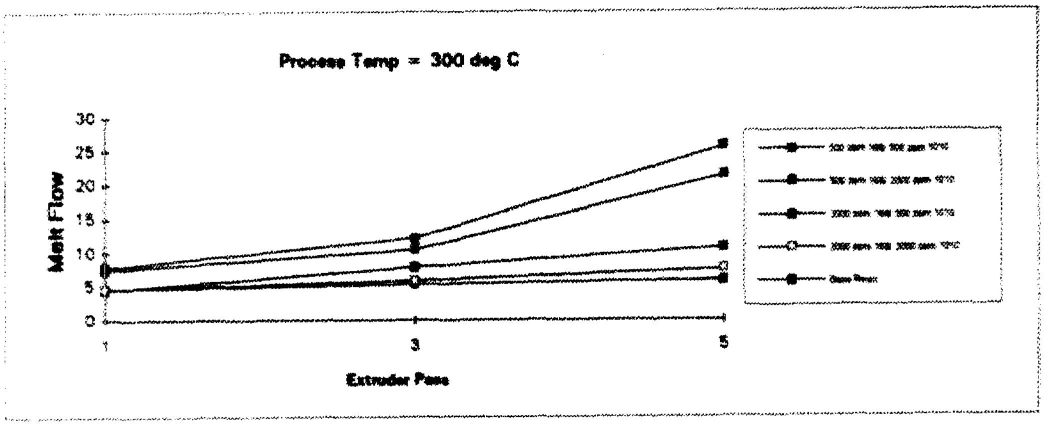
The antioxidants Irganox-1010 and Irgafos-168, both obtained from Ciba-Geigy, were mixed with PP resin by a multiaxial powder blender (Chemplex) for 1 hour prior to the extrusion experiments. The level of additives were confirmed by HPLC. The melt flow index of the extruded material was determined after the first, third, and fifth extrusion by a kayeness melt indexer (Dynsisco company) at 230°C and 2.16 kg. Discoloration (yellowness index) of the substrate was measured with Colorgrad system/05 colorimeter. The oxidation induction time was determined at 210°C under O_2 by a DSC 2920 from TA instruments. ^{31}P NMR spectroscopic analysis was done with a Varian Unity 400MHz NMR spectrometer at 130°C under nitrogen, using 1, 2 Dichlorobenzene, DMSO-D6 (9:1) as a solvent.

RESULTS AND DISCUSSIONS

Fig.1a - 1b shows the dependence of the Melt Flow Index (MFI) from the process temperature, the number of extrusions and different additive concentrations. It is very obvious and in accordance to the theory, that a high thermal-mechanical stress leads to an increase of the MFI, due to chain-scission and degradation, particularly with the formulations containing low levels of additives. The base resin, without stabilization behaves most sensitive towards



(F-1a)



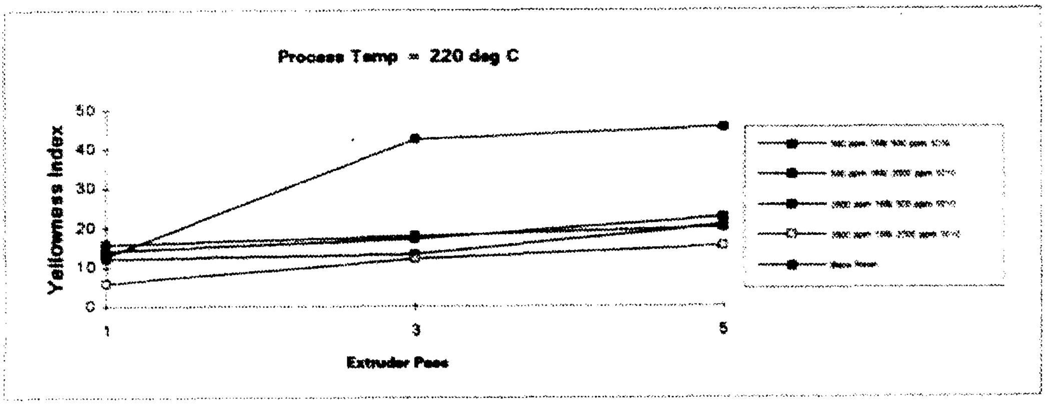
(F-1b)

multiple extrusion and temperature. It is a remarkable observation, that at the lowest processing temperature 220°C (Fig. 1a) the dramatic increase of MFI in the base resin needs an extrusion number of at least three. For that reason we assume that a very low stabilization is already present in the base resin without any antioxidant added. This may be due to stabilizing impurities from the production history of the product. A similar effect is known from unstabilized lube oils [8]. Regarding the highest processing temperature (Fig.1b), the lowest MFI values are obtained with high concentrations of the primary antioxidant, Irganox 1010.

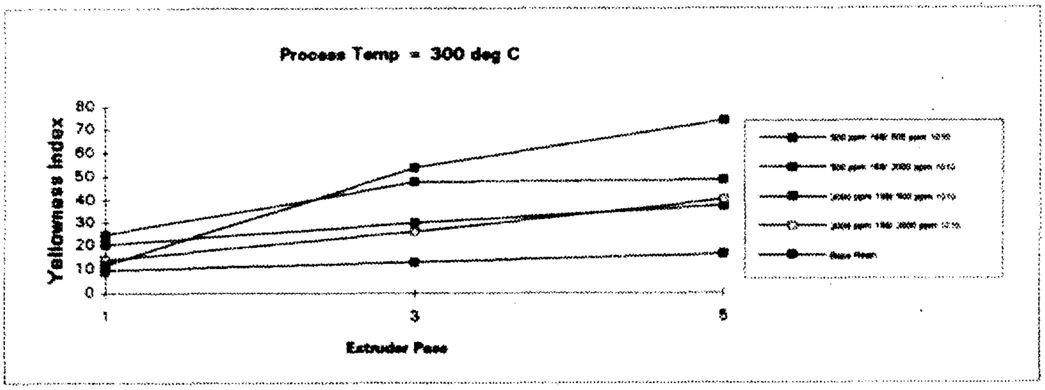
The best stabilization of MFI is achieved with the highest level of Irganox-1010, rather independently from the amount of Irgafos-168 added. However, at a low processing temperature, all additive-containing blends show quite similar stabilization of the MFI, even under high mechanical stress. The primary antioxidant, reacting with the free radical from the polymer formed during processing, obviously has the most stabilizing effect on the Melt Flow Index of the polypropylene. Generally, a polypropylene exposed to a high thermal-mechanical stress requires a much higher stabilization by antioxidants, particularly of the primary type, than polymer exposed to moderate stress. (Fig. 1b).

In Fig.2a - 2b, the color dependence (yellowness index) of the polypropylene with different additive concentrations and under different thermal-mechanical stress is shown. The base resin, without any antioxidant added, behaves worst and shows outstanding high yellowness, even at 220 °C and only three extrusion cycles. That is most probably due to the high degradation in the polymer chain itself. This undesired discoloring of the product is generated from multiple oxidized species, like diketones and other conjugated - electron systems, according to the theory of chromophores in organic molecules.

As soon as a low level of antioxidant has been added, the sensitivity towards discoloring decreases substantially and particularly under mild process temperature conditions. This correlates strong with the observed MFI behavior and shows clearly the stabilizing effect of the additives. However, at high temperature extrusion, the high Irganox-1010, but low-level Irgafos-168 added sample shows a rather high yellowness in comparison with the other additive-containing polymers, although that sample behaves best in the MFI test. This can be considered as a strong proof that the yellowness, observed in the high-level Irganox product is mainly due to the oxidized (degraded) form of the additive itself and not originated from degraded polymer. In comparison to this, a high-level Irgafos 168 but low in Irganox-1010 added product resists better towards discoloring and behaves moderate in MFI change. Obviously, the combination high Irganox-1010 / low Irgafos-168 protects the polymer itself better towards the increase in MFI and the detrimental effect of chain-scission and oxidation under severe thermal-mechanical conditions, than the reverse receipt. But the disadvantage of the high Irganox-1010 formulation remains in the discoloring tendency. This can be partly impaired by adding a higher level of Irgafos-168, which obviously prevents the Irganox-1010 to a certain degree from degradation and discoloring. For a product with recycling potential, therefore it could be advantageous choosing an antioxidant formulation high in phosphite to phenol ratio.

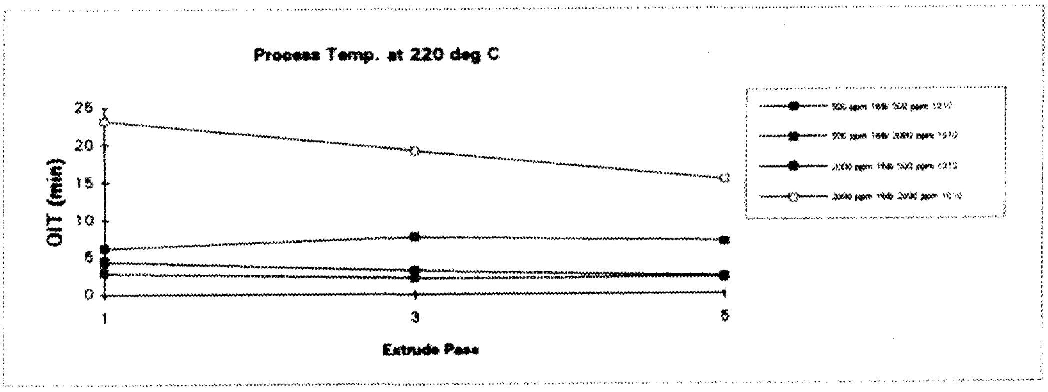


(F-2a)

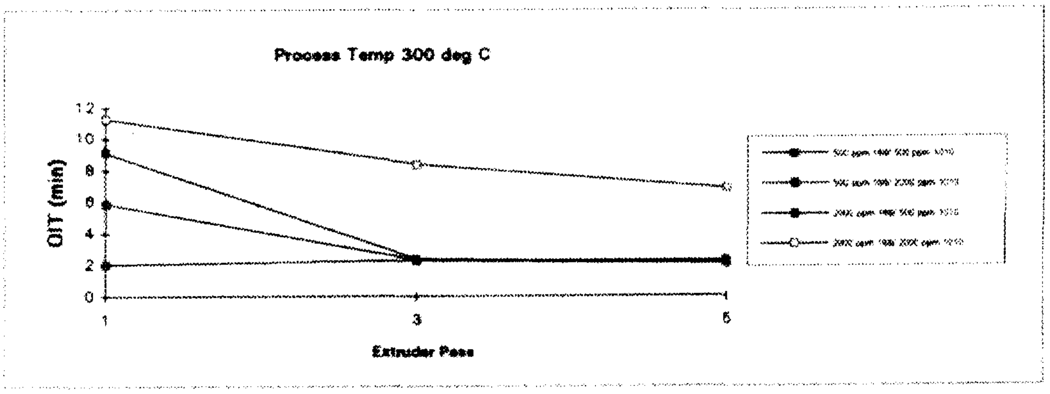


(F-2b)

Fig. 3a-3b shows the Oxidation Induction Time (OIT) dependence from thermal-mechanical stress and different additive formulations. The low-level additive formulations generally give shortest OIT, well in agreement with the observed increase in MFI. The OIT increasing effect of the blend with high Irganox-1010 and high Irgafos-168 is outstanding and shows the synergistic effect of that two additives on the oxidation stability of the product. Again, this is in agreement with the observed low MFI, for that particular formulation over a wide range of thermal-mechanical stress.

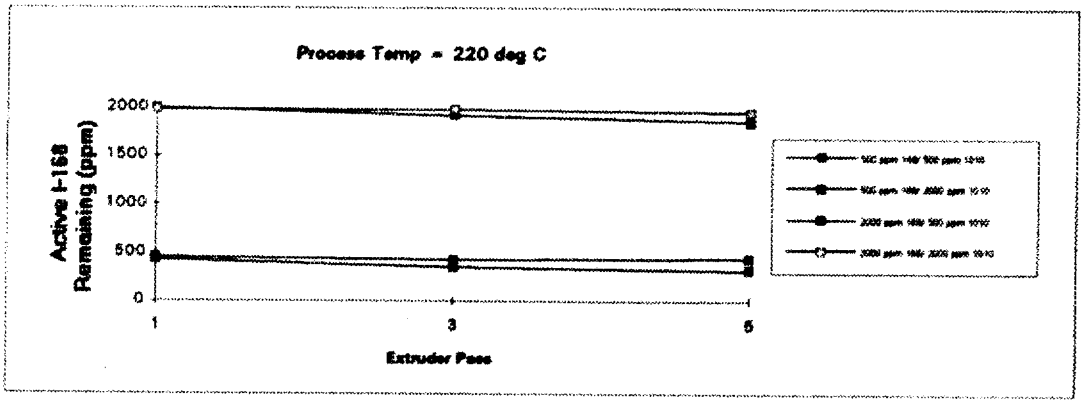


P 91 (F-3a)



P 91 (F-3b)

Fig. 4a - 4b shows the amount of remaining Irgafos-168 additive, measured by ^{31}P NMR after the extrusion experiment. At both process temperatures, a high formulation of Irganox-1010 is leading to a better stability of the phosphite additive. This effect is more significant at high process temperatures. At 220 °C process temperature, generally the Irgafos-168 degradation can be considered as relatively low. A comparison of these data with the MFI confirms that observation. All additive formulations show rather stable MFI at the low process temperature. At 300 °C, however, we already observed a rather strong increase of MFI after an extrusion number of three and an additive receipt of 500 ppm Irganox with 500 ppm Irgafos. The increase in MFI is nearly as strong as observed with the additive-free base resin. Although, the Irgafos-168 is not yet completely degraded and still present with a level of about 250 ppm after 5 extrusion cycles at 300 °C, it seems that this concentration of additive in its active form is too low to prevent the polypropylene towards the detrimental effect of thermal-mechanical stress, resulting in a dramatic increase of MFI.



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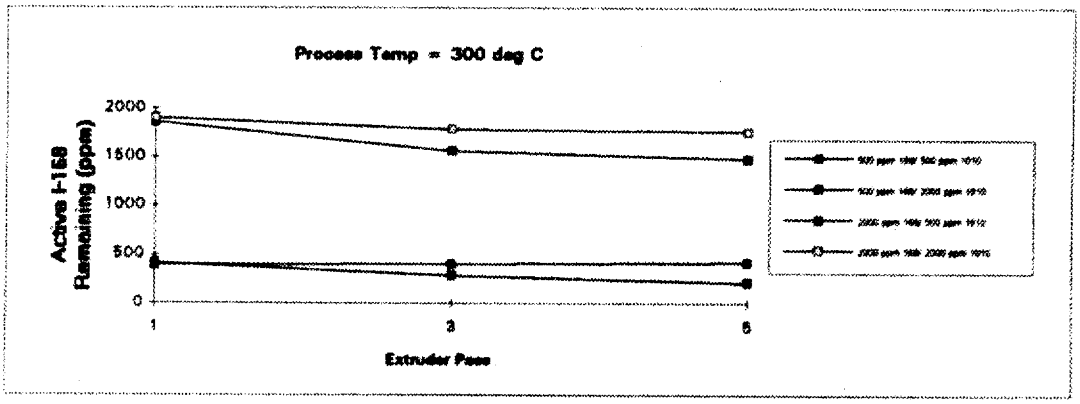

figure (4b)

CONCLUSION

The blends of Irganox-1010 with Irgafos-168 are commercially available products from Ciba-Geigy and known under the designation IRGANOX B 215, 220, 225 and 561. However, the user of these packages should make his own assessments of the additive formulations under his own conditions and his own requirements. Particularly a product which shall be reused further in a recycling process needs unconventional additive formulation and/or an additional additive booster during the recycling step.

The present study can be considered as a first approach to develop different additive formulations applied on one and the same base polymer for different applications. Design of Experiment (DOE) can be used as a powerful tool to assess the effect of the numerous parameters affecting the polymer properties during recycling.

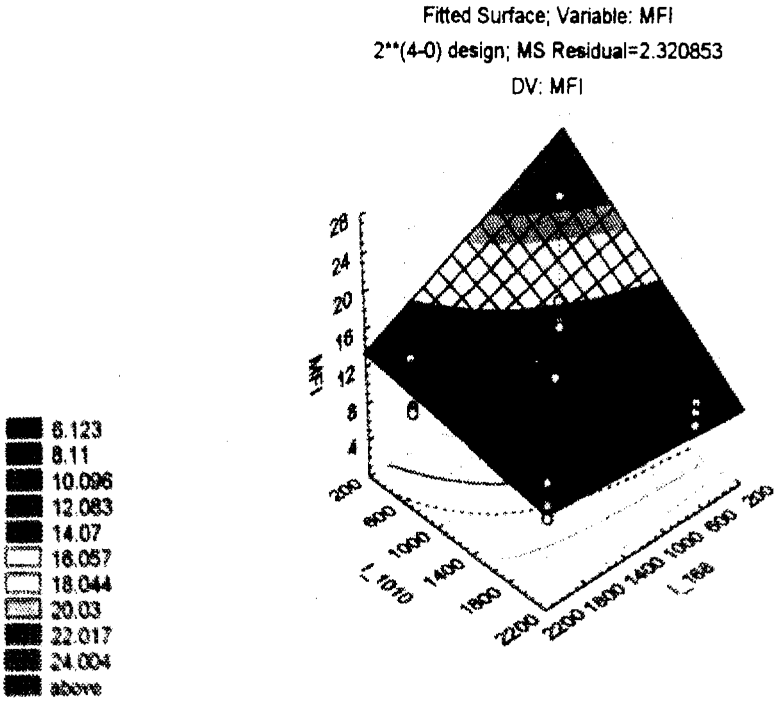

Figure 5a: The effect of the level of I-1010 and I-168 at 300°C after the 5th extrusion pass on the melt flow index

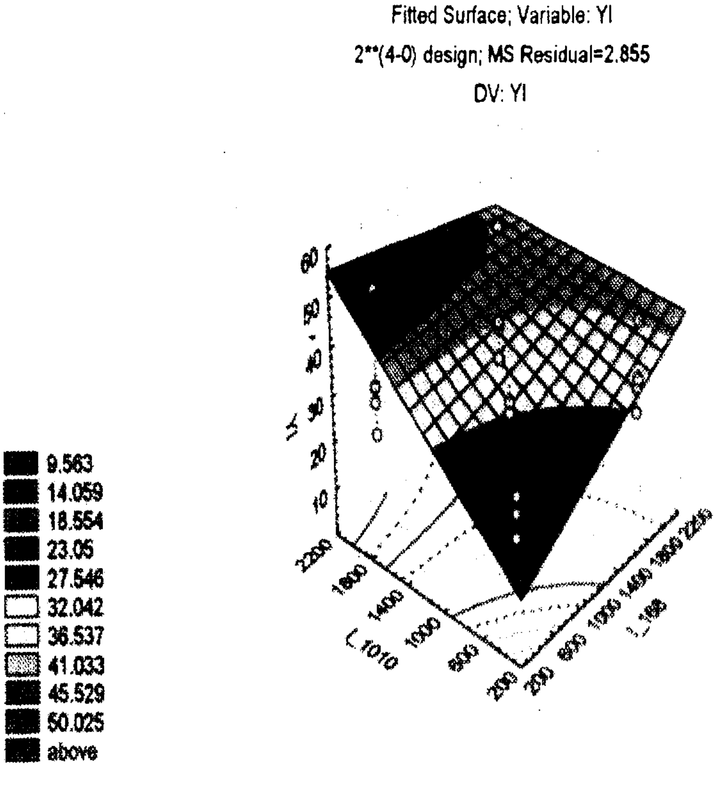

Figure 5b: The effect of the level of (I-1010 and I-168 at 300°C after the 5th extrusion pass on the yellowness index

A polypropylene product, e.g. designed to have lowest tendency of discoloring during a moderate process should be blended with low and equal levels of Irganox-1010 and Irgafos-168. (Fig. 5b). On the other side, if a certain discoloring is not a disturbing factor, but stability of the rheological properties during a high shear - temperature recycling process desired, a high Irganox-1010 formulation will fit that requirement. (Fig. 5a).

If both properties, color and rheology shall be little affected during recycling, high phosphate addition with moderate-low phenol content seems to bear the best compromise.

ACKNOWLEDGMENTS

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State of the Art and Future Perspectives of Starch-based Biodegradable Materials

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Abstract

Biodegradable polymers constitute a loosely defined family of polymers that are designed to be degraded by living organisms. They offer a possible alternative to traditional non-biodegradable polymers when recycling is unpractical or not economical.

Among the products already present on the still small market of biodegradables, starch-based materials are the most widely diffused. In this framework the concept of thermoplastic starch and the results obtained by Novamont on the behaviour of thermoplastic starch in presence of other synthetic polymers is revised. In particular the role of complexation between starch and synthetic polymer molecules is discussed.

As an example of the properties achieved by starch-based materials up to now, the various classes of Mater-Bi products currently available on the market are shown. Their processability, physico-chemical and physico-mechanical properties are described in comparison with polystyrene and low density polyethylene. Their biodegradation behaviour is also discussed.

The future market perspectives of biodegradable materials are finally presented as a function of both the legal environment and the need of establishing global energy consumption criteria, based on life cycle analysis parameters, when comparing the costs of biodegradable materials to those of traditional non-biodegradable plastics.

INTRODUCTION

The management of solid waste disposal with regard to the decreasing availability of landfills, the litter problem and the pollution of the marine environment is becoming very urgent in industrialised countries and may extend very quickly to the developing countries.

A solution is the valorisation of waste as a resource through its separation into specific fractions, to be transformed into new products with a certain market value.

Technological aspects such as the development of safer and more efficient recycling technologies, the development of materials easy to reuse or recycle and of biodegradable materials can significantly contribute to the solution of the problem.

Biodegradable polymers constitute a loosely defined family of polymers that are designed to be degraded by living organisms. They offer a possible alternative to traditional non-biodegradable polymers when recycling is impractical or not economical. Technologies like composting used for the disposal of food and yard waste, accounting for 25-40% of total municipal solid waste, are the most suitable for the disposal of biodegradable materials together with soiled or food-contaminated paper.

Starch-based materials are now industrial products and are leading the still small market of biodegradable products.

STARCH-BASED MATERIALS

Starch is an inexpensive abundant product available annually from corn and other crops. It is totally biodegradable in a wide variety of environments and can permit the development of totally degradable products for specific market needs.

Degradation or incineration of starch products recycles the atmospheric CO_2 trapped by starch producing plants during their growth, thus closing the biological carbon cycle.

Starch is constituted by two major components: amylose, a mostly linear alpha-D-(1-4)-glucan and amylopectin, an alpha- D-(1-4) glucan which has alpha-D-(1-6) linkages at the branch point. The linear amylose molecules of starch have a molecular weight of 0.2-2 million, while the branched amylopectin molecules have molecular weights as high as 100-400 million [1,2].

In nature, starch is found as crystalline beads of about 15 μm- 100 μm in diameter, in three crystalline modifications designed A (cereal), B (tuber), and C (smooth pea and various beans), all characterised by almost perfect left-handed, six-fold double helices.

Starch can be made thermoplastic applying sufficient work and heat to almost completely destroy its crystallinity. Equipment used for high pressure extrusion heats materials during processing, and continually compresses them [3, 6].

Thermoplastic starch alone can be processed as a traditional plastic; its sensitivity to humidity, however, makes it unsuitable for most of the applications.

The main use of thermoplastic starch alone is in soluble compostable foams such as loose-fillers, expanded trays, shape molded parts, expanded layers, as a replacement for polystyrene. Starch can be destructurized in combination with different synthetic polymers to satisfy a broad spectrum of market needs.

Thermoplastic starch composites can reach starch contents higher than 50%. [7-14]. Main producers of starch-based materials are Novamont with Mater-Bi trade-mark, ENPAC and National Starch.

MATER-BI PRODUCTS

Under the Mater- Bi trademark todayNovamont produces four classes of biodegradable materials, all based on starch and differing in synthetic components:

- Class Z: Biodegradable andcompostable, mainly for films and sheets. The biodegradation behaviour is reported in figs. 1-2. They contain thermoplastic starch and poly-epsilon-caprolactone and were introduced into the market at the beginning of 1992.

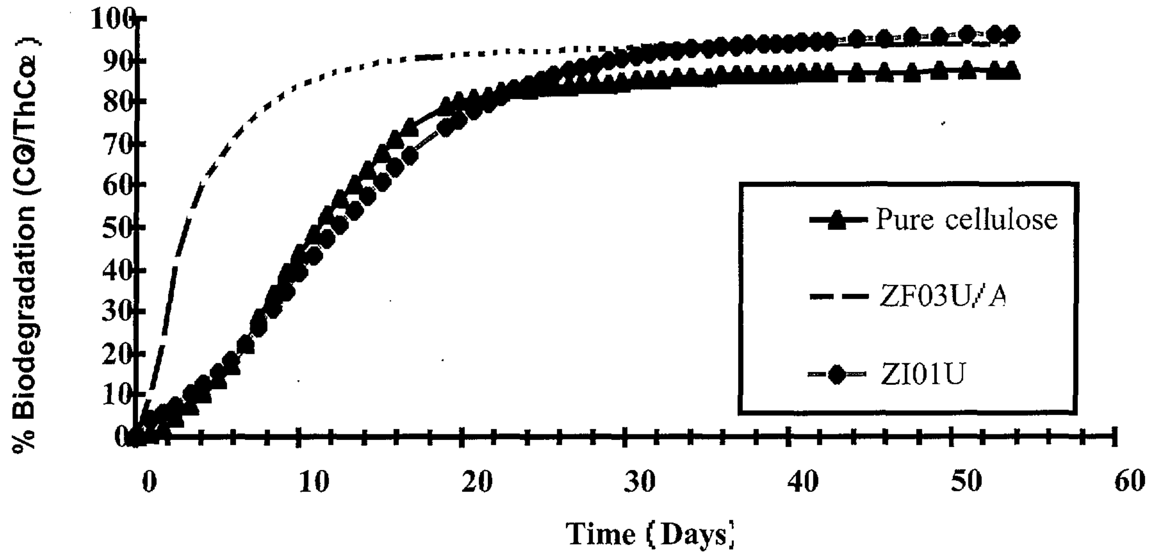

Figure 1 :Aerobic biodegradation of Mater-Bi products of class Z under controlled composting conditions (ASTM D 5338-92), in comparison with pure cellulose (test performed by VTT Institute, Finland)

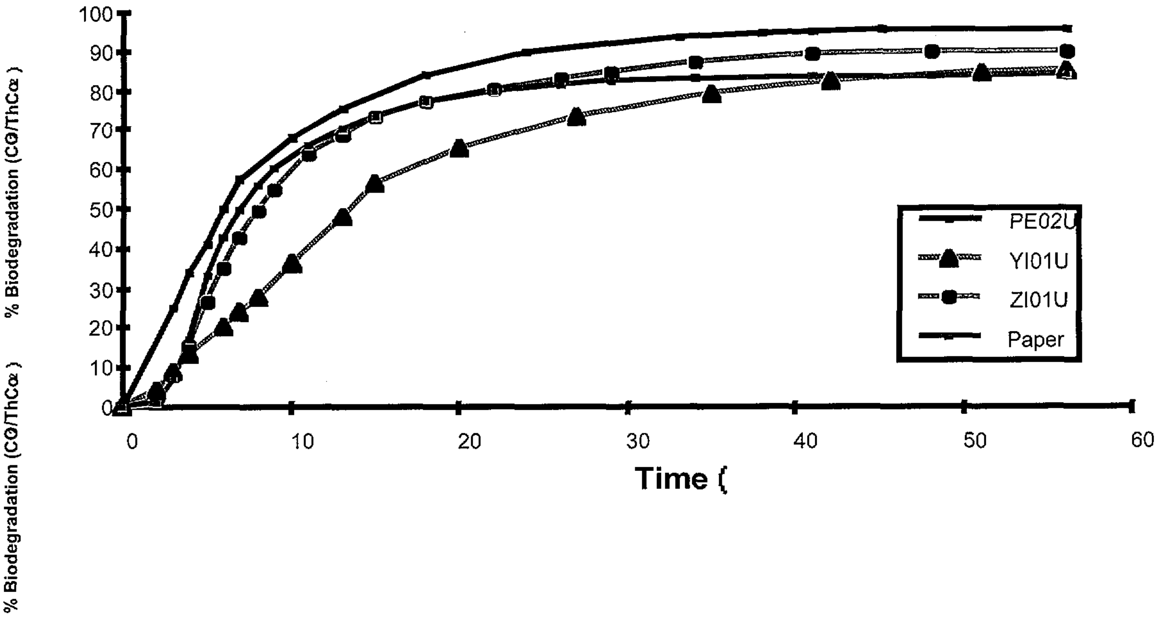

Figure 2: Aerobic Biodegradation of different Mater-Bi grades in presence of municipal sewage sludge (ASTM D 509-91 test)

- Class V: biodegradable,compostable and soluble, as a replacement of polystyrene packaging foams. They have a starch content > 85% and can be defined as thermoplasticplasticized starch. The biodegradation behaviour is reported in fig. 2 (see PE02U curve).

- Class Y: biodegradable andcompostable, for rigid and dimensionally stable injection molded items; they contain raw materials all from natural origin such as thermoplastic starch in a dispersed form and cellulose derivatives. Their biodegradation behaviour in different environments is reported in figs. 2-4. Mechanical properties andmoldability are very close to those of polystyrene. (tab. I).

- Class: Biodegradable, non- Acompostable materials (biodegradation time of two years in a liquid environment. They contain thermoplastic starch heavilycomplexed with ethylene-vinyl alcohol copolymers. Their main uses are in sectors werecompostability is not required.

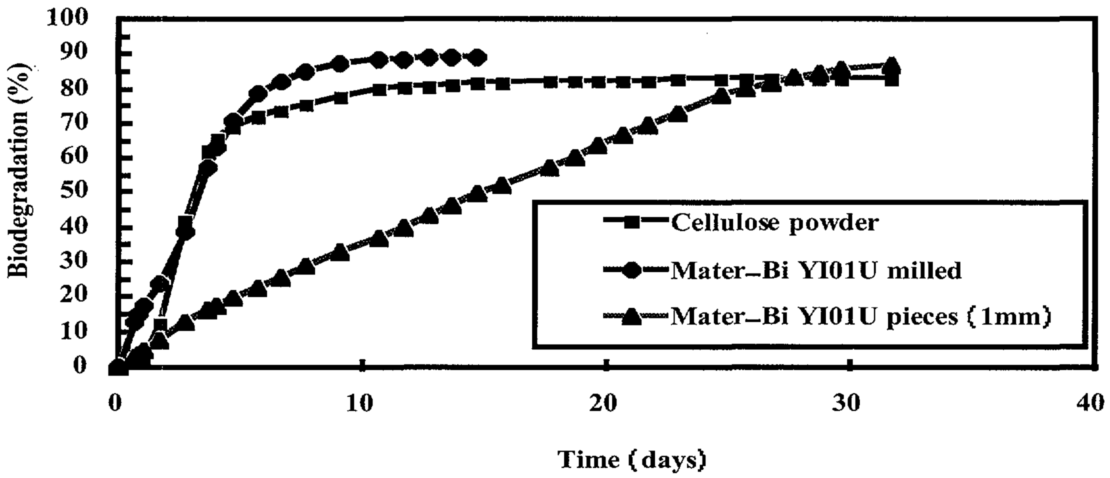

Figure 3: High solid anaerobic digestion of Mater-Bi YI01U in comparison with cellulose powder (ASTM D 5511-94 performed by OWS, Belgium)

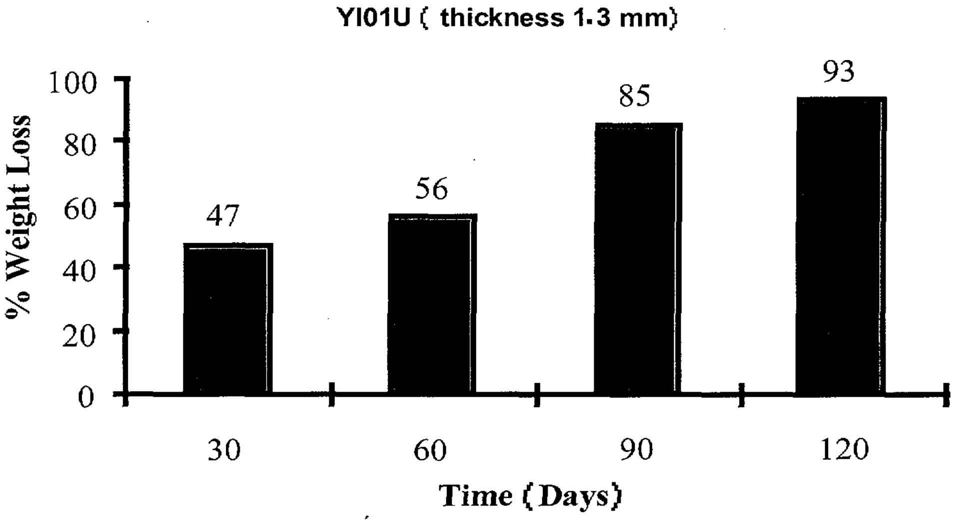

Figure 4: **Weight loss of Mater-Bi YI01U under composting condition (test method described in J. of.Env . PolymerDeg. 996 4:55-6)**

Novamont has recently launched two grades of Mater-Bi for films belonging to class Z, ZI01U and ZF03U/A, which have the _OK COMPOST_ certificate and comply with DIN 54900 draft norm part I and part II.

Moreover the biodegradability of the two materials in composting conditions has been measured by VTT, Finland (fig. 1) and by other institutes. Their mechanical properties are very similar to those oflow density polyethylene (tab. II).

Table 1: Some physical properties of Mater-Bi YI01U in comparison with traditional plastics

TEST	PROCEDURE	UNIT	YI01U	PS
Density	Pycnometer	g/cm^3	1.35	1.04 | 1.09
Melt fow rate	ASTM D1238	g/10 min	10 | 15 (at 190!C , load 5 Kg)	8 | 12
Tensile strenght	ASTM D882	Mpa	25 | 30	35 | 64
Elongation at break	ASTM D882	%	2 | 6	1 | 2.5
Tensile modulus	ASTM D882	Mpa	2100 | 2500	2800 | 3500

Table 2: Some physical properties of Mater-Bi grades belonging to Z class, in comparison with traditional plastics [68]

TEST	PROCEDURE	UNIT	ZF03U/A	ZI01U	LDPE
MFI	ASTM D1238	g/10 min	4 - 5.5	1.5	0.1 - 22
Strength at break	ASTM D882	MPa	31	28	8-10
Elongation at break	ASTM D882	%	886	780	150-600
Young modulus	ASTM D882	MPa	185	180	100-200
Tear strength	ASTM D1938				
. Primer		N/mm	68	55	60
. Propagation		N/mm	68	55	60

These Mater-Bi materials are industrial products designed for films and layers. An important example of a successful application of these two grades is represented by the compostable bags for organic and yard waste collection. The films and bags can be produced by means of traditional film blowing and sealing equipment for low density polyethylene with minor modifications, reaching similar productivities. Bags of different sizes are already used by millions of European citizens for the separate collection of the organic fraction of MSW to be composted.

Novamont's entrance on this market sector has been preceded by a comprehensive study on the behaviour of Mater-Bi bags in different composting plants (from static windrows to rotary fermenting reactors) and in "in-use" conditions, in cooperation with some European municipalities like Furstenfeldbruck (Germany), Korneuburg (Austria), Trento and Bellusco (Italy).

On behalf of the Swiss Composting Council and of the major Swiss distribution chains, Composto performed an overall study, including LCA, on different alternatives of separate collection of organic waste in Switzerland.

The study clearly showed that the collection with Mater-Bi bags has a much lower environmental impact than with PE bags or with bins without bags, requiring frequent washing.

Both the in use performance and compostability of Mater-Bi bags in full-scale composting facilities have been fully satisfactory.

Besides composting and yard waste bags, other main uses of Mater-Bi products are in the field of short-life applications such as shopping bags, mulch film, film for wrapping, loose-fillers and expanded shape molded parts as a replacement for polystyrene, soluble cotton swabs, nursery pots, cutlery, etc.

Mc Donald introduced in all their restaurants in Austria cutlery made of Mater-Bi of class Y from the beginning of 1997.

CONCLUSIONS

Starch-based materials in combination with aliphatic polyesters and copolyesters and cellulose and starch derivatives are available at industrial level. Their biodegradation rate similar to that of cellulose, their mechanical properties close to those of traditional plastics like polyethylene and polystyrene and the achieved reduced sensitivity to humidity, make these materials particularly suitable for the production of films, injection molded items and foams.

Mater-Bi products are the result of a significant investment made by Novamont in research and development, testified by the wide patent portfolio and by the leading position in the small market of biodegradable materials. In spite of these positive results, thermoplastic starch based materials are still at an early stage of development with many opportunities still to be taken.

The market potential for biodegradable products in the next 5 years can be estimated at about 30000-40000 ton/year in Europe in case of lack of legislative attention. USA and Japanese markets are of great potential, but still at a very early stage of development with the exception of starch-based loose-fillers.

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Environmentally Degradable Plastics: Poly(vinyl alcohol) - A Case Study

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Summary

Among the wide class of synthetic polymers poly(vinyl alcohol) belongs to the restricted number of truly biodegradable macromolecules that can be also processed as a thermoplastic polymer. Accordingly it has met increasing attention in the last few years for the production of environmentally friendly plastic items to be used for many applications mainly as hydrosoluble single-dose packaging and films. In the present contribution some physico-chemical features relevant to the thermal processing of the vinyl polymer have been reviewed. Biodegradation of commercial poly(vinyl alcohol)-based blown films has been also ascertained under different laboratory-scale conditions setup in order to simulating soil, composting and aquatic environments. These studies strongly evidenced the influence of the incubation conditions on the biodegradation of poly(vinyl alcohol), whose rate and extent of mineralization were comparable with those of cellulose almost exclusively under aquatic aerobic biodegradation tests, whilst the presence of solid matrices, such as soil and compost, seems to be impede the enzymatic attack to the polymer chains.

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a well-known synthetic polymer that has recently attracted renewed interest for the production of environmentally degradable plastic materials. The peculiar mechanical and rheological properties of PVA and its gradual reduction in cost, also account for its increasing production and end uses. Within the large range of applications, four main fields of PVA utilization can be identified: *warp sizing*, *paper coating*, *adhesives*, and *films* in textile industry, paper manufacture and packaging[1,2]. Consequently, PVA and PVA-based disposable items (*mulching films*, *laundry bags*, *single dose packaging*) can rather safely reach ecosystems with or without incorporation into any integrated system of waste and wastewater treatment[3]. Therefore the biodegradability of PVA and PVA-based materials has to be considered as a fundamental aspect to be ascertained. Basic properties of these systems depend upon degree of polymerization, degree of hydrolysis (Table 1), distribution of hydroxyl groups and stereoregularity (i.e. crystallinity) of PVA; thus also the relationship between biodegradability and polymer structure should be investigated.

Table 1: PVA properties as a function of molecular weight and hydrolysis degree

Molecular weight increase increase of:	**Molecular weight decrease** increase of:
Viscosity	solubility
Block resistance	flexibility
Tensile strength	water sensitivity
Water resistance	ease of solvatation
Organic solvent resistance	
Adhesive strength	
Dispersing power	
% Hydrolysis increase increase of:	**% Hydrolysis decrease** increase of:
Block resistance	solubility
Tensile strength	flexibility
Water resistance	dispersing power
Organic solvent resistance	water sensitivity
Adhesion to hydrophilics	adhesion to hydrophobics

PVA is considered to be a true biodegradable synthetic polymer since the mid thirties4). More recently single microorganisms5-9) and symbiotic bacterial cultures10) able to utilize PVA as carbon source have been identified. Suzuki4) and Watanabe7) proposed two similar degradation pathways by using different *Pseudomonas* strains. In both cases the polymer is oxidized by oxidase-type enzymatic systems with oxygen consumption and evolution of hydrogen peroxide; the result of this enzymatic attack being the production of carbonyl groups along the polymer chain. Activated β-diketones or α-keto groups are subsequently hydrolyzed with the breakdown of the carbon backbone and hence reduction of molecular weight. Membrane-bound dehydrogenases are claimed to be involved in the initial oxidation of the polymer chains in the two-member symbiotic biodegradation process11). It has been suggested that one of the microorganisms produces a PVA-dehydrogenase as *apo*-enzyme, which is converted into the active form (holo-enzyme) by the inclusion of an essential co-factor, produced by the other symbiont12). This cofactor was identified as pyrrolequinoline quinone (PQQ)11,13).

However the overall number of PVA-degrading microorganisms appears to be limited when compared with the widespread species capable of degrading aliphatic poly(ester)s, such as poly(hydroxyalkanoate)s (PHA's) and poly(ε-caprolactone) (PCL)14). Some species are found to be associated to PVA-contaminated textile or paper mill effluents6). Thus several *Pseudomonas* strains involved in the biochemical investigations of PVA degradation mechanism were isolated from soil samples5,7). In spite of this finding, only limited biodegradation rates and extent of PVA metabolization in soil burial tests have been reported15-17). Therefore the degradation mechanisms as well as the isolated degrading species previously reported, should be not considered as conclusive and exhaustive of the overall of the microbial species and biochemical patterns involved in the mineralization of PVA.

In the present paper some technical features relevant to the production of PVA films by blow molding are considered. Moreover, the degradative behavior of different commercial PVA-based blown films that can be used as hydrosoluble packaging was investigated in comparison with pure PVA under different test conditions. These studies led to the demand of acclimated microbial populations to achieve both significant biodegradation rate and extent of the polymer samples. Some aspects of the relationship between the polymer structure and its biodegradability were also investigated in the presence of a PVA-degrading bacterial mixed culture.

RESULTS AND DISCUSSION

PVA is the largest volume water-soluble polymer produced in the world. It can be commercially obtained by the hydrolysis of poly(vinyl acetate) (PVAc) (Scheme 1) by batch and continuous processes, thus is the latter the wider utilized in the large-scale productions. In the industrial continuous process a typical free radical polymerization of vinyl acetate is followed by the alkaline alcoholysis of PVAc. PVA molecular weight control is usually accomplished by choosing appropriate residence time in the polymerization reactor, vinyl acetate feed rate, solvent (methanol) concentration, radical initiator concentration, and polymerization temperature. Residence time, catalyst (base) concentration, and temperature can also control hydrolysis degree. The principal PVA manufacturers along the world are listed in Table 2.

Scheme 1: Synthesis of Poly(vinyl alcohol)

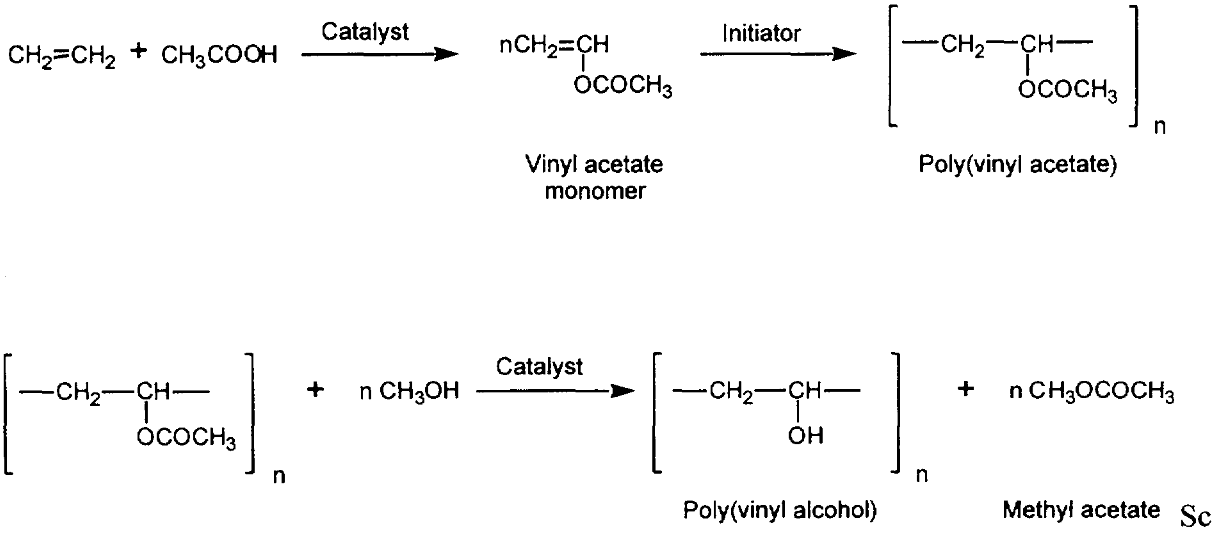


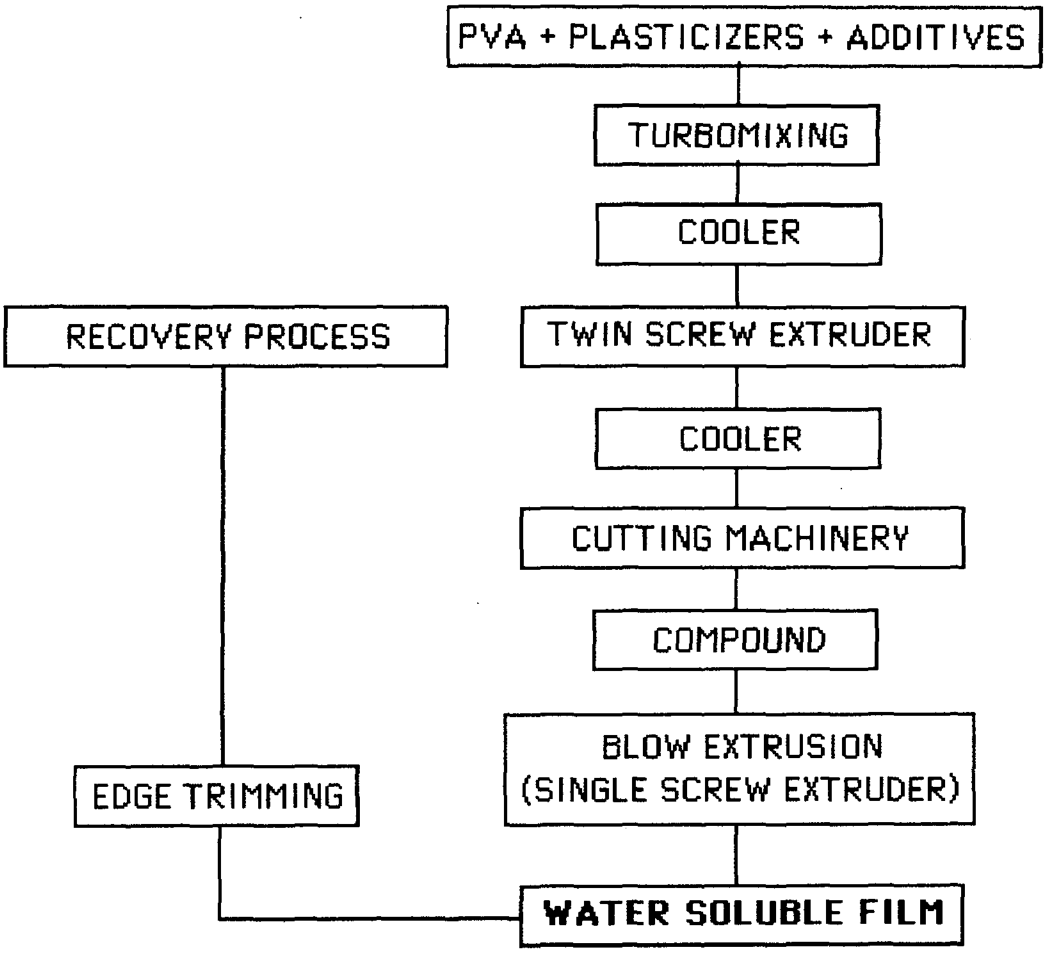
Table 2: Principal PVA Manufacturers

Producer	Trade name	Country
Wacker	Polyviol	Germany
Clariant	Mowiol	Germany
Erkol	@	Spain
Air Products	Airvol	USA
DuPont	Elvanol	USA
Kuraray	Kuraray Poval	Japan
Nippon Gohsei	Gohsenol	Japan
Unitika	Unitika Poval	Japan

Increasing interest in the production of disposable plastic items based on PVA and in particular PVA films stimulates the development of thermal processes in order to overcome the higher expensive casting technologies. The main difficult meet by thermal extrusion processing is represented by the close proximity of PVA melting point and decomposition temperature. The thermal decomposition of PVA begins at about 150°C or above, depending on the hydrolysis conditions (acid or alkaline), with the release of water from the polymer chains by cleavage, accompanied by the formation of volatile degradation products18,19,), leading to macromolecules with a polyene structure20). The water molecule release from the polymer chains is subject to a mass action equilibrium, which can be shifted toward the thermoplastic character of PVA by the addition of water and pressure application21). Consequently, a prerequisite for thermoplastic processing of PVA is its plasticization with plasticizers and waters prior to the extrusion. Several suitable PVA plasticizers capable to enhance its thermal stability such as glycerol, ethylene-diethylene and triethylene glycols, amine alcohols, and polyvalent hydroxyl compounds, have been, therefore, proposed22,23).

PVA films for several applications can be obtained by means of a fairly low expensive thermal processing represented by melt extrusion of mixtures of PVA, solid polyols, water, and other plasticizers24), followed by blow procedure (Scheme 2, Fig. 1). This manufacturing process, performed by Idroplast SpA (Montecatini Terme, Italy), do not require special conditions, both impulse welding and hot bar techniques, as well as other traditional welding techniques can be used, the obtained PVA films can be easily printed without any surface pretreatment. Moreover, films having graduated water-solubility can be produced depending on the degree of hydrolysis of the PVA used and the extrusion conditions.

Scheme 2: Flow sheet of PVA-based blown film manufacturing process



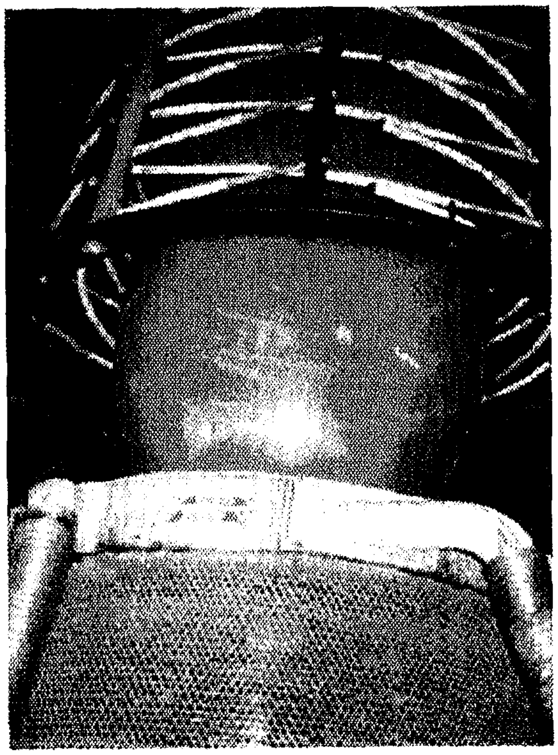


Figure 1: PVA film production by blow molding

From an industrial point of view, the described technology allows for the recycle of scraps generated at the level of the film production and during its conversion to various items. This effort was confirmed by means of molecular weight determinations by gel permeation chromatography (GPC) analysis carried out on film samples during repeatedly processing cycles. A very limited thermal degradation of the polymer matrix was thus ascertained as revealed by the fairly low variation in the molecular weight distribution recorded during subsequential extrusions (Fig. 2).

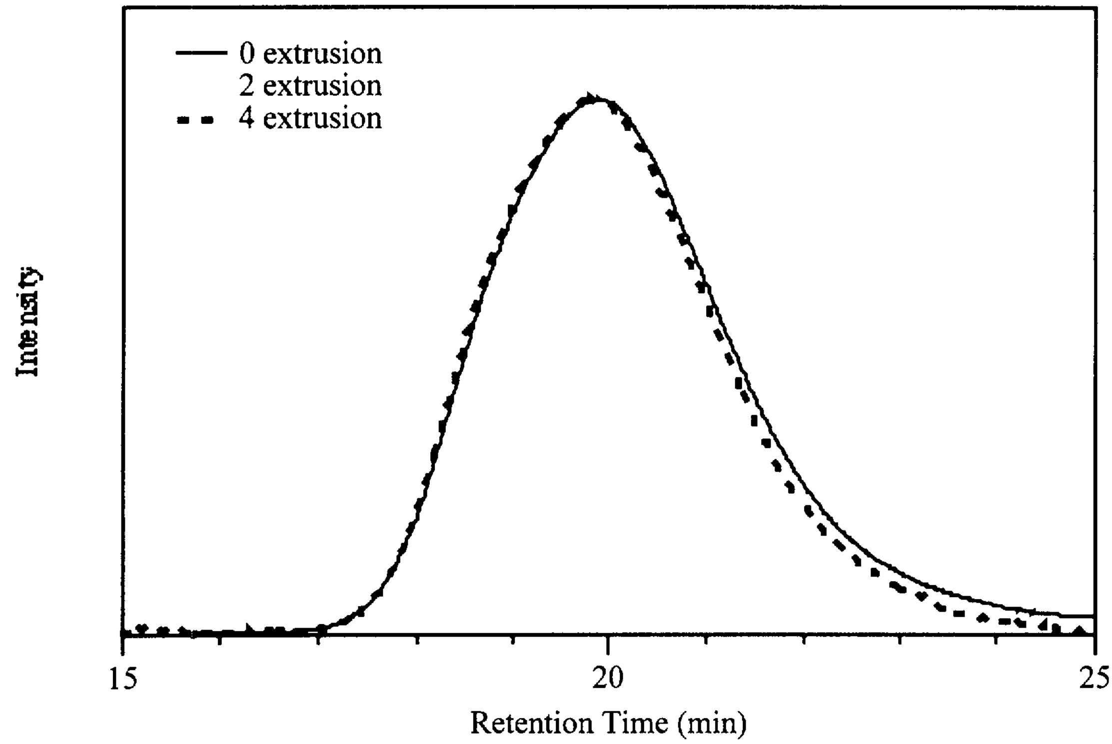


Figure 2: GPC chromatograms of PVA sample utilized for the production of low temperature water-soluble films after 4 sequential process

The biodegradation behavior of different PVA-based blown films and PVA samples was investigated by different laboratory-scale tests aimed at simulating different environmental conditions. Rate and extent of biodegradation were assessed both in respirometric tests (Fig. 3) and by titrimetric evaluation[25] of the polymer concentration in liquid cultures in the presence of several microbial biocenoses collected from different environmental sources. Accordingly, the effectiveness of both incubation conditions and microbial populations in biodegradation of PVA based materials, were compared.

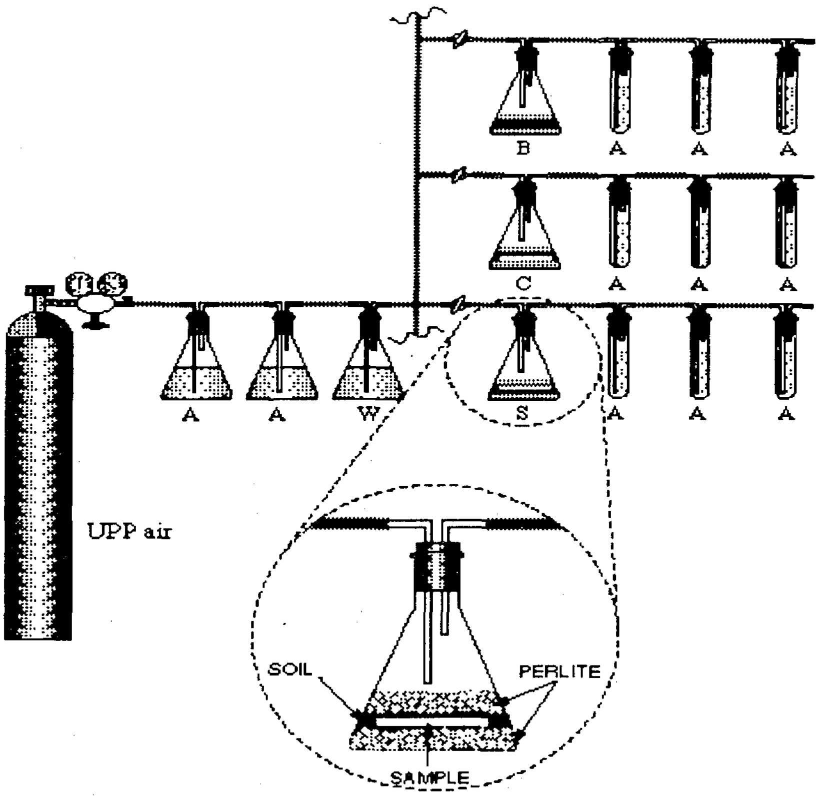


Figure 3: Schematic representation of a respirometric apparatus (A = absorbers containing 40 ml 0.025 N $Ba(OH)_2$, B = blank, C = positive controls, S = test compounds, W = water)

Respirometric tests were performed as simulated aerobic composting, aerobic biodegradation in liquid cultures, and simulated soil burial in respirometric flasks26). Stabilized compost from urban solid waste, river water microbial biocenose, activated sludge microflora of paper mill and municipal wastewater treatment plants, and a mixture of farm and forest soils were utilized respectively in simulated composting, liquid cultures, and simulated soil burial biodegradation tests as microbial inocula.

In Fig. 4 are shown the results, expressed as percent of net theoretical CO_2 productions within the time, recorded in simulated composting test. Biodegradation of PVA based plastic films did not exceed 7 % in 48 days. Moreover this result was obtained only in the presence of the K20 sample. In any case only small differences can be detected between PVA based films and a high density poly(ethylene) (HDPE) film sample utilized as negative control, indicating that under these conditions the polymer samples undergo an extremely limited microbial attack. Moreover the large CO_2 production recorded in the blank run (about 77 % of that of filter paper) could affect the accuracy of this test, as indicated by the fairly low extent of biodegradation of filter paper utilized as a positive control. A rather interesting feature observed during the incubation time was the lower CO_2 production, as compared to the blank, in cultures supplemented with PVA based plastic films in the correspondence of the thermophilic step of the simulated composting procedure. This phenomenon can be tentatively attributed to a toxic effect possibly exerted by the polymer samples, that resulted completely disperse in the compost bulk as a gel-like material, on the thermophilic microflora.

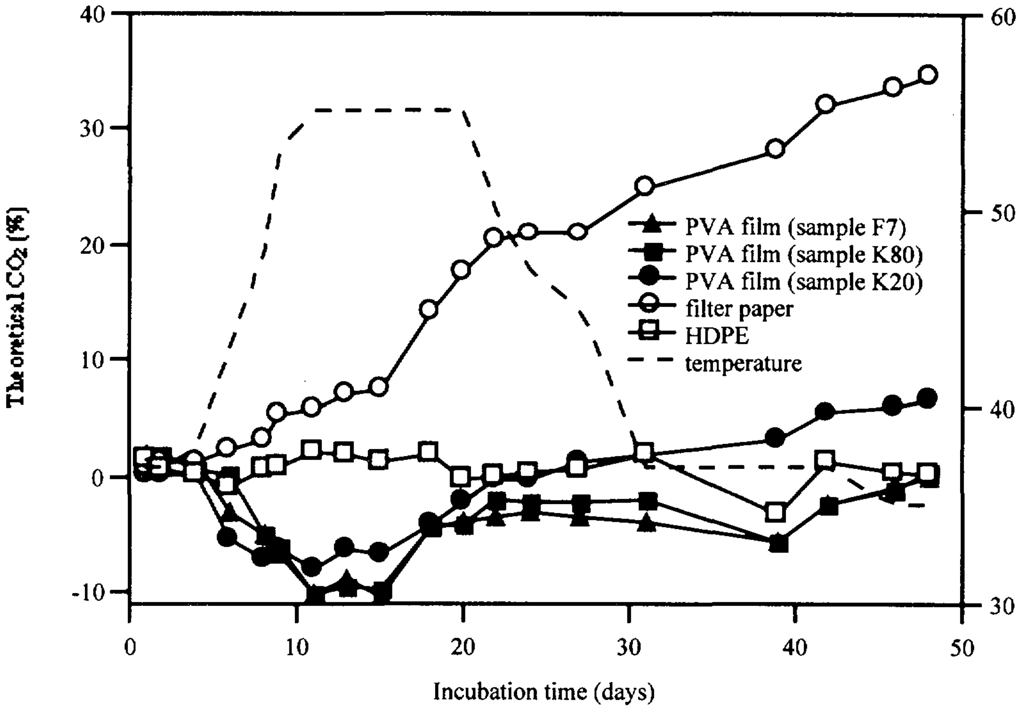


Figure 4: Biodegradation curves of PVA-based films, filter paper (positive control) and HDPE (negative control) in simulated aerobic composting test

Also in simulated soil burial respirometric tests PVA based films underwent a limited (8-9 %) biodegradation in 74 days (Fig. 5); however in this case the CO_2 production (about 27 % of that of filter paper) recorded in blank runs allowed for more reliable results. This was possible because the amount of soil introduced in any runs was limited by the specific adopted incubation conditions that provide a solid substrate constituted in the largest volume by inert mineral bulk (perlite). Moreover, rate and extent of biodegradation apparently were not affected by the polymer concentration or its physical state, as indicated by the almost identical results obtained in the presence of different amounts of polymer samples, as either film or powder. In another experiments, carried out in analogous soil burial simulation conditions, mineralization rate and extent of PVA88 samples resulted still limited as 7 % in a very prolonged incubation time (160 days), whereas other synthetic polymers utilized as positive controls still undergo to a significant mineralization.

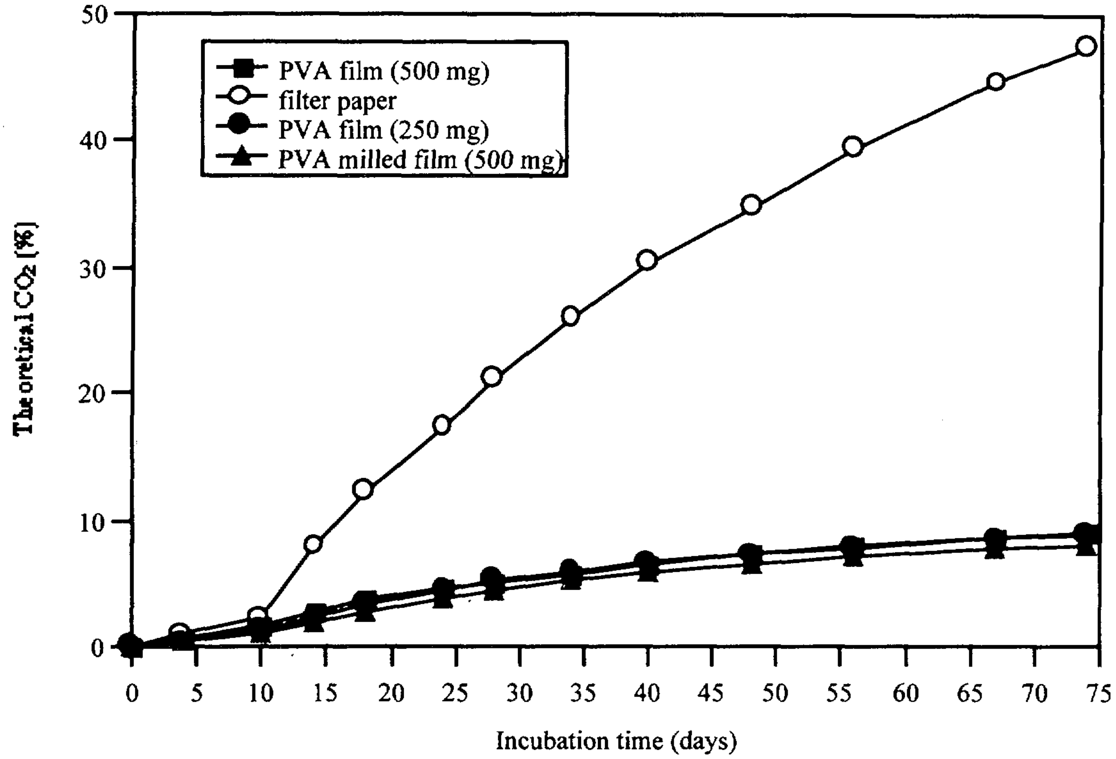


Figure 5: Biodegradation curves of a PVA-based films and filter paper in soil burial respirometric test

Limited biodegradation values of PVA based films (13 % after 21 days of incubation) were also obtained in aerobic biodegradation test carried out in liquid cultures inoculated with municipal sewage sludge (Fig. 6). However, due to the short incubation time the result obtained can not be considered as conclusive because a more active microbial population could be established within a prolonged duration of the experiment, as revealed by the significant level of biodegradation of the PVA based sample.

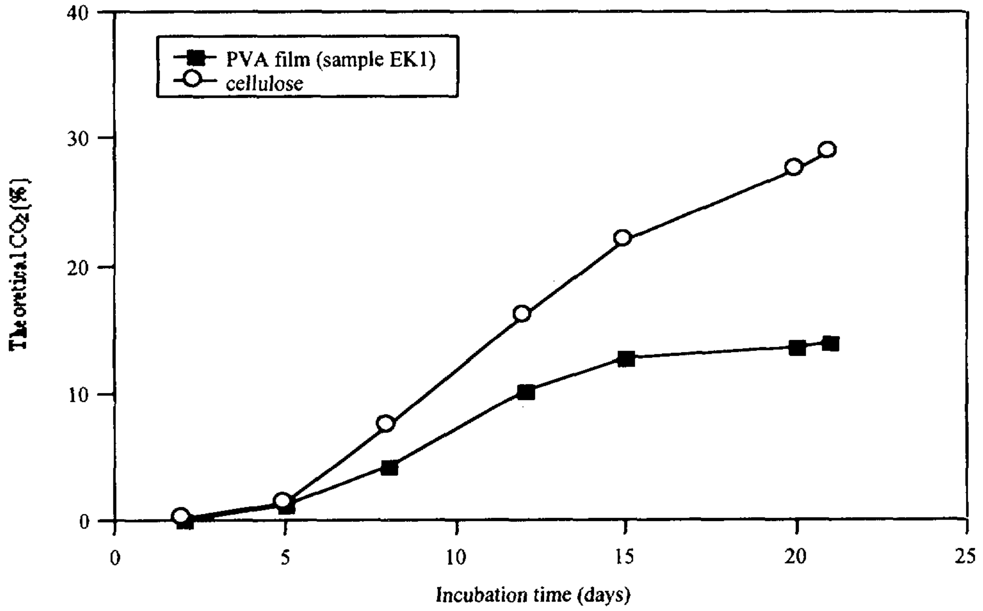


Figure 6: Biodegradation curves of a PVA-based film and cellulose in the presence of municipal sewage sludge

In the presence of sewage sludge from a paper mill wastewater treatment plant, the biodegradation extent of PVA and PVA based films reached values comparable to that of cellulose, even if this occurred only after a appreciably larger incubation time (Fig. 7).

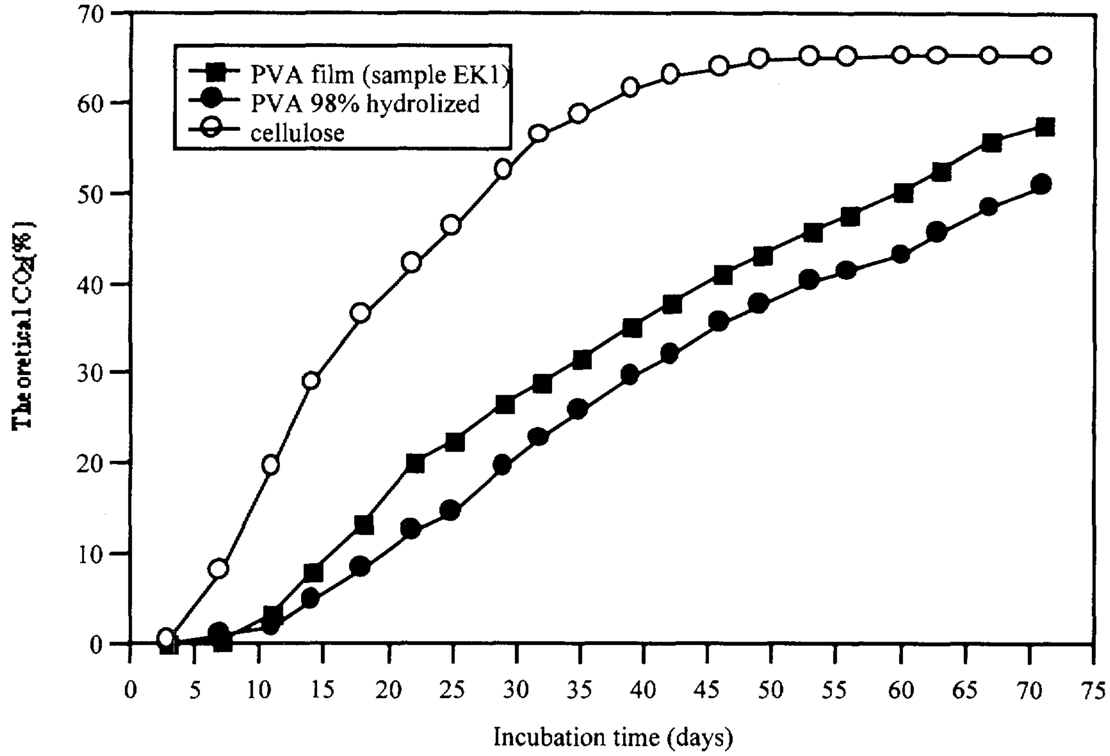


Figure 7: Biodegradation curves of PVA, PVA-based film and cellulose in the presence of paper mill sewage sludge

This last result can be explained by considering that microbial strains present in the paper mill sewage sludge are particularly active as a consequence of the selective pressure exerted by the large amounts of PVA in the waste-water reaching the treatment facilities of the paper factories.

According to the CO_2 evolution profiles, a significant decrease of the PVA concentration was also monitored in liquid cultures inoculated with paper mill sewage sludge samples (Fig. 8).

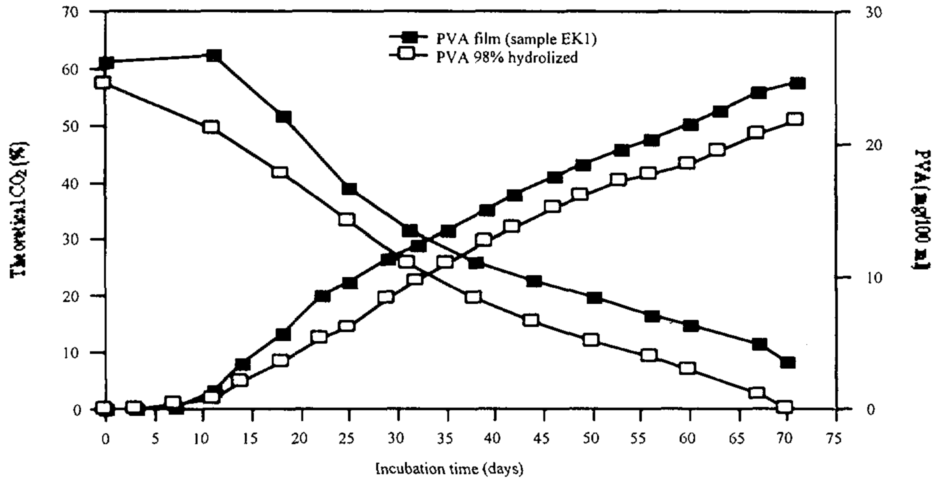


Figure 8: Profiles of PVA concentration and CO_2 evolution of PVA and PVA-based film in the presence of paper mill sewage sludge

PVA biodegradation studies in liquid cultures were also carried out by using compost, soil, and wood litter (one of the most microbial active environment, as well as paper mill sewage sludge as microbial inocula in order to establish if the lack of the biodegradability of PVA in solid matrices could be attributed only to absorption process, or to the absence of PVA-degrading microorganisms in the solid substrates, or both. Results obtained (Fig.9) allowed for the inexistence of active microbial species in the soil, litter, and compost samples utilized. However the hindrance to PVA enzymatic attack by absorption to the solid matrix can not be excluded at all, by considering that liquid culture condition are less suitable for the cultivation of fungal species which are the main agents of degradative process, at least in soil and wood litter.

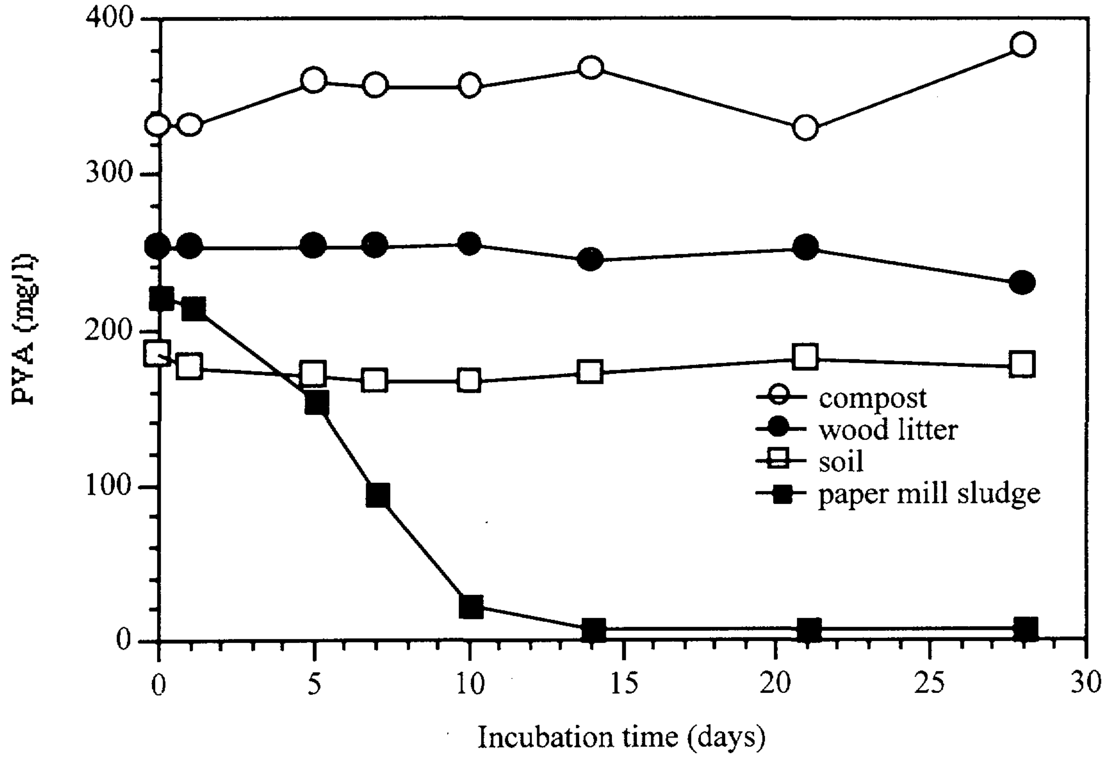


Figure 9: Variation of PVA concentration in liquid cultures inoculated with soil, compost, wood litter, and paper mill sewage sludge samples

Further experiments were carried out under soil burial conditions, by using PVA with 88 and 98% degree of hydrolysis, film samples inoculated with paper mill active microbial species. Also in this experiment, however only limited biodegradation extents of the PVA films were observed; moreover no significant differences could be found between the inoculated and sterile film samples (Fig. 10). Only limited differences, could be instead observed between the two PVA samples, the lowest degree of hydrolysis showing a slight higher propensity to biodegradation. GPC analysis, carried out on the PVA film with 98 % degree of hydrolysis, recorded before and at the end of the soil burial experiments, showed a significant increase of the average Mw, most likely due to the impossibility to recover the low molecular weight fractions (Fig. 11).

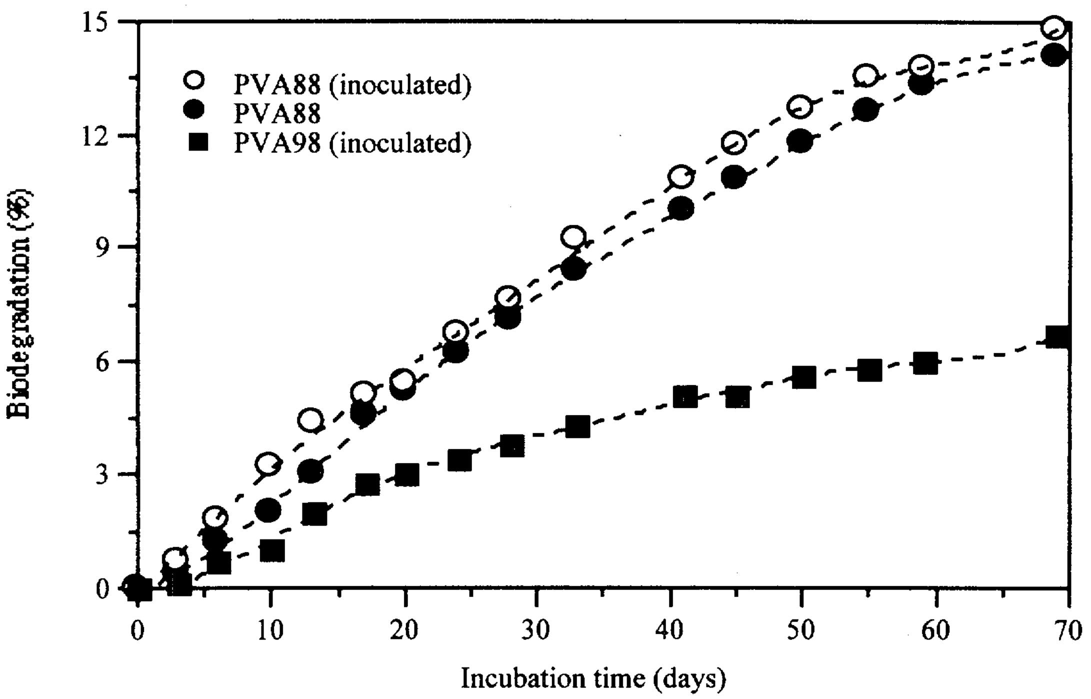


Figure 10: Biodegradation curves of two different PVA samples inoculated with selected mixed culture from paper mill sewage sludge, in soil burial respirometric experiment

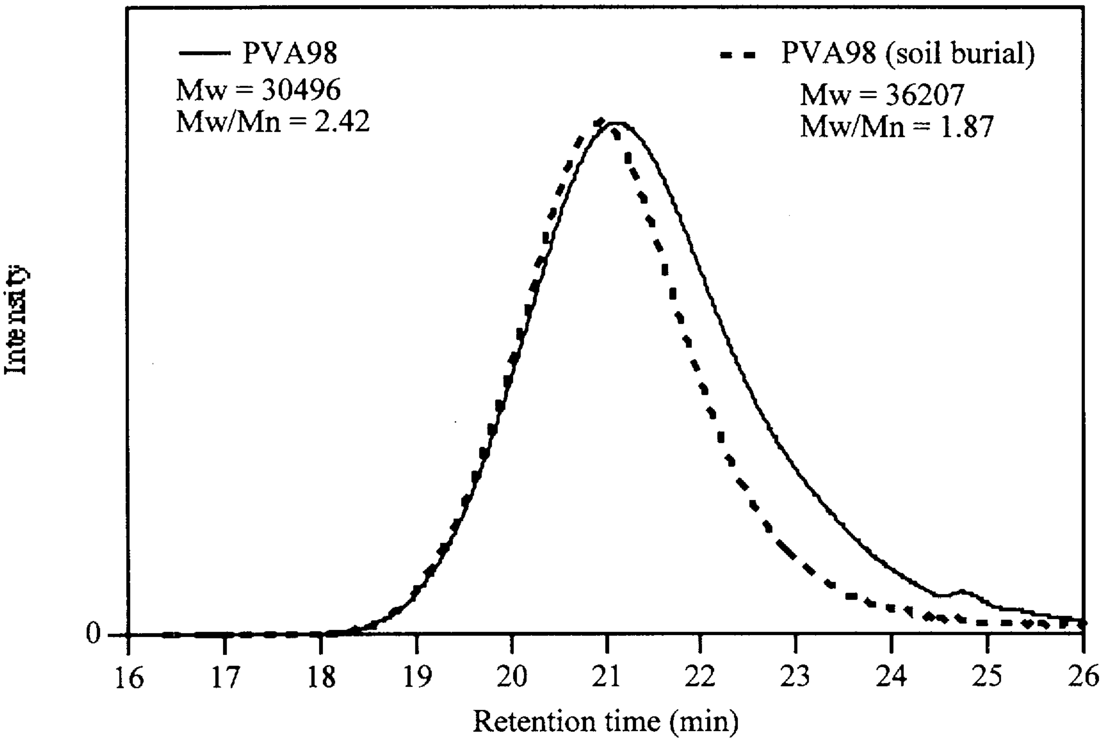


Figure 11: GPC profiles of PVA sample with 98% hydrolysis degree before and after soil burial respirometric experiment

By taking into account the above reported results, paper mill sewage sludge was enriched in liquid cultures in the presence of 250 mg/l PVA as sole carbon and energy sources and utilized, after repeated sequential transfers, as an acclimated inoculum in respirometric tests. As shown in Fig. 12, rate and extent of biodegradation of PVA samples attained in the presence of the acclimated inoculum were larger than those recorded in the presence of the previously tested inocula. Moreover the acclimation of the microbial population to PVA led to the failure of cellulose assimilation by the same microorganisms, as revealed by the very limited biodegradation (1.5 %) of the cellulose sample.

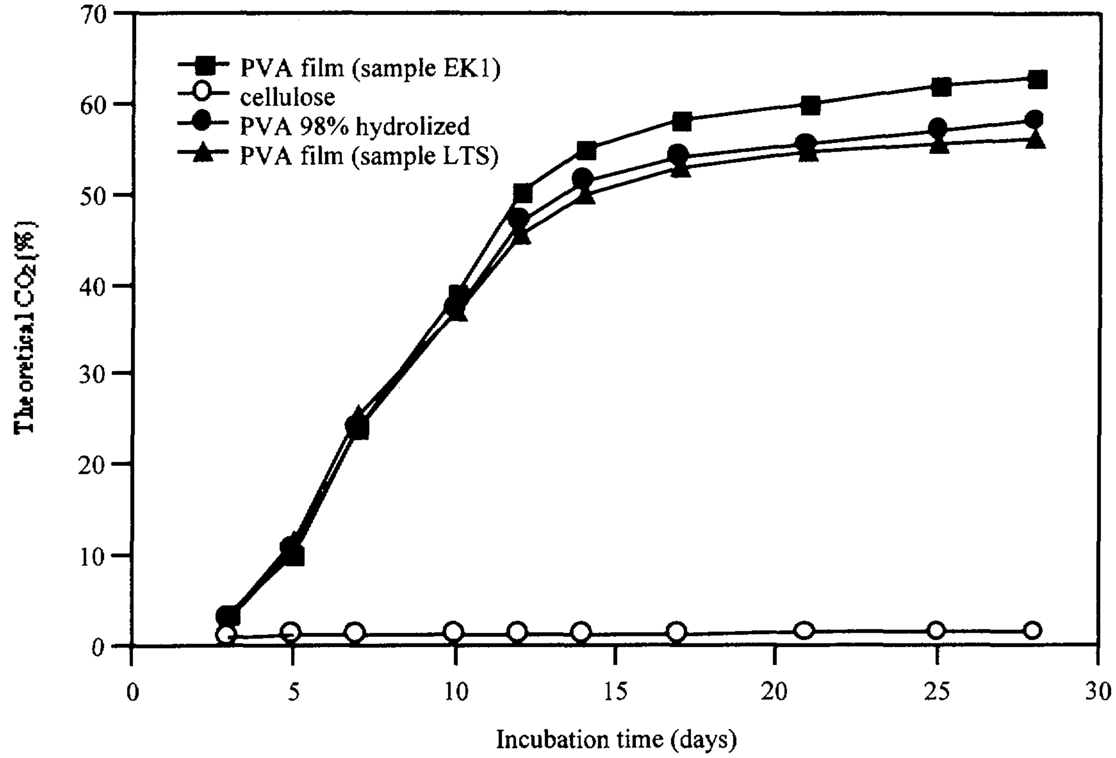


Figure 12: Biodegradation curves of PVA, PVA-based films and cellulose in the presence of acclimated mixed culture

The reported results indicate that the microbial attack of PVA is strictly related to the presence of selected microorganisms which can be found almost exclusively in environments continuously contaminated by PVA. The selective pressure exerted by the procedure utilized to obtain the acclimated culture tends to increase the populations of PVA degrading microorganisms.

According to these findings several degrading microorganisms previously isolated by different authors derived mainly from PVA polluted environments[8,9].

However, the ability to break the high energy C-C bond in the synthetic polymer, at the present seems to be restricted to a limited number of microorganisms, as revealed by the fairly low number of reports dealing on the isolation and characterization of microbial species involved in the biodegradation of PVA.

The acclimated mixed culture was also utilized in liquid cultures for testing the biodegradability of three different PVA samples having Mw 15,000, 88,000 and 36,000 respectively and correspondingly hydrolys degree of 72.5 (PVA72), 88 (PVA88) and 98% (PVA98). As represented in Fig. 13 both hydrolysis degree and molecular weight, did not exert any significant influence on the polymer attack by the selected mixed bacterial culture.

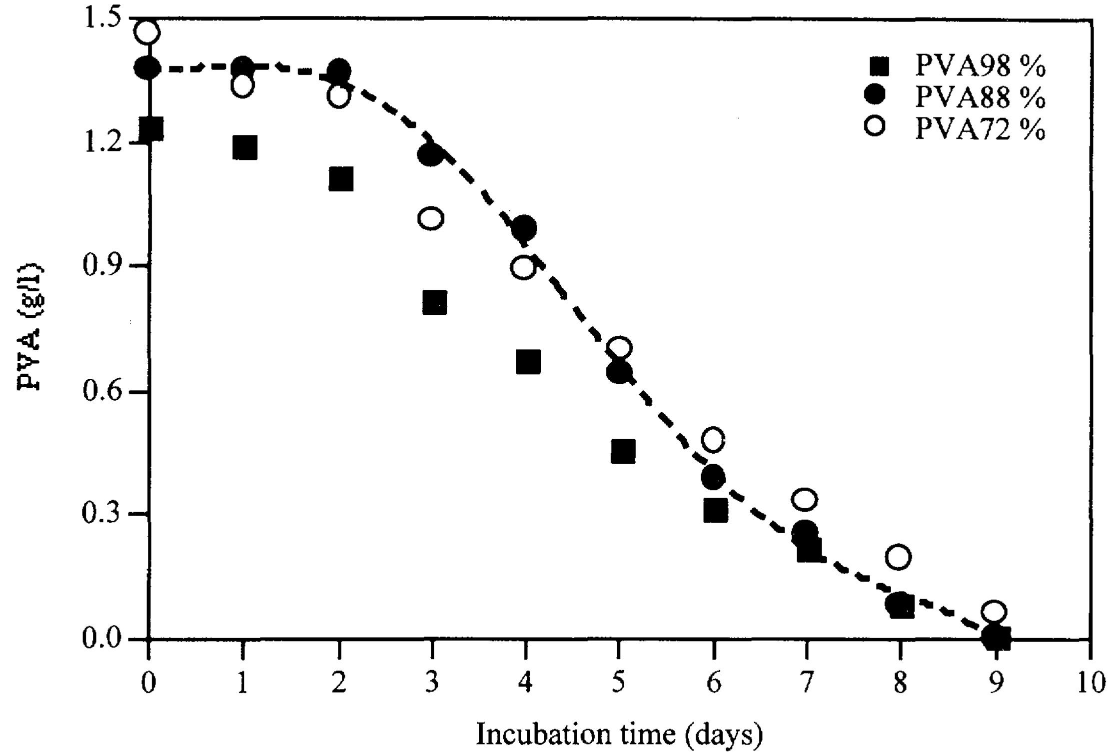


Figure 13: Variation of polymer concentration in liquid cultures supplemented with PVA samples having different hydrolysis degree, inoculated with a selected microbial culture

Moreover, the appreciable PVA degradation observed in the presence of a sterile culture filtrate of the mixed PVA-degrading culture seems to demonstrate that an extracellular degrading enzyme is present in the mixed active culture.

CONCLUSIONS

On the basis of the results obtained in the present investigation the following conclusive points can be highlighted.

PVA degrading microorganisms seems to be confined mainly into PVA contaminated aquatic environments, and a selective pressure (acclimation) is required to isolate single active microorganisms or mixed degrading microbial cultures.

The PVA degradation was rather limited under solid incubation conditions, controlled composting and soil burial simulation tests. However in the first case both the large amount of polymer samples and the high level of carbon dioxide production from the blank, negatively affected the results confidence. On the other hand under soil burial conditions the relatively small, but reliable, biodegradation of PVA, could be attributed either to the absence of degrading microorganisms in the soil microflora or to the polymer-soil interactions (e.g. hydrogen bonds) hindering the first enzymatic attack to hydroxyl groups. However, slight differences have been observed on the basis of the hydrolysis degree. These latter issue has to be confirmed by further investigations, also because of the increasing interest in the applications of PVA films as biodegradable mulching and soil conditioning films.

As a general conclusion one may stress that the assessment of the biodegradability of a polymeric material has to be referred to well defined time frame and environmental conditions.

ACKNOWLEDGMENTS

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Environmentally Degradable Plastic Composites based on Waste Gelatin

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Summary

Gelatin, a naturally occurring polymer, is currently used in various applications comprising manufacturing of pharmaceutical products, x-ray and photographic films development and food processing. However, gelatin scraps generated in the different manufacturing processes may constitute a concern for the environment. Basically speaking, waste disposal deriving from plastics based on synthetic as well as semisynthetic polymeric materials, is becoming an increasingly difficult problem for their unfavorable volume-to-weight ratio and extremely wide variability of type, shape and composition of post consume plastic items that hinder the way to a general unique option for a simple and economically feasible management.

As a partial solution to the global issue of plastic waste, in recent years much interest has been devoted to the formulation of environmentally degradable plastic items.

Biodegradable mulching films were formulated from blends and composites based on waste gelatin and other natural waste such as sugarcane bagasse or synthetic materials such as PVA. Also, crosslinked films were produced using external or inherent crosslinker. The films were produced either by casting method or spraying on soil surface. The composites were submitted to biodegradation trials. The results showed that the films were biodegradable and the crosslinking could delay and predetermine their biodegradation rate and extent.

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INTRODUCTION

Plastics have gained a unique position in materials technology for a number of reasons. Initially they were used as substitutes of paper, glass and metal because of their better physical properties 1) and because plastics are more economical than metals, wood and glass in terms of manufacturing costs, weight to strength ratio, and cost/performance convenience 2). Plastics have also achieved a dominant position in agriculture and horticulture, which has merited the new description 'plasticulture' to describe the use of plastics in greenhouses, tunnels and irrigation and in protective covers for crops (mulching films) 1).

Plastic waste may represents however a serious concern for the environment because of its recalcitrance to microbial attack 3,4). Recent estimates indicate that more than 200 million tons of municipal solid waste (MSW) is generated annually in the United States 5). This makes polymer waste management an urgent problem, needing environmentally compatible and friendly solutions; both short and long term, as soon as possible 2).

It is generally recognized that there is no single, simple solution to waste management but there is a fairly broad of options which comprise either reduction of the amount of material entering the waste stream and/or deal with its ways of disposal 6). Since plastic waste has caused serious, but often emotionally exaggerated environmental concern, there are nowadays increasing demands to develop environmentally degradable polymeric materials 7-9) The search for biodegradable alternatives to stubbornly bioresistant thermoplastics has led to the exploitation of the complementary properties of natural and synthetic polymers as blends, block copolymer, or graft copolymers 10).

Gelatin and starch are of particular interest since these biopolymers have no adverse impact on human or environmental health 11).

Gelatin, a naturally occurring polymer, is currently in use in various industrial applications. Gelatin scraps generated in the different manufacturing processes may constitute a concern for the environment due to strong swellability in water medium and high carbon and nitrogen content, that lead to high oxygen demand once they reach the sewage drainage system and waste water treatment plants.

The use of mulching films in particular, has led to a very substantial increase in the yields of soft fruits and vegetables in many areas all over the world, because plastics films not only helps to increase the temperature of the soil, but also reduce the usage of irrigation water and fertilizers with consequential beneficial economical and environmental returns 1). The disposal of agricultural mulching films can represent a key in the economy of the overall productive cycle, primarily caused by the advent of automated harvesting. Cropping equipment's are often rapidly put out of action by plastic based litter on the surface of the soil and residual undergraded plastics, once buried, may survive for long time and interfere with the root growth of subsequent crops. The intensive and costly labor to remove such debris from the fields by manual collection in large-scale plasticulture, may result in a drastic reduction of the benefits connected with the increased crop yields.

Herein, we report the development of biodegradable blends and composites based on waste gelatin and other natural or synthetic waste materials that can be used in agriculture for the fabrication of environmentally sustainable mulching films, and soil conditioners. The composite based on waste gelatin could constitute the basic matrix for the formulations of good biodegradable mulching and soil conditioning films and at the same time be helpful in solving the problems with the correct management of an yet energy reach plastic waste.

EXPERIMENTAL

Materials and methods

Materials used in this study were either waste material or commercially available materials. Polyvinyl alcohol (PVA) and scraps from the production of blown films for hydrosoluble biodegradable packaging and sizing wraps commercialized under the trade mark of Hydrolene® were supplied by Idroplast SpA-Italy. The PVA had an average molecular weight of 67 KD and degree of hydrolysis of 88 % and was used without further purification, also PVA with 98 % hydrolysis was used as received from the same supplier. Rp Scherer Egypt kindly supplied waste and virgin gelatin. The elemental microanalysis of waste gelatin, gave: carbon (43.55 %), nitrogen (11.62 %) and hydrogen (6.59 %). Brazilian sugarcane bagasse was kindly supplied by Prof. Miele, of the Faculty of Agriculture of the University of Pisa. Prior the use it was dried in an oven at 50 ^{o}C for 24 h and then grinned with a blade grinder. The grinned bagasse was sieved and the fraction passing through a mesh sive (0.212 µm) was collected. The carbon, nitrogen, phosphorous and organic substance content of the bagasse were determined by Kjeldahl method and were as following: organic substance (83.80%), carbon (48.72 %), nitrogen (0.34 %) and phosphorous (0.02 %).

Perlite, a naturally occurring siliceous stone, was supplied from BPB Italia S.p.A., Italy.

Air compressor: Films were sprayed on soil surface using a Fini compressor (Italy), type E.C. attack OL 195 23050 EU RC working at 3 bar pressure and with 2.5 mm nozzle.

Scanning Electron Microscope (SEM)

SEM inspections were carried out on a Jeol T300 apparatus. The film samples were prepared for SEM by critical point drying, sputtered with gold and observed at 10 keV[12).

Film preparations

Films were prepared by casting of water dispersions of all the ingredients or direct spraying according to a proprietary procedure. Table 1 shows the composition of the prepared films.

Table 1: Composition of films based on waste gelatin (WG), PVA (P), bagasse (B) and crosslinking agent (X)

Film Sample	Waste Gelatin	PVA	Bagasse	Crosslink Ratio (GLU)	Visual Characteristics	
	wt- %	wt- %	Wt- %	Wt- %	Color	Appearance
VGP0	0	0	0	0	colorless	rigid
WGP0	100	0	0	0	dark-red	very flexible
WGP2	10	90	0	0	light pink	flexible
WGP4	20	80	0	0	pink	flexible
WGP6	30	70	0	0	deep pink	flexible
WGP14	80	20	0	0	deep red	highly flexible
WGPX4	80	20	0	0.25	pale brown	very flexible, good film
WGPB10	80	20	20	0	brown-red	very flexible, good film
WGPB13X	80	20	20	0.25	brown	flexible
WGB2	80	0	20	0	red-brown	flexible
WGBX1	80	0	20	0.25	brown	very flexible, good film
WGX1	100	0	0	0.25	faint-brown	flexible

Coating of loamy soil surfaces

In this series of experiments the dispersions in water of the various components were sprayed on pots containing the loamy soil with an overall surface area of 154 cm^2 or by slow water evaporation from liquid films confined onto teflonized surfaces. The preparatory were aimed at testing the conditioning and mulching properties of the films obtained by in situ spraying on the soil samples. In Table 2 are collected the compositions of the films sprayed on the loamy soil samples. The pots were left outdoors under open-air conditions. A pot containing the loamy soil without any film was used as a control.

Table 2: Composition of sprayed films based on waste gelatin (WG), PVA (P),bagasse (B) and a low molar mass or high molecular weight dialdehydecrosslinking agent (X)

Film Sample	Waste Gelatin	PVA	Bagass	Crosslink Ratio (GLU)
	wt-%	wt-%	wt-%	wt-%
WGB5S	50	-	50	-
WGB5XS	50	-	50	0.25
WGPBS	40	10	50	-
WGPBXS	40	10	50	0.25

Crosslinking of waste gelatin containing films

Crosslinked films were prepared according to a proprietary procedure 13) by using high and low molar mass dialdhydes as crosslinking agents. Table 3 shows the composition of the prepared films.

Table 3: Crosslinked films based on waste gelatin and crosslinking agents (X)

Film Sample	Waste Gelatin wt- %	Crosslink Ratio wt- %	Visual Characteristics Color	 Appearance
WGX1	100	0.25	faint brown	very flexible
WGX3	100	1.0	coffee like	very flexible
WGX5	100	2.5	brown-yellow	very flexible
WGX7	100	5.0	coffee like	very flexible

Biodegradation studies

The biodegradation tests were carried out using a new respirometric procedure set up in the laboratory of the Department of Chemistry and Industrial Chemistry of the University of Pisa[14]). The test was carried out in 1 litre Erlenmeyer flasks containing a culture medium consisting of a bottom layer constituted by 20 g of Perlite and 35 ml water. On top of that layer a mixture of soils (forest and loamy soils) and grinned Perlite (5 g soil mixture and 7.5 Perlite) and 7.5 ml of water was layered. The test samples (6 strips 0.5 cm x4.9 cm) of known weight were placed on the top of the soil-perlite layer. The samples were then covered by another layer of the mixture of soil-perlite moistened with 7.5 ml water. Finally a layer consisting of 20 g of wet perlite was added. The Erlenmeyer flasks containing the samples were connected to a system for set for the determination of carbon dioxide developed within the time.

The flasks were discontinuously aerated with carbon dioxide-free air. The carbon dioxide-free air was passed through two flasks, the first flask contained a super-saturated solution of barium hydroxide and the second one contained filtered saturated solution of barium hydroxide. The two barium hydroxide flasks were used for trapping any traces of carbon dioxide in the air before passing to the flask containing the sample and the inocolum. Then the carbon dioxide-free air was humidified by passing through a flask containing water. The airflow was allowed to the different test flasks and regulated with plastic valves at a rate of approximately 30 ml/min.

At regular intervals barium hydroxide solutions in the CO_2 absorbers, were titrated with standard solution of HCl. The amount of CO_2 evolved from each sample was calculated from the amount of barium hydroxide consumed in the reaction with the released CO_2. The carbon content of each sample was calculated and the theoretical amount of CO_2 was calculated from the carbon content of each samples. Biodegradation was expressed as percent of evolved CO_2 (corrected for the CO_2 produced in the blank experiment) with respect to the theoretical CO_2. Filter paper was used as a reference standard.

Noncrosslinked gelatin films

A preliminary test of biodegradation of selected gelatin films was carried out using films; slightly humidified with water. Film samples VGP0, WGP2, WGP4, WGP6 and PVA as prepared according to the procedure described previously were investigated. Two strips of each film sample were used, the first was incubated between two layers of soil and the 2nd was incubated in the top of the soil, the results collected for the top samples are reported in Table 4.

Table 4: Behavior of some non-crosslinked PVA/gelatin films incubated on forest soil

Sample	Gelatin content (%)	Observations
VGP0	100	Growth of fungi noticed at the 4th day exposure
WGP2	10	Growth of fungi accompanied by almost total disappearance of the film at the 4th day of exposure
WGP4	20	Disappearance of the film after 24 hr exposure
WGP6	30	Disappearance of the film after 24 hr exposure
PVA	0	Disappearance of the film after 24 hr exposure

Crosslinked gelatin bases films

Film samples WGP0, WGX1, WGB2, WGBX1, WGPB10, WGPB13X, WGP14 and WGPX4 (Table 1) were selected for the submission to biodegradation trials with the aim of monitoring the effects of some fundamental structural parameters on biodegradation.

Film samples listed in Table 5 were selected for the submission to biodegradation trials with the aim of studying the effect of crosslinking on biodegradation rate and extent.

Table 5: Selected films based on waste gelatin (WG), and crosslinked waste gelatin (X) for the biodegradation experiment

Film	Crosslink Ratio	Weight of Sample	Visual Characteristics	
Sample	wt- %	mg	Color	Appearance
WGX1	0.25	95	faint brown	flexible
WGX3	1.0	99	coffee-like	very -flexible
WGX5	2.5	106	brown-yellow	very -flexible
WGX7	5.0	105	coffee-like	very -flexible
WG	-	79	coffee-like	very -flexible
PVA[a]	-	137	colorless	flexible

a) The sample used was from PVA 98% of hydroxyl content submitted prior the use to three freezing-thawing cycles.

RESULTS AND DISCUSSION

Gelatin containing films were cast from solutions or dispersion containing gelatin and the other components by slow evaporation of the water at room temperature and at atmospheric pressure.

Smooth films of a constant thickness were obtained whose size depending on the composition of the film, was ranging from 0.20 mm to 0.45 mm.

Films were also obtained by a direct spraying technique on soil with the aim of testing the feasibility of a single pot application in field experiments. It was expected that, the soil once sprayed could lead to improvement of the mulching character of the films by keeping the soil warm enough for the plant cultivation. The film evolution of film morphology formed on loamy soils was monitored for three weeks.

The results of sprayed film experiments showed that the films lasted for more than two weeks on the soil and the soil appeared to be conditioned and in a better state when compared with the control sample. It is worth mentioning that, during the experiment time the boots containing the sprayed films were exposed to outdoor condition that were monitored for all the duration of the experiment.

Low molar mass dialdehydes and high molecular weight dialdehydes are of the most popular crosslinking reagents, especially for proteic materials [14]). Because the amino groups arising from lysine react easily at room temperature with functional groups resulting in an obvious color change characteristic of the Schiff base linkages[15-17]). It was observed that, within a few minutes on treatment of the blend with a dialdehyde and casting the film, the color changed from the red color characteristic of our waste gelatin to color range from pale yellow to brown. This color change occurs only when preparing crosslinked films and it could be visually detected. The color change is due to the formation of aldimine linkage (CH=N), between the free amino group of gelatin and the dialdehyde.

In order to control the degradation rate of the gelatin containing films, it is worth having a physical stabilization by crosslinking. The crosslinking indeed increases the persistence of the films in the environment for the required period because crosslinking reinforces gelatin structure by introducing intra- and intermolecular bonds between gelatin molecules.

Biodegradation studies

The studies were carried out by using a respirometric method viable for the determination of the amount of the CO_2 released from the samples submitted to the action of soil microflora. The first trial was run for 30 days and the % of biodegradation extent was recorded as shown in Table 6. It was noticed that, for the first week, there is no much difference between the biodegradation rate of the crosslinked waste gelatin film and the non-crosslinked waste gelatin film. In general for the first week, the biodegradation rate for most samples was comparable. After the first week, the degradation rates changed and in some cases the crosslinking slowed down the rate of the biodegradation and in others was even higher than that observed in analogous uncrosslinked films. This might be due to the smaller ratio of the crosslinking. Figure (1) shows the integral biodegradation of the films selected for the first biodegradation trial within the time.

At the end of the biodegradation trial, most of the samples disappeared except for samples from film WGB2 and WGBX1. The recovered samples (WGB2 and WGBX1) once gently cleaned from soil by small brush and dried in an oven at 37 °C were analyzed by SEM. The changes in the surface morphology after submission to the biodegradation trial were compared with the original film surface.

The SEM for films before being submitted to biodegradation, showed smooth homogenous surfaces (Fig. 2). The SEM of some recovered films after biodegradation experiment showed cracks and fractures on the surface as indicated by increased surface area of the composite due to growth of the microorganisms on the film.

Table 6: Biodegradation various of the film samples based on gelatin

						Biodegradation (%) a)			
Time (days)	Cellulose	WGBX1	WGB2	WGPX4	WGP14	WGPB13X	WGPB10	WGX 1	WG
1	-0.1	1.3	1.2	1.1	1.7	0.8	1.4	1.6	1.5
2	-0.1	4.1	4.0	3.2	4.3	2.8	4.0	4.5	5.2
2.5	-0.1	5.2	5.7	4.2	5.7	3.7	5.1	5.4	7.2
3.5	0.5	8.2	8.9	6.6	8.6	6.2	8.4	9.6	11.5
4.5	1.6	12.9	16.6	11.5	13.3	11.5	14.7	22.1	19.7
5.5	2.5	20.2	22.5	17.1	18.4	17.1	19.1	29.3	29.3
6.5	3.1	22.8	25.6	21.4	21.0	19.7	21.7	37.3	33.7
7.5	5.1	26.2	30.1	25.5	24.2	22.1	24.2	42.3	36.1
8.5	6.2	28.8	32.8	29.0	26.4	23.6	26.1	46.0	38.1
11.5	8.4	32.3	37.4	33.4	30.0	25.7	29.3	50.6	43.0
12	10.7	35.3	40.5	37.0	32.4	28.5	31.4	54.8	47.0
14	14.5	38.1	43.2	40.3	35.1	31.8	33.9	60.4	51.4
16	17.6	40.4	45.5	42.5	36.5	33.4	35.6	63.8	54.0
19	21.0	43.6	48.1	43.4	39.1	34.8	37.7	67.2	56.8
22	23.5	44.6	48.9	44.9	39.7	35.5	38.5	68.5	57.1
27	25.4	45.5	49.9	45.8	39.9	36.5	39.4	69.8	57.3
30	27.5	46.3	51.1	47.1	40.7	37.7	40.7	69.9	57.6

a) Determined as $\frac{\text{Amount CO}_2\text{ (sample)} - \text{Amount CO}_2\text{ (blank)}}{\text{ThCO}_2} \cdot 100$

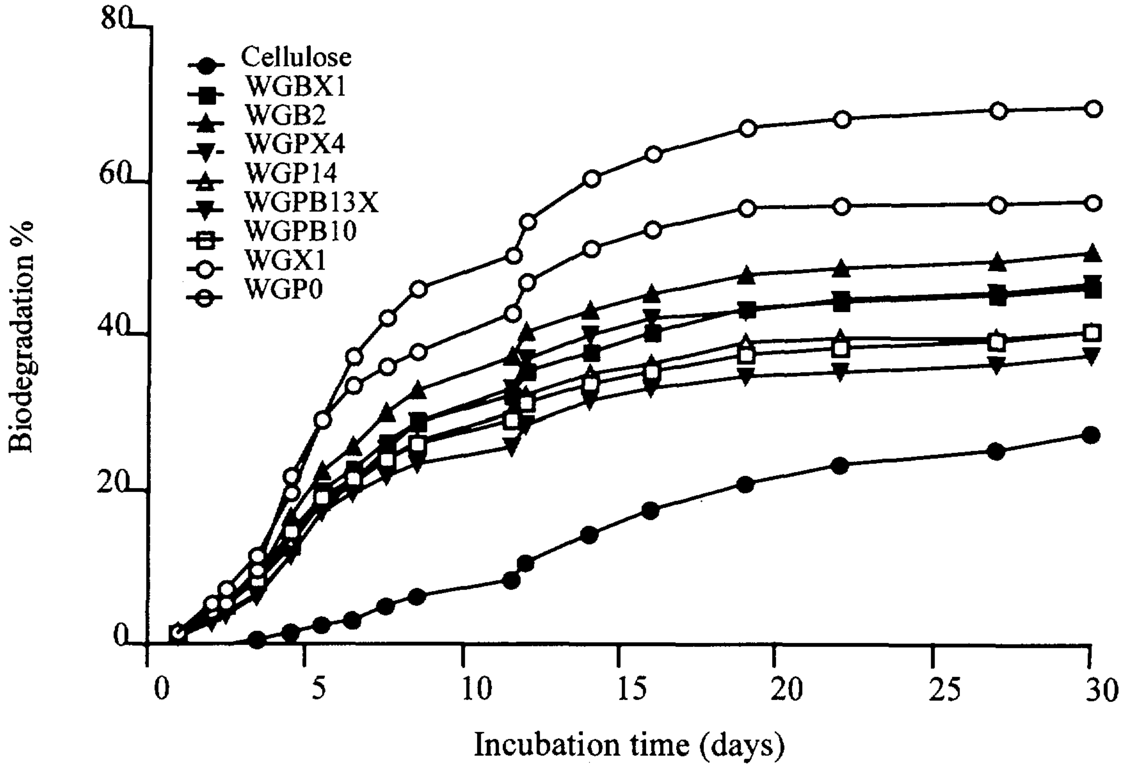


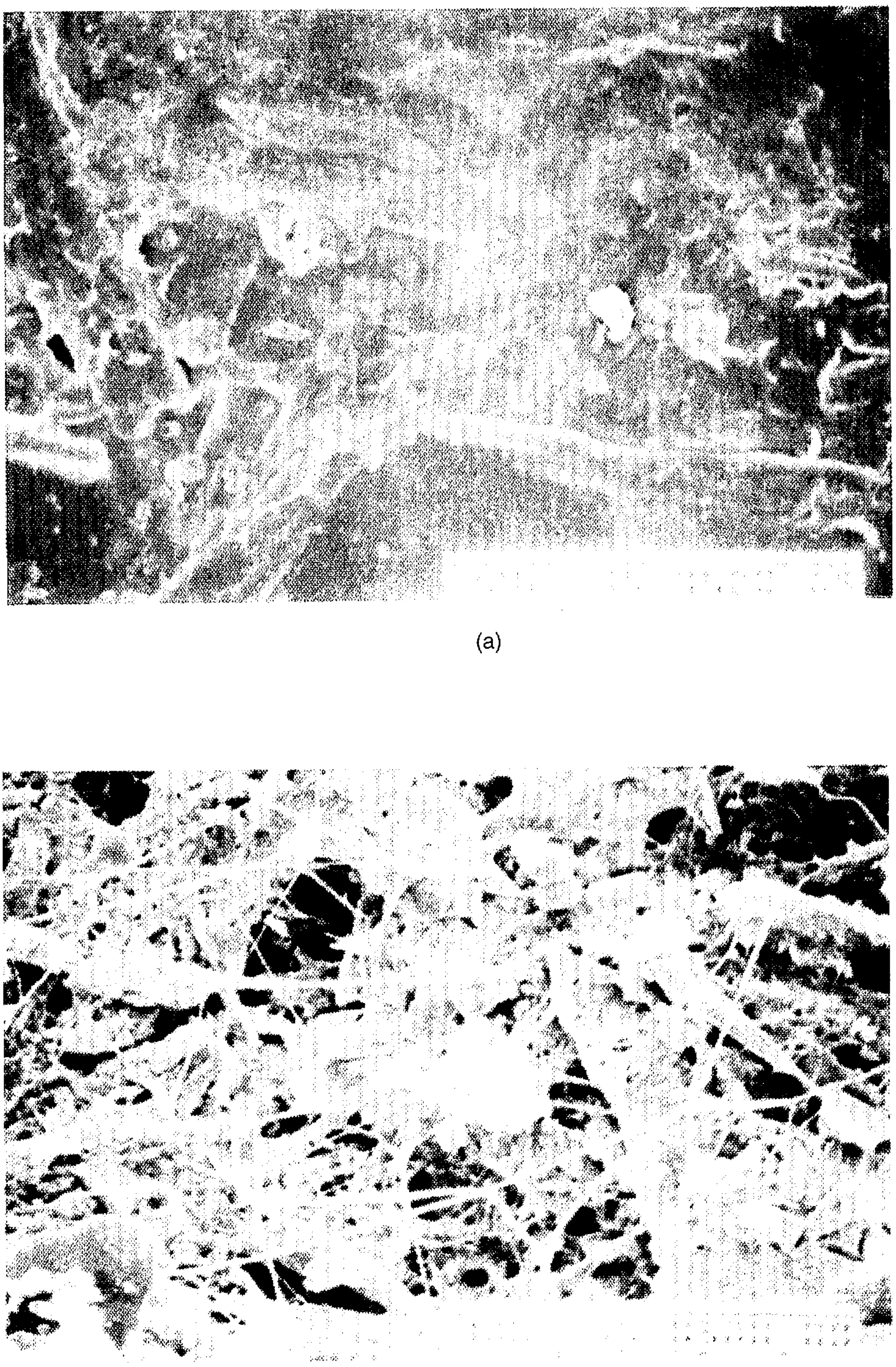
Figure 1: Trend and overall extent of biodegradation in waste gelatin films

Effect of crosslinking on the rate of biodegradation of films based on waste gelatin

Biodegradation trials were carried out in order to investigate the effect of crosslinking on the biodegradation of the film. In the first biodegradation trials, crosslinked samples used have a crosslink ratio of 0.25 %. At that relatively small crosslinking ratio, the effect of crosslinking on biodegradation was not specifically detectable. Therefore, in another trials we used samples with a crosslink ratio of 0.25-5.0 %.

Film samples (Table 3) and a blank were tested and compared with PVA. The biodegradation experiments related to the samples WGX3, WGX5, WGX7 were carried out in duplicate. The amount of CO_2 released from the samples was monitored by taking into account the CO_2 amount released from the soil itself. The trial was run for 39 days and the extent (%) of biodegradation was evaluated as shown in Table 7. At the end of the biodegradation trial, all the analyzed films lost their mechanical properties. From the data collected in Table 7 and from the integral profiles of the traces of CO_2 developed within the time (Fig. 3) a detrimental effect on the rate of the biodegradation and overall extent of biodegradation was detected with the increasing of the crosslinking degree.

In all cases the extent of biodegradation is larger than one order of magnitude with respect to that observed in the case of PVA 98 % degree of hydrolysis.



(a)

(b)

Figure 2: Scanning electron micrograph of WGB2 film sample before (a) and after (b) microbial attack during the first biodegradation trial

Table 7: Biodegradation % of crosslinked and uncrosslinked waste gelatin based films as compared to PVA sample

	Biodegradation (%) $^{b)}$					
Time (days)	PVA98 $^{a)}$	WGX1	WGX3	WGX5	WGX7	WG
1	-0.097	0.5264	0.50334	0.54162	0.2338	0
2	0.2921	4.0333	3.5225	3.10716	2.4937	3.1665
4	0.2921	11.925	7.38047	6.28947	5.377	9.2885
6	0.4868	21.92	12.6642	11.5584	10.131	18.155
8	0.404	31.175	18.7326	18.0249	15.305	26.96
10	0.7355	40.878	25.5149	24.7697	21.806	36.843
14	1.2328	54.323	39.5889	36.0963	35.081	54.286
16	1.677	61.523	46.7628	41.655	40.503	61.028
18	2.3432	68.923	55.1802	47.0662	47.613	68.973
21	2.3432	74.123	60.2498	50.1634	53.034	74.029
25	2.2322	78.123	65.415	52.6448	57.567	77.4
29	2.4543	80.723	68.0933	54.5044	60.5	80.048
32	2.5653	82.323	69.7193	55.2119	62.989	81.733
36	2.5677	84.736	71.3075	55.2766	65.135	84.639
39	2.7337	86.693	72.3872	56.817	67.008	86.455

a) The sample used was from PVA with 98% hydroxyl content submitted prior the use to three freezing-thawing cycles .

b) Determined as $\frac{\text{Amount } CO_2\ _{(sample)} - \text{Amount } CO_2\ _{(blank)}}{ThCO_2} \cdot 100$

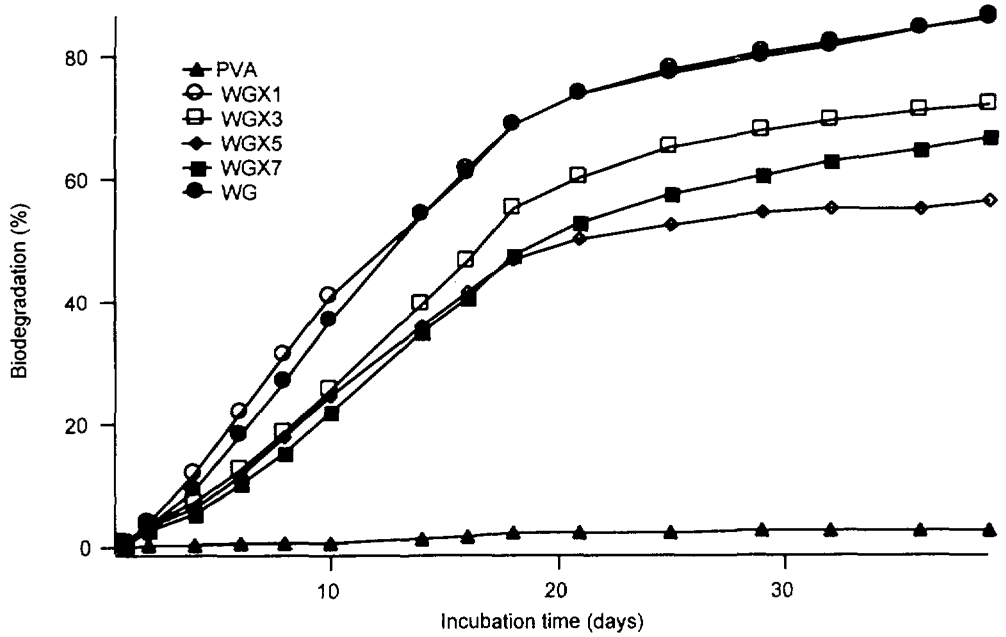


Figure 3: Trend and overall extent of biodegradation in waste gelatin films (mean values for duplicate trials), (PVA treated with freezing & thawing)

These results indicated that the crosslinking method is an effective procedure for controlling the biodegradation rate and biodegradation extent within the time in agreement with previous finding 17-19).

CONCLUSIONS

Cohesive, flexible biodegradable films based mainly on waste gelatin were prepared either by coating was water dispersions or direct spraying. Sugar cam bagasse and PVA were used as fundamental ingredients in the formulation of composite and blend films respectively. The structure of the films was reinforced by incorporation of various dialdehyde crosslinking agents in the polymer blends and composites. The prepared films resulted biodegradable and the crosslinking of waste gelatin with dialdehyde was found to be an effective mean to allow them to persist in the environment for the required period of time. These biodegradable blends and composites are on the way to be used in agriculture for the fabrication of mulching films and/or soil conditioners and self-fertilizers.

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The Status of Plastics Waste Management in Canada

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INTRODUCTION

Setting the Context - The Canadian Plastics Industry

The Canadian plastics industry has grown annually by more than seven per cent over the thirty-five year period of 1961 to 1996. This is five times faster than manufacturing in general in the country. Compared to the Real Gross Domestic Product of Canada, plastics growth has been double. In 1996, Canadian plastics processors and raw material, machinery and mould suppliers shipped product valued at $26 billion. Although large, the plastics industry comprises four principal industrial segments:

- manufacturers of plastic resins;
- manufacturers of equipment, moulds and related materials to convert resins into finished products;
- converters (plastic resins to finished products, including packaging); and
- recyclers

Together, these segments employ over 100,000 people in Canada, making the plastics industry one of Canada's largest employers.

Annual resin capacity in Canada is in excess of 3500 kilotonnes. Of the plastic resins converted to products in Canada, 40 per cent is used in packaging, 25 per cent in building and construction, 10 per cent each in automotive applications and furnishings and 5 per cent in electrical components. The remaining 10 per cent finds use in a host of miscellaneous products.

The primary purpose or objective of this paper is to document the status of plastics waste management in the residential sector. This is achieved by presenting, wherever available, information on a provincial basis and highlighting some of the major initiatives that have been undertaken by the plastics industry, in particular, the numerous initiatives by the Environment and Plastics Industry Council (EPIC), an industry initiative committed to the responsible use and recovery of plastics resources.

To place this objective in perspective it is necessary to understand that plastics are just one of many materials used to create packages and products that eventually require management as a secondary resource. Therefore, a secondary purpose of this paper is to document major waste management approaches and directions in Canada.

Not specifically addressed in this paper are waste management and diversion initiatives in the Industrial Commercial Institutional (IC&I) sector for general wastes or, more specifically, for plastic materials. It should be recognized, although no specific data respecting the exact quantities are currently available, the total diversion of plastics in the IC&I sector exceeds the diversion being achieved in the residential sector at the present time.

OVERVIEW OF WASTE MANAGEMENT IN CANADA

In any discussion of solid waste management issues in Canada, and particularly plastics waste management, it is important to understand some key perceptions and beliefs. Public attitude research indicates clearly that environment and resource conservation are important social and political factors, which will not abate. What was once a garbage crisis, or landfill crisis, has evolved into a resource conservation issue.

Householders want to do their part for the environment. They recognize the limitations on personally being able to do much about major environmental issues, but, through reduction, reuse and recycling, understand that they can help make a difference.

There is only a rudimentary understanding in the minds of the public and some government officials of the elements of environmental performance. Life cycle analysis and integrated waste management are important concepts in understanding environmental performance, but they are not yet fully understood or accepted.

Approximately 32 million tonnes of total solid waste are generated each year of which approximately 11 million tonnes are construction and demolition waste. The remaining 21 million tonnes is a combination of residential waste and industrial, commercial and institutional (IC&I) wastes. Approximately 70 percent of waste generated in Canada is landfilled.

There are 10 solid waste incinerators in Canada of which nine are classified as energy-from-waste facilities. Approximately 8 percent of total solid waste is incinerated.

Reduction, reuse, recycling (including composting) initiatives have resulted in 22 per cent of the waste generated being diverted. About two-thirds of all diversion comes from the construction/demolition sector.

Three main types of recovery and recycling programmes serve households in Canada:

1. Curbside collection: Householders place their recyclable materials into a container (either a plastic box, e.g. the Blue Box, or a bag) and set them out at the curb for collection.

2. Drop-off depots: Householders take their recyclable materials to a depot. On occasion, containers may be provided to householders to hold their materials, but generally no container is provided.

3. Deposit systems for containers: Householders pay a deposit on a container when they purchase the product (usually beverage containers) and receive part or all of their deposit back when they return the container to a central repository or to the point of purchase.

Specific activities within each province are described in the following table.

Table 1: Summary of Household Access to Recovery and Recycling Programmes

Percentage of Households with Access to/Served by....

Province/ Population / # households	**Curbside Collection**	**Depot Programmes**	**Deposit Programmes**	**Plastics Recycling (a)**	**Access to Curbside or Deposit Recycling (%)**
British Columbia 3,300,000 /1,335,600	65%	79%	100%	79%	79%
Alberta 2,600,000 /915,000	17%	7%	100%	17%	25%
Saskatchewan 990,000 I 366,000	2%	0%	100%	2%	2%
Manitoba 1,100,000/407,000	25%	68%	100%	0%	92%
Ontario 10,100,000/3,500,000	82%	0%	100%	82%	82%
Quebec 8,300,000 I 2,650,000	35%	9%	100%	44%	44%
New Brunswick 724,000/220,000	10%	30%	100%	39%	39%
Nova Scotia 920,000 I 263,000	61%	16%	100%	77%	77%
Prince Edward Is. 130,000/44,700	1%	6%	100%	0%	7%
Newfoundland 568,000/175,600	16%	2%	100%	2%	18%
Yukon Territory 28,000 / 8,000	0%	75%	75%	75%	75%
Northwest Terr. 58,000 I 16,300	0%	28%	0%	0%	28%
CANADA 28,818,000 / 9,901,200	5,148,845 52%	1,747,575 18%	9,882,955 100%	5,553,275 56%	70%

(a) Any type of plastic under curbside and/or depot collection programmes.

Sources:

Provincial or Territorial Governments, 1995; various reports and file information, Proctor & Redfern Limited.

A rapid flight over the country indicates that in:

British Columbia

- Curbside programmes exist in the two largest urban centres;
- Smaller municipalities use drop off depots;
- All households have access to a deposit system applied to a range of beverages.

Alberta

- Curbside collection in Edmonton;
- Drop off depots in Calgary and certain rural areas;
- Bottle depots for all beverage containers except beer which is handled by the Alberta Brewers Agents.

Saskatchewan

- Fee for service private curbside programmes in Regina and Saskatoon;
- Private depots in some areas;
- Extensive deposit system for beverages run by SARCAN.

Manitoba

- In a state of flux. Three private companies have been offering curbside collection in Winnipeg. A more widely based system is being implemented;
- Depots in rural areas;
- Levies on soft drinks and beer.

Ontario

- Curbside collection available to more an 80 percent of the population;
- Communities over 5,000 population required to provide service;
- Some municipalities collect more than 15 materials at curbside;
- Deposits on glass bottles for soft drinks and on beer bottles and cans.

Quebec

- More than 200 of 1,500 municipalities have curbside collection. Additional 250 municipalities have access to depots;
- Curbside collection is growing;
- Deposits on refillable and nonrefillable soft drink and beer containers.

New Brunswick

- Curbside programmes in Fredericton and Oromocto;
- Deposits on a wide range of beverage containers;
- Extensive network of redemption centres.

Nova Scotia

- Curbside collection in larger centres;
- Mobile and stationary depots.
- Landfill bans on glass, steel and some plastics.

Prince Edward Island

- Depots to collect variety of materials
- Refillable bottles required for soft drinks and beer.

Newfoundland

- Curbside programme in St. Johns;
- Depot collection service some rural communities.

Yukon Territories

- Drop off depots to service the population;
- Deposits on glass and aluminum beverage containers.

Northwest Territories

- Drop off depots service 4,500 households.

Each province has a different mix of each of the three generic recovery systems. Most curbside and drop-off depot programmes collect a wide variety of materials, whereas deposit systems are generally more restricted to a small number of materials.

More than 5 million households have access to curbside recycling programmes and an additional 1.7 million have access to depot recycling programmes. Overall, access to recycling programmes is available to approximately 70 per cent of all Canadians, with some provinces providing access to more than 80 per cent of their population.

The number of items that may be recycled varies from community to community. Five to ten items are most common although some programmes will accept up to seventeen materials collected at curbside.

It is estimated that more than 2.2 million tonnes of residential materials were recycled in Canada in 1996 with Ontario, British Columbia and Quebec accounting for more than 90 per cent of this figure. Approximately 6 per cent of the total, or 134,000 tonnes was plastics. About 26 per cent of the 134,000 tonnes was PET soft drink bottles.

A variety of methods are being explored to pull more materials from the waste stream.

User-pay waste systems have been effectively used in a small number of municipalities in Canada. A user-pay system is a method of charging people directly for waste collection and diversion based on the weight or volume of waste or number of bags of waste provided. Recycling is “free”. The result is that the householder has a disincentive to produce waste and, hence, reduces intake or recycles more.

Wet-dry and three stream waste collection systems are being introduced in a few communities. The City of Guelph, Ontario is building a major facility to handle a wet-dry collection system while the District of Lunenberg, Nova Scotia has a three stream process.

In the IC&I sector, material bans are sometimes used to force diversion of material. Dry wall, corrugated paper and wood have been banned in some localities. In most instances a ban is not imposed until a facility capable of recycling the specific material is operational.

Solid waste can have a relatively high calorific value, which can be recovered. In Canada EFW is not universally accepted. It is often seen as competing with reduction, reuse and recycling initiatives.

In Canada, 70% of all waste is landfilled. The siting of landfills requires environmental and social assessment which is a long process and can take up to five years or more. Modern landfill design now requires that the facility be lined, leachates collected and treated on site, a methane gas collection systems and have the costs of closing the landfill paid in advance.

The reality of the management of post consumer waste in Canada is two fold. It is oriented towards the diversion of packaging from waste and it is bound up in mechanical recycling.

Lip service is paid to reduction and reuse. Unfortunately gains made in reduction, e.g. light weighting, often go unnoticed. EPIC's brochure on source reduction is entitled "Source Reduction, the Invisible R." A two litre PET soft drink bottle today weighs 20 per cent less than it did in 1977, but when it is empty, it is just an empty bottle which, according to the public, must be recycled.

Since the imagination of the public has been caught by mechanical recycling, huge infrastructures of collection and processing have been set up to foster and promote it.

PLASTICS AND COLLECTION AND PROCESSING SYSTEMS

All common plastics are inherently recyclable. In fact, they have been recycled in plastics manufacturing plants for decades by transforming industrial scrap into a pellet or flake that can be extruded or molded into another product. Recycling industrial plastic scrap continues to be widely practiced by the plastics industry. The most commonly targeted plastics are those referred to as thermoplastics since they become soft and fluid when heated and can be remoulded into new products. The major thermoplastics in use in Canada include:

- LDPE & LLDPE
- PP
- PVC
- ABS
- Acrylics
- HDPE
- PS
- PET
- Polycarbonate
- Nylon

Post consumer plastic discarded by householders, institutions and the private sector has the potential to be a large and relatively consistent supply of material for plastic processors and/or end markets. However, the wide variety of plastic resins used necessitates the separation of the different plastic resins if they are to be returned to traditional manufacturing applications. In addition, household plastic scrap may be contaminated with food or other materials (e.g. paper labels, glues, etc.).

With the exception of PET soft drink containers, and to a lesser extent rigid plastic containers (RPCs), plastics are not as universally collected in recycling programmes as are aluminium, glass and steel food and beverage containers. Because of their low bulk density and resistance to compaction (i.e., high memory), plastics tend to take up a disproportionate amount of space in collection vehicles.

In Material Recovery Facilities (MRFs), the broad range of resin types, often within the same packaging application, results in lower sorting rates when compared to other food and beverage containers. The additional collection space required along with the lower processing rates may result in high recovery costs for plastics.

Restricting the number of plastic products that may be collected in a recycling programme helps reduce processing costs by reducing contamination from unwanted plastic resins. Collection efficiencies for plastics are being improved by streaming plastics with compatible materials. For example, collecting plastic film with newspaper allows the newspaper to act as a natural compactor, thereby improving utilization of vehicle space. During processing, because newspaper and film are readily distinguishable, they can be separated quickly at relatively low cost.

In the processing of plastic containers, almost all sorting is done manually although automated systems have improved to the point that they are both technically and economically feasible in large scale operations.

EPIC's role in Collection and Processing Systems

How to Establish a Recycling Programme

EPIC developed a guide for regional and municipal solid waste officials and recycling coordinators which outlined key factors (including what to collect and how to collect it) which should be considered when establishing a recycling programme. This 75 page guide features information for designing a plastics recycling programme.Topics that are covered include:

- locating markets for collected plastics;
- selecting appropriate equipment; and
- promoting the recycling programme.

Over the years EPIC has developed a number of guides and models to facilitate the more efficient collection and processing of plastics emanating from the household. The first of these was a computer model enabling the user to determine the cost of his collection process and to plan systems that reduced these costs.

Municipal Recycling Collection Cost Model

The Municipal Recycling Collection Cost Model (MRCCM) grew out of a 1990 EPIC-sponsored study of the incremental costs of adding rigid plastic containers to a curbside collection programme. Co-sponsored by EPIC and the Ontario Ministry of Environment and Energy

(MOEE), the MRCCM is designed to provide a planning and management tool to a wide target audience, including recycling programme operators and municipal representatives. It is available to municipalities free of charge and it allows the user to determine accurately the:

- cost per tonne of recyclable materials collected;
- cost per household;
- number of Blue Boxes/stops to be picked up per day;
- number of trucks required to service the municipality;
- fleet and cost requirements of adding new materials (e.g., RPCs, magazines, boxboard, etc.) to existing recycling programmes;
- fleet and cost impacts of adding new collection sources (e.g., multi-family dwellings, commercial establishments, etc.); and
- impact of increasing or altering participation rates (e.g., through public education and promotion, mandatory recycling, etc.).

Materials Recovery Facility - Processing Cost Model

The Materials Recovery Facility Processing Cost Model (MRF-PCM) as ointly ponsored project of EPIC and MOEE and is compatible with the MRCCM. The MRF-PCM has MRF operators as its primary target audience and is designed to be used as a planning or management tool in the examination of sorting and processing of recyclable materials. Again, it is available free of charge to municipalities and it allows the user to determine accurately the:

- manpower, equipment requirements and costs associated with starting a new processing facility;
- costs associated with expanding a programme by adding new materials or new sources of materials;
- costs associated with adding new mechanisms to increase material processing rates (e.g., new automated sorting equipment);
- costs of moving from a pilot scale to a full scale project; and
- estimated costs of sorting and processing individual materials or streams of materials.

Plastics Sorting Optimization Guide

The Plastics Sorting Optimization Guide, a project sponsored by EPIC, is a 100 page “hands-on” guide that provides the user with a variety of techniques to improve plastic sorting operations at municipal material recovery facilities (MRFs). Its primary target audience is MRF operators and recycling programme managers. The purpose of the document is to outline a variety of approaches and methods that can assist in:

- identifying curbside collection strategies, policies and procedures that will increase productivity at the MRF (i.e., optimizing system performance);
- assessing the performance, policies and procedures of an existing MRF;
- developing strategies to guide MRF operators to organize their plastic sorting operations to provide output streams of desired type and quality at optimal costs;
- examining changes to plastic sortation and other MRF functions and, consequently, the

economic impact of the change. Economic evaluation is done by using the MRF-PCM (see above); and
- designing of a MRF.

As a follow-up to the MRF Optimization Guide, the plastics industry worked with selected MRF operators across the country and demonstrated improvement in the quality of the sorted materials while at the same time reducing costs. Annual cost savings of over $ 1 million accrued to the MRF's which participated.

INTEGRATED SOLID WASTE MANAGEMENT

A number of European organizations have recently noted that only about 20 per cent of the plastics entering the waste stream may be handled in an economically sustainable fashion by mechanical recycling. Other means will have to be found to deal with the remainder.

Waste cannot be managed by a single simple process. Indeed, it cannot be handled in a cost efficient, ecologically sound manner by a number of freestanding techniques.

The management of solid waste requires an integrated approach which balances a very long list of Rs, of which Reduce, Reuse, Recycle are but three, and I might add, are not in a hierarchical order. A system of integrated waste management permits the use of any and all appropriate methodologies which can be validated as environmentally sustainable by Life Cycle Assessment.

Life Cycle Assessment

The benefits of plastics are generally not well understood. This lack of awareness leads to narrow, limited and often erroneous "solutions" which may result in serious and detrimental consequences to the environment and the economy.

EPIC is active with Environment Canada and other material sectors in the development of life cycle inventory data which will serve as the foundation for material life cycle assessment in Canada. Making use of third parties and peer-reviewed methodology, a life cycle inventory for the major commodity plastics manufactured in Canada has been developed from the perspective of oil and gas in the ground through to the formation of a plastic pellet. This database of energy and emissions is compatible with European, American and Japanese initiatives and it will find major application in improving the environmental performance of plastic products and processes.

EPIC and a partner Corporations Supporting Recycling have recently applied the concept of "life cycle thinking" to the subject of integrated solid waste management and have created a computer model which assesses the environmental impact and the economics of multifaceted waste management. The model which will be described in greater detail in another session of this workshop considers all of the waste management techniques available to municipalities such as landfilling, incineration, composting and recycling. It treats all of the materials commonly found in the residential waste stream such as paper, glass, steel, aluminium, plastics and organic matter. Environmental burdens are calculated for all activities engaged in from the time that the waste has been put out for pick up until it has been transformed into a useful material, energy or landfilled for final disposal. Environmental credits are applied where appropriate when recovered materials or energy displace virgin materials or primary fuels used to develop energy eg. electricity.

All plastics are energy banks. High density polyethylene has a calorific value within about 5 per cent of natural gas. The resin itself is probably freer of contaminants than natural gas straight from the well. The intrinsic energy of plastics can be recovered.

Any system of integrated waste management will allow for a consideration of the recovery of energy.

The Recovery of Energy

The recovery of energy is broader in concept than simply feeding material to a furnace and recovering the energy in the form of steam which powers a turbine, generating electricity.

The cracking of polymers to monomers, or even the precursors of monomers, is gaining attention in highly populated regions of the world which have large quantities of waste plastics. Condensation polymers are amenable to cracking processes involving hydrolysis, glycoloysis, methanolysis. In North America, PET is taken back to its basic feedstocks by methanolysis. The addition polymers are generally not susceptible to simple chemical attack and methods to recapture feedstocks from them are more complex and involve the sorts of equipment found in oil refineries and the like.

The European plastics industry is largely naphtha-based and about 80 per cent of those living in Northern Europe live within 100 miles of a steam cracker. As a result, a number of steam crackers are being adapted to convert plastic wastes back to chemical feedstocks. A European consortium has demonstrated conversion of waste to feedstock at a large facility in Scotland.

In addition to the use of steam crackers, waste plastics have been "recycled" using molten metal technologies where the materials are passed into pots of molten iron and the gases collected. The materials may also be converted through the use of heated, fluidized beds and commercial gas synthesis units such as those operated by Texaco. Feedstock recycling does not come cheaply. Pyrolytic processes all have "gate" fees associated with them. The gate fees may be as low as \$20/tonne at a cement kiln, to \$70/tonne at a municipal EFW facility, to as high as \$190/tonne at German hydrocrackers. In addition, there is always a certain amount of preparation of material required before the wastes can enter the process.

In Germany, funds are available from the "Deutsches Duales System" (DSD) which operates the "Green Dot" programme (a levy on packaging) to provide the gate fees. In North America no such subsidies exist and the current low prices for oil will probably limit the amount of feedstock recycling implemented.

There are, however, opportunities in North America to deal with waste plastics in the context of integrated waste management. The industry's philosophy is to mechanical recycle that portion of the stream which can be handled in an economically sustainable manner, e.g., PET and HDPE containers, as well as certain large volume films such as stretch wrap. Having done that, one should endeavour to recover the intrinsic energy of most of the remainder by using it as alternative fuels in cement kilns or energy from waste plants. The balance should be landfilled and the justification for doing this will be supported by a life cycle analysis that embraces environmental and economic considerations.

Integrated waste management is nothing more than common sense coloured with science.

Plastic Waste and Recycling in Qatar

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Abstract

The consumption of plastics, per capita, in Qatar was about 38 kg in 1996 and expected to reach 60 kg by the year 2000 which is comparable to some developed European countries. Plastic waste constitutes about 12% by weight of the total municipality solid waste which is approximately twice the world average, whereas the per capita solid waste is 1.30 kg/day, slightly less than USA but higher than many European countries. However only about 2% of town plastic waste is recycled and the rest is mostly dumped in sanitary landfills.

There are about twelve plastic factories in Qatar with a total production of about 14,000 metric tons producing various commodity plastic articles. Some of these factories use plastic waste as an important source of their raw materials but the main recycled waste (95%) is the industrial waste from the factories who usually recycle their own waste or sell them to other factories. However, some factories have recently established recycling units for the recycling of town plastic waste which is collected by individual rig pickers. Most of these wastes are processed into trash bags or converted to resins which are mixed with prime resins for manufacture of some low grade articles, or sold to some factories in the region or exported.

The main problem facing the recycling industry is the sorting and washing of the collected waste. Sorting is mostly mechanical (by hand) and depends on the experience of the workers. The government concern about the environment, and the activity of some environmental groups have raised the perception and created a gaining ground for recycling of solid waste. This has encouraged the plastic manufactures to increase the level and upgrade the available technology to further increasing the capacity of their factories to accommodate more town waste.

In this presentation, which is an outcome of several visits to most of plastic factories in Qatar, we will further shed light on the present situation, and on the main problems facing the recycling industry and its future perspectives.

INTRODUCTION

The Solid waste, mainly plastics, glass and paper, is growing much faster than the growth of world population due to the increase in utilization of disposable bottles and containers. Vance Packard state in his 1960 book "The Waste Makers" that the history will point out to our time as the waste era (4) which is still a valid description. It is a wonder what he has to write if he knew that so many developed countries have to rent spaces behind the borders for dumping their waste.

Gulf states consume about one million tons of plastic materials with a relatively high consumption per capita of about 38 kg /yr (1) with the consumption increased four times in the last 10 years. By the year 2000 it is expected to be 60 kg/yr (Table-1).

The average per capita solid waste is associated with the standard of living of population and the industrial development of the country. In the six Gulf States this average is about 1.5 kg/day (in Qatar the figure is 1.3 kg/day) (2) which is comparable to that of many developed countries, and which is mainly due to the high standard of living witnessed in the Gulf Region.

In Qatar, plastic waste constitutes about 12% by weight of the total municipality solid waste (Table- 4) which is about twice the average percentage of the waste of many developed countries. However, only about 2% of the waste is recycled and the rest is mostly dumped in sanitary landfills

The object of recycling is to reduce the amount of waste by recirculation of raw materials and to improve material utilization. Recycling is an established procedure for scrap, metals, glass and paper. It is, however, not always worthwhile; the cost of the process and the deterioration in mechanical properties have restriction effects on recycling as a dominant option for plastic waste management.

Most Governments are concerned with the management of solid waste rather than concentrating on the reduction of its volume and improving chemical and mechanical specifications of the resins to reduce the weight of plastic products. This strategy will lead to a more control of plastic consumption and an increase in recycling, but at the same time will raise the utilization of natural resources such as papers and wood. However despite of government's attempt to increase the percentage of recycled plastics, the recycling volume of plastic has not reached the level of that paper, steel and glass.

Plastic waste can be broadly classified into three categories - Industrial, agricultural and household. The first and the third are the main source of waste in the State of Qatar. The plastic waste produced by industry comes from manufacturers, processors and large end users.

In Qatar, the recycled plastic waste consists of 95% from plastic industrial waste and 2% from plastic town waste. Recently some factories have established or upgraded their machinery units to accommodate more town wastes which are collected by individual rig pickers. Most of these wastes are reprocessed into trash bags or converted to resins which are mixed with prime resins for manufacture of some low grade articles, or sold to some factories in the region or exported. In the following sections more aspects of this issue are further discussed.

PLASTIC CONSUMPTION

The plastic consumption could be determined by Per Capita Consumption:

The Per Capita Consumption in the Gulf States is estimated to be about 38 kg 1996. This amount was increased four times since 1985. It is expected to increase to 60 kg by 2000 and assumed to continue in growing by about 2% a year until the year 2015.

The consumption of plastic in Qatar is as shown in Table 1 below. It will be around 35,000 tons by the year 2000 and will reach 80 kg per capita by the year 2015. This consumption is about 2% of the total consumption in the GCC, as the population of Qatar is rated to the same percentage.

Table 1: The plastic consumption of Qatar

Year	Population (1000)[2]	Per Capita kg	Consumption Tons/Year
1996	450	38	17 100
2000	542	60	35 520
2005	590	66	38 900
2010	634	73	46 300
2015	676	80	54 000

PLASTIC AND RESINS PRODUCTION IN GCC AND QATAR

Plastic industry in the region started as early as 1956 in Saudi Arabia based on imported resins. Since then this industry is developed and improved to produce many plastic commodities, the number of plastic producers in the Gulf States were about 400 factories in 1996. These factories have produced about 1.8 million tons. The number of plastic producers About 85% of these factories are located in Saudi Arabia and UAE. About 40% of these producers are in the thermoplastic industry.

Plastic Commodities Industry in Qatar

The main plastic producers in Qatar were visited. A list of these producers are shown in Appendix 1.

These factories represent about 90% of the total plastic commodity producers in Qatar. From the above mentioned figure, the total plastic commodities produced in Qatar are:

LDPE +LLDPE	9100 tons/year
HDPE	1070 tons/year
PS	300 tons/Year
PP	155 tons/year
PVC	1900 tons/year

The total plastic produced in these factories is counted to about 12,500 tons/year. The total plastic produced in Qatar is around 14000 tons/year, which is equal to about 40% of total consumption of plastic. The rest of consumed plastic is imported from other Gulf countries or from India and Iran.

Resin Production

At present, most of the resins are produced in the GCC, such as :

PVC	Poly Vinyl Chloride
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
PP	Polypropylene
PS	Polystyrene
PET	Polyethylene Terphthalate

New projects in different stages are under consideration to produce new resins such as:

ABS	Acrylanitrile Butadiene Styrene
SAN	Styrene Acrylonitrile Nylon
PMMA	Poly(methyl Methacrylate)

Qatar, at present, produces only low density poly ethylene (400,000 tons/year). A new project is under implementation to produce in its first stage (by the year 2001) EDC - Ethylene Dichloride and MVC - Monovinyl Chloride and in the second stage will produce PVC. Other project is under consideration to produce LLDPE and HDPE (450,000 tons/year), and it is scheduled to start by year 2005.

The capacity of the GCC plants are presented in Table (2).

Table 2: Production of main resins in the GCC States (in thousand tons)(3)

Polymer	Year 1995	Year 2000	Producing Countries
Polyethylene (all types)	1290	2270	Qatar, KSA, Kuwait, Oman, UAE
Polystyrene	135	135	KSA
Poly Vinyl Chloride	300	550	KSA, Qatar
Poly Propylene	200	300	KSA, Kuwait, Oman
Total	**1925**	**3255**	

Almost two thirds of these resins are exported outside the region. See Table (3).

Table 3: Resins demand in GCC (1995)

Resins	Production 1000 tons/year	% Local Demand	% Export
LDPE, LLDPE and HDPE	1290	9.3	90.7
PP	200	39.0	61.0
PS	135	33.1	66.9
PVC	300	34.5	65.5

PLASTIC WASTE

The Town Waste

The per capita solid waste collected by the town waste collection authorities in the Gulf States is as follows: (2)

Country	kg per capita/day
Saudi Arabia	1.28
United Arab Emirates	2.10
Kuwait	2.10
Qatar	1.30
Bahrain	1.40
Sultanate of Oman	0.75
The average	***1.49***

The average value per capita of solid waste in GCC is almost the same as the per capita value in the United States of America (1.59), Norway (1.49) and Holland (1.37), but it is more than the per capita value in European countries (highest in Denmark 1.1 and lowest in Italy 0.68).

The total town solid waste in Qatar now is assumed to be about 257,000 tons/year. The waste analysis in Qatar stated that the plastic waste is 12% of the total waste, as shown in table (4), i.e. the plastic waste will reach the value of 31,000 tons/year.

Table 4: Qatar Waste Analysis (% by weight)(3)

Type of Waste	% wt
Textile	3
Bottles and Glass	3
Tins and Metal	5
Plastics	12
Paper and Cardboard	18
Vegetable and Putrescible	57
Miscellaneous (Wood, rubber etc)	2

Industrial Plastic waste

The main industrial plastic waste in Qatar comes from Qatar Petrochemical Company (QAPCO). The value of this waste is estimated to be about 500 tons/year of LDPE. The plastic waste from plastic producers is around 1000 tons/year of LDPE and about 100 tons/year of HDPE.

Waste Collection

The municipality solid waste in most big cities in the region, and in Doha is collected without any pre-collection sorting. Most of this waste is dumped in a sanitary landfill, and some waste is collected by individuals or companies such as paper, steel, plastic etc.

PLASTIC WASTE RECYCLING

The plastic waste recycling capacities in Qatar are 3350 tons/yr, 85% of these capacities to treat the LDPE and LLDPE waste, 12% for HDPE and 3% for PVC. The utilization factor of the available capacities is around 73%.

Most of plastic waste, recycled by plastic producers is based on their own waste, with the exception of two factories who also depend on some town plastic waste from QAPCO.

Most of the industrial plastic waste is recycled and reused (about 95%) to produce garbage bags and agriculture sheets, or exported outside Qatar. Only about 2% of the total town plastics waste is recycled.

In UAE, new plastic processors are now legally obliged to use 20% of their raw materials as plastic waste. This may also be implemented in other Gulf States in the near future.

ENVIRONMENTALLY DEGRADABLE PLASTICS

At present, no EDP is manufactured in any of the GCC States. Authorities in industry are cautious and not satisfied with the present performance and the future applications of EDPs,and, consequently the economic risk for industry. This is, in part, also due to the erroneous belief that there is no imminent plastic pollution problem (and therefore no need to substitute some of the present materials specially in harsh weather like that of the Gulf region) although there is a wide concern about other aspects of environmental pollution.

A recently proposed project is now under consideration in Qatar which involves establishment of a 6000 t/a plant, producing biodegradable plastic resins based on blending LDPE, HDPE or PP with calcium carbonate and chemical additives. The promoter of the project is a Korean company with a regional branch in Dubai.

The company claims that it has discovered a new biodegradable product by mixing certain additives with one of the above polymers according to the following recipe:

Polymer	59%
$CaCO_3$	40%
Additives	1%

The additives (stated to be 12 chemicals) are compounded separately, then mixed with the other two components and subjected to a compounding pelletizing machine. It is claimed that this polymer is biodegradable and posses comparable properties to, and cheaper by about 30% than the pure polymer. Further, it is possible to control its biodegradability, according to its application, by varying the composition of the additives. It can be used for a variety of applications such as shopping bags, disposable cups and trays, agriculture sheets, corrugated sheets, containers for diary products, water, juice, oil and other liquids. The Qatar Industrial Manufacturing company is cautiously considering the project.

CONCLUSIONS

1. The rate of consumption of plastic in Qatar and GCC is notably increasing leading to a high accumulation of the amount of plastic waste.

2. The procedure of solid waste collection, including plastic waste is still conventional without a suitable precollection sorting.

3. The recycling of industrial plastic waste in Qatar is well organized so that most of this waste (about 95%) is recycled.

4. The plastic town waste recycled is still negligible (about 2% only) depending on individual initiatives and rig pickers.

RECOMMENDATIONS

1. A comprehensive study is needed to determine the volume of waste and its main sources, and to elaborate available solution.

2. To encourage plastic producers for investing in the production of environmentally degradable plastics.

3. A precollection sorting system is required based on the following:

   i) The international coding system should be adopted to plastic products produced in Qatar which will facilitate the sorting procedure.

   ii) The resins and plastic producers should contribute in the cost of plastic recycling activities.

   iii) To implement deposit system based on reclaiming. This will encourage both the consumers and the rig pickers to collect more used plastics.

   iv) Raising the national perceptions of people about the hazards of pollution problems created by the growing volume of plastic waste. This should include educating school students and housewives.

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Appendix 1

The main plastic producers in Qatar are listed below:

1. Al-Rashid Plastic Factory

Products: Bags and Sheets
Resins: LDPE about 1700 tons/year
Recycling: 300 tons/year to be used by the factory 17.5% waste from the factory production.

2. Orient Plastic Container Factory

Products: Container, Bottles and Bags
Resins: LDPE (45%), HDPE(30%), PS(20%), PP(5%)
Total 1500 tons/year
Recycling: 150 tons/year, about 10% from the total production.

3. United Company for Manufacturing Plastic Items

Products: Pipes, Bags and Sheets
Resins: PVC, Polyethylene, LDPE
Recycling: 100 Tons of PVC
Small amounts of LDPE recycled and sold to other users.

4. Behzad Plastic Factory

Products: Bags, Sheets
Resins: LDPE, + HDPE
Recycling: No recycling. 6 tons/yr of own waste are sold to other users.
Capacity: 600 tons/yr
Production 450 tons/yr (75% utilization factor)
Manpower: 1 Engineer, 2 Supervisors, Total 12

5. Al-Zini Plastic factory

Products: Bags, Sheets
Resins: LDPE, HDPE and PP
Recycling: Capacity 1 ton/day
(300 tons/yr), production 0.6 t/day (60% utilization factor)
Capacity: LDPE 90 tons/month (1000 t/yr)
HDPE 40 tons/month (500 t/yr)
PP 7 tons/month (80 t/yr)

Products: Thrash bags HDPE 60% Prime Grade
40% Recycled Grade
+ Black Masterbatch

LDPE 100% recycled for thick bags and sheets, 60% Prime Grade and 40% recycled for LDPE thin bags and sheets + Masterbatch. Masterbatch about 16 kg/ton.

Manpower: 1 Supervisor - Total 80

6. Gulf Plastic Factory

Products: Bags (45 tons/month)
Resins: LDPE + HDPE
Recycling: 100 tons/month about 1000 tons/yr of HDPE and LDPE

7. Al-Aasima (Capital) Plastic Factory

Products: Recycled Plastics + Sheets
Resins: LDPE
Recycling: 1000 t/yr of HDPE and LDPE exported to UAE. The Sources of plastic waste are QAPCO, other plastic factories and Town plastic waste.
Capacity: 300 kgs/hr of sheets
Price: $550/ton, export prices CIF UAE

8. Qatar Plastic Products Company (QPPC)

Products: Heavy Duty Bags 2970 t/yr and shrinkable films700 t/yr.
Resins: About 2780 t/yr of LDPE and about 890 t/yr of LLDPE.
Recycling: 500 t/yr of LDPE and LLDPE.

9. National Plastic Factory

Products: PVC Pipes and LDPE bags
Capacity: 1800 t/yr of PVC Pipes
2100 t/yr of LDPE bags

Plastic Waste Management and the Position of EPDs in Slovakia

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Summary

Slovakia is a country with rather developed and extensive chemical industry. Production of plastics and plastic products is an important part of it. Thus, plastic waste disposal is an important issue in the policy of waste management of the country.

Landfill deposition is the prevailing way of waste disposal while recycling is the main process in the case of industrial plastics. Certain portion of waste is incinerated.

Environmentally degradable plastics are only used in rare special applications. The item is discussed on legislative level and few small research teams are active at universities and Academy of Sciences. The research done on biodegradable plastics is briefly described and some ideas are outlined on possibilities to attract an interest in EDPs of authorities, industry and public.

INTRODUCTION

Steady increase in plastic consumption in the world with growth rate 3.8 %/year indicates an important role of plastics in the daily life. While in 1994 total production of plastics was 108 million tons, the amount in 2000 is estimated to be around 135 million tons. With the increase of production and consumption the problem regarding plastic waste disposal is more pronounced. Although the portion of plastic waste in total amount of waste is not too high, being between 8 to 10 %, plastics industry is a target of severe criticism of green organizations. Therefore, the proper and efective management of plastic waste disposal is not only a technical and organizational issue but it is important also from point of view of the public image of plastics industry all over the world.

When discussing the situation in plastic waste management in Middle Europe, Slovakia may serve as a good example. Slovakia with its 5.5 millions citizens is a country with developed and extensive chemical industry. Chemical industry in Poland and Czech Republic is roughly at the same level, in Hungary it is less important, although many chemical plants are operating there as well. Nevertheless, the plastic waste disposal is of the same importance since the import of plastic goods is higher so that the portion of plastics in municipal waste is similar.

Chemical industry in Slovakia is the second largest industrial contributor (after machine industry) to gross national product of the country. Production of plastics and plastic products is an important part of it. Several large plants are producing plastics and some of them as well as numerous small companies make products from plastics by extrusion or injection moulding or using other technologies. The most important slovak chemical companies producing or processing plastics are Slovnaft (petro-chemistry, polyolefins), Matador (tires), Plastika (processing of polyolefins, pipes), Chemical plant Novaky (production and processing of PVC), Chemical plant Žilina (PMMA, polyamide 6), Chemosvit (fibers, mainly PP), Chemolak (adhesives and paints).

PRODUCTION AND DISPOSAL OF WASTE

Considering plastics production and consumption in Slovakia, it is not surprising that the portion of plastics in waste is close to that in highly developed countries, as seen in Fig. 1.

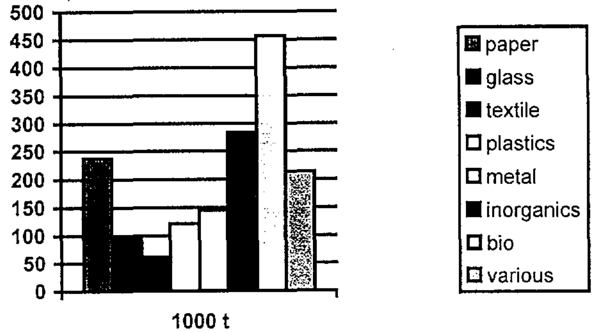

Figure 1: Municipal waste composition in Slovakia, data for 1995

The total amount of waste in 1995 was 1 620 000 tons. Plastics share was 121 000 tons, i.e. 7.5 wt. %. Considering density of various wastes, volume portion of plastics in waste represents 12 - 15%.

Of some interest regarding further discussion on environmentally degradable plastics (EDPs) are the data on the waste disposal. Primary industrial waste is usually recycled by the producers mixing a small amount of the waste with original polymer pellets. Municipal waste is disposed by various methods listed in Table 1.

Table 1: Municipal waste disposal methods. Data from 1996, total amount of municipal waste 1 685 964 t.

	Amount 1000 t	%
landfills	1 502	89.1
biological treatment	49	2.9
incinneration	85	5.0
energetic	0.06	0.003
various	20.7	1.2
exploitation	28.1	1.7

In the country there are 7 200 registered landfills, most of them unauthorized and in unappropriate technical shape. New landfills are built obeying the most advanced european standards. 76 incineration facilities serve for burning the waste. As seen in table 1, only very small portion of the heat generated is utilized for energetic purposes. Biological treatment and exploitation are mainly performed with agricultural waste, used as natural fertilizers or for a production of biogas.

LEGAL REGULATION SYSTEM

Legal regulation system is on rather high level, similar to or approaching to the most strict european standards. Ministery of Environment prepared a complex waste management programme and in 1991 a general Law on waste was approved by a parliament. Registration of wastes produced by companies and cities is required by law.

New laws and rules are prepared making the regulation system more and more compatible with EC.

In spite of the advanced regulation system, the application of the laws is not straightforward because of political (further increase of unemployment if the factories would be forced to stop production due to environmental requirements), economic (the economy is not strong enough, therefore it is difficult to force environmental actions which require a support from government) and local (lobbying, corruption, organized crime) reasons.

Dealing with plastics waste is focused mainly on recycling which is apparently, overestimated by the Ministery of Environment compared to other ways of dealing with waste. Several useful rules have been applied, e.g. a proposal for supporting the producers using recycled materials, or a discussion on a new law on packages. The primary plastic industrial waste is almost completely used mainly by the producers as an additive to original material or for less demanding applications. Many small and several larger companies are partially or fully involved in a business of plastics recycling. Recycling of automobile tyres has been developed, based on milling the tyres and application the rubber crumb as the additive in rubber mixtures or for special products.

ENVIRONMENTALLY DEGRADABLE PLASTICS

Taking into account the above mentioned points, the situation of EDPs is not on desired level in Slovakia. At present no application of environmentally degradable plastics is running. Main reason for this is a higher price of EDPs compared to conventional plastics used for the same purpose. The support from the Ministry of Environment is negligible, since, as mentioned above, the main stress regarding the plastic waste is aimed to recycling.

Economically less favourable but environmentally more friendly materials can be applied either if the loss due to a production is covered from external, mainly governmental funds or if public consumers are willing to accept higher price of certain product because they are aware of other benefits. Neither of these ways is promising in Slovakia at present : legal action, requiring the application of EDPs by law is questionable since there are no funds available necessary to finance such a regulation in situation when health care and education may be threatened by a collapse. A support from public opinion as a force to EDPs application seems to be too small at present. Therefore no producer is ready to start production of goods made from EDPs with high risk of long - term losses. Massive change of thinking could be a way to possible application of EDPs in the future.

At present the experts are discussing various aspects of EDPs application, such as the advantages of combination of bio- and photo-degradable materials or the effect of nondegraded remnants in soil. The former topic is related to more exact estimation and control of the lifetime of the EDPs to avoid premature extensive degradation during the application but fast degradation after expiring the lifetime of the product. The latter concerns mainly to the application of biodegradable LDPE/starch based foils in agriculture where the most important high volume application is expected.

Nevertheless, this discussion takes place exclusively on academic level. A discussion in broader range would be necessary, including governmental representatives, lawyers, and representatives of environmental NGO. The discussion should be broadly monitored by newspapers so that public would also be informed and influenced. A step towards this goal is going to be made by the organization of a workshop on EDPs in Smolenice, Slovakia, in October 1999.

CONCLUSION

Environmentally degradable plastics are rarely applied in Slovakia. In spite of a research done at universities and Academy of Sciences as well as a development in VUSAPL, Inc. resulting in original patents the industry is not willing to take a risk to start the production of biodegradable materials because of the high price of the products. No mechanism on governmental or NGO level was found up to now to promote the application of EDPs.

Plastic Waste Issues in Brazil and Some Countries in Latin America

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Abstract

Over the last few years the problem of plastic waste in Brazil and some other countries in Latin America has been receiving great attention since their production and consumption is growing fast. At present, about 76% of the urban solid waste produced in Brazil is discarded in open dumps. Despite the fact that they represent around 10% of the total solid waste, as compared with other waste materials, plastics take many years to degrade in the environment. Recycling is one of the most viable ways of decreasing the amount of plastic in urban wastes. In recent years, some kinds of plastic have gained significant importance in waste selective collection programs in Brazil; among them are LDPE, HDPE, PP and PET. A similar trend can be seen in Peru where the recycling of PVC and other thermoplastics materials from industrial and normal garbage has been carried out for the last 25 years. Other countries like Chile and Venezuela are working in the same direction, but unlike Brazil and Peru that have more than 300 companies devoted to recycling, they have few plants working on it. Recent research by the Brazilian Environment Ministry shows that great part of the Brazilian population is willing to cooperate with the selective collection and recycling involving the urban solid waste. Some programs developed by NGOs in South America are being recognized by the authorities as a standard model program to be adopted in other emerging countries. The utilization of EDPs is another viable way of continuing the sustainable development of plastics without causing environmental pollution. Therefore, the production of PHAs in Brazil will provide a promising alternative for all Latin Americans in the near future as demonstrated by the results obtained in the recent Workshop sponsored by ICS-UNIDO and some industries held in November 1998 in Campinas, São Paulo State - Brazil.

INTRODUCTION

BRAZIL (160 million inhabitants/1998)

As it is known, the recycling of plastics is classified as primary, secondary, tertiary or quaternary. The last two haven't attracted the interest of Brazilian industries due to important factors such as the high cost of producing monomers/oligomers and the lack of technology for chemical degradation and incineration. Primary recycling, which involves the reprocessing of non-consumed plastic pieces and parts rejected by quality control and secondary recycling, relating to mechanical processing of polymeric post-consumer materials, are being adopted now.

Recent studies by IBICT- Brazilian Institute of Information in Science and Technology - show that 150 projects are being implemented in the field of recycling in Brazil. 90% of this work is being carried out by about 300 researchers from 63 separate research groups inside the Universities, whilst the other 10% is being carried out by the Government and private Institutions.

Studies made by IBICT show that 500 technical scientific papers, 3 videos and 8 softwares packages on the subject have already been produced. A further 14 patents are already being used by some companies, are waiting approval. The know how in recycling that is being developed in the country will, with no doubt, put it in a distinguished position in future. Table 1 shows some of the active Institutions in this area at the moment.

Table 1: Some Brazilian Institutions working on recycling (1)

INSTITUTION	ADDRESS	RESEARCHES & PROGRAMME
Center of Packaging Technology CETEA	Http://www.cetea.ital.org.br Phone: +55-(19)241-5111 Fax: +55-(19)241 8445	Evaluation and policy of norms for packagings.
Macromolecules Institute/ Federal University of Rio de Janeiro	Hemais@acd.ufrj.br Phone +55-(21) 560-5455 Fax +55-(21) 590-0541	Recycling of polymers (plastics and elastomers).
3R Recycling of Plastics/ Federal University of São Carlos	Http://www.ufscar.br/portugues/projetos/3r-nrr/home.html Phone:+55-(16)260-8250 Fax: +55-(16) 261-5404	Recycling of plastics materials and statistical studies of the domestic solid waste.
USP (University of São Paulo) Recicla	Phone: +55-(11) 818-4428 Fax: +55-(11) 211-0922 Hwiebeck@usp.br	Educative programme regarding to the consumption and disposable of plastics. Developing of new technologies for recycling.
UNICAMP (State University of Campinas)	Lumeibit@dtp.feq.unicamp.br	
Laboratory of Solid Residues and Compounds of Paulista State University (UNESP-Botucatu)	Phone: +55-(14) 831-3883 , ext. 162/163. Fax: +55-(14) 821- 3438	Developing of new technologies for recycling of the urban waste.

The potential recycling of waste usually depends on economic factors, such as available quantities, market value of the reclaimed products and available reclaiming equipments.

Recent research developed by CEMPRE (Brazilian Business Commitment for Recycling) has shown that the willingness of Brazilians regarding selective waste collection is growing together with consumption that stands at 1.8 million tons/year, (Figure 1) (2).

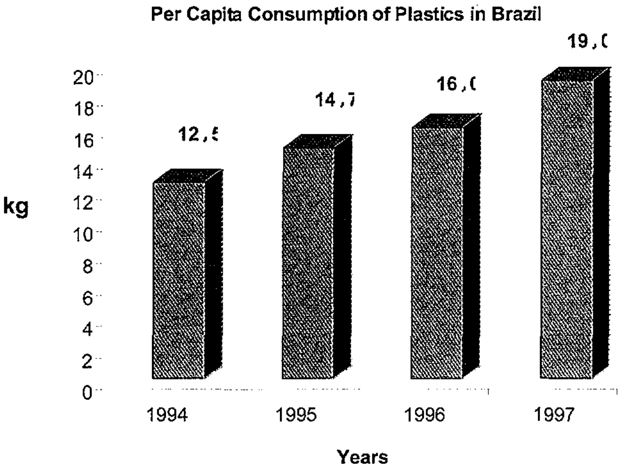

Figure 1

The increasing rate of consumption and the growing amount of discarded plastics containers in urban waste, is motivating the Brazilian industrial segment to think of recycling as a profitable business. Figure 2 shows commom plastics found in the Brazilian wastes in 1995.

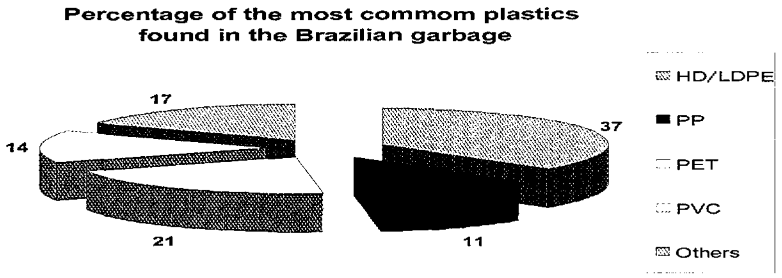

Figure 2

A survey conducted in 1995, showed that plastic made up around 18% of the total waste collected in 7 important cities in Brazil (Santos, S_o Paulo, Curitiba, Porto Alegre, Salvador, Florianópolis and S_o José dos Campos). Among the plastics found in the waste was PET, one plastic with an increasing rate of consumption. In Brazil, PET bottles were introduced in 1988, 12 years after their introduction in the American market. Despite this delay, the consumption of PET packagings has grown quickly, as shown in Figure 3, due to the relatively low price of the resin (3, 4).

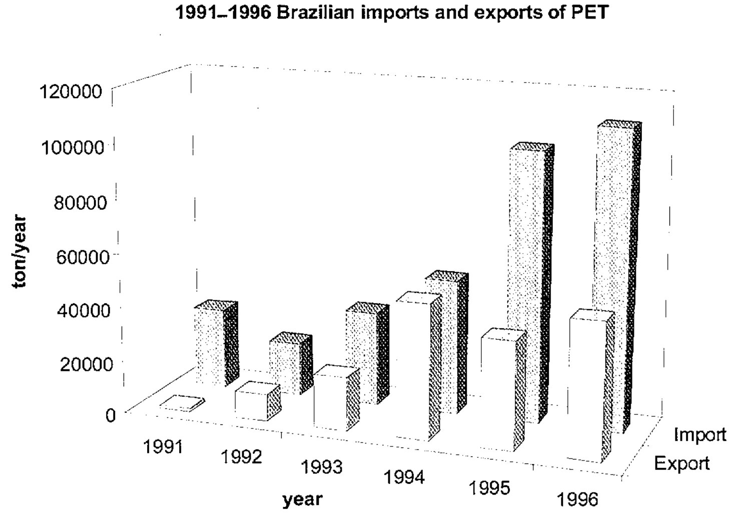

Figure 3

The privileged mechanical and thermal properties of PET, besides its aggregate value, also make this plastic very attractive.

The first PET recycling units appeared in the 90_s and since then the number of these units has been increasing year after year. In Brazil, the principal market for recycled PET is the textile market.

Jeans composed of cotton fiber and recycled PET are already being used in the country and the market for the client who is concerned about the environment is expanding greatly. In other countries this market has already been consolidated.

Table 2 shows the location, capacity and products made by PET recycling companies in Brazil. At present, these companies are concentrated in the south-east and south regions of the country. Although nominal capacity is over 40,000 ton/year, official information shows that about 30,000 ton was effectively recycled in 1997.

Another plastic that is at the center of many discussions is PVC, as some products made from this material, like tubes and pipes for drinking water, flooring, roofing, cable and wire coatings, doors,etc. have a lifetime of around 100 years. As presented by Edison Carlos (5), a Solvay representative in Brazil, this makes it difficult to develop formulations of a material with biodegrading characteristics. So, the best solution in this case is a stringent control of PVC waste. An important example of control actions, is the strong waste reduction by a major producer of PVC tubes in Brazil which accounts for more than 50% of the consumption of all PVC produced in the country. Efforts are directed to reduce this kind of waste such as the investments made to automate the resin transport and loading, the process of resins and additives blending, and others. Once blended, the PVC compound is automatically fed into the extruders and injection molding machines. The losses of this process used to be 5 or 6% before the investments, it is now around 1%. Even this amount is crushed and reintroduced to machines. When non-usable waste is generated, this material is sold for small recyclers. One good source of post-consumed PVC for recycling are the cables coated with this plastic. PVC, after being separated from the cable and crushed it worths up to R$500.00 per ton (~$300.00). This makes this kind of market very profitable and makes it difficult to find great quantities of PVC waste in the market. In Table 3, some PVC recyclers at Great São Paulo are listed.

Table 2: PET Recycling Companies in Brazil (1988) (3)

Company	Location (City, State)	Nominal Capacity (Ton/year)	Products
RECIPET	Indaiatuba,SP	18,000*	Pelletes for multilayer packaging, bottles, sheets, fibers and geotextiles
REPET/UNNAFIBRAS	Mauá,SP	10,000	Pellets for fibers/fibers
ARTEPLAS	Itajaí,SC	4,000	Pellets, ropes and yarns
ECOFABRIL	Jundiaí,SP	4,800	Flakes for fibers
FIBRASCA	Joinville,SC	2,400	Fiberfill for pillows, plush, ropes and yarns.
BETTAMIN	Esteio,RS	-	Bristle for brooms and brushes.
RIOPET**	Rio de Janeiro,RJ	6,000	Flakes for multilayer packaging.

* Production in 1997 : 15,000 ton
** Starting December, 1998

Table 3: PVC recyclers at São Paulo city (5)

RECYCLING COMPANY	SOURCES OF RAW MATERIAL	FINAL PRODUCT
CAPP	Wire and cables and industrial scraps.	Hoses, shoe soles.
LUMAPLASTIC	Packagings, tubes,ceiling, industrial scraps.	Tubes.
Arteplás	Scraps from extrusion and injection processess and coating of wire and cables.	Flexible sheets.
Waltubo	Post-consumed: (100%) of thermosetting	Conductors for electricity.
	Scraps from electric guides, shoe soles, vinyl balls.	Electric outlets, hoses, shoe soles.

In spite of all the efforts of the ONG's like CEMPRE and some other educating programmes, total control of plastic waste pollution is still a dream. As can be seen from Figure 4, the destination of the majority of urban waste in Brazil is still the open dumps.

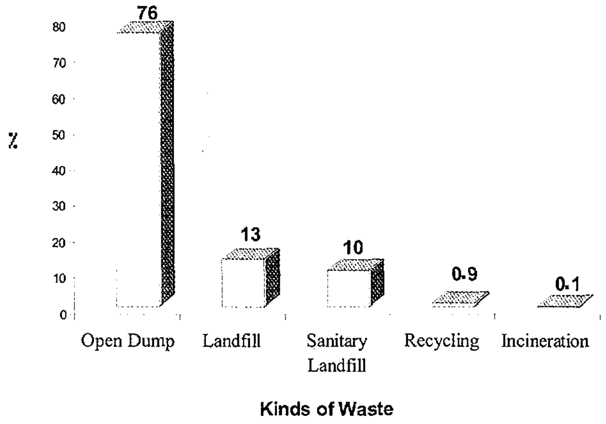

Figure 4: The Destination of Urban Waste in Brazil

It is easy to understand this situation when we compare the price of the selective with normal collection of waste. In Brazil, the average cost of a waste selective collection programme is around $240 per ton of waste collected, while the cost with normal collection is $20 per ton collected. In recent years, some kinds of plastics have gained significant importance in waste selective collection programmes in Brazil, reversing the trend of low-added value and the resulting lack of interest. Among these plastics are LDPE, HDPE, PP and PET. Figures 5 and 6 show some pictures of selective collection.

Figure 5: Warehouse of sorting in Campinas / S_o Paulo State

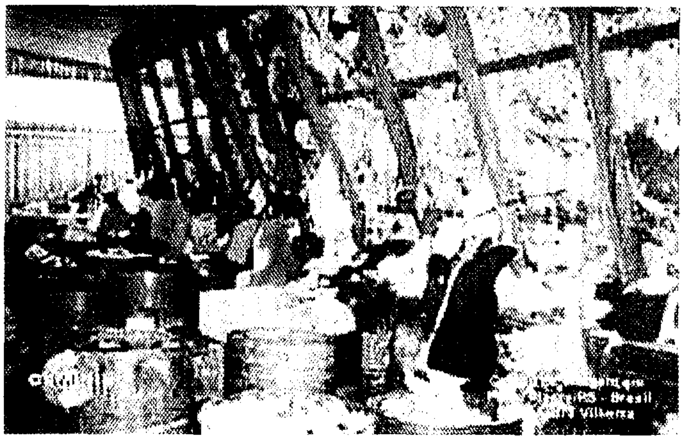

Figure 6: Warehouse of sorting in Porto Alegre / RS

According to Dr. André Vilhena (2), trade in plastic scrap can vary significantly with the direct involvement of cooperatives of street scavengers, scrap dealers and recyclers. The consumption per capita of plastics in Brazil is growing. The supply of this material is expected to increase as a result of waste selective collection programmes scattered around the country. This is expected to ensure greater regularity and quantity of the supply to the recycling industry. Yet, better operating conditions at the majority of plastics recyclers in Brazil are needed since the conditions now are not desirable, as shown in Figure 7 .

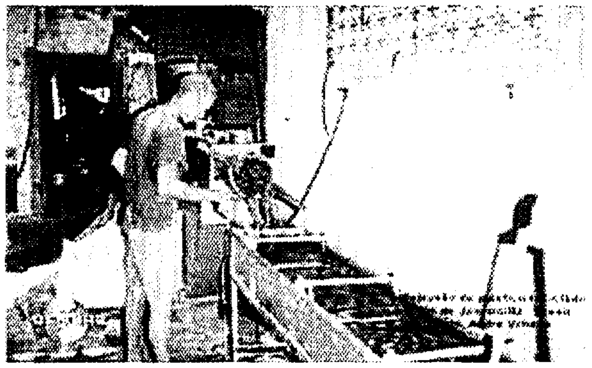

Figure 7: Extrusion of recycled plastic in Rio de Janeiro / RJ

The relevant economic aspects of the present and the future market of recycling in Brazil are shown in Table 4 below, (1);

Table 4: Variation of prices of trash in 1994 (US$/ton) *

MATERIALS	JUNE	AUGUST	OCTOBER
PET	94	133	126
Film plastic	107	93	103
Rigid plastic	83	136	123
Glass	132	37	31
Aluminum	635	495	478
Steel can	72	76	49
White paper	150	123	117
Cardboard	125	128	81

* Average price of 11 consults to programs of seletive collection and cooperative of collectors in various regions of the country.

Regarding the Brazilian situation on plastics recycling, some important points are essential for the success of the recycling companies and the educating programmes:

-First, more investments should be made in order to improve the selective collection and increase the supply of raw materials for the recycling industries. This could be done by offering better conditions to the poor people that earn a living from the selective collection of the waste. Regarding this, there are in Brazil some incentives to the recyclers that come from NGOs like CEMPRE; companies from other industrial segments and foreign government donations.

-Second, an improvement in the technological sector is necessary to improve and increase the installed capacity. Finally, the expansion and discovery of new markets and applications for the final recycled product is the key for the future. We believe that these points are the aim of every country in Latin America too, in spite of our differences.

A look at the situation of some countries in Latin America indicates that the recycling is the main alternative for plastic wastes, as it is in Brazil.

PERU (23, 7 million inhabitants/1995)

Plastics such as HDPE, LDPE, PP, PS and compounds of PVC, from sanitary and industrial landfills, have been recycled for more than 25 years. According to Velarde and Pérez (6), the lack of a Petrochemical facility as well as proper policy regarding environmental issues in Peru means more than 500 companies are dedicated to the recycling of plastic garbage.

As those companies are not afilliated to the Society of Industries in Peru, it becomes difficult to get any data about the production or volume of plastics produced. In any case, it is known that about 75% of these industries produce the ground of plastic and the remaining 25% work up to the final products such as bags, buckets, washtubs, toys without quality control. These are mostly illegal enterprises producing about 80% of black bags, and 50% of toys products in Peru. Their contribution is not significant due to the low performance of production and degradation of their products.

Detailed research shows that the economical situation is more important than the environmental necessity, basically because of the economic value of the systems of recovery, storage, transport, etc. At the beginning, raw materials didn't have to pay freight, but as the demand went up, this cost became important. Table 5 shows the prices of raw materials in the landfills according to ESLIMP (Empresa de Limpieza Pública del Distrito de Callao).

Table 5: Prices of Raw Materials in the Sanitary Landfill in Peru

MATERIALS	PRICE ($ / KG)
PE and PP	0.09
Bottles of oils (PVC)*	0.14
Films (PE and PP of extrusion)	0.12
Tennis shoes or sneakers (PVC)	0.21
PVC for shoes without canvas or toe-cap	0.38

OBS: PVC bottles are now replaced by PET

These are increased by about 30% by the wholesalers depending on the grade of quality and contamination of the materials. Furthermore, recycling is expensive since in Peru there is no equipment specially designed for plastic recycling but only old machinery adapted to these process. Therefore, bad quality materials with high costs are processed and its consumers represent a small group of the industry dealing with the processing of plastics. It is difficult to determine the amount of plastic consumption and the record of production as many manufacturers are illegal and work with people who are not authorized by Peruvian Law to collect garbage. Yet, the central Government and the city halls do not incentivate recycling nor do they take political actions to face the problem and establish a mandate organizing the process. The present conditions are considered inadequate and the enterprises that deal with the segregation do not pay taxes on the raw material or other social benefits to their workers and some of them do not pay taxes to the city halls. According to Velarde and Pérez, the recycling process will constitute a form of reducing the environmental contamination but the import of new technologies are needed in order to optimize the productive processes in such a way that they will be more efficient and economical.

VENEZUELA (22,3 million inhabitants/1996)

A presentation by Rojas de Gáscue (7) at the WEDPLA'98 showed that only few companies (around 20), localized in the middle-western region of Venezuela are dedicated to the recycling of plastics. The majority of plastic materials that are recovered come from industrial waste. Less than 30% of this amount corresponds to post-consumption waste. There are few centers dedicated to collection, separation and cleaning of plastic waste performed by workers without any advanced technology. Normally these materials are sold after being grounded. The final consumers of these recycled materials are the companies that produce toys, pipes, brushes,etc. These companies are responsible for only 2% of total plastic consumption in Venezuela. This low rate of recycling is due partially to the lack of awareness of the consumers about the necessity of practicing plastic waste selection as this represents a high cost process for recycling companies. So, it would be very appropriate for the Venezuelan industries that work with plastics to motivate and raise the perception of the population about the social and environmental benefits of recycling.

CHILE (14,887 million inhabitants/1997)

Data presented recently by Cárdenas at the WEDPLA_98 shows that in Chile the situation is not so different from its neighbours in Latin America.

As shown by Cárdenas (8), the amount of plastics used in packaging is about 32% , being followed by 20% consumed by industries, 14% in construction and 5% in other areas (toys industries, tools, transport, etc).

From 1992 to 1997, the consumption per capita of plastics has increased by about 50% as shown from Figure 8 below;

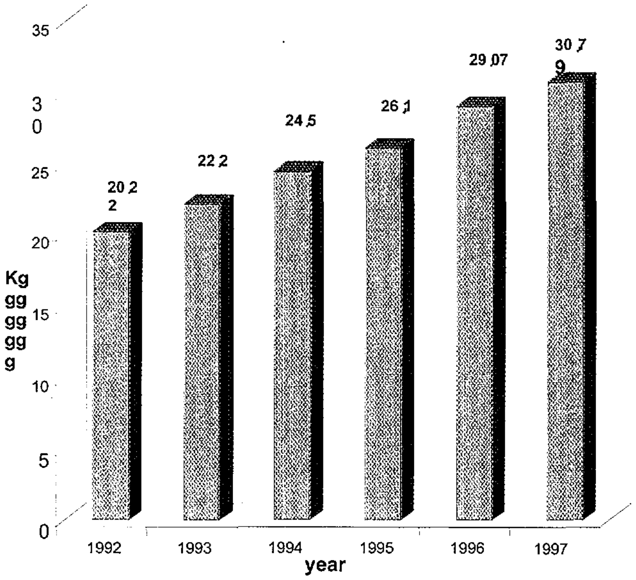

Figure 8: Chile Consumption of Plastic per capita

It is interesting to note that, despite the fact that their production and consumption of plastics is growing fast, there is no legislation to control the environment, safety of the workers and the areas around plastic plants. At the moment, there are few companies working on recycling of polymers and re-using raw materials, as can be seen from Table 6.

Table 6: Polymers Recyclers in Chile

INDUSTRIES	PRODUCT	VOLUME (TONS/MONTH)
Eletroquímicas Unidas	HDPE (75%) LDPE(25%)	50
Polymer S.A.	PP (30%) PS (70%)	184
Williamson Balfour	PET PE	12.6 1
Plastic Chile	HDPE LDPE PP ABS	30 30 15 10

According to Cárdenas, the selective collection of plastics from the garbage deposits has only started in Santiago. The use of toxic monomers without safety is a problem to be considered and the industries such as the polyurethane foam industry are more concerned about this issue. Environmentally degradable plastics (EDP's) is an interesting area that should be explored in Chile as the country has a great demand for the utilization of EDPs.

COLOMBIA (35,1 million inhabitants/1995)

The discussions on plastic wastes are as recent in Colombia as they are in Chile. According to Zuluaga (9), in 1995 a study on solid waste disposal in Colombia was promoted by the Ministry of the Environment, in collaboration with the World Bank, and the World Health Organization. However, only in August 1997, the Ministry produced a document entitled "Policy for Integral Management of Waste", after a meeting with representatives of some Associations of Plastic Producers, NGOs, Regional Corporations and others. As a result of this meeting, four regional groups were formed with the general objective to "avoid or minimize any risk for the population or the environment caused by solid waste and to minimize the amount of dangerous solid waste reaching disposal sites...". In spite of this, no specific policies were proposed regarding plastic recycling. This issue is just starting to be discussed in Colombia. If we don't take into account the amount of organics in the solid waste, using the data supplied by EMSIRVA (Municipal waste collection and cleaning company) in Table 7, it is clear that the amount of plastics is significant and certainly will be more in the future as the projection of plastic waste generation in the near future (Table 8) shows.

Table 7: Distribution of Solid Waste in Colombia according to the type of material

TYPE OF MATERIAL	DISTRIBUTION (% weight)
Organics	79.92
Paper and paper boards	7.60
Cotton fabrics	2.00
Bones	0.23
Plastics	**5.71**
Glass	1.59
Metals	1.02
Others	1.92

Table 8: Projection of the plastic waste generation from 1996 to 2000 in Colombia

YEAR	EXPECTED POPULATION	PLASTIC WASTE (ton/year)
1996	1,946 200	27,817
1997	1,992 100	33,167
1998	2,078 800	39,760
1999	2,078 800	46,375
2000	2,161 400	57,765

As presented by Zuluaga (9), the CDT-ASTIN (Center for Technological Development) has proposed a 10 years project (1998-2008) dedicated to plastic recycling. The main candidates for recycling are the commom packaging polymeric materials used in Cali (the second largest city in Colombia) for instance , where we may find plastics as PS, PP, LDPE, HDPE and PET. A PET recycling plant in Medellín was built by COODESARROLLO. The goal at first was to produce 120 tons in 1997; 200 tons in 1998 and 5000 in 2007 but following personal contacts with the company, Zuluaga states that minimal success has been achieved in the collection of PET. The Ministry of the Environment, in June/1998, promoted a project to recover PET. The goal was to get 15 industries to participate but up to now there are only 8 involved. Each of them have invested US$10,000 and with the advice of a Brazilian company, they have started economic feasibility studies.

It is important to note that there is no official or private campaign relating to the selective collection of these wastes from the whole trash. However, as in other countries in Latin America, many poor people have made a way of living from recovering solid waste including plastics.

In conclusion, recycling in Colombia seems to be a promising business but the discussion on national policies on this subject , with the participation of the Ministry of Environment, and some private and official organizations, has just started.

MEXICO

The plastic markets in Mexico are not mature according to Oscar Carrillo (1). However, the markets are waiting to be developed. Mexican plastics producers are interested in importing U.S. recovered plastics and produce finished products with inexpensive labor costs. The commercial opening of NAFTA offers numerous opportunities for exporting finished plastics products duty free to the U.S.

Nowadays, growing concerns in the environment is bringing greater opportunities in the area of recycling without the need to invest in new resins. Figure 9 shows the general composition of the Municipal Solid Waste (MSW) in Mexico city.

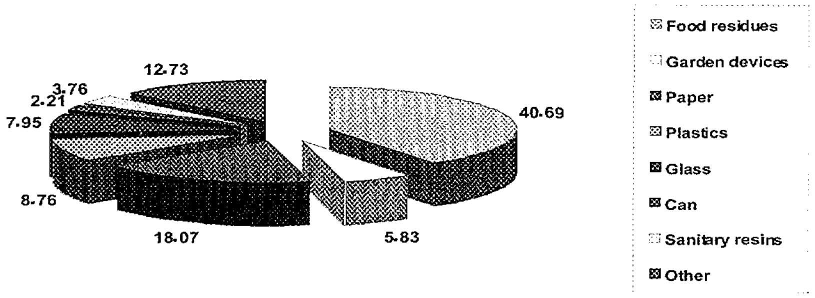

Figure 9: General Composition of the Solid Municipal Waste in Mexico City on 1995

In 1987, it was estimated that 10,000 inhabitants of the Federal District, of all ages, were involved directly in scavengers operations without legal protection or social security, receiving low incomes and living under unhealthy conditions. At that time, the products obtained by recycling wastes are summarized in Table 9.

Table 9: Products obtained by recycling waste in Mexico in 1987

WASTE MATERIAL	FINAL PRODUCT
Remains of sugar cane	Paper
Waste paper & cardboard	Reprocessed paper & cardboard
HDPE	**Plastic stands**
Scrap pieces of tyres rubber	**Fenders for lorries**
Natural rubber, nylon cord and steel wire	**Tyres**
PE other densities and PVC	**Water pipes and electrical conduits**
Pine wood	Fuel briquetts
Glass pieces	All types of glassware
Fiber glass	Fiber glass for isolating thermostats
Hard plastic	**Games, sandals,etc**
Plastic films	**Cellulose**
Bottles	Returned to bottling manufacturers

More recent data, published in the ecological folder #5, of the "Associacion de Tiendas de Autoservicio y Departamentales" linked to the International Institute of Recycling in Mexico, show the products obtained by recycled plastics in Table 10.

Table 10: Types of Resins Recycled in Mexico, in 1995, and the products generated

TYPES OF RESIN	RECYCLED PRODUCTS
PET	Polyester fibers, screens, carpet Fibers for stuffing of clothes,brushes, tacks, video cassette boxes.
HDPE	Botellas para cosmetics and shampoo. Envases for motor oil and chemical products.
PVC	Electrical cables covering Cones for traffic guides, garden hose.
LDPE	Plastic bags for domestic wastes. Mulchs. Sticks for broom and brushes .
PP	Cones and coils for textile industry. Toys. Automotive devices.
PS	Shoe heels, office accessories, building industries devices.
Mixed resins	Tables, chairs, kiosks, sign posts.

ARGENTINA (35 million inhabitants/1995)

According to Bertolino (1), there was no National Plan in Argentina to advise the population about the problem caused by waste. Some Universities and Environmental Associations have been working but there is no effective interest from the local authorities or financial support to develop educating programmes. Despite of this, in the last years, some advances were witnessed in the field of recycling with the participation of some industries, schools, city councils and the media.

A study on 30 small cities in Argentina provided important data about the types and the amount of wastes found in the domestic wastes, as can be seen in Table 11 below.

Table 11: Composition of the domestic wastes/ person /year, generated in 30 small and middle cities in Argentina (1996-1997) (1)

TYPES OF RESIDUES	Kg /Inhabitant/Year	%
Organic Materials	130.7	48.3
Inorganic Materials	70.1	25.9
Plastics	20.1	7.4
Papers & Cardboards	14.2	5.2
Glasses	12.0	4.4
Clothes	1.8	0.7
Metals	1.8	0.7
Others	20.1	7.4
Total	270,8	100.0

If we look at the capital of Argentina, Buenos Aires, alone we can see that the composition of plastics in the domestic waste is significant, as shown in Table 12.

Table 12: Composition (in %) of the domestic wastes generated in Buenos Aires in 1997 (1)

MATERIALS	%
Plastics	10
Organics	55
Papers and cardboards	18
Metals	10
Others	7

Nowadays, there is a plan for the utilization of the domestic solid residues (PUPRSD) to the collection and selection of the waste that is growing time by time with the adhesion of the population. The main topics of this plan are;

- To spread the idea of selective waste collection in the whole country;
- To reduce the environmental contamination;
- Composting of the organic wastes that are not contaminated with pathogenic components;
- Generation and diffusion of knowledge;
- Organization of Ecoclubs;
- Norms to dispose the residues.

MISCELLANEOUS (1)

Appendix A1: Total Population of Latin America and Caribe (x 1,000)

COUNTRIES	1980	1990	1995
Antigua and Barbuda	61	64	68
Antillas Netherlands	174	190	199
Argentina	114	32,547	34,587
Bahamas	210	256	276
Barbados	249	257	262
Belize	146	189	215
Bolivia	5,355	6,573	7,414
Brazil	121,286	148,477	161,790
Chile	11,147	13,100	14,210
Colombia	26,525	32,300	35,101
Costa Rica	2,284	3,035	3,424
Cuba	9,710	10,598	11,041
Dominica	74	71	71
Ecuador	7,961	10,264	11,460
El Salvador	4,525	5,172	5,768
Granada	89	91	92
Guadalupe	327	391	428
Guatemala	6,917	9,197	10,621
Guyana	759	793	835
Haiti	5,353	6,486	7,180
Honduras	3,569	4,879	5,654
Jamaica	2,133	2,366	2,447
Mexico	67,570	83,226	91,145
Nicaragua	2,802	3,676	4,433
Panama	1,950	2,398	2,631
Paraguay	3,136	4,317	4,960
Peru	17,324	21,596	23,532
Republica Dominicana	5,697	7,110	7,823
Saint Kitts and Nevis	47	42	41
Santa Lucia	115	133	142
San Vicente las Granadinas	98	107	112
Suriname	355	400	423
Trinidad and Tabago	1,082	1,236	1,306
Uruguay	2,914	3,094	3,186
Venezuela	15,091	19,502	21,844
TOTAL	**355,1**	**434,1**	**474,7**

* OBS: These data may vary according to the source of information.

Appendix A2: Composition of municipal solid waste in various countries of Latin America (% weight)

COUNTRY	PLASTICS	METALS	ORGANICS	PAPERS	GLASSES
Argentina (96)	**8.2**	3.9	53.2	20.3	8.1
Bolivia (94)	**4.3**	2.3	59.5	6.2	3.5
Brazil (96)	**3.0**	4.0	-	25.0	3.0
Chile (92)	**10.3**	2.3	49.3	18.8	1.6
Colombia (96)	**14.2**	1.6	52.3	18.3	4.6
Costa Rica	**11.0**	-	58.0	19.0	2.0
Ecuador (94)	**4.5**	1.6	71.4	10.5	2.2
El Salvador	**6.1**	0.8	43.0	18.0	0.8
Guatemala (91)	**8.1**	1.8	63.3	13.9	3.2
Mexico	**6.1**	3.2	43.0	20.0	8.2
Peru	**3.2**	2.1	50.0	10.0	1.3
Paraguay (95)	**4.2**	1.3	56.6	10.2	3.5
Trinidad & Tobaco	**20.0**	10.0	27.0	20.0	10.0
Uruguay (96)	**13.0**	7.0	56.0	8.0	4.0

ACKNOWLEDGEMENT

This work wouldn't be possible without the contributions of all participants of Latin America in the "Workshop on Environmentally Degradable & Recyclable Polymers in Latin America-WEDPLA'98", held in Brazil, November 15-20 / 1999 under the auspicious of ICS-UNIDO and the special collaboration of Profs. Stanislav Miertus and Emo Chiellini from ICS, and Dr. André Vilhena from CEMPRE.

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* All these authors published their contributions in the Proceedings of the "Workshop on Environmentally Degradable & Recyclable Polymers in Latin America- WEDPLA'98", held in Brazil on November, 1998.

Plastic Waste Management in Austria

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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 (20 kg less), and the Netherlands had the highest consumption of such materials (210 kg). Details are given in Figure 1, but it can be said, that these quantities are in the same range that can be found in other countries of the western world, even though it has to be mentioned, that the Austrian data have been influenced by strict laws starting to bring first results in 1995.

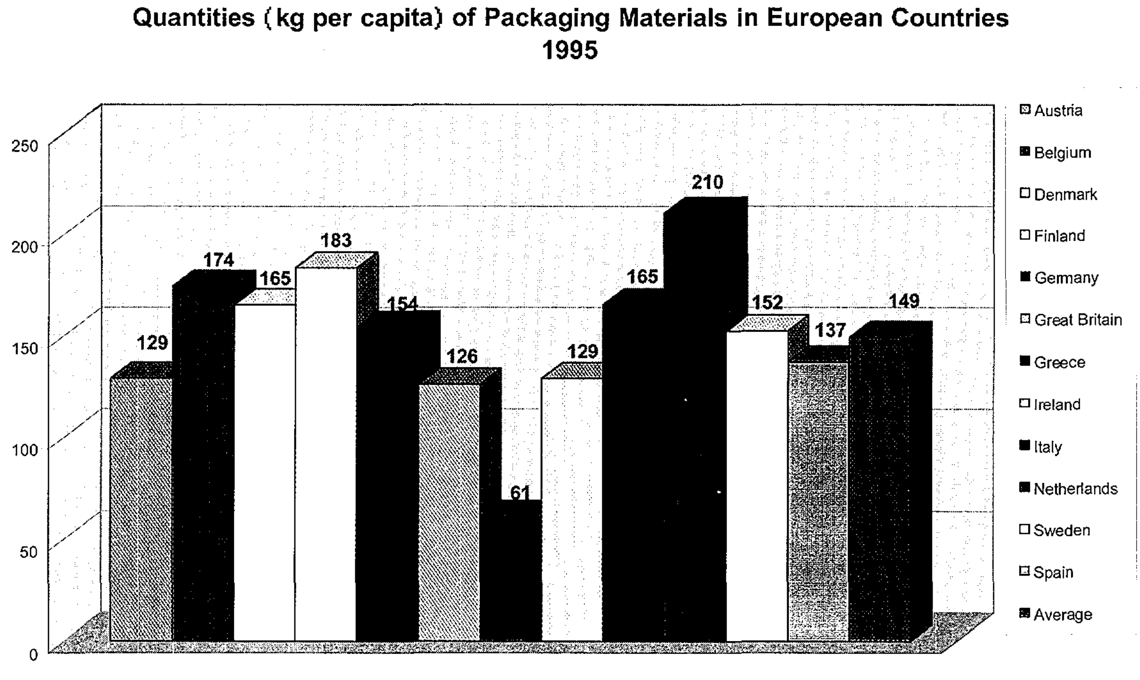

Figure 1: Quantities of plastic packaging materials (kg per capita) used in European countries in 1995

Rising Quantities of plastic waste materials have started to become a problem in Austria in the early 90. As can be seen from Table 1, a total of 763500 tons of plastic waste had to be handled. Part of it 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%).

handled. Part of it 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%).

Table 1: Treatment of Plastic Waste (in tons) in Austria (1994) before governmental regulations

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

Due to strict regulations 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 is 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 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

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 licence-fees and transfers the money to ARGEV and ÖKK, ARGEV: organizes collection and sorting of plastic packagings, execution then is done by disposal companies, that are contract-partners,

ÖKK: organizes, coordinates, and controls the recovery of all collected plastic-packaging materials. Recovery is executed in seven national and two international plants situated in Switzerland and in the Netherlands.

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. License tariffs are divided into three groups, depending on the volumes of waste plastic packagings. 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 have been spent as is shown in Table 3.

Table 3: Money spent 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 4) of this collected waste could be reused, the rest (46101 tons) was used for energy recovery under strict governmental regulation and control.

Table 4: 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 2 and 3)

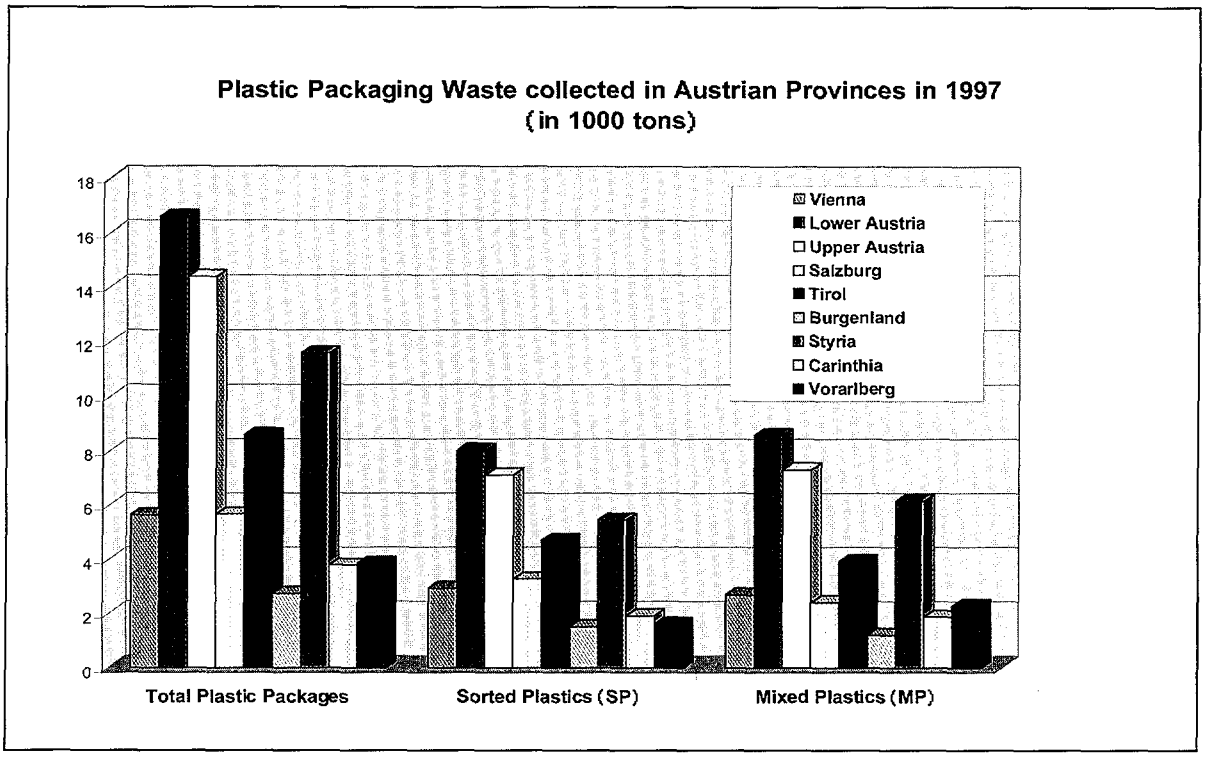

Figure 2: Plastic Waste collection in Austrian Provinces

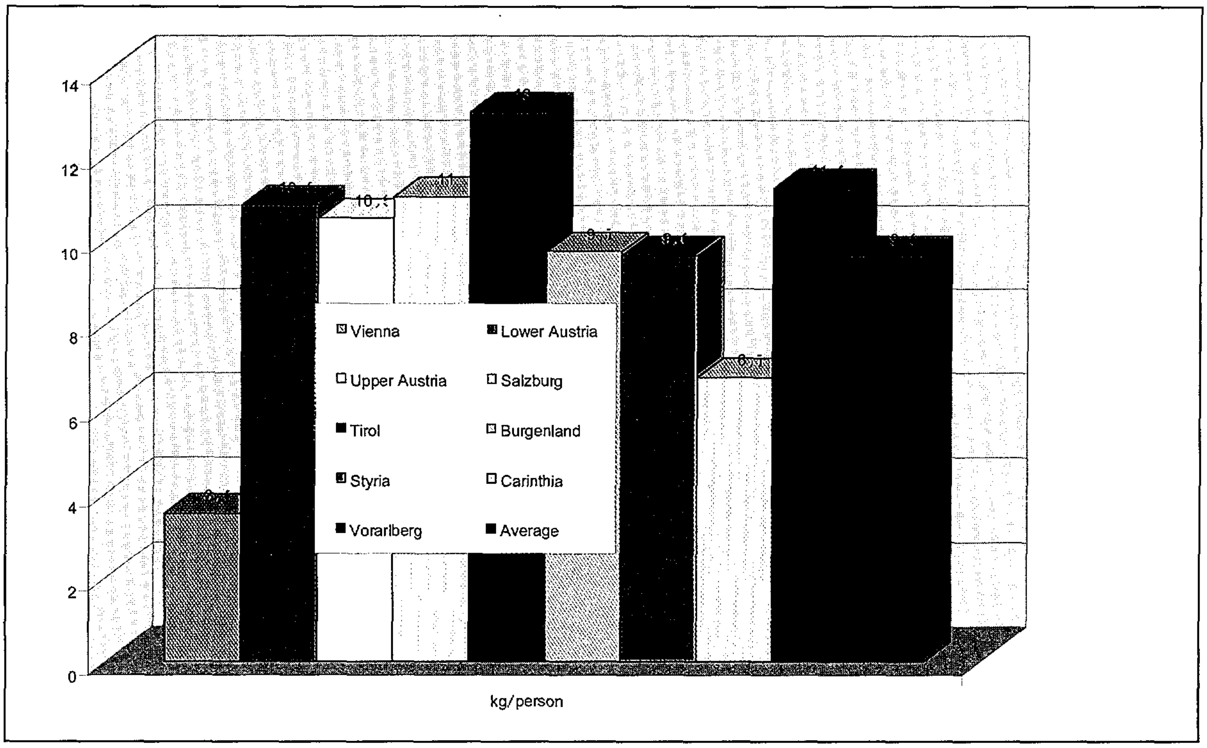

Figure 3: Plastic Packaging Waste Collection 1997 per capita in Austrian Provinces

Incineration of plastic packaging waste is of course of interest for energy recovery from such materials. Heating values are compared in Figure 4.

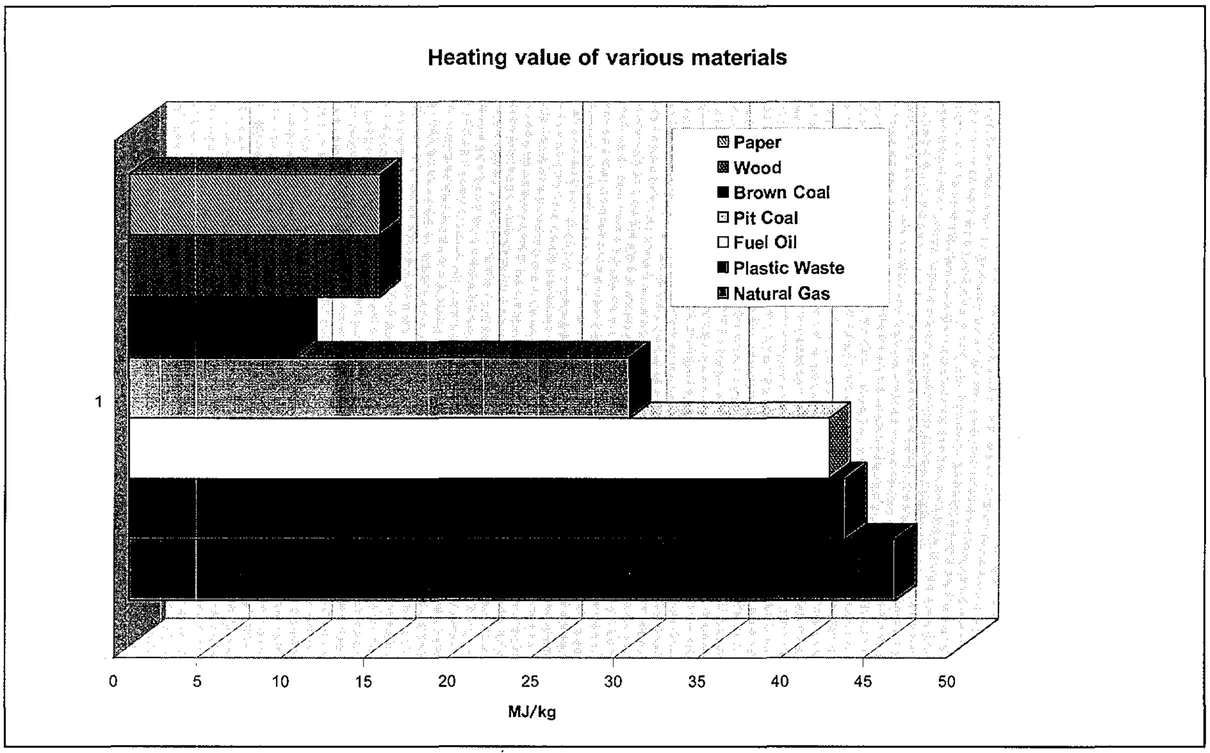

Figure 4: Heating values for various combustible materials

However, there are concerns 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 5) have to be followed for specialized plants, having the allowance for plastic waste incineration (Table 6).

Table 5:Requirements for Energy Recovery from Plastic Waste

- Observance of Emission Standards
- No Increase of Emissions of Harmful Substances
- A Maximum Emission of 0,1ng Dioxin TE/m^3 allowed
- Direct Substitution of Conventional Fuels by Packaging Waste and therefore Reduction of the Consumption of Natural Resources has to beProved
- Optimum Recovery of the Energy
- Defined Quality of the Material to be Incinerated is Needed

Table 6: Energy Recovery from the Mixed-Plastic-Fraction

1994: Cement producers started adaptation of their plants for the use of shredded plastic waste (mixed fraction)

1998: 3 cement factories 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 quantities for land filling will be further reduced, and hopefully environmentally degradable polymers and plastics will be integrated into the Austrian Packaging Order. In the moment such packaging material is used in rather low quantities, but does not show up in statistic data separately.

Plastic Waste Management in Egypt

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Abstract

Plastic waste is becoming a serious problem and needs an urgent environmentally friendly solution. Plastic production, waste generation and waste recovery in Egypt are discussed in this article.

Plastic production in Egypt is expected to reach 75 million kg/year by the year 2000 and plastic waste will reach 38 million kg/year. The % of plastic waste in MSW in Egypt is 9%.

Analytical cases for plastic waste generation in hotels, hospitals and student hostels are reviewed.

Also, traditional practices, new trends and technology for plastic waste management in Egypt are cited.

INTRODUCTION

Solid waste management is becoming an increasingly difficult problem as traditional landfills are becoming scarce and, more importantly, environmentally undesirable.[1]

Plastic materials have helped to improve the quality of human life. They offer improved performance, comfort, safety, functionality, durability, versatility, freedom of design and adaptability to special needs.[2]

The use of plastics can make a significant contribution to conserving natural resources and to minimizing the generation of waste.[3]

The production of plastics constitutes only four percent of Western European oil consumption (Figure 1).

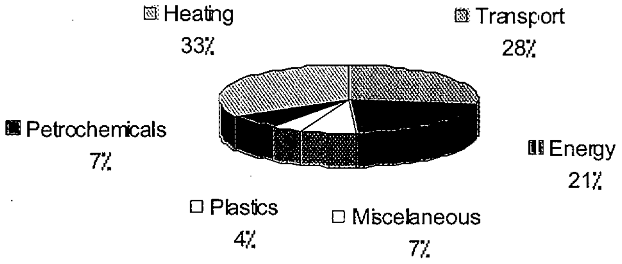

Figure 1: Different Uses of Western European Oil

PLASTIC PRODUCTION

The estimated world plastic consumption is shown in Table 1.

Table 1: Plastics Production (Estimation) in x 1000 tons

Region	Production (in 1000 ton)						Change (in %)	Share (in %)		
	1983	1984	1985	1990	1995	2000	83/90	1983	1990	1995
Western Europe	23010	23910	24210	28600	31577	34864	3.47	34.42	28.56	24.54
North America	20808	22602	23590	26500	29258	32303	3.91	31.13	26.47	22.74
Asia	11328	12966	13742	16200	26090	42019	6014	16.95	23.60	29.58
Eastern Europe	8099	8797	9140	10489	12897	15858	4.22	12.12	11.67	11.16
Latin America	2565	2943	3088	5018	8156	13256	13.66	3.84	7.38	9.33
Oceania	686	700	800	1192	1776	2646	10.54	1.03	1.61	1.86
Africa	350	385	400	565	198	1127	8.78	0.52	0.72	0.79
Total	66846	72303	74970	88564	110552	142071	4064	100	100	100

Many uses of plastics have long lifetime and plastics can often be recycled into a second life application. The polymer types which are likely to enter the waste stream as plastic waste are listed in Table 2.

Table 2: Common Polymers

Polymer	Typical Applications	Typical Lifetime Range
High density polyethylene (HDPE)	Packaging and industrial film, bottles, tubes, cups, closures, toys Tanks, drums, cable insulation, pipes, gasoline tanks, shipping containers, seating.	Up to 2 years Up to 30 years
Low density polyethylene (LDPE)	Packaging film, cling-film, bags/sacks, lids, toys, Coatings, flexible containers, tubing, Irrigation pipes	Up to 2 years Up to 5 years Up to 20 years
Linear low density polyethylene (LLDPE)	Packaging film, lids, coatings	Up to 2 years
Polyethelenterephthalate (PET)	Bottles, food packaging films, strapping, recording tapes, Carpets, vehicle tire cords	Up to 5 years Up to 10 years
Polypropylene (PP)	Yogurt and margarine pots, sweet and snack wrappers, packaging films, bottles/caps Automotive battery cases, parts and body components, Electrical components, carpet pile and backing Milk and beer crates	Up to 5 years Up to 10 years 15 years
Poly styrene (PS)	Packaging applications, dairy product containers, Ciups and plates Electrical appliances, tape cassettes	Up to 5 years Up to 10 years
Expanded poly styrene (EPS)	Shock resistant packaging, cups and plates Thermal insulation, building components	Up to 5 years Up to 30 years
Polytetrafluroethylene (PTFE)	Cable insulation, heat-resistant coatings, electrical components	Up to 30 years

Table 2: Common Polymers (contd.)

Polymer	Typical Applications	Typical Lifetime Range
Polyvinylchloride unplasticized (PVC-U)	Window and door frames, ducting, water supply and drainage pipes, rainwater goods	Up to 50 years
Polyvinylchloride expanded (PVC-E)	Building components, building facades	Up to 50 years
Polyvinylchloride plasticized (PVC-P)	Flooring, cable and wire insulation	Up to 50 years
	medical tubing and bags, shoes, cling film, food packaging, beer, and milk and food processing tubing	Up to 5 years

Plastic waste is a particularly evident problem as it represents 20-30% of the waste stream by volume (although only ~ 7% by weight (4).

The percentage of plastics in MSW in industrial countries is different from that in developing countries. Figures 2 and 3 show that the percentage of plastics in industrial countries is 7% whereas in developing countries it is 2%.

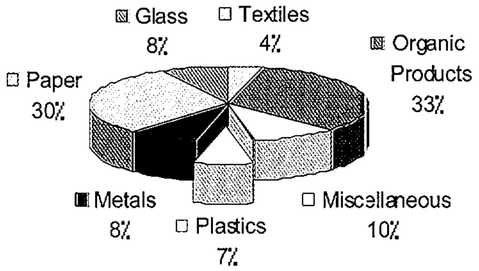

Figure 2: Percentage of Plastics in MSW in Industrial Countries

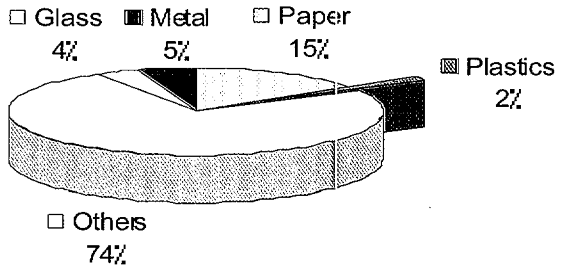

Figure 3: Plastics in Municipal Solid Waste in Developing Countries

A flow sheet showing the stages of production of plastic materials, is presented in Figure 4.

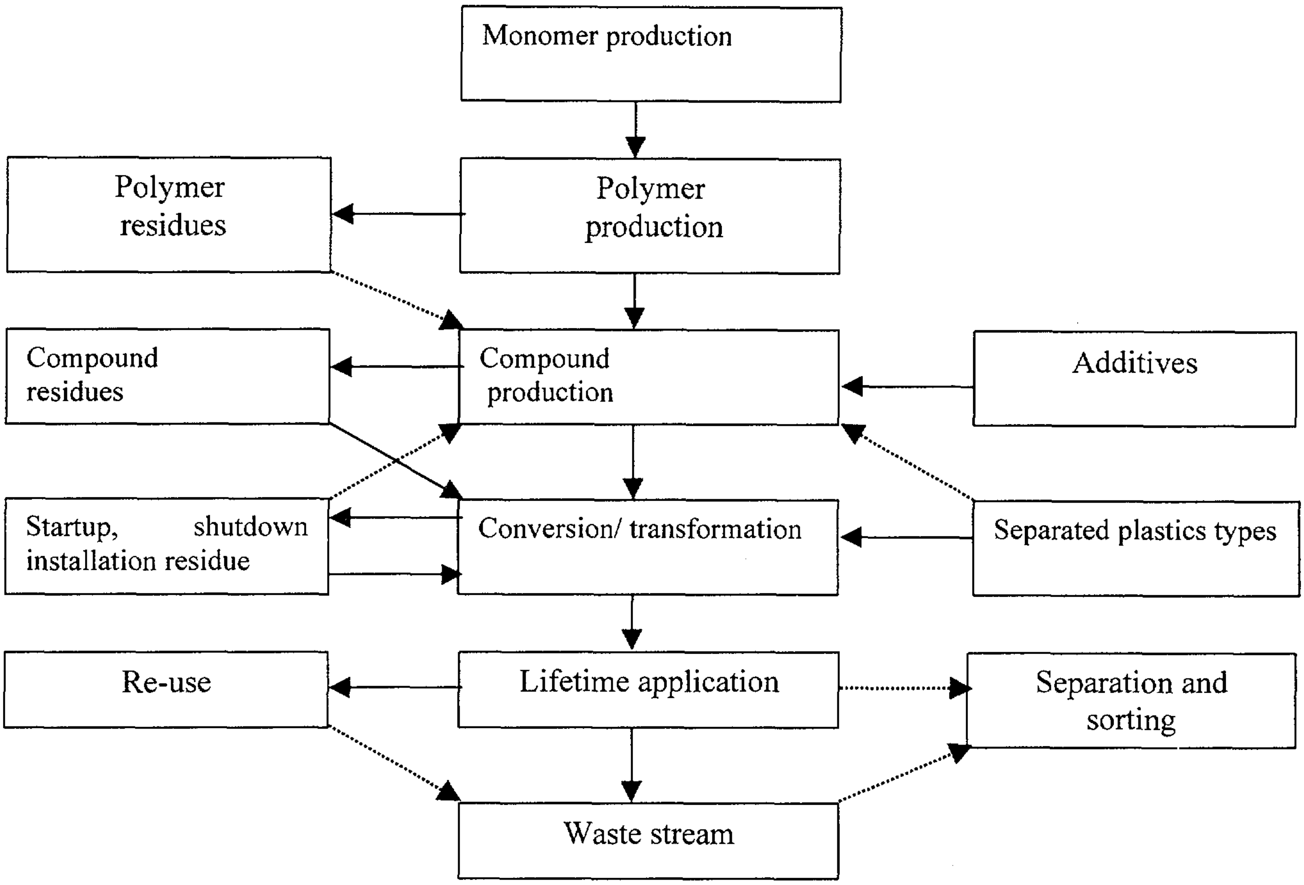

Figure 4: Manufacture, Use, Re-use and Re-cycling of Plastics

To meet the wide range of needs of polymer applications, many plastics end products are composed of a blend of polymers and additives. Typical polymer additives are listed in Table 3.

Table 3: Typical Plastics additives

Material	Typical concentration ratio : up to
Antioxidants	1%
Fillers	40%
Foaming agents	2%
Impact resistance enhancers/tougheners	10%
Pigments and dyestuffs	5%
Plasticisers	40%
Heat/light stabilizers	5%

In spite of their various applications in packaging, automotive, building and construction, electric and electronic equipment, in sports and leisure, medicine, etc., only 4% of global crude oil production is used for the production of plastics (3). However, plastic waste represents a problem of environmental concern. Since these plastic wastes are non-degradable or at least take very long time to degrade, they cause serious environmental problems.

It is generally recognized that there is no single, simple solution to waste management (4).

A range of waste management options exist which either reduce the amount of material entering the waste stream or deal with its disposal.

PLASTIC WASTE MANAGEMENT: CONCEPTS AND PRACTICE

Sources of Plastic Waste

Plastics contribute to reduction in the consumption of natural resources (e.g. lighter packaging materials means less losses and shipments of products; better building insulation, lighter cars etc.) and to waste prevention. Nevertheless, although industries across the world are producing or converting the polymers in a continuously sound and more efficient manner, waste will continue to be produced.

a) ***Plastic Waste from the Agriculture Sector***

Agriculture primarily uses PE, PP and PVC plastics. The plastic materials used in agriculture generally have a short to medium life span (5).

Examples for short-life plastic applications are greenhouses covers and fertilizer sacks. Irrigation pipes, drums and tanks, represent examples for medium lived plastics.

b) ***Waste during Polymer Production***

While industry strives to produce only first-grade material, it is likely that a small proportion will be off-specification and unsuitable for the chosen customer. This polymer may nevertheless find a proper usage in other specified applications (3).

Also during polymer compounding, polymers with additives may give rise to other material outside the specifications required by one customer but suitable for other applications. Examples might be the wrong color, wrong hardness or wrong processing characteristics.

Molding and extrusion factories may produce waste materials start-up, shutdown and running conditions which cannot be re-used on-site because of quality or specification limitations. Nevertheless, such materials may be used in other applications. The plastic wastes generated during the plastic production constitute one type of plastic waste.

c. ***Plastic Waste from the Automotive Sector***

d. ***Plastic Waste from the Construction Sector***

The construction industry uses mainly PE and PVC plastics.

e. *Plastic Waste from the Industrial Production and Packaging Sectors*

This sector produces large amount of plastic wastes such as bags, drums, containers and packaging films.

f. *Plastics in Municipal Solid Waste*

Municipal/domestic waste is regarded as a waste requiring special consideration. Municipal Solid Waste (MSW) has only a small plastic proportion (around 8% by weight). The most important potential source of plastic waste is to be found in consumer wastes, arising from trade and industry and from private households.

This waste consists mainly of packaging materials, consisting of various grades of PE, PP, PVC, PS, PET. Engineering plastic is also present (3, 5).

g. *End-of-Life Plastics*

Plastics often come to the end of their first-life application with the character of the plastic material substantially unchanged. Several countries now have legislation requiring that end-of-life plastics are recovered for recycling. The return of end-of-life components to suppliers may also form part of commercial transactions. Extracting the plastics from equipment at the end of its life may be difficult and expensive but such materials are recycled. End-of-life plastics components from long life-time applications, such as window frames, may contain additives which are no longer used. It is common practice to recycle these materials into new, environmentally sound applications where the additives remain sealed away from the environment within the plastics matrix. Examples of end-of-life plastics are shown in Table 4.

Table 4: Examples of End-of-Life Plastics

Potable water and drainage pipes	PVC-PU, HDPE
Window frames and construction off-cuts	PVC-PU, PVC-PE
Computer enclosures and key board frames	PVC-PU, PS
Bottles	PET, HDPE, PVC-PU
Packaging Film	PP, LDPE, HDPE, PVC-PU
Cable/cable insulation	LDPE, PVC-PP, PTFE

PU = Poly Urethane

Options for Plastic Waste Management

a. *Mechanical Recycling*

Mechanical recycling is widely practiced for recycling of maximum amount of plastic waste. It involves collection, separation, cleaning, size reduction and melt processing of waste in a conventional manner. Mechanical recycling has got an edge over other modes of waste disposal such as incineration, land filling, and sea dumping since it offers eco-friendly and economical solutions, generates employment potential and results in a considerable saving in oil. Most of the thermoplastics waste are being recycled by this technique.

b. ***Feedstock Recycling***

Feedstock recycling, unique to plastics, is a process which breaks down polymer molecules into petrochemicals feedstock which can be used, among other uses, to make new plastics. Feedstock recycling technologies have an important role to play in helping to meet the plastics industry goal of resource optimization and maximum recovery. In particular, it offers new ways to recycle plastics overcoming some of the limitations faced by mechanical recycling, where large quantities of clean homogeneous plastics waste are necessary for success.

Three. Energy Recovery

Energy recovery, alongside these recovery options, can ensure that we no longer waste our plastics waste. Eco-balances show, in many circumstances, that combustion of plastics waste to create energy is the most environmentally beneficial option. Figure 5 shows energy content of municipal waste.

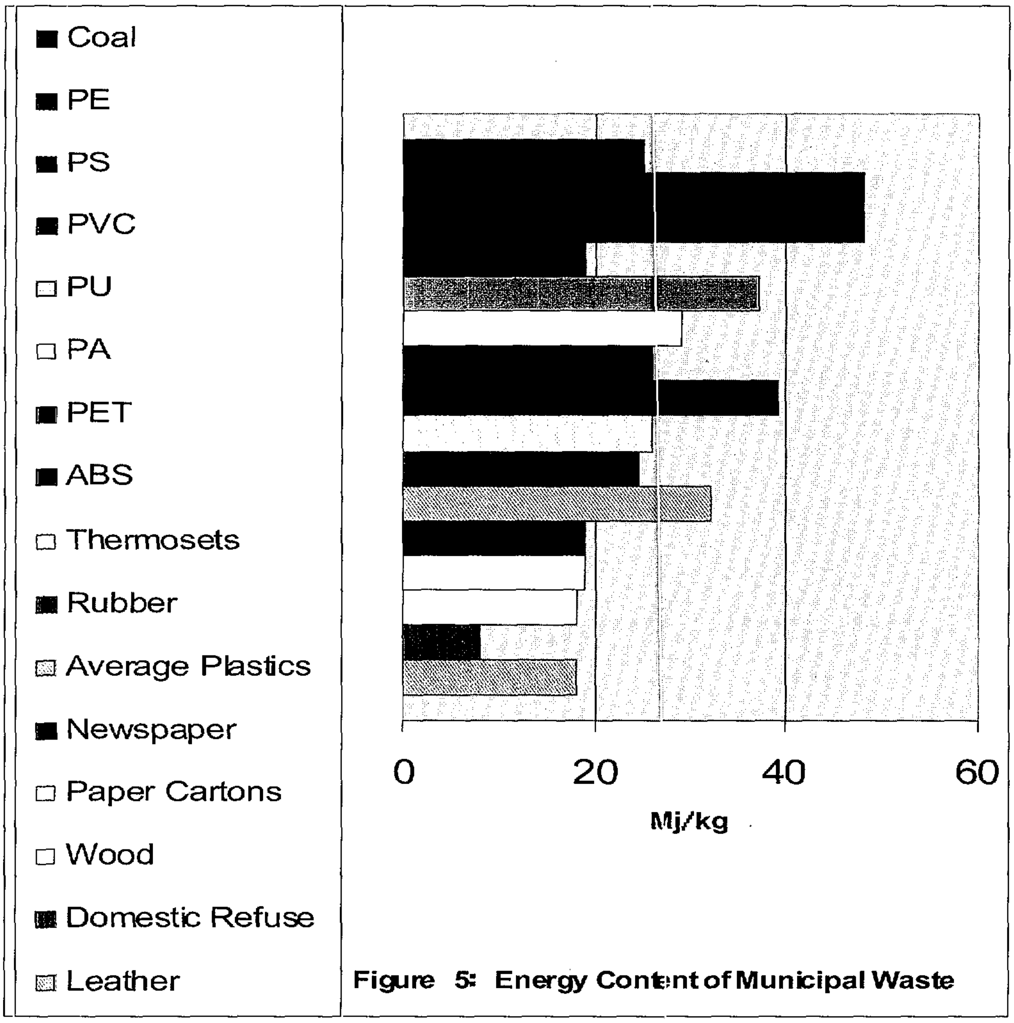

Figure 5: Energy Content of Municipal Waste

d. *Disposal by Landfill*

The reaction against landfill, as the primary method of waste disposal, is part of the general upsurge of concern about the state of the environment. More specific difficulties related to potential shortages of capacity have resulted in a near-crisis situation in parts of the Asian countries and have given impetus to re-cycling and other methods of waste disposal.

Landfill is still the predominant waste disposal method in the Asian countries, but its share is declining rapidly. Many landfill sites have closed and a number of the remaining sites have only a limited life-span. Landfill will generally decline, not only because land shortages but because environmental concerns, which are particularly directed towards plastics.

e. ***Biological Treatment***

Biological treatment is mainly performed with agricultural waste, used as natural fertilizer or for production of biogas.

SITUATION OF PLASTIC WASTE IN EGYPT

Plastic production in Egypt in 1994 was estimated to be ~55 million kg/year which consequently produced ~22 million kg of waste plastic. The amount of solid waste generated in 1995 in Egypt was 11×10^6 kg and the percent of plastic waste in solid waste was ~8-9%, i.e. 8×10^5 kg.

It is expected that in the year 2000, plastic production in Egypt will increase to 75 million kg/year and the plastic waste is expected to reach 38 million kg/year.

Plastic waste represents 9% by weight and 20% by volume from the solid waste in Egypt (6). MSW fractions in Egypt are shown in Figure 6.

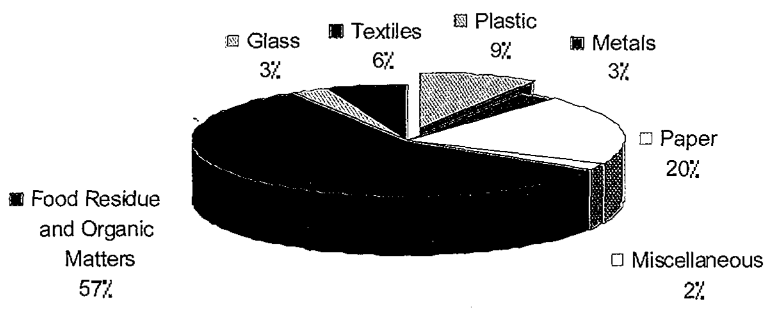

Figure 6: Municipal Solid Waste Fractions

The percent of major types of plastics in the Egyptian MSW are represented in Figure 7.

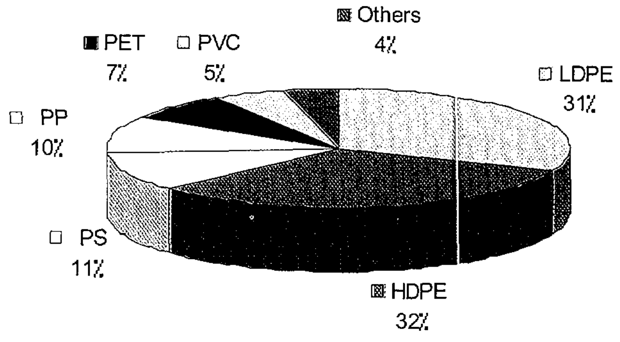

Figure 7: Major Types of Plastics in Egyptian MSW

It is shown that PE represents the highest percent of plastic waste found in the Egyptian household waste (Table 5).

Table 5: Major Types of Plastics in Egyptian Household Waste

Plastic Type	Percent	Product Type
LDPE	27	Plastic bags
HDPE	21	Toys, oil bottles, milk bottles
PS	16	Cups
PP	16	Plates, food packaging
PET	5	Water bottles, soft drink, bottles
Others	15	Miscellaneous
Total	**100**	

Production and Consumption of Plastic in Egypt

Packaging represent 30% of plastic industry in Egypt. Table 6 shows the consumption of different types of plastic in Egypt during the period 1980-1998 (in 1000 ton).

Table 6: Plastics Consumption and Production in Egypt

Material	1980	1985	1990	1993	1994	1995	1996	1997	1998
PVC	45	54.5	87.4	96	89.2	95.9	103	110.8	119
HDPE	30	42	59	68.8	73.9	79.5	84.5	91.9	98.9
LDPE	80	115	162	177	190	204	219.9	236.5	254
PP	15	27	63.6	77.5	83	89.6	96.3	103.4	111
PS	17	30	57.7	65	69.9	75	80.7	86.8	93

Table 7 gives a summary of a study conducted by Sobhy et al (7) on solid and plastic wastes produced by an average Egyptian family in Cairo and suburbs.

Table 7: Average of Solid Waste and Plastic Waste produced by Egyptian Family (4 persons)/day in Cairo

Place	Total Waste (kg)		Plastic Waste Weight (kg)		% of Plastic Waste	
	1992	1994	1992	1994	1992	1994
Zamalk	520.03	550.42	104.11	146.44	20.02	26.605
Mohandisene	560	600.233	100.8	129.34	18	21.548
Doki	326.333	360.54	53.257	63.094	16.32	17.5
Heliopolis	245.25	300.147	28.939	43.101	11.8	14.36
Maadi	221	233.83	26.696	30.633	12.08	13.1
Naser City	196	216	20.26	26.25	10.336	12.15
Agoza	173.33	184.93	24.125	25.133	13.045	13.59
Middel Town	230	222.6	19.987	18.4	8.69	8.26
Giza	190.61	194.51	14.961	16.72	7.85	8.59
Mokatam	160.315	177.681	11.35	13.42	7.08	7.55
Manial	157	159.9	9.996	10.946	6.37	6.85
El-Haram	230.15	250.15	25.613	28.57	11.13	11.42
El-Orman	210.375	251.47	25.157	39.56	11.96	12.196
Helwan	74.54	90.573	3.816	6.557	5.12	7.239
El-Kalaah	86.6	92.574	9.446	11.239	10.9	12.25
Total	3581.533	3795.56	478.514	609.503	13.36	16.06
Average of plastic waste/person/day	0.663	0.754	0.089	0.113	13.42	16.07

From the table we can see that the amount of waste and plastic waste differ from one place to another according to the economic level of the family.

The average of solid waste/person/day in Cairo is 0.754 kg/day and the average of plastic waste/person/day is 0.113 kg/day.

Generally speaking, it was found that the amount of solid waste increases with the increasing income of the family. This is similar to various studies conducted in different countries (8).

Specific Analytical Cases for Plastic Recycling

a. *Plastic Waste in Hotels and Restaurant*

The study was carried out by separation and identification of plastic waste in nine hotels in Egypt during October 1993 (6). The results of this study are summarized in Table 8.

Table 8: Weight of Plastics consumed in Nine Hotels in October 1993

Item	Total/wt. (kg.)
Water bottles	6000
Oil bottles	2313
Vinegar bottles	25.2
Plastic foil	11.3
Spoons	25
Plastic cups	43
Foam plastic	200
Stirrers	355
Straws	793
Laundry bags	150
Suit bags	330
Dress bags	330
Shirt bags	330
Rubbish bags	5200
Hygienic bags	1025
Cup bags	30
Plastic hangers	395
Plastic brooms	1.8
Detergent bottles	27.3
Shampoo bottles	365
Shower gel	365
Shower cap	365
Large plastic baskets	14
Total	18693.6

b. *Plastic Waste in Hospitals*

Medical applications of polymers represent one major field of plastic industry. Many medical tools such as syringes, blood tubes, catheter, medical bottles, urine collection bags, and gloves are made of plastics. Most of these tools are short lived and become a waste after few minutes from their uses.

A survey (6, 9) was carried out in 20 hospitals in 1994, the different amounts of plastic waste are shown in Table 9.

Table 9: Consumption of Plastic Bag in 20 Hospitals in 1994

Item	Total Number
Syringe	261163
Catheter	18679
Naso gastric tube	3859
Infusion set	25857
Urine collection bags	7644

Table 9: Consumption of Plastic Bag in 20 Hospitals in 1994 (contd.)

Item	Total Number
Canula	23864
Triple junction	2880
Butterfly	5530
Endotracheal tube	1897
Negative pressure suction drain	565
Plastic mackintosh	9135
Gloves	30523
Plastic boxes	5257
Plastic cups	33583
Solution bottles	68460
Yogurt cups	133460

From the above table, the consumption of plastic by hospitals is 12.55 ton/month and 3.4 kg/bed. From these data, the estimated consumption of the health sector in Egypt is 327 ton/month.

The study also showed that there are only two hospitals using incinerators, to get rid of their waste, but without recovery of energy. Other hospitals do not have incinerators, they leave their waste to garbage collectors.

c. *Plastic Waste at Cairo University Student Hostels*

The results of a study on Cairo University student hostels (boys) during the academic year 1994-1995 showed that the amount of plastic waste/year was 24 ton for 7500 students i.e. the average consumption for each student was 3.2 kg/year (6).

Different types of plastic items used in the student hostels (boys) are shown in Table 10.

Table 10: Different Types of Plastic Articles used in Student Hostels (Boys)

Type	Number of Units/Year	Weight of Unit (in Gm.)	Total Weight (kg.)
Cups	126×10^4	7	8820
Yogurt	864×10^3	6	5184
Jam bottles	162×10^4	3	4860
Chicken bags	234×10^3	7	1638
Salt bags	18×10^3	4	72
Oil bottles	405×10^2	60	2430
Vinegar bottles	18×10^2	40	72
Garbage baskets	25×10^2	350	875
Others	15840	9	142.56
Total			24093.56

Similar study was carried out on girls student hostels at Cairo University, the results of the study showed that each girl consumed 2.9 kg/year of plastic. Table 11 shows the different types of plastic found at the University hostels for girls.

Table 11: Different Types of Plastic found at the University Hostels for Girls

Type	Total Weight (kg.)
Cups	3043.485
Yogurt	1818.54
Jam bottles	157.442
Chicken bags	530.82
Salt bags	37.26
Oil bottles	715.5
Vinegar bottles	36.45
Garbage baskets	3.0
Others	105.05
Total	6447.547

From these studies, it was found that the average consumption per student in the hostels is 3.1 kg/year, and for the consumption of 80000 student is 248 ton/year.

Recovery of Plastic Waste in Egypt

Traditional practices of plastic recycling versus immerging environmental awareness:

a. *Traditional Practices*

i) *Collection and Sorting of Plastic Waste*

Through a large number of rag pickers and waste dealers, there is a highly efficient but unorganized system of plastic waste collection from municipal solid waste. Sorting of plastic waste is performed by the individuals who collect the waste, and finally by recyclers. Figure 8 shows some plastics collected from municipal solid waste.

Figure 8: Different Types of Plastic Waste

The collection and sorting of plastic wastes are typically the first two steps involved in post-user plastic waste recycling. Figure 9 shows sorting of plastic waste after collection.

Figure 9: Sorting of Plastic Waste

In the traditional practice, the sorting process usually require manpower to separate and sort the plastic waste.

ii) ***Traditional Recycling of Plastic Waste***

Up to the time of writing this article, recycling plastic waste in Egypt means mechanical recycling, other methods such as chemical and energy recycling are not in application.

- Washing

  After sorting of plastic, washing of waste is performed manually in a tank containing hot water to remove dirt. After thorough washing for two or three times, the plastic waste is dried.

- Size Reduction

  The washed plastics are reduced to small sizes using a shredder. The shredded pieces are fluffy in nature which are sent for melt recycling. Figure 10 shows the most common shredder used in the mechanical recycling of plastic waste in Egypt.

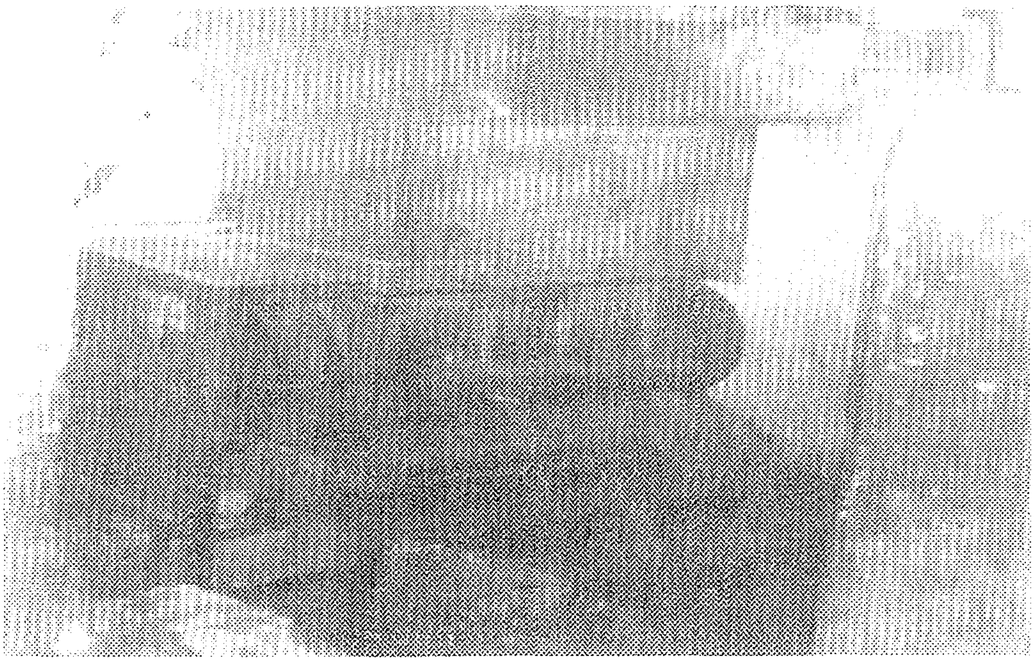

Figure 10: The Most Common used Shredder

After shredding the plastic waste, it is washed using tanks containing hot water. The shredded washed plastic is usually dried using centrifugation drier (Figure 11).

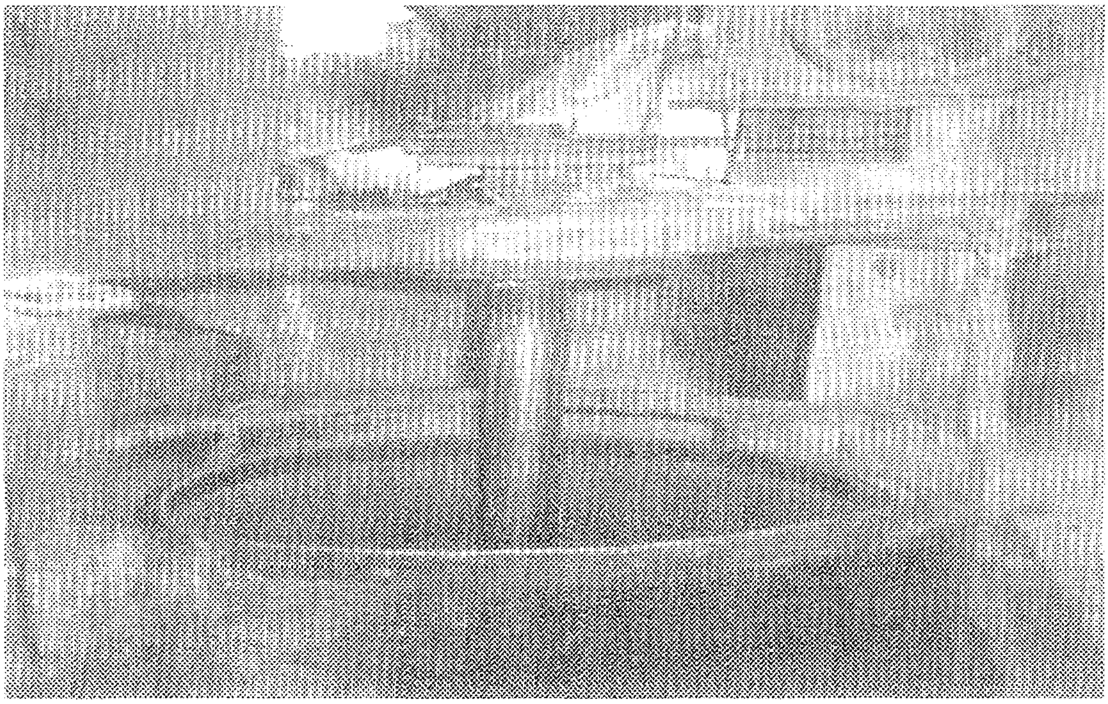

Figure 11: The Most Common used Drier in drying the Shredded Waste Plastic

Figure 12 shows samples of final products treated by the traditional way described above.

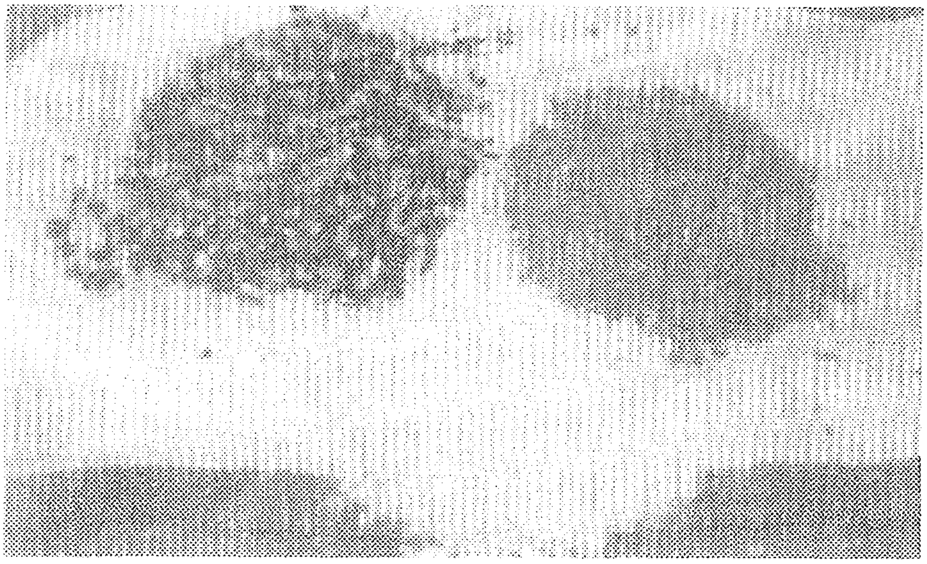

Figure 12: Samples from the Final Product

b. *New Trends in Recycling Technique*

On increasing the awareness of plastic waste problem in Egypt, new technology started in plastic waste recycling.

In this, they only feed the line with the waste and receive the pelted product at the end of the line. All steps are carried out automatically in the line (Figure 13). Samples from the final granulated product and the manufactured product are shown in Figure 14.

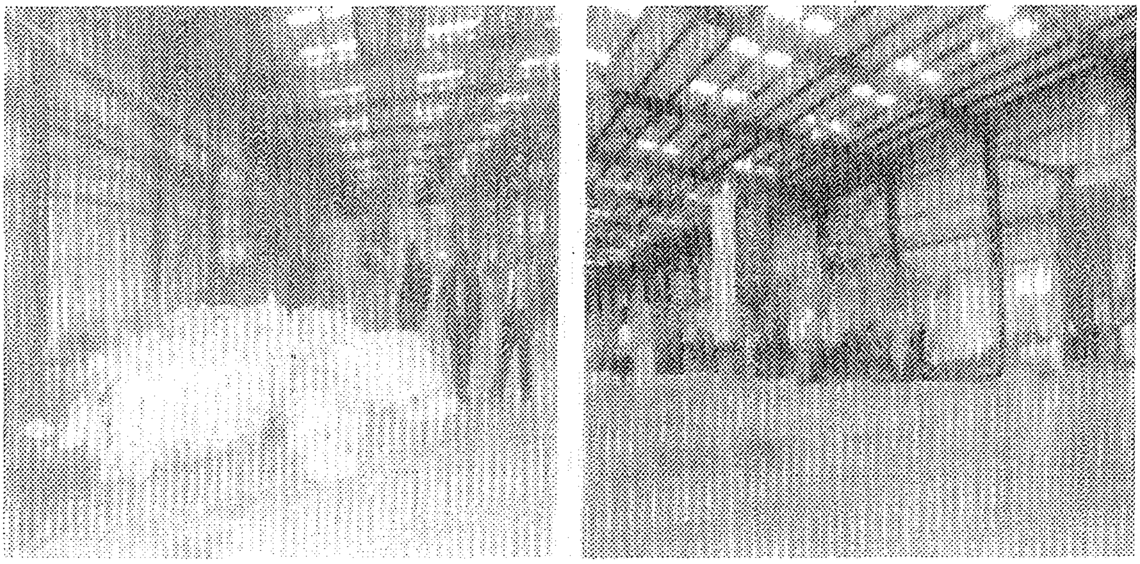

Figure 13: General View of the New Recycling Line

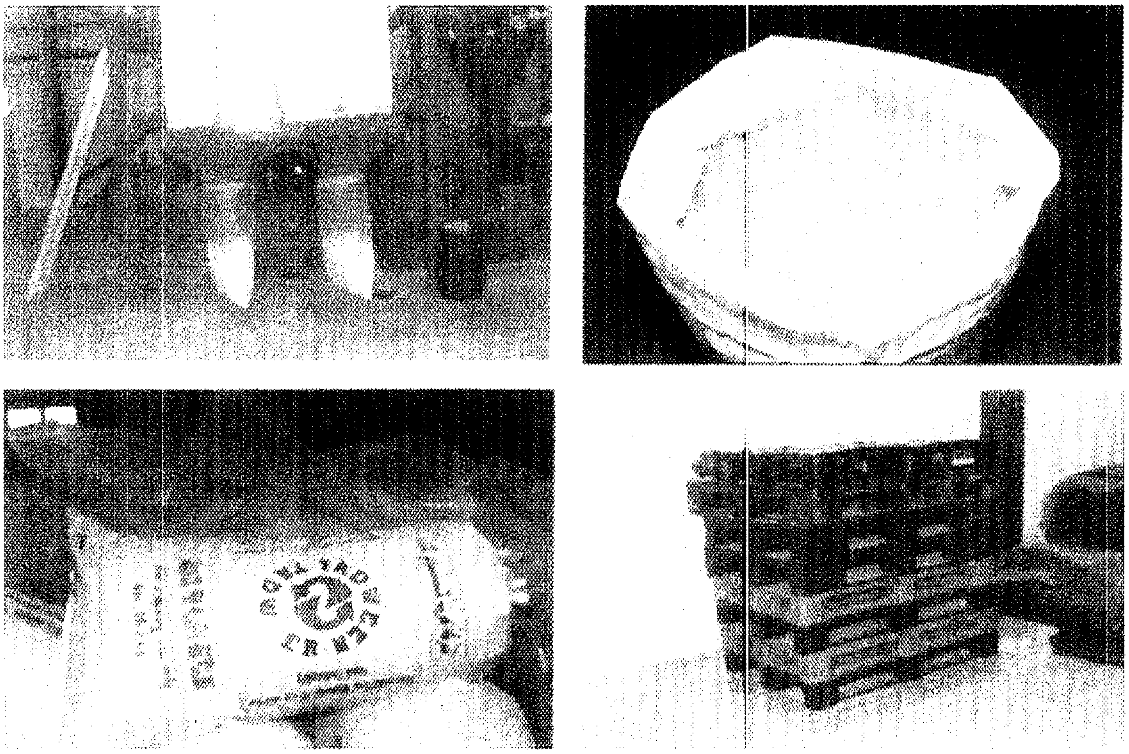

Figure 14: Final Products from the New Recycling Technology

CONCLUSION

Plastic recycling is receiving more attention in Egypt. It used to be a black industry in economic, as well as, environmental sense. However, the situation is changing as environmental laws are implemented and environmental awareness is raised. Research activities within the universities and research centers are addressing this problem and looking for new benefits from plastic recycling.

Moreover, the economic derive for recycling have attracted new generation of industrialists who are environmentally conscious to be involved in this industry. New plants have been recently established which look into plastic recycling as a mean for clean environment. It is envisaged that this new move of environmentally conscious industries take over and set spread all over Egypt.

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Plastic Waste Management in Yemen

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Abstract

In Yemen; plastics are produced from imported resins. There are five types of plastic resins used: Low density polyethylene (LDPE), high density polyethylene (HDPE), poly vinyl chloride (PVC), poly propylene (PP) and poly styrene (PS).

Plastic companies do not generate plastic wastes since all scrap and byproducts are recycled. Other forms of re-use of plastic materials do not exist in Yemen, except for the recycling of PVC shoes.

Plastic wastes can be seen all over the country. In the major cities, collection of plastic waste is part of the municipal garbage collection system. In rural areas and cities no garbage collection systems exist.

There are many options to replace the current used plastics by other plastics or materials. Poly (ethylene terphthalate) (PET), poly carbonate (PC) or photolytic and biodegradable plastics can be used instead of PVC plastics. The other replacements are the use of glass, tins, papers and use of cardboard materials.

Plastic waste in itself does not pose an environmental risk in the sense that chemically or biologically may directly pollute surface water, ground water, air or soil although it produces long term pollution. However, the overall presence of plastic litter is regarded as visual pollution and a nuisance. Furthermore, it does not enhance the national image of the country and tourism.

INTRODUCTION

Solid waste refers to everything that goes out in trash and is handled as solid in contrast to what is flushed down the drain and handled as liquid. The volume of municipal solid waste produced each year has grown steadily with increasing population and with increasing affluence.

The problems that exist in waste disposal system are rather complicated and specific. Waste is the source of environmental pollution, but it is also the source of secondary raw materials and energy.

In recent years, there has been a trend toward the use of disposable products such as paper, plates, cups, plastic or aluminium food containers and wrappings. Therefore, the generation of a solid waste has increased much more rapidly than the growth of population. On average, municipal solid waste consists of the following items shown in Table 1 below (1, 2):

Table 1: Composition of Municipal Solid Waste

Solid Waste	% by weight
Paper	41
Food wastes	21
Glass	12
Ferrous metals	10
Plastics	5
Rubber and leather	3
Textiles	2
Aluminium	1
Other metals	0.3

ENVIRONMENTAL PROTECTION COUNCIL IN YEMEN

In 1987, the Environmental Protection Council (EPC) was established by Decree No.7 of the Council of Ministers.

The most efficient way to effectuate institutional development and environmental awareness is to undertake all the dimensions of environmental management. One of the selected subjects is the dissemination of plastics as solid waste.

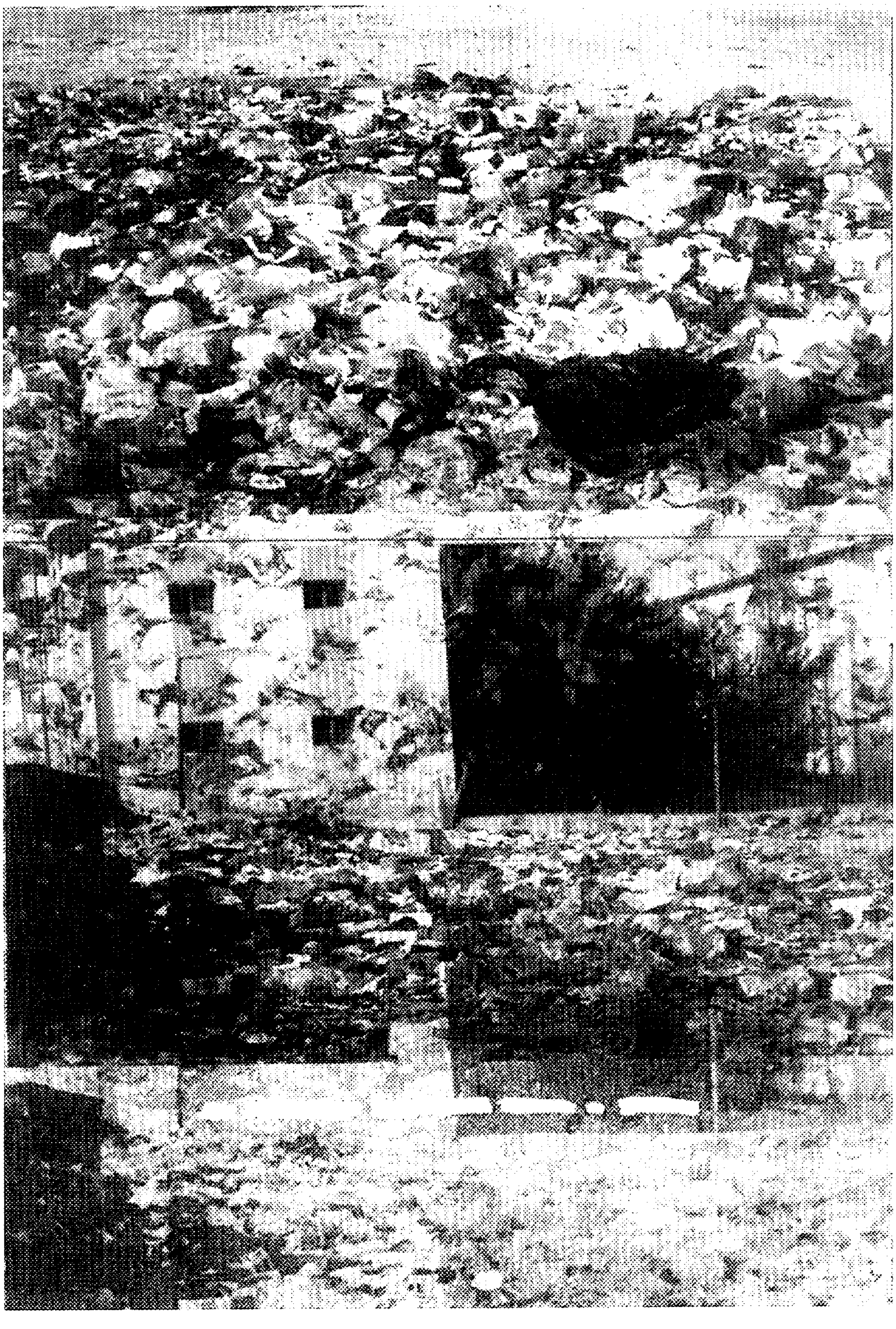
Stepping ahead

Between June 12 to July 2 1990, a short term commission was formulated under the Technical Assistance Program "Support to Environmental Protection Council" in the Republic of Yemen to formulate practical recommendations for the collection and recycling of plastics. "Support to the Environmental Protection Council" is being implemented by Haskoning Royal Dutch Consulting Engineers and Architects under the bilateral development co-operation program between Yemen and Dutch Governments (3).

The objectives of the mission are to clarify the fundamental reasons leading to the dissemination of plastics into the environment and to recommend the most feasible approach to the problem.

PLASTIC WASTES

Visitors to the Republic of Yemen will notice the abundant and defacing presence of litter, mainly composed of plastic bags and plastic bottles. The plastic bottles are mainly empty mineral water bottles. The dissemination into the environment is apparently caused by:



1. A lack of suitable means (e.g. containers) to collect and dispose of the waste,
2. A lack of awareness of the need to dispose of domestic waste by an organized system.

PRODUCTION AND USE OF PLASTICS

In Yemen, plastics are produced from imported resins. There are five types of plastic resins used: Low density polyethylene (LDPE), high density polyethylene (HDPE), poly (vinyl chloride) (PVC), polypropylene (PP), and ploystyrene (PS). The annual consumption of plastic resins is shown in Table-2. Data were provided by the main industries (3).

Table 2: Consumption of Plastic Resins during 1989

Type of Resin	Consumption (tons)
LDPE	5,000
HDPE	20,000
PVC	4,000
PP	600
PS	40

The main use of plastic materials in Yemen are bags (in shops), bottles (mineral water) and other packing materials. The production of plastic products as pipes, crockery, windows, etc. is very limited (4).

Table 3: Main Uses of Plastic Materials

Type of Plastic	Main Use
LDPE	Bags, Cups, Toys, ...
HDPE	Bags
PVC	Bottles, Shoes, ...
PP	Large and Heavy Duty Bags
PS	Package Materials

Re-use of Plastics

Plastic companies do not generate plastic wastes since all scrap and byproducts are recycled. Other forms of re-use of plastic materials do not exist in Yemen, except for the recycling of PVC shoes.

DISSEMINATION OF PLASTIC WASTES

Plastic wastes can be seen all over the country. The waste contains mostly empty mineral water bottles and plastic bags. In the major cities collection of plastic waste is part of the municipal garbage collection system. However, only a limited number of cities do have a garbage collection system and in all these cities the provided facilities are not sufficient to collect all wastes. In rural areas and smaller cities, no garbage collection systems exist.

Empty mineral water bottles are, mostly, present along the highways and in urban areas. Plastic bags can be found anywhere since the wind disseminates them over long distances even after collection and disposal at landfills. Additional factors are the excessive use of plastic bags as wrapping material in shops and the use of bags to wrap Gat (a herbal drug popular in Yemen).

The major reasons for the dissemination of plastic waste are:

1. A lack of garbage collection and disposal facilities

2. An excessive use of cheap quality plastic bags as wrapping material in shops and for Gat.

3. Large consumption of mineral water.

4. Indiscriminate disposal of plastic materials (public awareness, social behavior) absence of a market to recycle plastic bags and bottles.

5. Absence of a system of taxes/refunds on one-off used plastic products.

6. Relatively low prices of plastic compared to other packing materials (bottles, paper, card boxes and cans).

7. Dissemination by wind.

8. Scavenging of waste containers and dumps by animals (dogs, cats, goats, sheep) and people.

RECLAMATION OR RECYCLING

One solution is to look at municipal solid waste not as waste to be disposed of but as a resource to be recycled back into the same or other useful products.

In industrialized countries, suitable plastic collection systems are introduced, plastics are cleaned, cut, mixed and remelted to generate low grade granules which are used as packing

materials, or for the production of plastic tubes and window frames. This system is used when different types of plastics are collected together.

a *Re-use of PVC Bottles*

In principle, PVC bottles can be re-used and put into their original use, however cleaning and sterilization is hampered because PVC melts at 70°C. Sterilization of the bottles is important precondition for re-use. Therefore PVC bottles should not be re-used for e.g. mineral water.

b *Baling of Plastics*

If a plastic collection system would be introduced and re-use facilities are not yet available, it can be considered to bale the plastics. The bales can be easily stored at depots or can be used as a kind of fence at disposal sites. A stock of bales will make it also interesting for private companies to start re-use of plastics.

c *Refund System*

A refund system can be introduced for plastic bottles and bags, similar to the refund system for glass bottles. A refund system offers many advantages such as additional financial arrangements, collection facilities and re-use facilities have to be organized as well.

d *Tax System*

A tax can be introduced to be paid by plastic factories to the central government. The tax can be used to cover the additional costs for collection and to re-use of plastic waste.

OPTIONS FOR REPLACEMENT

There are many options to replace the current used plastics by other plastics or materials such as:

1. Poly (Ethylene Terphthalete) (PET)

Advantages of using PET plastics as packing material

a. PET is a good substitute for PVC.
b Gives good recycling to high quality products.
c High re-use potential (PET bottles can be re-used over 20 times).
d Low emissions during both production and final incineration.

Disadvantages of using PET

a. High production cost
b. PET has a limited use

2. **Poly Carbonate (PC)**

Advantages for using PC

a. High potential for re-use
b. High purity grade of recycled PC products
c. Non-hazardous gaseous effluents during incineration

Disadvantages of using PC

a. High production cost
b. The use of toxic compounds during production (phosegene, phenol, chlorine)
c. Emissions during production of methylene chloride and phenol
d. The production requires high safety measurements for people and environment which is not available in Yemen

3. **Glass and Paper**

Glass bottles could be used for mineral water and beverages. It is easy to collect, clean and re-use. The problem in Yemen is the lack of glass bottle production facilities. Import of glass bottles is not attractive from a financial point of view. Paper can substitute but its production is expensive compared to plastics.

4. **Tins**

This option is not feasible in Yemen for replacement of plastic materials for economic and technical reasons.

PROJECTS FOR SOLUTION

A workshop for sanitation, held in February 1990 in Sana'a – Yemen, concerned with domestic waste collection suggest a number of solutions:

1. Introduction of degradable plastics.

2. Financial stimuli in order to reduce the use of plastic bags.

3. Financial stimuli (taxes, refunds) to provide a stimulus to return plastic bottles to shops.

4. Collection and recycling of plastic wastes.

5. Collection and incineration of plastics in pits in rural areas.

6. Enhance the quality of the materials in order to enhance the reuse.

7. Enhancing awareness in combination with taxes.

RECOMMENDATIONS

Few recommendations can be considered to reduce the dissemination of plastic wastes in Yemen such as:

1. To start a campaign to reduce the present excessive use of plastic bags.
2. To start a health promotion campaign to enhance a civilized public awareness on solid waste.
3. To introduce a tax or a refund system.
4. To start a genuine collection system of plastic waste.
5. Construction of depots in major cities where plastic wastes can be delivered.
6. Introduction of EDP's for certain plastic items.

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Plastic Consumption, Plastic Waste Management and Development of Environmentally Degradable Polymers in China

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THE PRODUCTION AND CONSUMPTION OF PLASTICS IN CHINA

Because of low price, lightweight and good durability, plastic productions have been grown quickly in pace with the development of petroleum industry and have been widely used worldwide. In China, the production and consumption of plastics also increase rapidly along with development of the economy and the improvement of people's living standard. The volumes of output, import, export and consumption of major plastics (five general-purpose thermoplastics) in recent years in China are listed in Table 1. Employees involved in plastic production, the production capacity and the requirement amount of some synthetic resins and plastics are listed in Table 2.

The total output value of synthetic material manufactured in China was about 4.89 billion US Dollar in 1996. Among them, 26%, which valued at 1.27 billion US Dollar are from manufacturing of polyolefin plastics; 16.8%, at a value of 0.82 billion US Dollar from thermosetting resins; 4.8% (about 0.23 billion US Dollar) from engineering plastics; 5.9%, that is 0.29 billion US Dollar from functional polymer and 2.9%, worth 0.12 billion US Dollar from Organosilicon or (and) organofluorine material manufacturing. The rest go to synthetic rubbers, synthetic fibers and other synthetic materials.

Korea, Japan, Taiwan Province of China and USA are usually regarded as China's major sources of the imported plastics. It should be noted that recently Saudi Arabia and Thailand have exported more and more plastics to China. In 1995, Saudi Arabia became the fourth exporter for PE to China, surpassing Taiwan Province of China for the first time. Five general-purpose plastics imported from Thailand increased annually as well. It could be foreseen that this trend of large importation would maintain for a long time.

Table 1: Output, import, export and consumption of synthetic resins and plastics in China (kt)*

Year		1995	1996	1997	1998, Jan-Oct	2000**
Output	PE	1322	1714	2152		2300
	PP	1064	1409	1881		2000
	PS	255	306	340		500
	PVC	1374	1389	1534		1800
	ABS	40	28	16		20
Total		4055	4846	5923	5695	6620
Import	PE	1823	2194	2284	1780	
	PP	1068	1128	1253	1229	
	PS	1067	1289	1398	1105	
	PVC	389	860	1173	1253	
	ABS	804	992	1031	860	
Total		5151	6463	7139	6227	
Export	PE	14	16	29	33	
	PP	14	5	19	26	
	PS	66	47	119	95	
	PVC		46	52	26	
	ABS	8	54	56	34	
Total		102	168	275	214	
Consumption	PE	3131	3892	4407		
	PP	2128	2532	3115		
	PS	1256	1548	1619		
	PVC	1763	2203	2655		
	ABS	836	966	991		
Total		9114	11141	12787	11708	
Degree of self-Sufficiency		44.5%	43.5%	46.3%	48.6%	

Note: * Not include Hong Kong and Taiwan Province of China (hereinafter, with no further Explanation.

** Estimated data.

Table 2: Production capacities and recent demands for some synthetic resins and plastics in China

	PE	PP	PVC	PS	ABS
Number of main manufacturer	17	15	79	7	5
Production capacity in 1996 (kt)	2170	1480	1680	400	250
Demand in 1997 (kt)	3640	2500	2000	1500	800

	Phenolic resin	Epoxy resin	PC	Polyformaldehyde
Number of main manufacturer	Over 100	19	8	4
Production capacity in 1996 (kt)	150	50	~15	13
Demand in 1997 (kt)	120	60	30	

Figure 1 shows the price trend of plastics in Chinese domestic market from January 1997 to November 1998. It could be seen that from August 1997, prices of major plastics dropped sharply, and slumped to the lowest point in July 1997. Since last August, prices have been gradually rising again, prices of PP and PE even have enjoyed remarkable increase.

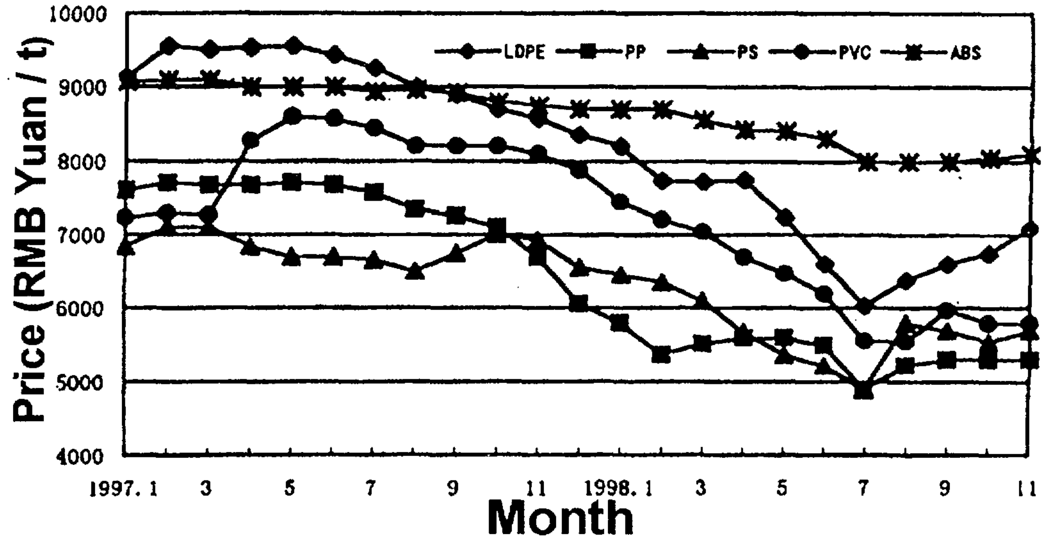

Fig1. The prices of selected synthetic plastics in China from Jan. 1997 to Nov. 1998 (1 US$=8.3 RMB Yuan)

It can thus be deduced that in pace with continuous enlargement of market of plastic products in China, the production capacity and output value will increase correspondingly, and consumption will go up continuously as well. According to statistics from Chinese Light Industry Union, the consumption of plastics in China rose from 1220 kt in 1980 to 8,100 kt in 1994, and will probably reach 14,000 kt in 2000, with per capita consumption rising from 1.24 kg/a to 6.67 kg/a. It is estimated that such a high growth rate of 10% will be maintained in the coming 20-30 years.

Still there are some problems in terms of manufacturing, consumption and selling of plastics in China.

- The product mix of plastic is inappropriate. Products for general use are much more than that for special use. Most of these products are of low grade. Advanced plastic products that can be used in special professions, such as high tension cable, drum of washing machine, auto mobile, electronic and electrical household appliances et al still are relied on import, while products for general use have been stocked up because of relative overproduction.
- Production cost is high, price system inflexible and ability for meeting market contingencies poor.
- Quality of plastic products in unstable. Properties of different batches of same kind of product varied remarkably.

- A good system of market feedback and efficient before and after-sale services has not been built up thoroughly. Because of inharmonious relations and insufficient cross-links among the departments of technique, production and sale, a virtuous circle of "production – sale – market feedback – production" has not been established yet. This resulted in delay in supply, poor before and after-sale service, slow improvement of quality and little choices of products in the market.

- The way of settling accounts is not flexible. For imported goods, payment can be made within 3 to 6 months after delivery with credit guarantee. However, because of the serious problem of "debt-chain" in China, domestic enterprises try hard to avoid selling on credit and only deliver after receiving payment.

SURVEY ON PLASTIC WASTE AND ITS DISPOSAL POLICY IN CHINA

At present, solid garbage of livelihood generated per capita in Chinese cities is about 440kg/a. The total amount of livelihood rubbish in urban areas in China was 110,000 kt in 1997. Increasing with a rate of 8% ~ 10% annually, it is going to reach 150,000 kt in the year 2000. The amount will go up to 600,000 kt plus tremendous industrial garbage.

For the time being, waste plastics produced in China are about 4% of total solid wastes, i.e. 5,000kt/a. And big cities have a much higher ratio than medium or small ones. For example, the proportions of waste plastics to livelihood trash in Shanghai and Beijing are about 11% and 9%, with 290 kt/a and 140 kt/a of waste plastics, respectively. Among waste plastics, PE comes the first, PVC and PP follows (see Table 3).

Table 3: The constitution of waste plastic in China

	PE	PVC	PP	PS	Polyester	Others
Ratio (%)	52	22	15	4	1	6

Because disposal facilities of solid garbage are not perfect, and formulation as well as implementation of relative state laws and regulations is not strict in China, only 10% of waste plastics are recycled and reused. 25%~30% of them are incinerated or deeply buried. Nearly 60% of waste plastics are not treated properly, some of them are abandoned or stacked wantonly, some are even dumped at rivers, lakes or sea.

Figure 2 is the scheme of life cycle assessment on plastics in China. All statistics in the scheme were of 1994.

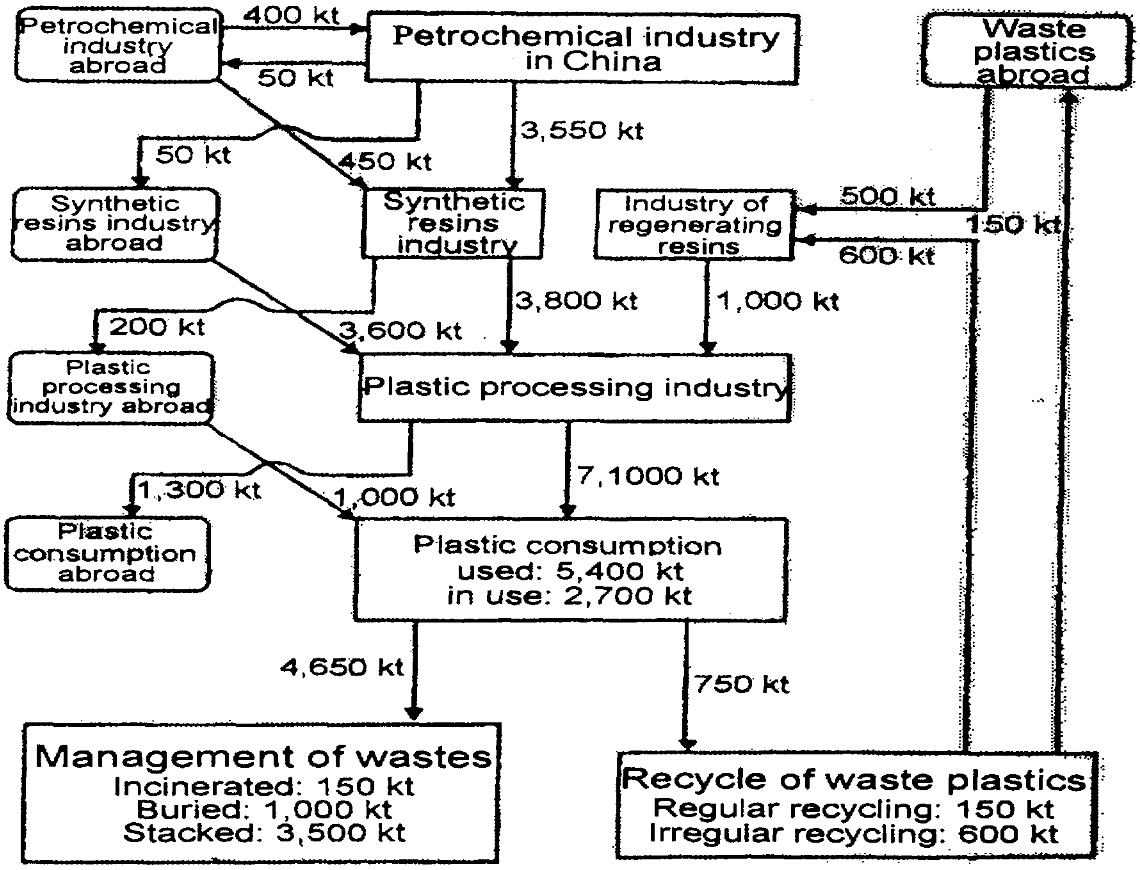

Figure 2: The scheme of life cycle assessment on plastics in China. All statistics in the scheme were of 1994

So far there is no specialized institution for waste plastics treatment in China. Normally waste plastics are managed in following ways:

- **Deep Burial.** Safely deep burial is considered to be an efficient resolution for waste plastics in China. However whether it will affect environment or not is still unclear. Moreover, since general plastics are uncompressible and non-degradable, they occupy lots of precious arable land when deeply buried.

- **Incineration.** Incinerating plastic wastes for generating electricity is considered as one of the best choices for waste plastics management. However, garbage incineration industry is only in its preliminary stage in China recently. One of the reasons is that in our solid wastes there are few flammable components and much kitchen trash which contains relative high moisture. Energy gained from burning such garbage is not enough for generating electricity. Another reason is that because of financial and technical limitation, most of the incinerator in China can only burn less than 20 tons of solid garbage a day. It is not cost effective for generating electricity. Even worse, the harmful gas produced by waste plastics in the process of incinerating, if not controlled strictly, will cause serious secondary pollution to environment.

- **Recycle, Regeneration and Reuse.** This method has been greatly encouraged in China (some details are reviewed in the next section). However, so far in China most of the manufacturers involved in regeneration of waste plastics are small or medium sized village and township enterprises, lacking in advanced technique and short in fund. Since they are large in number and scattered all around, it is not easy for the state to carry out environmental control and management. Therefore it may bring about pollution to rivers and do harm to the health of employee in a certain degree.

◆ **Stacked Wantonly**. The direct consequence of this irresponsible behavior is: that waste plastics and other domestic litter in China have been piled up to 600,000 kt, seizing over 500 km² of precious arable land, with almost 2/3 of the cities (more than 200 cities) being surrounded by litter. This does not only seriously pollute surface and ground waters, endanger the cities' environment and people's living conditions, but also hinder further development of urban and rural areas.

So far there is no special state laws and regulations with regard to the use of plastics and management of waste plastics. However, the 17th and 18th articles of *The Law of People's Republic of China on Environmental Prevention and Management from Pollution of Solid Wastes*, which was put into effect on 1st April 1996 clearly stipulates: "All products should be packed with materials that are easy to be recycled and reused, to be disposed or to be cleared up in natural environment. Product manufacturers, sellers and users should recycle and reuse those recyclable and reusable packing materials and containers according to relative state laws and regulations". "Chinese government encourages research institutes and manufacturers to study and produce agricultural films easy to be recycled and reused, easy to be disposed, or to be cleared up in natural environment. The enterprises and individuals who use the agricultural films should recycle or reuse these materials to prevent or reduce pollution to environment". In addition, the *Notification on Several Preferential Treatment of Income Tax for Enterprises*, jointly issued by Chinese Ministry of Finance and State Tax Bureau, clearly stipulates that enterprises whose products are mainly made from three wastes (i.e. waste gas, waste water and industrial residues), may enjoy income tax reduction or exemption in the first five years of its production.

Lately, the problem of plastic wastes pollution (also called "white pollution", referring to harms done to the outlook or natural landscape of cities and destruction to the ecological environment caused by wantonly disposal of waste plastic packing materials and used agricultural films) is extremely serious in China. For instance, the output of plastic production in Shanghai is about 600 kt/a, around 10% of the state's total. Daily consumption of plastic bags and non-reusable containers for fast food is about 6 millions and 600,000 pieces respectively and daily generation of waste plastics is over 600 tons. In Beijing, plastic wastes in livelihood trash include plastic packing materials, plastic bags and disposable tableware, and used agricultural films in the suburb areas as well. It is estimated that there are 2.3 billions pieces of plastic bags (at a weight of 18.7 kt) in the livelihood trash and 6.75 km² of used agricultural films (at a weight of 3.0 kt) in suburbs each year in Beijing. This problem has drawn great concerns for both public and government at all levels in China. Relevant authorities in China have listed this problem as one of the imperious environmental issues. 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 recycle and reuse, and to produce degradable materials."

In many cities in China, white pollution mainly refers to wantonly littering plastic packing materials and foamed plastic boxes for fast food, which cause "visional pollution" and "potential harm". At the moment, due to powerful voice of news media and public opinion calling for a ban on foamed plastic boxes for fast food, dozens of local governments in China have issued local prohibition since 1995. Meanwhile, the Environmental Protection Bureau of P.R. China is working together with relative state departments on a timetable for banning of foamed plastic boxes for fast food. Laws and regulations are to be formulated and submitted to the State Council of China for examination and approval in 1999, and become effective in 2002. Apart from that, a circular letter on gradually introducing degradable plastic production in all regions of Liaoning has been issued by The Municipal People's Government of Liaoning Province in November 1997.

Although the implementation of prohibition alleviated "white pollution" to some extent in certain areas, practice has showed that prohibition alone can not thoroughly solve this problem. Since most of the substitutions such as paper tableware or degradable tableware for general plastics are not recyclable and have to be buried after use, thus putting a heavy load on burial treatment. Secondly, their prices and durability could not compete with general plastic products, therefore they are not welcomed in the market. So generally speaking the prohibitions are not well performed all over the country.

Supported by the State Bureau of Environmental Protection, the authorities of Beijing, Tianjing and other cities have suggested to take recycling, regenerating and reusing of non-degradable plastics as a major treatment while incinerating, burying and producing degradable substitutions as a supplement. The circular letters issued in June 1997 and November 1997 clearly stated that wasted non-reusable plastic food boxes and plastic products should be recycled and regenerated properly. In Beijing, the circular letter stipulated that recycling rate of wasted plastic food boxes must reach to 30%, 50% and 60% in 1998, 1999 and 2000, respectively. Now, a production line of regenerating polystyrene particle with a capacity of 1800 tons/a has been installed and 11 recycle stations for PS food box have been built in Beijing. The total amount of recycled PS food boxes is more than 2 tons/day and the recycling rate is over 30% in the market. The Environment Protection Bureau of Shanghai also worked out a draft plan on prevention and control of "white pollution" in Shanghai in August 1998, aiming at establishing a system of recycle, regeneration and reuse of waste plastics to pave the way for circulated economy and sustainable development in Shanghai. The project of recycling and regenerating of PS food boxes is scheduled to be formally run into operation in June 1999.

CURRENT SITUATION OF PLASTICS RECYCLING, REGENERATION AND REUSE INDUSTRY IN CHINA

The industry of recycling and regenerating waste plastics in China started in the fifties, and has undergone great changes since eighties. A number of processing factories for plastic recycling and regenerating mushroomed in coastal areas with investments from Hong Kong, Taiwan and the foreign countries. The scope of the industry has been enlarged and the technique has been improved as well. Up to this date, more than 20 sets of equipment for regenerating waste plastics with melting method have been introduced from Japan and Germany. In addition, with an increase of imported waste plastics the industry of plastic regeneration is developing vigorously in China.

Recently, the industry of refining fuel oil from waste plastics by thermal catalytic cracking is developing quickly in China. A dozen of such units have been built in Beijing, Shanxi, Shandong, Hebei and other provinces. It is estimated that these units can treat more than 20 kt of waste plastics and produce 15 kt of fuel oil each year. Though many of these units claimed that most of the waste plastics such as PE, PP, PVC and PS can be treated, practice showed that it is more suitable for PE and PP disposal. So far there is no details on producing fuel oil from PS by directly cracking in China.

China is only in its preliminary stage in treating waste plastics with thermal decomposing technique to obtain monomers and raw material for chemical industry. There is only a few research equipment for thermal decomposition, with capacity of 1000 tons/a for producing monomers. Industrialized production has not been formed. Also it is only on a trial base with regard to utilizing combustion heat of waste plastics in China.

The Chinese government always encourages the use of regenerated resources. Great attention has been paid to the high pressure brought by pollution of waste plastics to environment protection. With support from the Government, a number of the universities and research institutes are actively engaged in doing research on establishing plastic recycle system and regenerating and reusing waste plastics. However, though the total amount of recycled and regenerated plastics increase quite remarkably, the rate of waste plastic recycling and regenerating are relatively low at about 10% and 15%.

SITUATION ON RESEARCH AND MANUFACTURING OF ENVIRONMENTALLY DEGRADABLE PLASTICS IN CHINA

Since photodegradable plastics was developed in some of universities and research institutes in 1970s, the production of degradable in China has undergone following development stages. From the 70s to the middle of 80s, addictive-style photo-degradable plastics was developed by adding photosensitizing agent to ordinary PE; from the middle of 80s to the middle of 90s, the application of above mentioned plastics were extended. From the end of 80s to 1995, a new technique of blending starch to ordinary PE to form biodegradable plastics was introduced and redeveloped. From 1990 to this date, photo-biodegradable plastics on the basis of creation of the above two plastics were developed. Up to now, quality of various photodegradable, biodegradable, photo-biodegradable plastics has been greatly improved and the costs relatively reduced. Meanwhile, mechanism 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 institute have started to study on artificial materials which are thoroughly biodegradable, such as polyhydroxy acid (Qinghua University), polyhydroxy acetic acid (University of Science and Technology of Beijing) and polylactic acid (The College of Light Industry of Beijing) et al.

In recent years, production of degradable plastics has grown rapidly in China, over 50 raw material production lines have been installed. Among which, most are for starch blended plastics with a capacity of 50 kt/a; 6~7 lines are for photodegradable plastics with a capacity of 6000 tons/a; nearly 10 lines are for photo-biodegradable plastics with a capacity of 4000 tons/a. With regard to the raw material of degradable plastic products, its capacity is much higher than market need in China because of limitation of market and intrinsic shortcomings of degradable plastics.

Photodegradable Plastics

Early in the middle of 70s, research has been made on additive photodegradable plastics. In recent ten years, more and more institutions are engaged in this research and technique is relatively advanced. The principle method is to add chemical additives such as photosensitive compounds of transit metals or ferrocene derivative. There are over 15 manufacturers of photodegradable plastics in China, with a capacity about 9 kt/a. However, there is no research and manufacture on synthetic photodegradable plastics at present.

Biodegradable Plastics

Since 1990s, destructive biodegradable plastics have become focus of domestic development. The main products are plastics of starch blended or grafted PE, PP, PS, PVC or PVA. Research on thoroughly biodegradable plastics is being carried about in the labs of several universities. Apart from that, cellulose derived for straw, wheat-straw and bark are used as raw material for agricultural ground film. However, there is still a long way to go to industrialization. All together there are 60 research and production units of biodegradable plastics in China, with a capacity about 60 kt/a.

Photo-biodegradable Plastics

The research on photo-biodegradable plastics is quite advanced in China, however, efforts should be made on accurate control of time of degradation and partial degradability. Research and development of ground films with photo-biodegradable plastics has been listed as one of the key research projects of state. Ten or so institutions have adopted different methods and accorded satisfactory results. Of late, photo-biodegradable plastics have been applied to tableware, trash bags, purchasing bags, etc. There are around 40 research institutions and manufacturers in China, with a capacity of 5000 tons/a.

CONCLUSION

The consumption of plastic in China is more than 12,000 kt/a, rapidly increased with the improvement of people's living standard during recent years. The large amount of plastic waste has brought huge pressure to environment protection in China. The Chinese government and the public have paid great attention to this problem, and made gigantic efforts for a better resolution. A series of local laws and regulations concerning the management of plastic waste have been promulgated with consideration to present conditions of China. To retrieve the waste plastic for recycling, regeneration and reuse is considered to be the most practical way to reduce the environmental pollution. Research and development of environmentally degradable polymers are also encouraged prudently.

Environmentally Degradable Polymers in Brazil. A follow-up of ICS-UNIDO Workshop held in Brazil in 1998

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Abstract

The PHAs production in Brazil, a family of EDPs, was born in this decade and it seems to be promising in the near future. However, to get a final product, with all thermo- and physico-mechanical properties found in commodity plastics, it must be deeply investigated. In this sense, the Workshop on Environmentally Degradable and Recyclable Polymers sponsored by ICS-UNIDO and held in Brazil in November 1998, put together many of the best specialists in this area in order to discuss and show the viable alternatives that may be adopted to reach this goal. As a result of the Workshop follow-up, some Research Institutions and Companies in Brazil, including COPERSUCAR, are convinced that the EDPs may occupy a very important niche in the plastic market and its utilization cannot be postponed. They believe that the development of projects involving advanced research groups of countries, that are interested in this same issue, is a good alternative to gain time, experience and keep in touch with the specialists on EDPs throughout the world.

INTRODUCTION

The programme to produce EDPs in Brazil was born almost at the same time as theprogramme developed by the Brazilian government looking for alternatives for fossil fuel. The goal to produce methanol as a derivative of sugar cane resulted in a big revolution in the automotive industries, accustomed until now to project cars moved by fossil fuel. All the efforts to stress their knowledge and experiences on sugar cane and its derivatives gave to some groups of researchers the know-how necessary to make them potential experts in this issue. So, the developing of a technology for the production of anecological thermoplastic resin didn't take much efforts from them and the aim to produce PHB, one EDP from thePHAs family, established a partnership of the COPERSUCAR CENTER OF TECHNOLOGY (CTC) and the INSTITUTE OF TECHNOLOGICAL RESEARCH OF THE STATE OF SÃO PAULO (IPT) in 1992.

After a period of laboratory development, followed by bench scale tests, a technology for producing the bioplastic was established, with two main steps. The first was a biological one, the fermentation of a culture broth based on sugar cane syrup and mineral salts, that leads to a large mass of microorganisms containing a high percentage of the polymer. The second step is a series of physicochemical procedures in order to recover and purify the resin (Figure 1).

After aerobic fermentation, the final microbial mass is harvested by sedimentation and thickening. The biopolymer is solvent extracted from the biomass sludge. The extract is filtered to remove the residual biomass debris and then to a crystallization subjected process where the PHB obtained is recovered. The remaining solvent is removed and the PHB obtained is dried. Chlorinated or other solvents toxic to human being, or harmful to the environment, are not used in any stage of the process. The solvent currently used does not present any restriction from the environmental viewpoint or for food uses. The plant for future Industrial Production is being planned to avoid any environmental problem related to VOC emission.

Protection patents for this process were claimed and an economic feasibility study was carried out showing that the proposed process could be profitable. It was decided to scale up this process to a pilot unit, with the aim of developing and optimizing an industrial process for the production of the polymer on a large scale. Such scale would make it possible to standardize a final resin, develop applications and evaluate the potential market.

The pilot unit was designed and assembled, starting its operation in the second half of 1995. It is located in a sugar mill and was entirely financed by COPERSUCAR. At present, the pilot unit is operating normally and the bioplastic produced is being tested by plastic processors that are developing applications and trying to replace petrochemical plastics by the biodegradable PHB. In this way, COPERSUCAR has far stablished several agreements with plastic processors to develop uses and market for its product.

The main targets for PHB are the food package and filmes industries, as well as products for personal care, cosmetics, automotive parts, chemical containers, surgical and odontological disposable devices and many others where recycling is difficult and disposability is necessary. There is a market of large proportions (greater than 300,000 tons/year) and a demand for such a product so far is restrained.

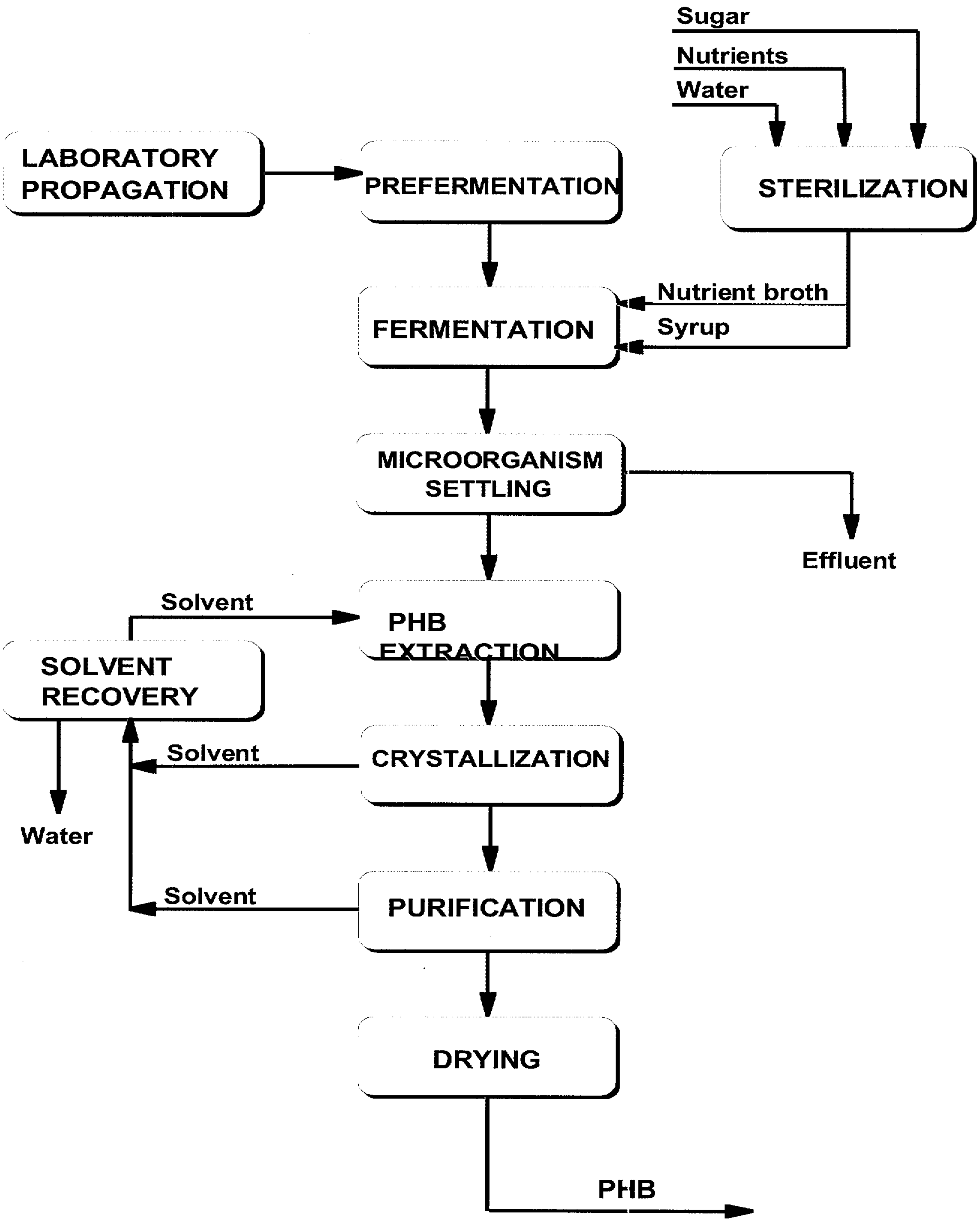
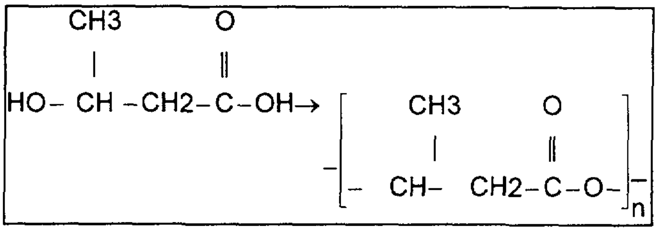


Figure 1: Simplified Description of Biodegradable Plastic Production from Sugar Cane

COPERSUCAR activities are focused on the production of the polymer, whose properties are specified below.

Product properties

PHB COPERSUCAR is a homopolymer of 3-hydroxybutiric acid obtained by aerobic fermentation of a bacterium of the genus Alcaligenes, with the following chemical structure (Figure 2).



$$\mathrm{HO{-}\overset{CH3}{\overset{|}{CH}}{-}CH2{-}\overset{O}{\overset{\|}{C}}{-}OH} \rightarrow \left[\mathrm{-\overset{CH3}{\overset{|}{CH}}{-}\;CH2{-}\overset{O}{\overset{\|}{C}}{-}O{-}}\right]_n$$

Figure 2: Chemical structure of PHB

Some technical data of the production of PHB, as well as the data related to the pilot plant and its physicochemical properties may be seen in Tables 1, 2 and 3.

Table 1: Basic data related to the Pilot Unit for Biodegradable Plastic (PHB) Production

Site	USINA DA PEDRA S/A –Serrana /SP
Capacity	30-60 tons per year
Investment	US$ 2, 500 000.00
Products	Bioplolymers (PHB , PHBV)
Product characteristic	Yellowish white powder with purity higher than 99,5%. Mw (250,000 – 600,000).
Engineering project	CENTRO DE TECNOLOGIA COPERSUCAR (CTC)
Technology	CTC – IPT (Institute of Technological Researches)
Basic raw material	Sucrose
Microorganisms	Bacterium of the genus Alcaligenes
Process	Polymer biosynthesis by aerobic fermentation. Extraction and purification of the polymer by solvent.
Start-up of the unit	September/1995

Table 2: Technical coefficients of the PHB Production Process

Sugar consumption	3,0 kg/ kg of PHB
Biomass yield (dry basis)	100 Kg dry biomass/ m^3 of fermentation wine.
Fraction of biodegradable plastic	70 – 75%
Fermentation time	45 hours
Yield related to PHB extraction	~95%
Energy consumption	2,9 kW.h/Kg PHB (provided by cane bagasse remaining after sugar extraction)
Steam consumption	40Kg/Kg PHB

Table 3: Physicochemical properties of COPERSUCAR's PHB at present

PHB content	99,5% (dry basis)
Moisture	near 0,3%
Nitrogen	below 0,1%
Ashes	near 0,25%
Residual solvents	below 10 ppm
Molecular weight	near 250,000
Specific gravity	1,200 Kg/m^3
Melting point	169-172 °C
Glass transition temperature	1 - 5 °C
Decomposition temperature	250 °C
Crystallinity	70%

According to COPERSUCAR, the properties of polymer to be achieved next year are summarized in Tables 4 and 5.

Table 4: Some physicochemical parameters of PHB to be reached in 2000

PHB content	higher than 99,5% (dry basis)
Moisture	less than 0.2%
Nitrogen	" 0.05%
Ashes	" 0.1%
Residual solvent	" 2 ppm
Molecular weight	250,000 to 650,000

Table 5: Mechanical properties expected for PHB

Impact resistance	25.4 J/m
Strenght at break	31.5 kgf /cm^2
Tensile strenght	7.6 kgf / cm^2
Elongation to break	10.4%

Studies on biodegradability in vitro were developed with samples of the polymer and of compounded resin injected to standard test probes submitted to DIN 53739 (ASTM G21/G22 - 90) norms. The results has shown a biodegradation of the samples in 29 days and attended these norms. In order to know the behaviour of the same samples in the field, samples of compounded resin injected to standard test probe were introduced in IMHOFF chambers. They showed 75% loss of weight in 180 days. When buried in several types of soil, they showed surface microbial attack after 2 to 4 weeks depending on the soil characteristics.

FUTURE PROSPECTS

COPERSUCAR is looking for partners that could have technology to compound the polymer and develop opportunities for commercial application of this unique polymer in various fields related to plastic processing, such as injection molding, extrusion process, processing by injection and blowing, plastic film development and any other.

Partners, could be companies that develop technology for polymer processing, polymer processing equipment suppliers and plastic processors.

COPERSUCAR wish to know from those companies what are the physical, chemical and mechanical standards that must fulfill in order to be usable for their commercial purposes.

Also, it wishes to know which properties must be corrected or improved to attain partners expectances or if there are some properties, which their standards could be more tolerant, than those proposed by COPERSUCAR. In case there is an interest in any collaboration agreement or commercial venture between the potential partner and COPERSUCAR, some information are required , as listed below:

- Raw biopolymer demand per year, actual and projected needs for,1999, 2000 and 2001 years.
- Size of the companies involved in terms of annual gross income or equivalent parameter.
- Markets to which the companies direct their activities, such as:
  medical applications, personal care products, cosmetics, consumer goods, packaging, food industry packaging, agriculture and vehicle production.
- Raw polymer needs for the initial step of application development, considering:
  Quantity (Kg) to be delivered under previously defined specifications and the frequency of delivering.

State of Rubber Industry in Iran and Its Environmental Impact

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INTRODUCTION

Rubber wastes generated from the used tires and rubber goods has been one of the sources of pollution caused by polymeric products.

Although different techniques such as landfill, incineration, pyrolysis, reclaiming, reuse and retreading has been developed to handle the problem but huge amount of tires and rubbers are discarded as waste, in the environment.

With regard to the considerable amount of used rubber to be disposed of, incineration and dumping on waste sites are still the most frequently used techniques, but dumping is on the decline. On the other hand, recycling of used rubber still plays an important role for environmental protection.

The present paper is an attempt to analyze the state of rubber industry in Iran and its quantitative and qualitative developments during the past twenty years. Due to high demands for tires and rubber articles and their useful life, measures and approaches has taken to either retread or recycle them, would be discussed.

TIRE INDUSTRY IN IRAN

Tire industry in Iran started its production from beginning of 60^{th}, when the first tire production company called B.F. Goodrich started its production. Until 1978 three other production units came in to operation, producing totally 42,000 tones of tires per year. From 1978 onwards due to importance of tires in transportation, the renovation, expansion and development of tire industry from quantitative and qualitative point of view was given the priority and Table 1 shows the plants with their capacities producing passenger, light duty, heavy duty, agricultural and off the road tires, operating in the country.

Table 1: Existing Plants and New Projects

Plant Name	Production Capacity (tones/year)
Kian Tire	32,000
Iran Tire	32,000
Dena Tire	45,000
Pars Tire	45,000
Kerman Tire	45,000
Yazd Tire	15,000
Kavir Tire	25,000
Artawheel Tire	25,000
Khozestan Tire*	10,000
Zagross Tire*	25,000
Iran Yasa Tire and Rubber	15,000
Total	314,000

*Will start production from the year 2000.

It is forecasted that the consumption for the country would be about 180_-200,000 tones/years.

The remaining capacity is exported to different countries in Asia, Africa and Middle East.

Figures 1, 2, 3 and 4 shows the production of passengers, light duty and heavy duty tires respectively per year. It is clear from Figure 4 the production has been continuously increasing from 1978 till today (five times) and is expected to become seven times compared to 1978 year_s production, by the year 2000.

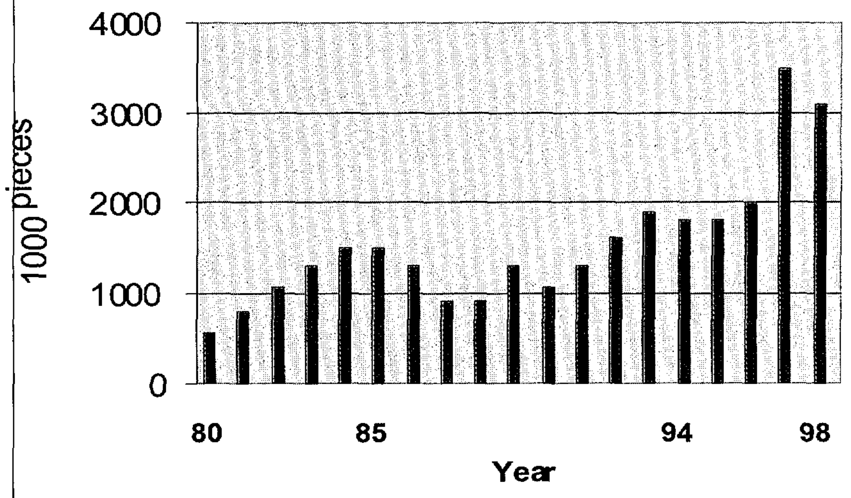

Figure 1: Production of Passenger Tires from 1981 -1998

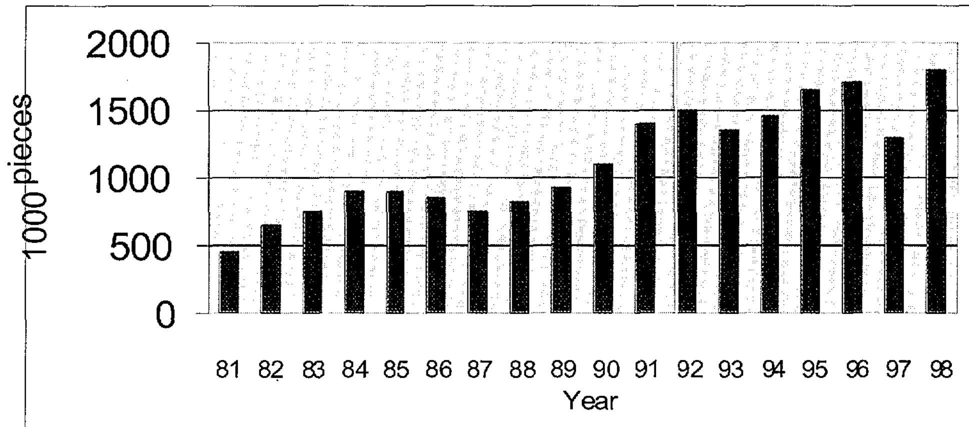

Figure 2: Production of Light Duty Tire from 1981-1998

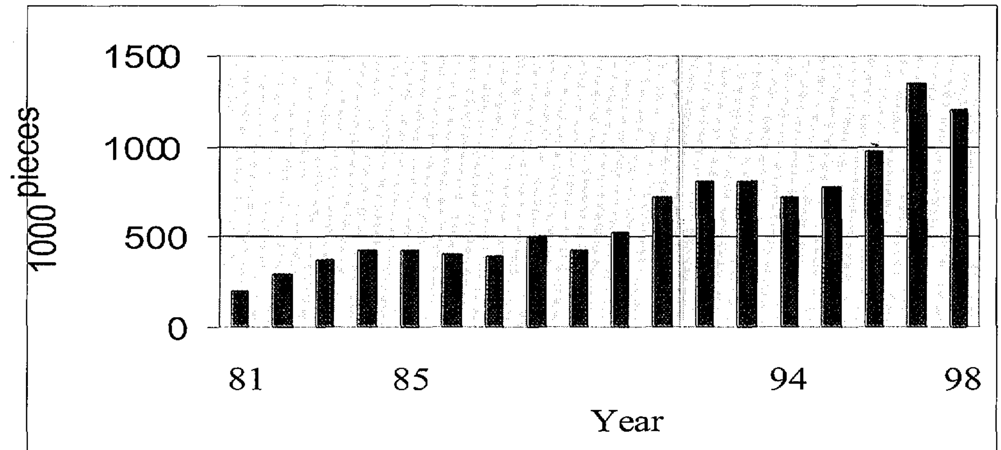

Figure 3: Production of T.B. Tires from 1981-1998

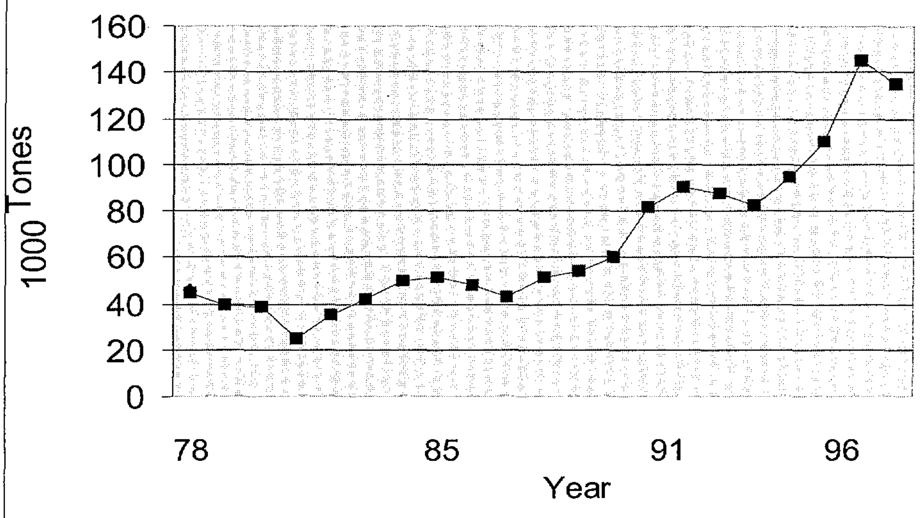

Figure 4: Production of Tire and Tube in Iran from 1978-1998

Regarding qualitative development, the existing bias technology is being changed to steel belted radial tires and plans for production of all steel tires are in program. With regard to quality system, few of the plants has obtained ISO 9001 certificate and others are in process of establishing the ISO 9000 quality systems.

It is expected that around 150,000 tones of tires are annually corded as waste. The increasing quantity of tires and rubber goods product as waste, have caused severe environmental pollution and disposal problems, in the country, forcing policy maker to study and find right solutions for the problem.

As it can be seen from Tables 2 and 3, the main material composition of tires are rubbers and other materials which are economically very valuable and can be recycled to useful products. From different techniques of tyre waste handling such as landfill, incineration, pyrolysis, retreading and reclaiming. The last techniques (retreading and reclaiming) have been found to be useful to make better use of waste tires in our country. The important point is that tires can be retreaded, which are not damaged and are suitable for retreading. The damaged and worn ones could be taken to the reclaiming plant, to produce rubber granulates or rubber reclaims.

Table 2: Material Composition of a Tire

Material	%
Natural Rubber (NR)	25
Synthetic Rubber (SR)	25
Carbon Black	25
Cord (Steel / Textile)	15
Others	10

Table 3 shows the rubber composition of tire apart from the cord (steel or textile) and bead wires. During the reclaiming process the cords and bead wires are separated, the remaining is shredded and granulated, then chemically depolymerised and refined as reclaim rubber.

Table 3: Rubber Composition of a Tire

Composition	%
Rubber Polymer	50
Carbon Black	25
Oils (Softener)	20
Zinc Oxide	2
Sulfur	2-1
Accelerators	0.5
Antioxidants	1.5

Around 20 plants of retreading with the cold and hot retreading technology exists in the country with a total capacity of around 1,500,000 tires/year. The total retreading units are listed in Table 4 with their capacity.

Table 4: Retreading Units

Number	Retreading Technique	Capacity Tires
10	Cold Recaping	500,000
10	Hot	1,000,000
Total: 20	Cold + Hot	1,500,000

At present cold retreading is preferred due to its lower investment, production flexibility, simplicity, safety and better performance in service of tires retreaded. Table 5 shows the percentage of different type of retreading in some European countries. It is clear that cold retreading technology is having a better market due to its advantages.

Table 5

Country	Hot Retreading %	Cold Retreading %
Austria	35	65
U.S.A.	25	75
Denmark	45	55
Sweden	15	85
Switzerland	50	50

Retreaded tires can be used as replacement tire in different types of vehicles. It can be seen from Figure 5 that majority of retreaded tires are used in truck tires (48%) of light truck tires 20%.

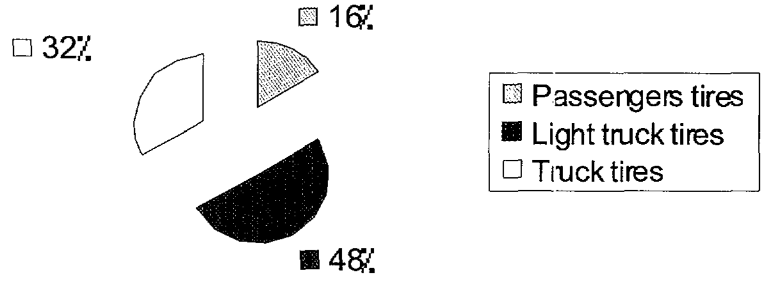

Figure 5: Share of Retread in the Replacement Business

Two reclaiming plants in the country are in production. One is producing about 10,000 tones of reclaim per year plus 6,000 tones of granulated or powered rubber.

Next plant is about 3,000 tones capacity and produces butyl reclaim. All these products are being used in rubber industry as a source of raw materials and some are exported to other countries.

CONCLUSION

Tires are very important in transportation industry for the development of the society and their consumption increases leading to used tires as waste. In order to prevent or scale down the pollution caused by used tires, it is found that retreading and reclaiming are a suitable way to reuse rubber waste. Also producing longer lasting tires, better care of tires and making better road surface to reduce the wear, increasing life of tire casings by retreading, using granulated rubber and using tyres as a source of energy could decline the pollution problems caused by rubber waste.

Recycling of Waste Latex Products and Its Utilisation

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Abstract

Due to the unstable nature of the latex compound and the strict specifications in the quality of latex products such as examination and surgical gloves, the rejection in the latex industry comes to as high as 10 to 15 percent of the rubber consumed. These rejects have created a major disposal problem for the rubber industry. In addition the used examination and surgical gloves from the laboratories and hospitals are of a sizable quantity which requires a systematic disposal arrangement without causing a major environmental problem. Moreover the local authority prohibits the open burning or burial of these rejects due to environmental pollution. But it represents a source of high quality rubber for reclamation and reuse. One of the utilizations of this latex reclaim was undertaken by developing polymer alloys with thermoplastics. Thermoplastic elastomers of isotactic polypropylene and latex reclaim were prepared using a Brabender plasticorder torque rheometer. The mechanical properties of these blends are comparable with those of the conventional thermoplastic elastomers based on natural rubber and polypropylene. The effect of dynamic crosslinking of these blends has shown that it increases the mechanical properties like tensile strength, modulus of elongation and impact strength. Scanning electron microscopic examination of the tensile fracture surfaces has been used to correlate the test results. Viscosities of the dynamically vulcanized thermoplastic elastomers showed that they have good processing stability and are processable as thermoplastics.

INTRODUCTION

Thermoplastic alloys and blends represent one of the fastest growing sectors of the plastics industry. Physical modification of thermoplastics by addition of an elastomer is one of the most important ways of producing thermoplastic elastomers with special properties. Thermoplastic elastomers are materials having the characteristics of thermoplastics at processing temperature and those of elastomers at service temperature (1-4). This unique combination of properties of vulcanized rubber and the easy processability of thermoplastics bridge the gap between conventional elastomers and thermoplastics. Blending of an elastomer with a thermoplastic in an internal mixer at a temperature above the melting point of the thermoplastic has certain definite advantages (5-7). The desired properties can be achieved by the proper selection of elastomer and thermoplastic components and their ratios in the blend. It has been further shown that the addition of a small quantity of crosslinking agent during melt mixing of the polyolefin and the elastomer phase improves the technical properties of the thermoplastic elastomer. The crosslinking efficiency of polypropylene can be increased by the addition of a co-agent together with organic peroxides (8-11). Since the crosslinking of polypropylene initiated by thermal decay of organic peroxides is a more complicated task due to the nature of the microradical reactions occurred by β -scission and disproportionation. This leads to molecular weight decrease, branching the originally linear macromolecules and an overall chemical change of polypropylene due to an increase of the double bond concentration as well as of the amount of degradation and oxidation products. Recombination of microradicals occur simultaneously with the degradation process and can lead to crosslinking under certain conditions. Microradical fragmentation is apparently retarded by coagent presumably because of macroradical addition to the reactive centre of the coagent and a more stable radical is formed. The latter decays either by recombination with another radical or by transfer reaction. Polyfunctional monomers are the most used coagents for polypropylene crosslinking like divinyl benzene, diethylene glycol dimethacrylate, diallyl maleate, unsaturated esters and ethers of pentaerythritol, triallyl cynaurate together with organic peroxides (12,13). But the efficiency of these coagents is not high enough especially at high additive concentration. Various side reactions, mainly homopolymerisation of coagent, take place if the amount of additive is high. p-Benzoquinone and bisphenol were found to be highly effective coagents for polypropylene corsslinking (14).

This paper reports studies on thermoplastic elastomers prepared from natural rubber latex waste [hereafter referred to as latex reclaim (LR)] and isotactic polypropylene (iPP). The mechanical properties like Tensile strength, modulus of elongation and impact strength of the PP/LR blends were compared with those of PP/NR blends. The effect of dynamic vulcanization on mechanical properties was also studied. Scanning electron microscope (SEM) has been used in explaining the effect of basic components of the blends on the physical properties of thermoplastic elalstomer (15-18). The tensile fracture surface of the blends have been analysed by SEM.

EXPERIMENTAL

Materials

The experiments have been carried out using isotactic polypropylene (iPP) having melt flow index of 4.2g/10min at 190°C/49 N and natural rubber having mooney viscosity of 85.2 at ML(1 + 4) 100°C. Latex reclaim was prepared from waste latex gloves having volatile matter of 0.12%; Ash content of 3.99% and Acetone extract of 4.86%.

Additives used are zinc oxide, stearic acid, Benzoyl peroxide, Dicumyl peroxide, p-benzoquinone and Accinox ZC(N-1,3 dimethyl N' phenyl p-phenylene diamine) were all commercial grade.

Preparation of thermoplastic elastomers

Thermoplastic elastomers were prepared on a Brabender plasticorder torque rheometer as per the formulations given in Table 1. The blend ratios are denoted by the letters A, B and C. Letters a-f denote the blends containing various additives as specified in the table.

Table 1

Material	A	B	C
PP	90	80	70
NR or LR	10	20	30
Additives	a, b, c, d, e, f	a, b, c, d, e, f	a, b, c, d, e, f

a) Blends containing 1.0 phr Accinox ZC for the rubber phase.

b) Blends containing 4.0 phr zinc oxide, 2.0 phr stearic acid and 1.0 phr Accinox ZC for the rubber phase.

c) Blends containing 4.0 phr zinc oxide, 2.0 phr stearic acid, 1.0 phr Accinox ZC for the rubber phase and 2.0 phr Benzoyl peroxide for the plastic phase.

d) Blends containing 4.0 phr zinc oxide, 2.0 phr stearic acid, 1.0 phr Accinox ZC for the rubber phase and 2.0 phr dicumyl peroxide for the plastic phase.

e) Blends containing 4.0 phr zinc oxide, 2.0 phr stearic acid, 1.0 phr Accinox ZC for the rubber phase,2.0 phr benzoyl peroxide and 1.0 phr p-benzoquinone for the plastic phase.

f) Blends containing 4.0 phr zinc oxide, 2.0 phr stearic acid, 1.0 phr Accinox ZC for the rubber phase, 2.0 phr dicumyl peroxide and 1.0 phr p-benzoquinone for the plastic phase.

Note:

Indices 1, 2 denote the blends containing NR,LR respectively (e.g., a_1 denotes the blend containing NR with ‘a’ type additives and a_2 denotes the blend containing LR with ‘a’ type additives).

Mixing was done at 190°C and 40 rpm. PP was melted in the mixer for 1 minute and then NR/LR containing the additives was added and the mixing was continued for 5 minutes. For the blends containing benzoyl peroxide,dicumyl peroxide,p-benzoquinone curative system,BPO,DCP and p-benzoquinone were added after four minutes blending of PP and NR/LR. The mix was then taken out and sheeted on a laboratory mixing mill at 2.0 mm nip setting. The sheeted material was cut into small pieces and again mixed in the plasticorder at 190°C for two minutes so as to get uniform dispersion of the ingredients. After mixing, it was compression moulded in an electrically heated hydraulic press at 190°C for 3 minutes. The mould used was provided with bolts and nuts so that the materials inside could be held under pressure even after taking out from the press. At the end of the moulding time, the sample still under compression was immediately cooled by plunging the mould into cold water. Aluminum foils were used between the mould surfaces to minimize shrink marks on the sheets.

The impact strength of the blends was determined by a Dynstat apparatus. Other mechanical properties of the blends have been measured on a typical universal testing machine.

Viscosity measurements of the uncrosslinked (b) and crosslinked (f) blends were done on the Brabender plasticorder at a temperature of 190°C and 40 rpm rotor speed. The dependence of the viscosity (torque/rpm) of these blends with the percentage of polypropylene was evaluated by taking the torque values of the blends after mixing for 5 minutes.

Microscope observations were carried out with a scanning electron microscope (SEM). For this purpose the tensile failure surface of the crosslinked (f) blends were carefully cut out from one of the test pieces without touching the surfaces and then sputter coated with gold within 24 hrs of testing. The specimen were stored in a desiccator before and after gold coating until the SEM observations were made inorder to avoid contamination.

Results and Discussion

Figure 1 shows the variation in tensile strength of uncrosslinked PP-NR blend (a_1 & b_1) and PP-LR blend (a_2 & b_2) with the amount of polypropylene. The tensile strength of the blends decreases with an increase in the rubber content of the blends as expected (18). In blends containing a higher proportion of PP, the elastomer phase remains as dispersed particles. Smaller size and uniform dispersion of the dispersed phase improve the tensile properties of the blends (19). In uncrosslinked blends, the molecular entanglements in the rubber particles alone are unable to prevent rapid flow and fracture in response to an applied stress (20. This results in the lower tensile strength of the uncrosslinked blends. It is seen that the tensile strength of the blends with LR is slightly higher than those of the blends with NR. This is possibly due to the presence of crosslink precursors and/or unreacted curatives in the latex reclaim (21)

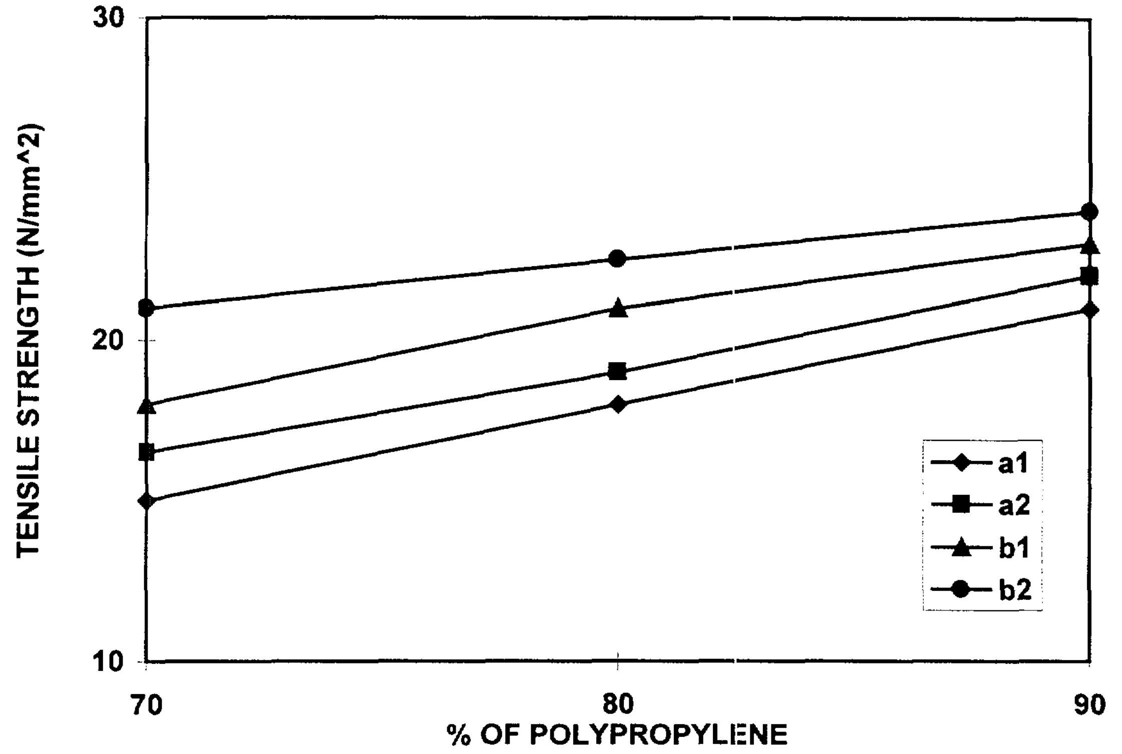

Figure 1: Variation in Tensile Strength with Percentage of Polypropylene of uncrosslinked a1, b1 (PP-NR); a2, b2 (PP-LR) Blends

Figure 2 presents the variation in tensile strength of the crosslinked PR-NR (c_1 , d_1 , e_1 , & f_1) with the percentage of polypropylene. The tensile strength of the dynamically crosslinked blends are found to be higher than those of the uncrosslinked blends. Crosslinking allows the polymeric particles to reach higher strains and at the same time confers mechanical strength to the particles (20). In the case of benzoyl peroxide cured blends [c], the reduction in tensile strength is probably due to the molecular degradation of PP at the processing temperature. Curing with P-benzoquinone (e) improves the tensile strength of these blends and acts as a stabilizer of polypropylene thermodegradation i.e., if quinone is present, it inhibits the degradation process and further crosslinking occurs. The maximum improvement in tensile strength was observed for the thermoplastic elastomer containing ‘f’ type curatives. It means that small amount of quinone is sufficient to produce crosslinking network along with the organic peroxides. Moreover the role of quinone as the coagent of crosslinking can consist in the ability of binding the fragments, i.e., the end microradicals into a primary formed polymer network besides diminishing the fragmentation of microradicals.

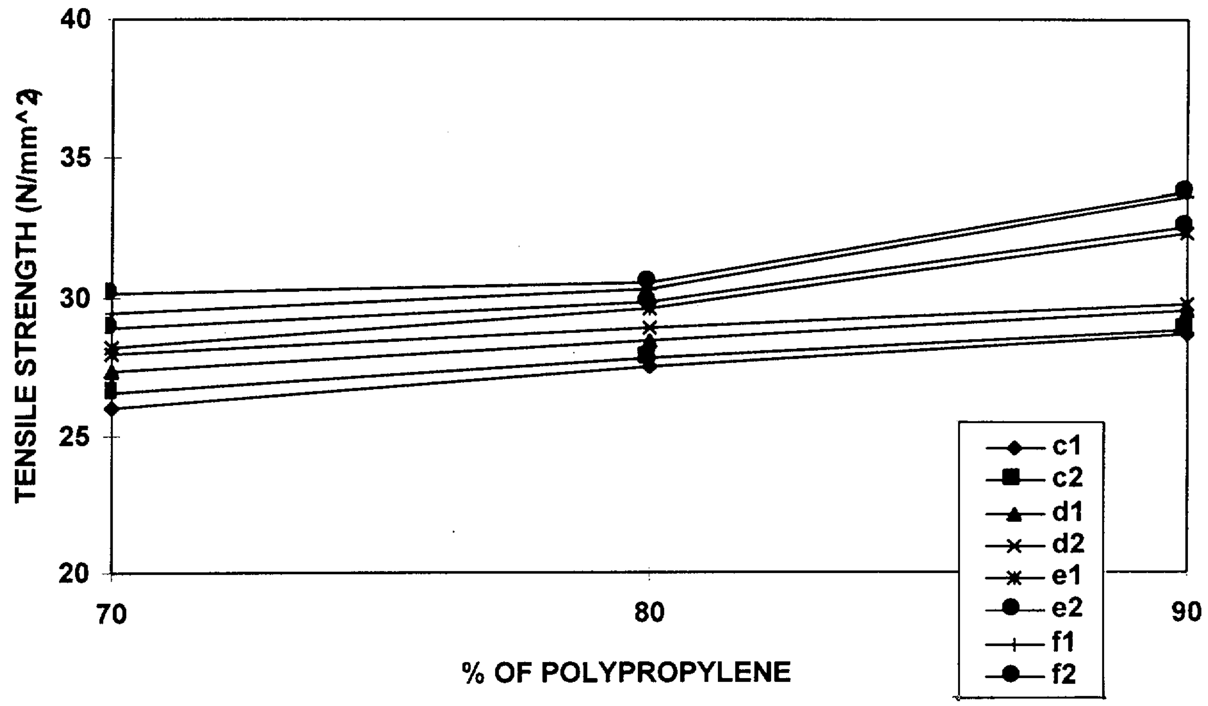

Figure 2: Variation in Tensile Strength with Percentage of Polypropylene of crosslinked c 1, d1, e1, f1 (PP-NR); c2, d2, e2, f2 (PP-LR) Blends

Figures 3 and 4 show the variation of modulus of elasticity with polypropylene content of uncrosslinked and dynamically crosslinked blends respectively. The modulus of elasticity is found to be higher for the crosslinked blends and the maximum improvement is observed for the blends crosslinked with dicumyl peroxide and p-benzoquinone. For both uncrosslinked and dynamically crosslinked blends, the modulus of elasticity of the PP/LR blends is found to be higher than those of the PP/NR blend. This may be attributed to the partially crosslinked nature of LR (22,23).

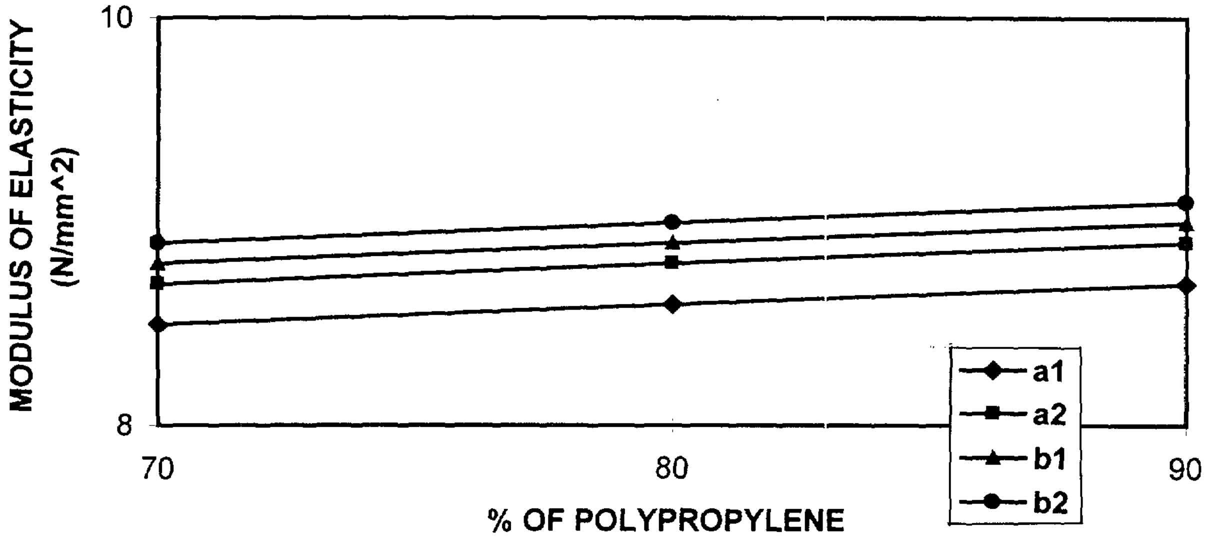

Figure 3: Variation in Modulus of Elasticity with percentage of Polypropylene of uncrosslinked a 1, b1 (PP-NR); a 2, b2 (PP-LR) Blends

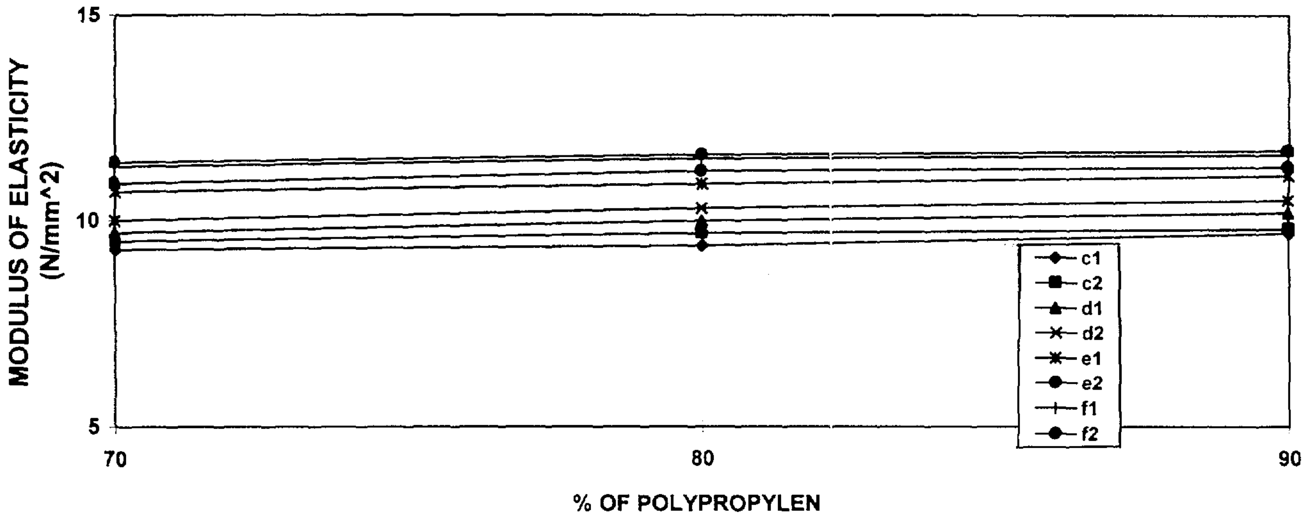

Figure 4: Variation in Modulus of Elasticity with percentage of Polypropylene of crosslinked c1, d1, e1, f1 (PP-NR); c2, d 2, e 2, f 2 (PP-LR) Blend

The impact strength of the thermoplastic elastomers with the percentage of polypropylene at different temperatures (293K,273K and 253K) of uncrosslinked (b) and Crosslinked (f) blends is shown in Figures 5 and 6. At about 293K, i.e., above the glass transition temperature of PP, a minimum of the impact strength at 10% rubber content can be observed. At low temperatures (below the glass transition temperature of PP) the minimum vanishes. It seems that the variations of the impact strength with temperature can be explained by assuming a mechanism that is analogous to the case of blends in the fluid state (24): at lower NR/LR content the blend essentially consists of isolated NR/LR elastomeric molecules assembled in the amorphous region of PP. In isolated form these molecules are characterised by much lower capacity for energy absorption. Simultaneously, they can be treated as a factor that disturbs the PP structure. Because of the increased mobility of PP chains above the glass transition temperature, this behaviour can lead to a decrease in impact strength. This effect gradually vanishes owing to the increase in the number of energy absorption centres at higher concentrations of the elastomeric phase. Below the glass transition temperature of PP, the effect related to the capacity for energy absorption of isolated molecules becomes stronger compared with that resulting from the disturbance of PP structure by these molecules. As a consequence of this behaviour, the minimum vanishes and an increase in impact strength can even be observed. The impact strength of PP/LR blends are comparatively higher than those of PP/NR blends.

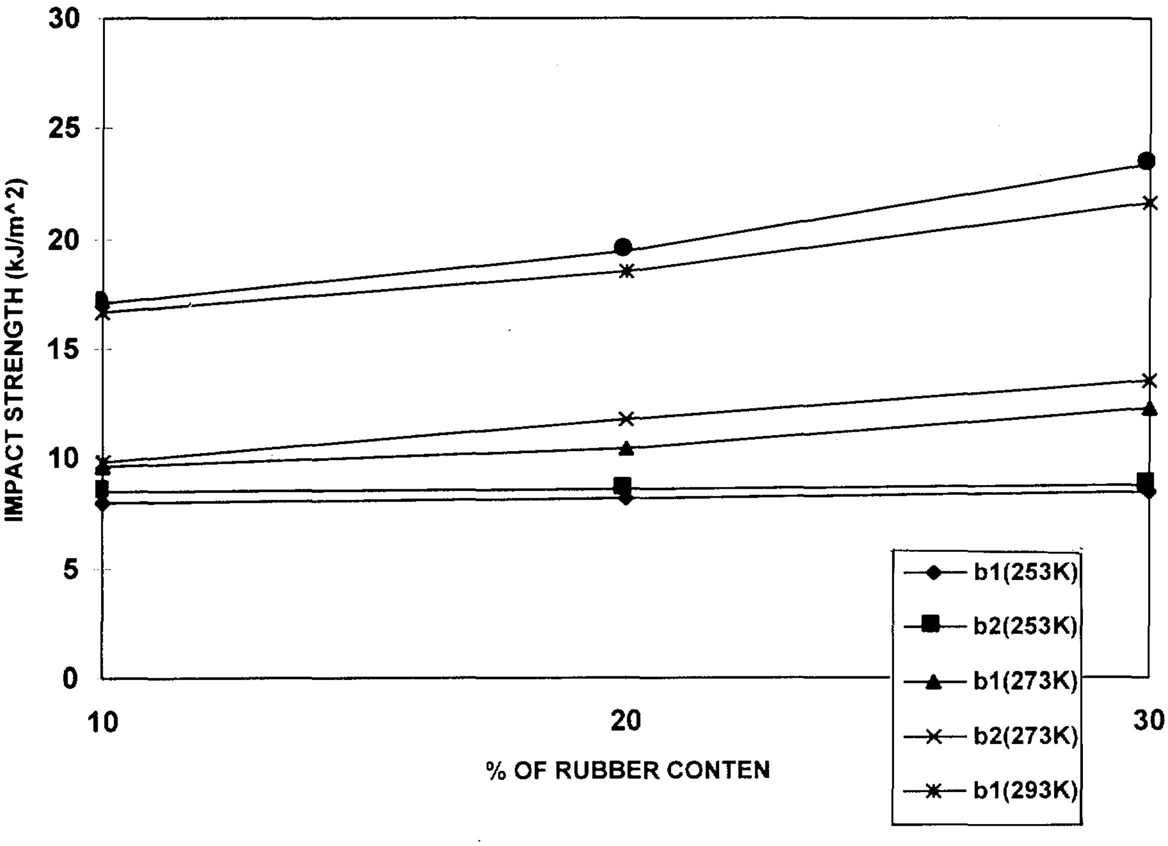

Figure 5: The Influence of Rubber Content on Impact Strength of uncrosslinked b1 (PP-NR); b2 (PP-LR) Blends at Different Temperatures

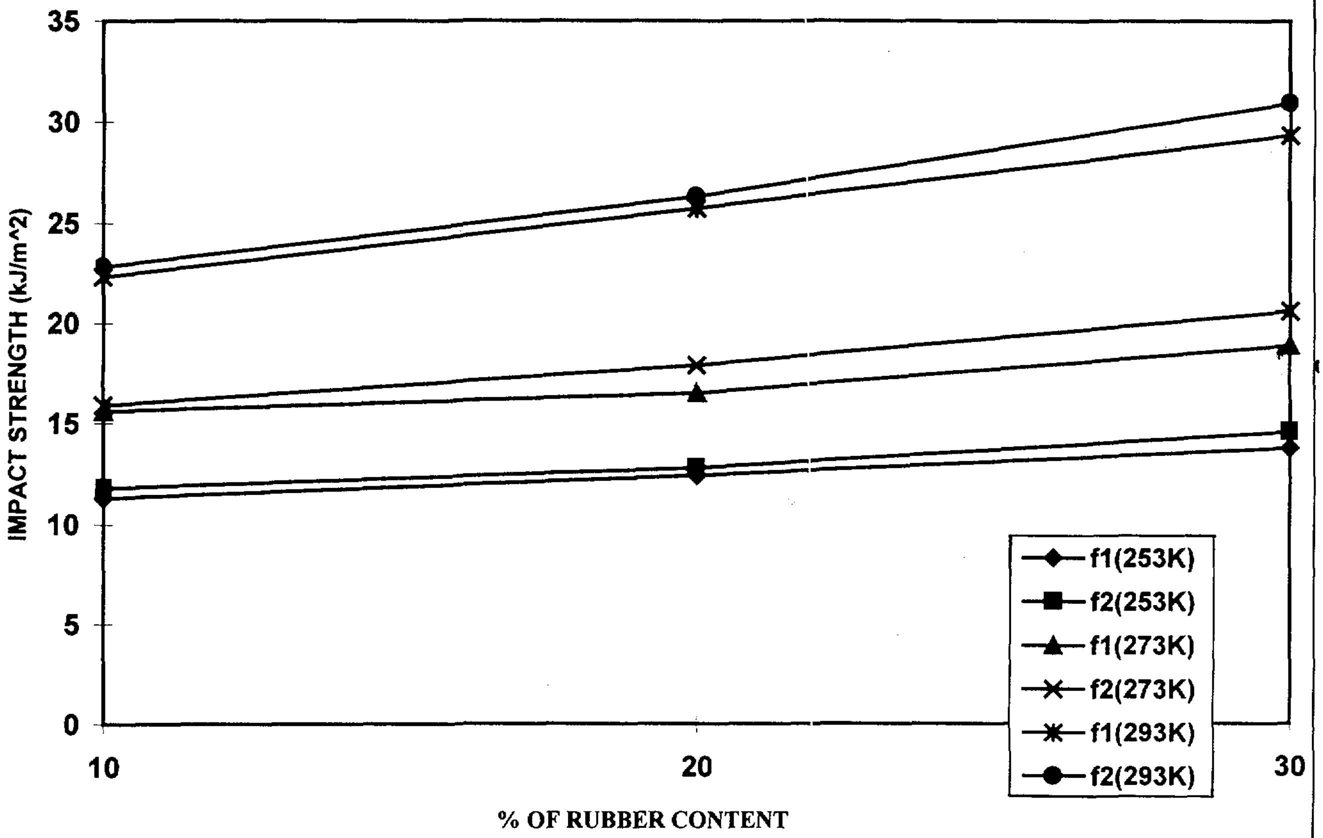

Figure 6: The Influence of Rubber Content on Impact Strength of crosslinked f1(PP-NR); f2(PP-LR) Blends at different Temperatures

Figure 7 presents the effect of blend viscosity (torque/rpm) with the percentage of polypropylene of uncrosslinked (b) and crosslinked (f) blends. It is seen that the proportion of elastomer phase in the blend and the extent of dynamic crosslinking have a profound influence on the viscosity of the blends . The uncrosslinked blends show lower viscosity compared to that of the crosslinked blends. The viscosity increases with the percentage of rubber in the blends. Crosslinking of the thermoplastic elastomer increases its viscosity and decreases the deformation of the dispersed particles as indicated by the increase in Brabender mixing torque values. The viscosities of the PP-LR blends are found to be slightly higher than that of the PP-NR blends as expected.

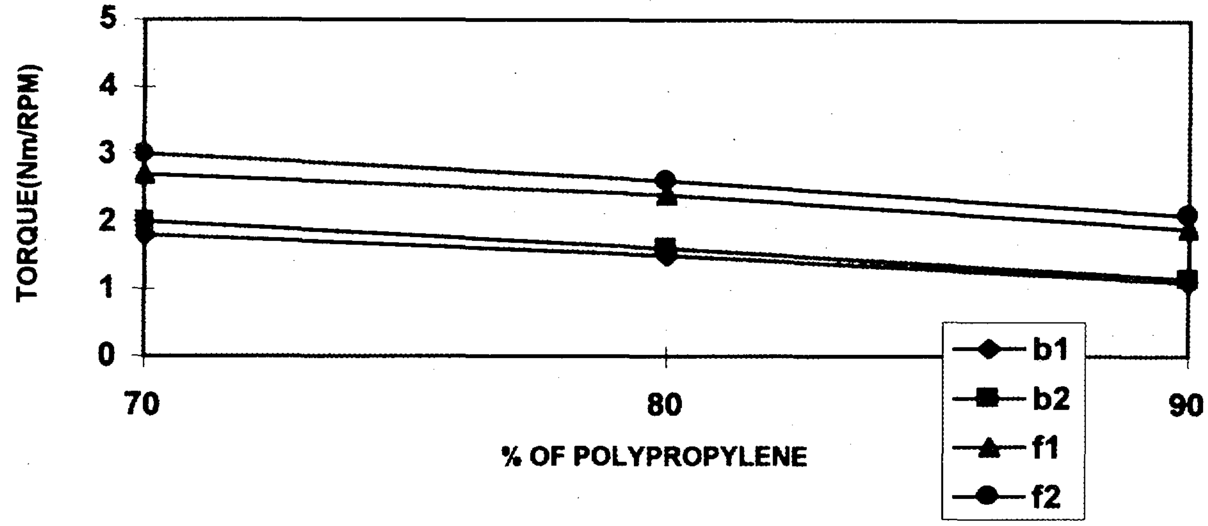

Figure 7: Variation in Viscosity with percentage of Polypropylene of uncrosslinked b 1 (PP-NR); b 2 (PP-LR) and crosslinked f 1 (PP-NR); f 2 (PP-LR) Blends

The morphological studies of the PP-LR blends were made using the crosslinked blends (f). Fig 8 shows the tensile fractograph of 90/10, PP/LR blend. The failure is of a brittle nature with multidirectional cracks. Figure 9 shows the fracture surface of PP/LR (80/20) blend. It indicates that the initiation of fracture is propagated concentrically as the shear advances. Increasing the rubber content in the blend (Fig. 10) increases the continuity of the rubber phase. Due to the partially crosslinked nature of the latex reclaim, it reduces the particle size and improves the dispersion of the rubber phase in the blend. The resistance to high deformation of this crosslinked particles restricts the flow under stress, as shown by the presence of many short curved shear lines on the fracture surface (Fig. 10).

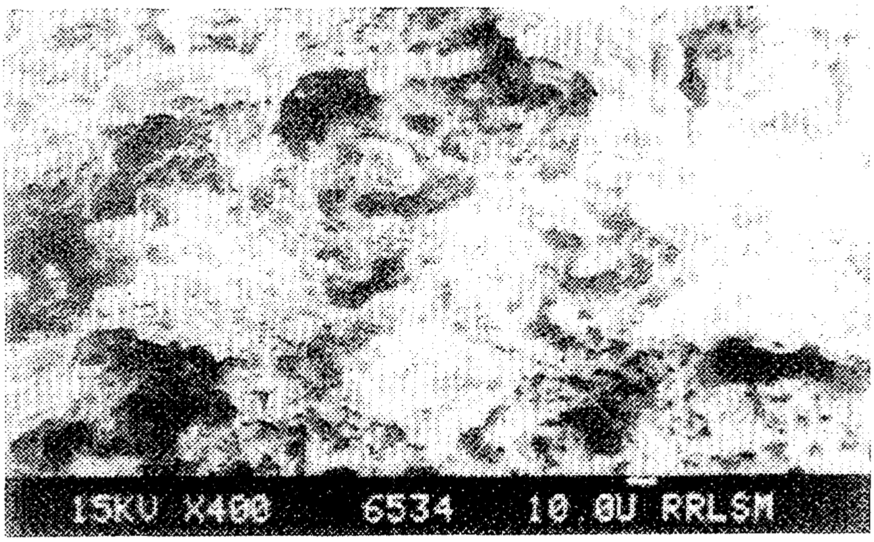

Figure 8: SEM photograph of the tensile fracture surface of crosslinked (f2) PP/LR (90/10) blend

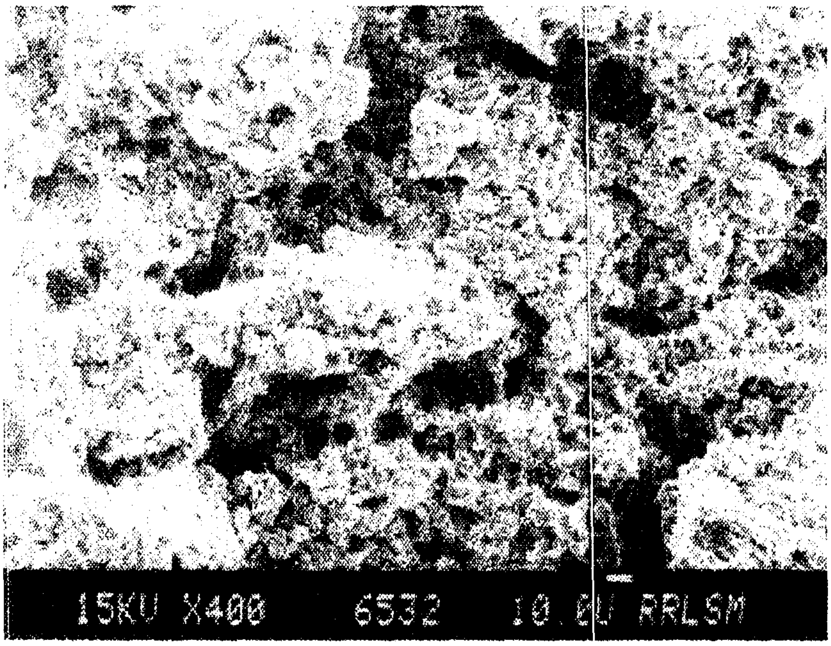

Figure 9: SEM photograph of the tensile fracture surface of crosslinked (f2) PP/LR (80/20) blend

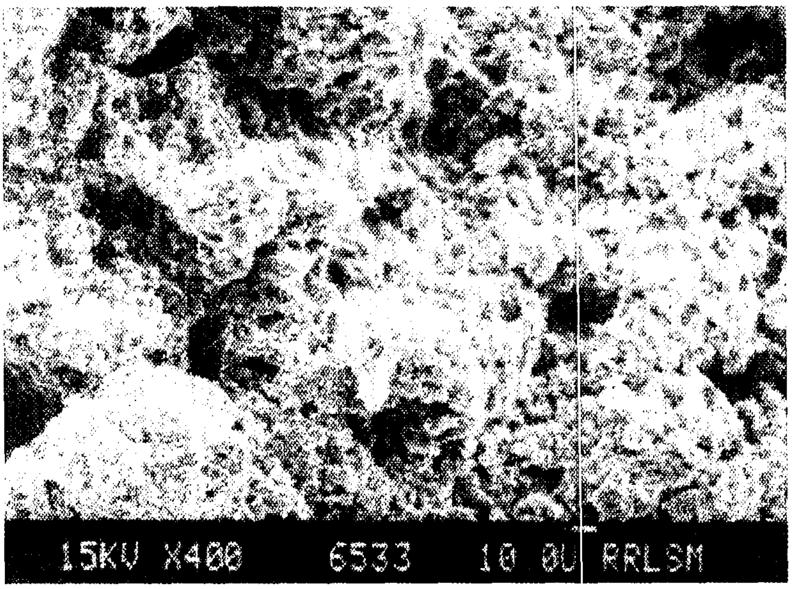

Figure 10: SEM photograph of the tensile fracture surface of crosslinked (f2) PP/LR (70/30) blend

CONCLUSIONS

1. Thermoplastic elastomer can be developed economically from latex product waste and isotactic polypropylene.

2. The mechanical properties of polypropylene/latex reclaim blends are comparable with those of the blends based on polypropylene and natural rubber.

2. The dynamic crosslinking improves the tensile strength, modulus of elasticity and impact strength of the polypropylene/natural rubber and polypropylene/latex rubber blends.

4. Addition of latex reclaim minimises the brittle failure of polypropylene as observed in the PP/NR blends and moreover dispersed particles of latex reclaim restrict the matrix flow in polypropylene/latex reclaim thermoplastic elastomers.

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Fluorescence Probes for Polymer Characteristics, Degradation and Molecular Weight Determination

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Abstract

Demands on developing polymers implies on researchers to use various techniques to understand their properties not only on macro- but on micro-levels. Fluorescence spectroscopy techniques (steady state fluoresence, fluorescence lifetimes, time-resolved fluorescence, red-edge effect, etc.) is a line in this direction. In this context we have used various fluorescence probes, Figure 1, to study polymers (polyvinylalcohols, polyalkylmethacrylate, etc.) heterogeneity : (probes 1, 2 and 3); polymers micropolarity and microviscosity : (probes 4-9). Lately we have suggested the use of twisted intracmolecular charge transfer (TICT) fluorescence , occurring in probes 6-9 and related compounds, as molecular weight detectors of polyalkylmethacrylate polymers. We are in the process of generalizing the idea to include other polymers using various fluorescence probes. The fluorescence properties of PRODAN #10 and dewar-anthracene # 11 are under study and are promising in investigating polymer dynamics.

INTRODUCTION

The advancement of applied sciences in general and polymer science in particular made humans to enjoy various products (especially those made of polymers) which is found to be necessary in our daily life. This is nothing if its compared with the suffering, we are going to face, resulted from the waste produced out of these products. This implies a duty on researchers to use various methods of investigation to prolong the lifetime of these polymers products, understand their properties and urgently put solutions to limit or prevent their danger on environment and humans life.

As a line in this direction we find fluorescence spectroscopy techniques to be useful tools to understand various properties of some (if not all) polymers, on the micro- and macro- levels. We actually found polymers to be useful probes to study certain photophysical phenomena like the red-edge effect (REE) and the twisted intramolecular charge transfer (TICT) occurring in the field of fluorescence spectroscopy. It turned out to be that these and others (excimer, exciplex, energy transfer etc.) phenomena are useful probes to study various characteristics of local polarity, local free volumes, T_g, energy migration along polymer chains, volume changes (swelling/contraction) etc [1]. Moreover, fluorescence probes are enjoying themselves in controlling polymerization processes and most probably will find their ways in limiting polymer degradation.

RESULTS AND DISCUSSION

The fluorescence spectroscopy is a powerful technique: it is highly sensitive (clean), it uses molecular probes and labels (spy), and it covers a wide range of measurements channels [2]. In this context we have used various molecular fluorescence probes (polar, nonpolar and flexible molecules), Figure 1, to probe various aspects (like microenvironmental heterogeneity, local polarity and local viscosity etc.) of various polymers [3-8]. Our tools of investigation were the steady state fluorescence, the fluorescence decay lifetimes, the time resolved fluorescene (TRF) spectra, the REE, etc. The fluorescence results obtained were rationalized to various microscopic properties of polymers. As examples:

a. The fluorescence results of a merocyanine dye (probe 1, fig. 1), of 4-amino-4′-nitrobiphenyl (AND) (probe 2, fig.1) and of 4-amino-4′-nitrofluorene (ANF) (probe 3, fig.1) in poly (vinyl alcohol) (PVA) and in polyalkylmethacrylate polymer matrices were used to demonstrate the presence of different solvation sites in the bulk of the polymer matrix [3,9]. Since these probes undergo either a decrease, probe 1, or an increase, probe 2 and 3, in dipole moment upon electronic excitation, therefore these dipoles are expected to occupy various polymer sites, of different sizes and shapes at any given time giving rise to a broad electronic absorption spectrum of the probe in a particular polymer matrix. It must be noted that exciting the probe using the maximum absorption wavelength ($\lambda_{maz.}$) doesn't reveal detail information on polymer sites. However moving the excitation to include the whole range of wavelengths at the red edge of the first electronic absorption band lead to a gradual red shift (accompanied sometimes with sharpening of the vibrating bands) of the fluorescence spectra.

   These shifts are observed only if the orientational motion of polymer sites, around solute dipoles, are slow compared to fluorescence lifetimes of the probes.

   A qualitative potential energy diagrams were built, on the basis of interaction energy that depends on the orientation and intermolecular separation between the solute dipole and the solvent cage (site), to emphasise and explain the role of micro-environmental heterogeneity of a polymer matrix on the fluorescence of these probes.

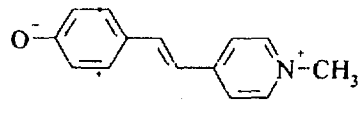
b. Fluorescence of flexible molecules that undergo geometrical changes upon electronic excitation, such as the methyl and tertbutyl esters of 9-anthoic acid, 9MA and 9TBA (probe 5, fig.1) and tetraphenylbutadiene (TPB) (probe 4, fig.1). These molecules undergo different degrees of geometrical changes (motions) from nonplanar (degree of non planarity depends on the size of the ester group in case of 9TBA and 9MA and on the degree of conjugation in the case of TPB) to planar conformation upon electronic excitation. This motion is retarted by the local friction imposed by the medium and thus is sensitive to local free volumes and their distribution within the matrix. We found the fluorescence spectra of 9TBA in PVA of high molecular weight (M.Wt.) (M.Wt. = 125000) to be blue shifted and are more structured as compared to its fluorescence spectra in the lower M.Wt PVA (M.Wt.) = 15000) polymer matrix [10]. In contrast the fluorescence of 9MA, was found to undergo a red shift as compared to 9TBA in all polymers studied. This emphasizes the role of the rotatable moeity size in probing phenomena. These observations are confirmed with the REE results. Similar conclusions were withdrawn from the fluorescence spectra and the REE results of TPB, probe 4, fig 1, in PVA and PMMA polymer matrices [4,11].

c. Fluorescence from molecules that undergo twisted intramolecular charge transfer (TICT) in the excited state such as 4-dimethylaminobenzonitrile (DMABN), 4-dimethylaminoethylbenzoate (DMAEB), diaminodiphenylsulfone (APS), 9,9′-bianthryl (BA), probes 6, 7, 8 and 9, fig.1. These molecules were found to emit one or two fluorescence bands depending on the polarity and viscosity of the medium [12]. The long wavelength fluorescence band is assigned to a structural changes in the excited state resulting from twisting of the donor moeity (the dimethylamino-group in case of DMABN and one of the anthracene-groups in case of BA etc.) to a perpendicular geometry relative to the rest of the molecule. This motion, leading to a TICT state, is accompanied with electron transfer (from donor to acceptor) and orientational motion of the solvent cage (polymer site), only if the medium is polar and have some degree of fluidity [12]. The short wavelength fluorescence band is coming from a nonpolar state and called B-band (or normal fluorescence band). This class of molecules covers classes **a** and **b** mentioned above. This is because the TICT phenomenon has two significant features as mentioned above. First, it is a dynamical process that involves twisting of the donor group and therefore can probe local microviscosity (local free volume) similar to 9TBA and TPB; second, it is a charge separation process and hence is sensitive to environmental polarity similar to merocyanine dye, AND and ANF probes. So these photophysical properties invited researchers to utilize the TICT phenomena to probe media of appreciable viscosities and polarities, such as polymers [3-11] and cyclodextrins (CD) [13-15].

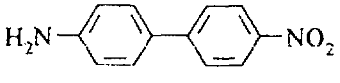
As examples, using the fluorescence of DMABN and related compounds in various polymers we found:

1. The relative intensity of the TICT band (relative to the B-band) to enhance in the lower M.Wt. PVA (M.Wt. = 15,000) relative to the higher M.Wt. PVA (M.Wt. = 125,000) polymer matrix. This leads us to conclude that as these matrices have the same chemical character, it is only the free volume (mobility in the matrix cage) which controls these emission. These steady state fluorescence results were confirmed and found to be consistent with the REE and TRF spectra results [7,16].

2. The TICT fluorescence of DMABN was hardly observed or undergoes any appreciable change when studied in polyalkylmethacrylate polymer matrices of various side chain lengths (PMMA, PEMA, PBMA and PHMA where M = methyl, E = ethyl, B = n-butyl and H = n-hexyl). These observations were attributed to the opposite roles of the local polarity and local free volume of a polymer site on the TICT emission of DMABN and related compounds [16]. On one hand, as the polarity of the methacrylate polymer decreases from PMMA to PHMA, the TICT is expected to be suppressed. On the other hand, as the rigidity (which reflects local free volume) of these polymers decreases from PMMA to PHMA, the TICT fluorescence is expected to be enhanced. Therefore the opposite roles of these effects on the TICT fluorescence of DMABN make it hardly to be observed. However, using the REE and TRF spectroscopy techniques we were able to observe a large change in the relative intensity of the two bands [7 , 16].



pyridine merocyanine
1



AND
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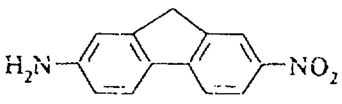
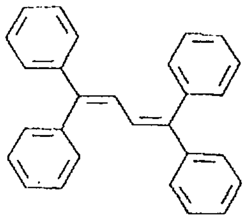
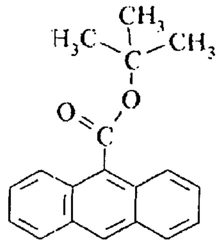


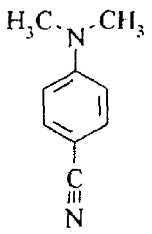
ANF
3



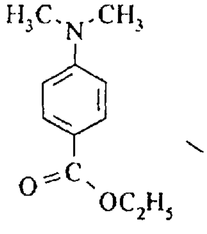
TPB
4



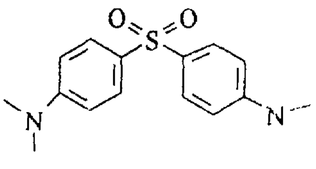
9TBA
5



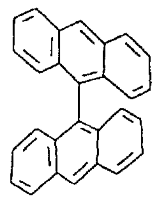
DMABN
6



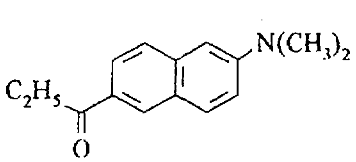
DMAEB
7



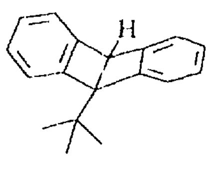
APS
8



BA
9



PRODAN
10



D-anthracene
11

Figure 1: Various molecular systems that can be used as fluorescence probes in polymers.

3. In order to separate the effect of the local polarity from that of the local free volume of a polymer site we studied the TICT fluorescence of DMABN and related compound in various PMMA polymer matrices of different molecular weights. We found the relative intensity of the TICT fluorescence, which appears only under edge excitation, is highly enhanced in the lowest M.Wt. polymer matrix [8]. This focuses attention on the use of the fluorescence of these compounds or other compounds as a reference (standard) to calculate or (measure) the M.Wt. of a polymer matrix using various fluorescence techniques.

d. We are currently engaged in using 6-probionyl-2-N,N dimethylamino naphthalene (PRODAN) and Dewar-anthracene (probes # 10 and 11, respectively Fig.1) as probes for various polymers. The fluorescence of PRODAN was found to probe the gelation process of the widely used tetramethylorthosilicate-derived sol-gels. The red shift of the fluorescence of PRODAN which was followed by blue shift was attributed to expulsion of ethanol molecules first (water content will be larger and hence more polar), followed by removal of water molecules [17]. We found the same thing to happen if PRODAN is introduced in cyclodextrin (CD) aqueous solutions [15]. These results encourage us to investigate its fluorescence in various polymers. Moreover since Dewar-anthrancene undergoes a large geometrical change upon excitation [18] we expect its fluorescence to be promising for studying polymer dynamic and distribution of polymer sites.

Last, but not least, as we are being involved in this kind of research since early 80's, the accumulation of polymer samples (prepared at different time intervals which cover ~ 15 years) implies on us to correlate the emission of the above probes (fig 1) to life time of the polymer. Our goal is to find a way to study and control polymer degradation.

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