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Advances in Materials Technology: MONITOR

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ADVANCED POLYMERS FOR ENVIRONMENT

Dear Reader,

This is number 34 of UNIDO's state-of-the-art series in the field of materials entitled *Advances in Materials Technology: Monitor*. This *Monitor* is devoted to **ADVANCED POLYMERS FOR ENVIRONMENT**.

The main article for this *Monitor* was written for us by Dipl. Ing. Dr. Christa Fritscher from the Austrian Plastics Institute in Vienna, Austria.

The degradation of polymers is an important part of modern polymer technology. At times when concern for the environment is great and basic knowledge of polymer chemistry allows the designing of new interesting materials with unique characteristics, there are many applications where the degradation process of the polymer must be known. Many of the traditional bulk polymers are quite resistant towards environmental degradation, but different modifications can render the materials susceptible to, for example, photo-oxidation and biodegradation.

With this *Monitor*, we start a series of publications with regard to environmentally sound technologies in materials science and engineering.

We invite our readers to share with us their experience related to any aspect of production and utilization of materials and especially comments on the subject of this *Monitor*. It would be appreciated if you could answer the questions on the "Reader Survey", which you will find at the end of this *Monitor*, and return it to us. Thank you for your cooperation.

Technology Development and Promotion Division

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1. DEGRADABLE POLYMERS

by

Dipl.-Ing. Dr. Christa Fritscher

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1. The Austrian Plastics Institute

The Austrian Plastics Institute (Österreichisches Kunststoffinstitut, "OKI") is the oldest division of the Austrian Research Institute for Chemistry and Technics (Österreichisches Forschungsinstitut, "ÖFI") in Vienna. Established in 1953 as a private research and testing institute in the fields of plastics, it grew up to one of Austria's most important testing laboratories. Since summer 1991 Dr. Dietmar Loidl has been head of the institute, Prof. Hinterhofer being managing director of the ÖFI.

Although the OKI is not State-run, it has been authorized by certain Austrian Ministries for doing testings in the whole field of plastics and rubbers, its certificates being approved as official documents. Since

1992 the ÖFI is also an accredited European testing laboratory according to the qualification criteria of European Standard EN 45.001.

This authorization includes testing and analysis of thermoplasts, thermosets, elastomers, bonding agents and coatings, it also includes examinations on polymer composites, on semifinished and finished products and the controlling of production processes for these articles.

The Plastics Institute's unique situation is the fact of being associated with five other divisions of the ÖFI working in different fields of plastics applications. One of them is in charge of varnishes and coatings (ÖLI), others deal with materials used in the building industry (ÖBI), in sports (ÖIST) and in medical applications (ÖIBW); public relations work for plastics as valuable materials is done by the ÖIWK. Most of these other divisions of the ÖFI are, as well as the Plastics Institute, authorized for their special field of work and so offer an extensive catalogue of possibilities to the customer. An overall of about sixty employees allow quick handling of all orders.

The Plastics Institute's special field is not only all kinds of mechanical, physical and chemical, but also microbiological examinations of plastic or rubber materials and components, the analysis of products with respect to environmental properties, information and advice in questions concerning engineering and construction and finally the recycling of plastics; different kinds of databases provide the properties of most materials, online-searching in scientific literature databases gives access to latest publications. Also within the last few years questions concerning quality insurance of plastic products has become an important factor of the Institute's work.

Beside the above-mentioned work as a testing laboratory, the OKI is involved in different research programmes, most of them either standing in a very close relationship to industrial problems and applications or aiming at the development of new testing methods. Some examples of such research programs are the development of testing methods for degradable polymers especially used in agriculture and for the classification of recycled plastics, the comparison of methods for the redevelopment of sewers and drains, the long term behaviour of reinforced plastics, the recording of the composition of the plastic fraction within garbage, a study about volatile pollutants from plastic building products or the optimizing of a testing method for determining the thermal conductivity of tube-like plastic insulation foams.

Much emphasis is put on teaching: Some members of the Plastics Institute's staff give lectures at Austrian universities. In addition training courses for students, teachers and other interested people take place at the ÖKI as well as seminars about special current developments and scientific advances.

On the occasion of the Herman F. Mark award ceremony each year in October an international symposium is organized by the ÖKI. In October 1992, "Advances in Degradable Polymers" were presented and discussed by leading scientists from all over the world.

2. Sense and importance of degradable polymers

The degradation of polymers is an important part of modern polymer technology. Degradable plastics, only a few years ago little more than a novelty, are now a hot topic within the plastics industry.

Traditional applications of synthetic polymers are mostly based on their relative inertness to biodegradation compared with natural macromolecules such as cellulose and proteins. First incentives for the study of the biodegradation of polymers were to prevent or retard attack on polymers by bacteria, fungi, insects, rodents, and other animals. Now the use of synthetic polymers has accelerated to the extent that the disposal of the polymeric products currently in use, most of them bioresistant, has become increasingly difficult. One of the important current incentives for the study of biodegradable polymers is their easier disposal. Moreover, biodegradable polymers are useful for applications such as sutures, surgical implants, controlled-release formulations of drugs and agricultural chemicals, agricultural mulch, etc., and interest in them continues to increase. Current trends in polymer research and the marketing of plastics indicate an increasing demand for the development of a diversity of degradable polymeric products with predetermined survival time.

The interest today is focused on degradable polymers and their transformation into low molecular weight degradation products and the changes in the long-term properties of the materials. The term "environmental degradation" denotes several degradation factors (physical, chemical and biodegradation) working synergistically towards mineralization. Deterioration and degradation of polymeric structures in nature are the basic mechanisms ensuring recycling of the elements of the biosphere.

Many of the traditional bulk polymers are quite resistant towards environmental degradation, but different modifications can render the materials susceptible to, for example, photo-oxidation and biodegradation. Metal complexes are used, triggering a photo-oxidation with a possibility of later biodegradation. Starch-filled LDPE with metal complexes and an unsaturated additive shows promising results as a material which can undergo both photolysis, thermolysis,

oxidative and biodegradation. For biomedical use the attempts to develop degradable polymers have been focused on the synthesis of new biodegradable polymers, and also the modification of natural polymers. There have been synthesized, for example, aliphatic polyesters, polyanhydrides and polycarbonates. These are interesting materials with potential use as suture filaments, ligature clamps, bone fixation plates and drug-releasing systems. These new materials are often too expensive for non-medical use and therefore, for non-medical applications the modification of synthetic polymers has been more usual.

3. Definitions of terms

The occurrence of polymer degradation is recognized by its effects on the appearance and properties of the material. Common effects are discolouration, embrittlement, tackiness, loss of surface gloss or crazing or chalking of the surface. From a practical point of view, degradation is any change which has an adverse effect on polymer properties. To the polymer chemist, the term "degradation" refers to any chemical change in the polymer structure. Nevertheless no standard definition about the meaning of this term exists.

Deterioration involves physical changes caused by cracking, embrittlement or disintegration. Environmental degradation occurs in the natural (outdoor) environment.

The biodegradation involves living organisms or their secretions and can be defined as a molecular phenomenon in which a biological system mediates at least one step of the overall transformation of the polymeric molecule into gaseous products and biomass.

Photodegradation can be defined as a breakdown of polymeric molecules initiated by sunlight. The photo-oxidative degradation involves sunlight and oxygen (change of oxidation-stage) in combination.

4. The mechanisms of polymer degradation

4.1 General aspects of polymer degradation

Polymers can be divided into natural polymers of plant, animal or micro-organisms and synthetic polymers. A second important distinction, which proves to be important in relation to degradation behaviour, is based on the repetition unit. Macromolecules are made up of many chain units which are repeated many times along the length of the chain. Most polymers contain a single type of repeat unit and are described as homopolymers. There is, however, a large group of polymeric materials (both natural and synthetic) in which two or more different structures are repeated in the chain: these are described as copolymers and include such examples as some synthetic rubbers and lacquers, and natural protein-based materials. Very important in relation to degradation behaviour is also the distinction between polymers with a purely carbon-carbon back-

bone such as polyethylene, polypropylene, polystyrene, cis-polyisoprene or poly(vinyl alcohol) and those with heteroatoms. Heterochain polymers have more complex structures. Those of animal origin are usually proteins and have a polypeptide chain structure. This is a special type of α -aminoacids with different alkyl groups. Wood, silk, casein and albumin are examples of materials with this type of structure. Those of plant origin will typically be polysaccharides with structures related to cellulose or starch. All of these materials have the common feature that the backbone of the macromolecule includes other atoms as carbon such as oxygen and nitrogen. Synthetic heterochain polymers range from relatively simple structures such as that of the polyamide, Nylon-6, and the silicone rubber, polydimethylsiloxane, to very complex structures such as are present in alkyd and epoxy resins.

4.2 Degradative Agents

Polymers may be degraded as a result of exposure to various agents, which can be listed under five headings:

1. *Heat*: Every polymer will undergo degradation at some stage if the temperature is increased sufficiently and the differences in stability are considerable. It has to be stressed that polymer stability can be dependent on the history of the sample, its purity and, in some cases, on molecular weight.

2. *Light*: The spectrum of radiant energy from the sun which reaches the surface of the earth in summer extends from about 290 nm into the infrared region and the ultraviolet component of this radiation is sufficiently energetic to break bonds and cause degradation in many polymers. They are even more sensitive to more energetic radiation such as X- and γ -rays.

3. *Atmosphere*: Degradation of polymers can also occur by chemical attack by gases in the atmosphere. The most important case is attack by oxygen, but aggressive gases such as ozone, sulphur dioxide and nitrogen dioxide can have an important effect even in low concentrations. Oxidation often accompanies the primary effects of degradation induced by heat and light, especially in the surface layer of the polymer, in the common situation of degradation in air.

4. *Hydrolysis*: Certain polymers are susceptible to this specific type of chemical attack under appropriate conditions.

5. *Biodegradation*: Most natural polymers, but relatively few synthetic polymers, are sensitive to attack by micro-organisms, again under appropriate conditions.

4.3 Some Important Polymer Characteristics

Some general features of particular importance in relation to degradation processes may be highlighted at this point.

(a) *Amorphous or crystalline state*: Most polymers are amorphous solids, i.e. they have a very disordered structure in which the chains are randomly coiled. It is easier for atmospheric gases but also for water and enzymatic systems to diffuse into the surface layer of an amorphous polymer, than in the case of a crystalline polymer.

(b) *Glass transition temperature*: This is a very important property of any amorphous, linear polymer. If the temperature is gradually raised, this is the temperature at which the physical state changes from glass to rubber. The change is reversible on cooling. At the glass transition temperature (T_g), the macromolecules receive just enough thermal energy from the surroundings for movement to begin within the chains. Some types of degradation reaction cannot proceed to any significant extent below T_g , because the macromolecules are "frozen" in their random coils.

(c) *Functional Groups Present*: Functional groups are specific chemical structures within the polymer chain which provide sites for reaction. Examples of functional groups are carbon-carbon double bonds, -OH groups and -CO-O (ester), -CO-NH- (amide) and -O-CO-O- (carbonate) linkages. Polymers containing ester and amide linkages may be susceptible to hydrolysis, for example, and those with OH substituents may undergo dehydration at elevated temperatures. Structures containing the carbonyl (-CO-) group are also particularly important as chromophores, i.e. sites which certain types of light may be absorbed.

(d) *Presence of Tertiary Hydrocarbon Atoms*: The CH groups in polypropylene, polystyrene, polyacrylates and various other polymers are sensitive to certain types of reaction during degradation, in which free radical species are present.

4.4 Stability and Degradation Behaviour

It is possible to predict sites of chemical attack in reactions such as hydrolysis in suitable polymers from examination of available functional groups, but it is much more difficult to predict general patterns of degradation due to heat and light. Bond energies give a good guide as to which bonds would be first to break. Some typical average values of bond energies are shown in table 1.

Table 1

Average Bond Energies at 298K (in kJ mol⁻¹)

C-S	273	C=C	612
C-Br	280	C=N	617
C-N	307	C=O	732
C-Cl	340		
C-C	349		
C-O	361		
C-H	416		
C-F	485		

Another important factor involved in polymer degradation, apart from bond energies is the fact that a macromolecular chain is a unique reaction environment. In most chemical reactions, in order for reaction to occur, reactant molecules must collide and do so with sufficient energy. In the long chain of a macromolecule, however, repeat units are held in proximity to one another. This has the consequence that suitable functional groups in adjacent units may be able to react or that the reaction proceeds systematically along the chain. Furthermore the stability of a long macromolecule can be acutely sensitive to the presence of a very small number of structural abnormalities, where deviation from the repeat structure occurs. The simplest such abnormality is the chain end itself and there are important examples of end-initiated thermal degradation. Other common abnormalities are oxidized structures, possibly introduced during processing, and these can be sites both for thermal and photolytically induced degradation. At least polymers are seldom used in the pure state and impurities or additives can have a profound effect on the stability of a polymer and on the pattern of degradation.

Photodegradation

The bonds in macromolecules typically have energies between 300 and 500 kJ per mole. Visible and infrared radiation is of insufficient energy to break such bonds, but it can be seen that UV light with wavelengths lower than about 400 nm is of suitable energy. Some of the sun's radiation, however, is absorbed in the atmosphere of the earth. There is insufficient energy to break C-H or C-F bonds, but that suitable C-C, C-O and C-Cl bonds could be broken.

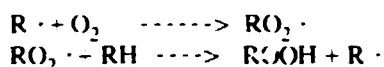
In order for UV light to cause photolysis of a polymer, it must first be absorbed. This requires a chromophore. This may be a group within the polymer structure, of which the most important examples are structures containing the carbonyl group. An alternative pathway in photodegradation, however, involves

absorption of an excited polymer molecule which undergoes homolysis. The radicals so formed can then undergo various possible reactions, such as disproportionation, chain scission and following intermolecular transfer, depropagation to monomer or crosslinking.

Several polymers which do not contain a chromophore in the repeat structure are nevertheless found to be unstable in use in sunlight, unless protected by added photostabilizers. These polymers include PVC, polyethylene, polypropylene, natural rubber, polyamides and polypeptides. The explanation is the presence of some carbonyl groups in the chains formed as a result of oxidation.

Atmospheric degradation

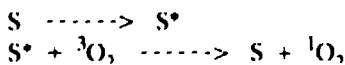
The ground state of the oxygen molecules is a triplet state in which there are two unpaired electrons. Oxygen usually participates in degradation reactions of polymers as a free radical species. Although oxidative degradation can occur at normal temperatures and in the absence of UV light, the most common effects result from the combined effect of oxidation and thermal or photodegradation. The oxidative chain mechanism is of prime importance whenever there is a source of free radicals:



In the second step, RH can be a suitable polymer molecule. Because of the chain nature of this reaction, even small concentrations of free radicals can result in significant amounts of oxidative degradation. The primary oxidation product, the hydroperoxide ROOH, is thermally and photolytically unstable. It decomposes to give two radicals, each of which can participate as R· in the chain process:



A second type of degradation due to oxygen arises when, in the presence of a suitable photosensitizer (S) capable of efficiently absorbing ultraviolet light, energy transfer occurs to produce an excited state of the oxygen molecule, singlet oxygen (¹O₂):



Hydrolytic and biodegradation

Hydrolytic degradation is possible in synthetic polymers containing ester, amide, urethane and carbonate links and in natural polysaccharides and proteins. Apart from the case of polymers with ester and amide structures in the side groups rather than in the backbone, hydrolysis leads to a rapid loss of physical properties as a result of cleavage of the chains. Because of the hydro-

phobic character of most polymers, hydrolysis, even where feasible, may proceed slowly. Humid conditions and pH less than 7 will favour this type of degradation reaction.

The most important agents of environmental biodegradation are micro-organisms, particularly bacteria and fungi. These organisms are extremely versatile and adaptable in their action; they produce a tremendous variety of degradation-promoting enzymes, which are highly specific towards particular chemical structures. The rate of biodegradation depends on environmental conditions. A population of suitable micro-organisms must be present; it may well be that more than one type of organism must be present at the same time. To function effectively, the environment must provide the proper temperature, moisture level, oxygen (except for anaerobic bacteria) and nutrients. Even if the micro-organisms can utilize a polymer as a source of carbon, other essential elements - including nitrogen, phosphorus, sulphur, and trace metals - are unlikely to be present in usable form in the polymer itself. The several types of micro-organisms have different requirements for effective action. Fungi require oxygen and quite acidic conditions, pH 4.5-5, and the optimum temperature is about 30 °C. Bacteria prefer less acidic conditions, pH 5-7, and will operate over a wider temperature range up to 60 °C. Bacteria can operate under aerobic or anaerobic conditions.

Micro-organisms may also be specific in their attack, but may be able to adapt to new substrates such as synthetic polymers. Polymer structures sensitive to attack by micro-organisms are aliphatic polyesters, polyethers, polyurethanes and polyamides. Two commonly used types of polyurethanes are poly(ester urethanes) and poly(ether urethanes). The former are more susceptible to biodegradation than the latter.

In addition to the functional group requirements, it has been found that biodegradation is strongly influenced by chain length and branching. Short, linear chains are more susceptible. Polymers which are initially resistant to biodegradation may become susceptible after the chain size has been reduced by photo-oxidation.

Recent attempts to develop new biodegradable polymeric materials have centred in three areas: (1) development of new methods for modifying natural polymers, (2) development of new synthetic polymers that are inherently biodegradable, and (3) use of biodegradable materials as additives to common non-degradable polymers.

5. Types of degradable polymers and commercial products

5.1 Natural Polymers

Common natural polymers such as cellulose, starch, and proteins are biodegradable.

Commercial products:

Starch based foamed materials: The structural composition of starch is an amylose-amylopectin-grain structure. The hydrophilic nature of starch permits only limited applications. Properties such as the gluing quality or degradability under aerobic and anaerobic conditions are the positive sides of this material. The porous structure is obtained by coordination of steaming and structuring due to gluing of starch.

Depending on product and application purpose, different values in elasticity, mechanical stability and wall thickness can be predetermined. The density is between 0.15 and 0.25 g/cm³.

Due to their polysaccharide structure, the products exhibit high stability against light or oxygen. In contrast to extrusion technologies, starch is not depolymerized during processing and is therefore not water soluble. Water has a plastifying effect. Long term influence of moisture renders the product unfit for use. In this case coating is necessary.

Applications: Trays for small products with low moisture content, which need mechanical protection and have an additional barrier against environmental influences during transport and storing, such as sweets, bread and pastries or technical articles and trays and containers for fast food.

Source: Franz Haas Waffelmaschinen GmbH, Haasstraße, A-2100 Leobendorf, Austria
Product manager: Dr. K. Tiefenbacher
Biopac Biologische Verpackungssysteme

5.2 Modified Natural Polymers

Several new polymeric materials have been prepared by chemical modification of natural polymers. Biodegradable block copolymers have been prepared by depolymerization of cellulose triacetate, followed by reaction with diisocyanates or diisocyanate diol combinations. Similarly, starch and related glycosides have been used as polyols in the synthesis of polyurethanes. Biodegradable films have been prepared from cross-linked and grafted amylose.

Commercial Products:

Based on Cellulose acetate: It is generally known that secondary cellulose acetate (with 53 to 56 per cent acetyl groups) is suitable for thermoplastic processing. With appropriate plasticizers a plastic material is obtained which excels in transparency and pleasant texture and is therefore often used for tool handles, combs, spectacle frames and the like.

Cellulose acetate with such a degree of substitution is in principle biodegradable, although degradation proceeds extremely slow. However, when

common plasticizers are substituted by specific esters and other low molecular components (at least 30 per cent by weight), the material has still got the same thermoplastic properties but will decompose in soil or water within a few years.

Cellulose acetate can be processed on conventional injection moulding machines or on extruders adapted to its specific processing properties. It can be turned into granular materials, strips and films and into injection moulded and extrusion blow moulded shapes.

The material properties are comparable to those of the known cellulose ester-based plastics: Films and thin-walled hollow bodies are highly transparent. Mechanical properties compare well with those of conventional packaging materials. The thermal resistance is somewhat lower, but the permeability to steam and oxygen is relatively high compared to that of standard plastics. The material is resistant to oils and fats and, for a short while, even to weak acids and alkalis.

Source: Franz Rauscher GmbH & Co.,
Chemiewerkstoffe KG, Bergisch-Gladbach
Managing director: Dipl. Ing.
Ingo Schwarz-Quandt

Batelle Institute G.V., Am Rainerhof 35,
P.O.B. 900160, D-6000 Frankfurt, Main 90,
Germany
Technical manager: Dr. Alexander Ach

Starch-vinylalcohol-copolymer: e.g. with around 60 per cent starch is produced by Mater-Bi, Montedison Germany GmbH, Eschborn, Marketing director: Dr. Stefano Facco

5.3 Biodegradable Synthetic Polymers

Although common low-cost thermoplastics such as polyethylene, polypropylene, polystyrene, and PVC resist biodegradation, aliphatic polyesters, such as polycaprolactone, polyethylene adipate, and polyglycolic acid, are readily attacked. Several patents have disclosed the use of polycaprolactone, alone or in combination with other materials, in biodegradable containers for planting of seedlings. Certain aliphatic polyesters are reported to be useful for the fabrication of absorbable sutures. Polyurethane block copolymers and graft copolymers containing aliphatic ester groups are similarly susceptible to biodegradation. Recent work has led to the development of newer polyamides having enhanced biodegradability.

Copolymerization of a common monomer (e.g., ethylene or styrene) with a monomer possessing polar functional groups (e.g., acrylic acid, acrylamide, or vinyl acetate) offers a conceivable route to enhance biodegradability; the polar functional groups might serve as points of attack for microbial enzymes. Other novel synthetic approaches to biodegradable polymers include

the preparation of acrolein-acrylic acid copolymers, polyamidotriazoles, polyphosphazenes derived from amino acid esters, and hydrolyzed acrylonitrile copolymers.

Commercial products:

PHB V: Hydroxybutyrate (HB) is found widely throughout nature where it is produced by bacteria as a carbon and energy store. Polyhydroxybutyrate-valerate (PHB V) is a completely biodegradable thermoplastic polyester composed of hydroxybutyrate units with between 0-30 per cent hydroxyvalerate units incorporated randomly throughout the polymer chain. The properties and biodegradation of PHB V vary with the polymer hydroxy valerate (HV) content, molecular weight, degree of crystallinity, surface area and presence of biodegradable additives.

This material can be processed on conventional equipment, using conventional technology, to produce moulding, containers, coatings, laminates, films and fibres. Just like conventional plastics, products made from PHB V are stable in use, durable and moisture resistant. They may be reused or recycled and upon incineration release only CO₂ and water.

Polyhydroxybutyrate is particularly compatible with mammalian tissue and blood. It is recognised by the human body where the monomer of polyhydroxybutyrate is itself a normal metabolite in mammalian blood.

A disadvantage of PHB V products is their expensive production process, which is based on the fermentation of glucose by e.g. *Alcaligenes eutrophus* species and a following clean up. Recently the gene which is responsible for the synthesis of HB has been successfully transferred into special plant cells by Dr. A. Steinbüchel (Georg-August-University, Göttingen, Germany).

Commercial products:

BIOPOL, ICI Bio Products and Fine Chemicals,
Billingham, Cleveland, UK

BIOMER, PCD Polymere GesmbH., A-4021
Linz Austria, St.-Peter-Str. 25

5.4 Biodegradable Additives

Flexible PVC compositions containing organic esters as plasticizers are susceptible to microbial attack.

Another example of unintentional use of a biodegradable additive is the practice of using wood flour as a filler in thermosetting resins (e.g., phenolic and melamine-formaldehyde resins). In some instances, this may lead to a composite material in which both ingredients exhibit some biodegradability; melamine-

formaldehyde resins themselves are reported to be biodegradable.

More recently, attention has been focused on the international use of particulate solids such as starch as degradable "fillers" in common thermoplastics. Starch-polyethylene composites, prepared by conventional compounding and processing, resulted in "biodegradable" paper-like materials. Similar results have been reported in the case of mixtures of starch with ethylene-acrylic acid copolymer. PVC compositions filled with starch or with starch graft copolymers are readily attacked by soil micro-organisms; the physical properties of these materials are similar to those of PVC compositions containing inorganic fillers. In addition to starch, a variety of other particulate natural materials - cellulose, lignin, sawdust, peat, casein, lactose, etc. - have been suggested as degradable fillers.

Use of biodegradable particulates (e.g., starch, regenerated cellulose, or natural gums), in combination with polyvinyl alcohol as a synthetic film-forming polymer, has been proposed as a route to degradable agricultural mulch or degradable barrier layers for use in disposable diapers and sanitary napkins.

When a biodegradable additive is employed, probably only the additive undergoes rapid biodegradation; a porous and mechanically weakened, but undegraded, polymer is left behind. While the increased surface area of the residual porous polymer would be expected to enhance its degradability, there is as yet little convincing evidence that the remaining polymer is truly biodegradable.

Commercial products:

Polyethylene-starch copolymers:

Ecostar Plus Masterbatch Kunststoff-Zusätze VertriebsgesmbH. "ÖKO-Plast", starch content up to 25 per cent, some types with an additional UV-sensitizer, auto-oxidants and/or unsaturated fatty acids

Weilamstr. 28, D-4434 Ochtrup, Germany
Managing director: Eberhard Bierbaum

Archer Daniels Midland Co., (ADM) P.O.B. 1470, Decatur, IL 62525 USA: with around 6 per cent starch and photosensitive additives; Agri-Tech Industries (USA): films based on starch and acrylic acid

St. Lawrence Starch Co. Ltd., 141 Lakeshore Road East, P.O.B. 1050, Port Credit Postal Station, Mississauga, Ontario L5G 1E8 Canada

5.5 Water-Soluble/Water-Degradable Plastics

Problems with the use of water-soluble plastics for disposable packaging are that the material will be

water-sensitive prior to disposal, actual contact with liquid water will be required for removal of the plastic material but no removal will occur under dry conditions and the dissolution of the polymer may lead to a water-pollution problem.

Polyvinyl-alcohol is hot or cold water-soluble, in water completely biodegradable and can be blown to films.

Applications: laundry bags for infectious laundry in hospitals, bags for water-soluble pesticides, detergents or washing agent, labels for multi-path-glass bottles

Commercial products:

Browing & Frick AG: PVA-films and products, Bahnhofplatz 9, P.O.B. 7587, CH-8023 Zürich, Switzerland

Hoechst AG, P.O.B. 80 03 20, D-6230 Frankfurt am Main 80, Germany

Bellard AG, Solothurn, Switzerland: thermo-plastics copolymer based on ethylacetate and acrylic acid or a vinyl ether-maleic-acid-anhydride-system

5.6 Modification of Polymer Structure to Enhance Photodegradability

In plastics designed to be photodegradable, absorption of radiant energy by the polymer molecule, an additive, or an impurity leads to formation of an "excited-state" molecule, which then initiates reactions leading to the rupture or cross-linking of molecular chains.

Numerous materials of varying types have been reported to accelerate the photodegradation of common plastics.

Principal classes of photodegradation-promoting additives are:

- Transition-metal compounds
- Aromatic ketones
- Quinones
- Readily oxidized organic materials
- Aromatic hydrocarbons
- Organic sulfur compounds
- Organic peroxides
- Dyes, pigments

The use of transition-metal compounds as additives deserves special comment. Compounds of chromium, manganese, iron, cobalt, nickel, and copper are powerful accelerators of thermal oxidation of hydrocarbon polymers. Consequently, such additives can cause difficulties in melt processing by reducing the

thermal stability of the molten polymer. To counteract this difficulty, antioxidants have been used in combination with transition-metal compounds. Iron dialkyldithiocarbamates are particularly promising additives. Unlike most transition-metal compounds, these act as stabilizers with respect to thermal autoxidation. Yet they are effective sensitizers of photo-oxidative degradation. Compositions displaying an "induction period" can be formulated, so that accidental short-term exposure to sunlight will not cause deterioration of polymer properties.

Also compositions containing more than one type of additive have been developed to further enhance and/or control photodegradability.

Applications: agricultural use (mulch films), bags, six-pack yokes in USA

Commercial products:

Ecoplastics: Ecolyte: photodegradable ketone copolymer

Dow Chemical, Midland; Du Pont Co., Wilmington; Union Carbide Corp., Danbury; USA: photodegradable ethylene/carbon monoxide comonomer

Ampacet, Corp., 250 S. Terrace Ave., Mt. Vernon, NY 10550 USA: masterbatch containing TiO₂

Agri-Tech, Ind., USA

Plastigone Technologies Inc., P.O.B. 165618, Miami, FL 33116, USA

6. Test methods for determining the degradability of polymers

Because of the different mechanisms of degradation and types of materials and a missing standardized definition of the term "degradable", there have been only a few standard test methods developed. There are two ASTM-standards which should be mentioned:

ASTM 5209-91, January 1992: Determining the Aerobic Biodegradation of Plastic Materials in the Presence of Municipal Sewage Sludge

ASTM D 5210-91, January 1992: Determining the Anaerobic Biodegradation of Plastic Materials in the Presence of Municipal Sewage Sludge

These test methods cover the determination of the degree and rate of aerobic respectively anaerobic biodegradation of synthetic plastic materials (including formulation additives) on exposure to activated municipal sewage sludge from a waste-water plant under laboratory conditions.

Several general methods can be used for measuring the biological decomposition of polymers. These measurements provide such information as rate of polymer weight loss (determined by Size Exclusion Chromatography), loss of physical properties, such as tensile strength, and change of the chemical structure of a polymer, which could be determined with e.g. ATR-FTIR-technique, Differential Scanning Chromatography, Nuclear Magnetic Resonance or X-ray-Spectroscopy. Also the rate of increase in colony size of micro-organisms in contact with the polymer can be determined. In accordance with ASTM G 21-70/G 22-76 the specimens are placed in or on a solid agar growth medium that is deficient in available carbon. After inoculation with the test micro-organisms (mixture of fungus spores or bacteria, e.g. *Pseudomonas aeruginosa*), the medium and samples are incubated. Any growth of the colony is dependent on utilization of the polymer specimen as a source of carbon. After the exposure the samples are examined for evidence of colony growth on the polymer sample surface, weight loss or loss of physical properties can also be measured.

Soil Burial can be performed either under laboratory conditions or in a natural setting. Uniformly sized samples are buried in a mixture of equal parts of sand, garden soil, and peat moss in laboratory containers which are kept at high humidity away from sunlight. Outdoor testing affords a means of testing plastic samples for rate of breakdown in a given soil type containing a native microbe population and in variable geographic regions. Samples retrieved from soil burial may be tested for weight loss or deterioration of mechanical properties or they may be examined by scanning electron microscopy for evidence of attack. Although soil burial testing affords a way to test samples for breakdown close to actual conditions of waste disposal, it lacks reproducibility because of the difficulties in controlling climatic factors and the populations of various biological systems that are involved. For more reproducible results, degradations by cultured fungi and bacteria as well as degradations by purified enzymes are used.

A very accurate but not always practicable method is the ¹⁴C tracing of polymers and measuring of labelled carbon utilized or released by micro-organisms. Although this method is not subject to interference by biodegradable impurities or additives in the polymer or in the soil, it is very sensitive to the presence of labelled low molecular weight polymer molecules which may be present in the sample.

7. Pro and contra degradable polymers

Degradable polymers are a very important development in some special fields of agriculture (e.g. mulch films), medicine and pharmacy. There are also some benefits for the use of degradable packaging. But its usage cannot solve every packaging problem. A main problem is the high costs caused by additional

ingredients employed in the manufacturing of degradable polymers and of changing the process by which the polymer is synthesized. It will also be necessary to change storage and distribution systems to keep degradable and nondegradable products separate. In many countries, landfill and incineration are the only environmental solid-waste disposal methods which are practiced widely. In the case of landfills, degradability can cause complications - settling, generation of gases and possible contamination of groundwater or a possible release of additives or degradation products having unknown impact to the environment. Degradable polymers may also complicate recycling of undegradable polymers. In case of incineration there are no significant differences between degradable and undegradable polymers. The best solid-waste disposal for biodegradable polymers would be composting. Another problem in the use in packaging applications is the increased risk of contamination, damage, or spoilage of packaged goods.

However, the costs and risks should be weighed against the benefits before concluding that introduction of degradable plastics would "solve" the general problem of littered packaging materials.

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2. TRENDS IN RESEARCH AND RECENT DEVELOPMENTS

Development of biodegradable plastics

Objectives

This project aims to develop biodegradable plastics that are degraded by micro-organisms in the environment (in soil), thereby reducing the burden on the natural environment. This will help to harmonize human activities with the natural environment and aid in solving the most serious and urgent global environmental problems as we approach the 21st century.

Scope of the project

1. *Development of biodegradable plastics through cultivation of polymer-producing micro-organisms - Biosynthesis*

Bioplastics produced by micro-organisms will be developed through screening of micro-organisms with polymer synthesis functions, clarifying their synthesis mechanisms, and studying cultivation methods.

1. Screening and breeding of useful micro-organisms to produce plastic-like polymers;
2. Development of property-improvement and processing technologies;
3. Development of high-density, large-scale cultivation technologies.

2. *Development of biodegradable plastics by utilization of natural polymer materials - Natural polymer derivation*

Technology will be developed for large-scale synthesis of biodegradable polymer materials by utilizing natural polymer materials. Concurrently, research will be undertaken to develop a processing method and provide water-resistant properties.

1. Development of technologies for functionalizing and improvement of natural polymers;
2. Development of technologies for synthesis and processing.
3. *Development of biodegradable plastics through molecular design technology and finely controlled polymerization - Chemical synthesis*

Useful biodegradable synthetic polymers such as polyesters based on molecular design through an understanding of the biodegradation mechanism of existing polymers will be developed.

1. Screening matter for synthetic materials and accumulating data on physical and chemical properties;
2. Development of technologies for molecular design and finely controlled polymerization;
3. Development of technologies for function improvement and processing.

Evaluation of biodegradability

To develop biodegradable plastics, it is necessary to establish a method of evaluating and testing biodegradability.

Biodegradability of plastics is evaluated through these methods:

- (a) Evaluation in natural environment;
- (b) Evaluation with micro-organisms;
- (c) Evaluation with enzymes.

Each of these methods has its own special characteristics. Therefore, it is essential to evaluate the biodegradability of plastics by combining several different evaluation methods. (See diagrams, page 20) (Source: *JETKO*, April 1993)

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Biodegradable material

A new Japanese type of biodegradable material made from clay and recycled milk cartons has been produced by the Science and Technology Agency's (STA) National Institute for Research in Inorganic Materials (NRIM).

The new material, a clay/fibre composite porous material, is extremely light, with a reported specific gravity of 0.1.

The new material degrades rapidly when discarded, and can be dissolved in water for re-use. Although the material is not water-resistant, it is expected to be a useful alternative to foamed polystyrene.

Coating it with a water-resistant substance would enable the material to be used in heat insulating and cushion materials.

During production, a 10 per cent aqueous solution of smectite, a clay mineral, and a 10 per cent aqueous

solution of fibre, prepared from recycled cardboard such as that derived from old milk cartons, are mixed in a ratio of 85:15, frozen by liquid nitrogen, and vacuum dried.

The material produced is 95 per cent porous, and has numerous pores several hundred microns in diameter which are filled with water. Using liquid natural gas, the energy source during freezing is said to reduce the production cost, but it is unclear if the new material will be competitive in price with foamed polystyrene.

However, because the new material is environmentally compatible, it may be competitive if the cost of disposal is considered.

In the future, the institute plans to check the acoustic, temperature control and deodorant properties of the material, as well as its ability to keep fruit fresh. (Source: *iti International Technology and Innovations*, Vol. 29, No. 5, May-June 1992)

* * * * *

SEAGEL - Made by processing agar derived from kelp

Scientists from Lawrence National Laboratory have invented this material lighter than air which is biodegradable and non-toxic when burned. Production begins dissolving the agar in water and adding an organic solvent and an emulsifying agent to disperse the agar evenly throughout the liquid. After the mixture sets into a gel the researcher hardens it by freeze-drying. Some grades of Seagel contain 40 mg to 50 mg of material per cubic centilitre of product, compared with 60 mg per cubic centilitre for balsa wood. (Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94551)

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Synthesis of new type of biodegradable plastic

The Fermentation Research Institute has developed a new type of biodegradable plastic the molecules of which have ester linkage and which is produced from petrochemical ingredients.

The research institute has already developed various kinds of biodegradable plastics by using biodegradable polycaprolactone (PCL), micro-organism-produced polyester and starch. There are two methods for developing biodegradable plastics from petrochemical ingredients. One uses in combination an existing biodegradable plastic (PCL, etc.) and a conventional plastic (polyethylene, nylon, etc.), and macromolecules are reformed by the alloying (blending) technology to develop plastics of excellent biodegradability (micro-organism degradation). The other is a method of developing new types of biodegradable plastics by using a low molecular weight chemical substance as the

starting material and performing a polymerization reaction.

In this experiment, the latter was used to develop the new biodegradable plastic. As the starting material used inexpensive diethylene glycol to produce the monomer (MTC: 2-methylene-1, 3, 6-trioxocane) and synthesized a polyester including ether linkage by radical ring-opening polymerization. Furthermore, a new type of vinyl-based polymer with ester linkage was synthesized by radical copolymerization of MTC and general purpose monomer such as styrene and vinyl acetate. These polymers are decomposed by the lipid-decomposing enzyme lipase that exists in various kinds of micro-organisms. Copolymer of esterether-styrene was decomposed by 10 per cent after 16 hours reaction with lipase.

The radical copolymerization reaction has a broad range of applications and has the advantage of readily introducing ester linkage into conventional polymers. This indicates the possibility of providing biodegradable characteristics to conventional plastics such as polyethylene and polystyrene. Also, the quantity of introduction of ester linkage can be adjusted with ease by changing the raw material mixing ratio, so it will become possible to produce various kinds of biodegradable plastics featuring a variety of properties.

The research institute plans to adjust the raw material ratios to enable the biodegraded fragments to be further decomposed. (Fermentation Research Institute, AIST, 1-1-3, Higashi, Tsukuba City, Ibaraki Pref. 305, Japan. Tel.: +81 298-54-6089; Fax: +81 298-54-6009) (Source: *JETRO*, July 1992)

* * * * *

Foaming resin made of biodegradable plastic

The Nippon Synthetic Chemical Industry Co. Ltd. and Novamont SpA of Italy have jointly developed a biodegradable foaming resin consisting primarily of starch.

The Nippon Synthetic Chemical Industry plans to develop applications for the substance as a packaging material for home electric appliances and electronic equipment as well as for use in the sectors of civil engineering and gardening. The minimal adverse influence on the natural environment is to be advertised as its sales point, to raise demands as an expanded polystyrene (EPS) alternative. The foaming technology was developed jointly with Suzuki Sogyo Co. Ltd., a technology development venture company, and applications are to be developed jointly with Hitachi Transport System, Ltd.

The foaming resin is based on the biodegradable plastic Mater-Bi developed by Novamont and consists primarily of starch and denatured polyvinyl alcohol.

The total energy necessary for production, which is an ecobalance yardstick, is less than 50 per cent that of general-purpose plastics, so its influence on the natural environment is extremely small during manufacture. Also, the combustion heat per gram is 5,000 calories, less than one half the calorific value of EPS. Toxic gases, black smoke and soot are not generated, so the substance can be incinerated by households in general and with ordinary incineration furnaces, and when buried in the ground, its volume is decreased to about one half in a week and almost completely degraded in three months.

In addition, Mater-Bi is usable as a composting material. Mixed with garbage or fallen leaves and gardening rubbish, it can be composted with a household composter or in a composting factory belonging to a local government.

The new foaming technology is fundamentally different from the technologies for manufacturing buffer materials in bulk or for foaming polystyrene beads. CFC or hydrocarbon gases are not used as the foaming gas, only water, and no toxic gas is generated in the process of foaming.

Mater-Bi has almost the same buffer capability as the foamed polystyrene EPS-50 or EPS-70, and can be incorporated flexibly with a buffer characteristic suitable for both heavy loads and light loads. Users can use the substance intact simply by partly remodelling injection moulding machines and moulds.

To discriminate Mater-Bi from foams substances made of polyethylene and other plastic materials when recycling, the plan is to propose an original colour system.

The new foaming resin domestic selling price is about 1.5-1.8 times that of EPS, but the price can be suppressed to the same level as EPS in the future through mass production. (The Nippon Synthetic Chemical Industry Co., Ltd., Advanced Film Development Department, 9-8, Nozaki-cho, Kita-ku, Osaka 530, Japan.) Tel.: +81 6-314-3175; Fax: +81 6-314-0244 (Source: *JETRO*, July 1993)

Biodegradable polycarboxylate

Assoc. Prof. S. Matsumura and his research team of the Faculty of Science and Engineering, Keio University, have succeeded in synthesizing a biodegradable polycarboxylate by incorporating successive vinyl alcohol groups for use in detergents.

Calcium ion reduces the activities of surfactants which removes soiling, so it was necessary to suppress the calcium activity. Polycarboxylate reacts with calcium ion both in soils and tap water, making it inactive. However, conventional polyvinyl-type polycarboxylate

is not biodegraded when drained into sewage treatment plants or rivers, so zeolite has been used primarily, but this material shows an insufficient builder effect and contains fine particles which are not dissolved in water and may settle in the washing water.

Therefore, research is in progress to incorporate the function of biodegradability into water-soluble polymers which are used as detergent builders, just like the biodegradable plastics which are degraded into carbon dioxide and water by the action of micro-organisms.

The new polycarboxylate contains biodegradable successive vinyl alcohol moieties in the polymer chain which are cleaved by micro-organisms to produce low-molecular weight fractions. The resultant low molecular weight substances are further biodegraded to some extent, followed by complete decomposition. The synthetic method is to mix the raw materials of methyl acrylate and vinyl acetate, followed by the addition of a polymerization initiator to start the polymerization reaction, then terminating the reaction immediately by dry ice-acetone cooling. Experiments showed that when more than about five to six successive vinyl alcohol groups were present in the polymer chains, biodegradability was achieved in environmental conditions. The new polycarboxylate displays a maximum biodegradability of 80 per cent. The detergent builder performance is reduced only by about one fourth when compared on an equal weight basis, so by increasing the volume of the polymers in the detergent formulation, the new polycarboxylate will become a suitable detergent builder. (Keio University, Faculty of Science and Technology, 3-14-1, Hiyoshi, Kohoku-ku, Yokohama City, Kanagawa Pref. 223, Japan. Tel.: +81 45-563-1141; Fax: +81 45-563-0446) (Source: *JETRO*, December 1992)

New catalyst system for synthesizing biodegradable plastic using CO₂

Prof. Y. Yoshida and his research group at the Toyo University Faculty of Engineering have developed a catalyst system for synthesizing biodegradable plastic from CO₂ with over 40 per cent higher efficiency compared to conventional methods. The new plastic can be used as a drug carrier for drug delivery systems (DDS).

The newly developed system uses a catalyst made from a mixture of diethylzinc, zinc hydroxide and water (1:2:0.3) in dioxane under CO₂ at 50 atm. The presence of water in the mixture is a significant difference from existing methods.

Propylene oxide was then added to the catalyst system in dioxane, which was again put under CO₂ at 50 atm. At 40° C, the copolymerization of propylene oxide and CO₂ occurs. As a result, more than 50 per

cent of the propylene oxide was copolymerized compared with only 35 per cent using conventional catalyst systems consisting of diethylzinc and zinc hydroxide (without water). The copolymerization of CO₂ and propylene oxide forms an aliphatic polycarbonate and the resultant copolymer is expected to be a biodegradable plastic.

The researchers also conducted an animal study using rats to examine if a pellet based on the copolymer containing ftorafur (a carcinostatic agent) can be applied as a DDS drug carrier. The pellet containing the carcinostatic agent at a concentration of 40 per cent was implanted into rats and the time course of ftorafur concentration in the blood was examined.

The ftorafur concentration was maintained in a range between 0.5 and 2.5 µg/ml over 40 days, showing the copolymer can be used for slow release of the agent over a long time. (Toyo University, Department of Applied Chemistry, Faculty of Engineering, 2100, Nakanodai, Kujirai, Kawagoe City, Saitama Pref. 350, Japan. Tel. +81 492-31-1132; Fax: +81 492-31-1031) (Source: *JETRO*, December 1992)

MITI to work out standard for test method for biodegradable plastics

The Ministry of International Trade and Industry (MITI) will standardize test methods for biodegradable plastics. While diverse biodegradable plastic products have been marketed in Japan, there is no common method to examine their biodegradability.

MITI intends to work out a standard for the said tests as the Japan Industrial Standard (JIS) on the basis of "Testing methods for biodegradability of new chemical substances" specified under law concerning screening of chemical substances and regulation of their manufacture, etc. MITI is thinking of finishing the task by 1994 at the earliest.

The said test method is to examine the biodegradability of a given plastic in the presence of micro-organisms by means of the standard active slurry which has been prepared by cultivating the slurry collected from more than 10 different places in Japan. The biodegradability can be determined by electrically measuring the amount of oxygen consumed by micro-organisms in a flask.

This method has so far been adopted here most frequently and is believed to be the closest to success in practical application among many methods. The method, however, can never indicate the precise state of actual decomposition of a given plastic disposed of on a specific site as soil condition differs from place to place.

MITI will thus continue research on the other test methods too. (Source: *Chemical Business*, September 1993)

European research on biodegradable plastics

A Franco-British study headed by the University of Clermont-Ferrand is investigating the complete decomposition of plastics. The researchers are examining commercial polyethylene products in the advanced abiotic (degradation caused by light, heat, oxygen or water) phase, to determine ways of increasing the "bioassimilation" of residues of polyethylenes in the ground. Experiments have shown that the breakdown of these plastics can be "programmed" in time.

Using commercial (or laboratory) polyethylene products, whose phototransformation can be increased by modifying their structures or by introducing additives, the study has shown that residues left after abiotic degradation can be bioassimilated. This is proven by the growth of certain micro-organisms and some erosion of the polyethylene particles, in culture conditions where the polymer was the sole source of carbon. Research is now continuing into the extent of bioassimilation.

European Community research is also under way into a new biodegradable polymer which is produced from biomass, through fermentation. This is an ecological solution (a plastic that is not only biodegradable, but also of biological origin) and requires extensive research in order to reach the technical and economic performances level of polymer petrochemistry. (Source: *Performance Materials Technology*, November 1993)

Following are 11 summaries of speeches presented at the XI. International Herman F. Mark-Symposium in Vienna from 6 to 7 October 1992.

Degradation of polymers

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The degradation of polymers is an important part of modern polymer technology. At times when concern for the environment is great and basic knowledge of polymer chemistry allows the designing of new, interesting materials with unique characteristics, there are many applications where the degradation process of the polymer must be known.

Current trends in polymer research and the marketing of plastics indicate an increasing demand for the development of a diversity of biodegradable polymer products with predetermined survival time. Four main fields can be distinguished: packaging materials, generally lightweight items for one-trip applications; mulch films for weed suppression, moisture retention or microclimate stabilization in agriculture; sacks and bags for the disposal of rubbish, litter and garden waste and medical applications, *in vivo* in the human or animal body.

Many of the traditional bulk polymers are quite resistant towards environmental degradation, but different modifications can render the material susceptible to, for example, photo-oxidation and biodegradation. Metal complexes are used, triggering a photo-oxidation with a possibility of later biodegradation. Starch-filled LDPE with metal complexes and an unsaturated additive shows promising results as a material which can undergo both photolysis, thermolysis, oxidation and biodegradation. Both types of materials discussed above are subjected to long-term (bio)degradation tests, in parallel with quick photo-oxidation and thermolysis tests.

For biomedical use the attempts to develop degradable polymers have been focused on the synthesis of new biodegradable polymers, and also the modification of natural polymers. We have been synthesizing aliphatic polyesters, polyanhydrides and polycarbonates. These are interesting materials with potential use as suture filaments, ligature clamps, bone fixation plates and slow-release systems. Important parts of our projects concern different characterizations *in vitro* and *in vivo*, along with optimizing synthetic routes. These new materials are often too expensive for non-medical use and therefore for non-medical applications the modification of synthetic polymers has been more usual.

Biodegradable polymers from nature are a class of high molecular weight compounds where the polyhydroxyalkanoates are perhaps the most interesting materials at the moment. They are produced as nutrient storage compounds by several micro-organisms and they have characteristics similar to polypropylene.

The interest today is focused on degradable polymers and their transformation into low molecular weight degradation products and the changes in the long-term properties of the materials. The term "environmental degradation" denotes several degradation factors (physical, chemical and biodegradation) working synergistically towards mineralization. Deterioration and degradation of polymeric structures in nature are the basic mechanisms ensuring recycling of the elements of the biosphere.

Recent progress in the synthesis of polylactones and their applications as degradable engineering materials

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In the last few decades a great deal of research has been done on the synthesis of "heavy duty" polymers and polymer materials for long-term service. In particular many kinds of high temperature stable and chemically stable structural polymer materials have been developed. Essential contribution to this field is due to Professor Herman Mark's remarkable ideas and research carried out by himself and the group of his former students, including Carl Marvel, Charles Overberger, Pearce and many other outstanding scientists.

However, nowadays a new field of research has been developed concerned with degradable polymers. This new field is growing continuously due to the strong demand for biodegradable polymers as packaging materials and in particular as biocompatible materials for various applications in biology and medicine, e.g. as bone-fixing plates and endoprostheses, pharmaceutical materials for controlled drug release and so on. Research on these materials continues at an extraordinary pace. Recent reports and publications focus attention on theoretical aspects, new methods of synthesis, physical and chemical properties, as well as on new applications. Several findings about reactivity patterns and reaction mechanisms are noteworthy. The general development of this research and recent experimental data will be discussed in this paper.

Various polyesters obtained via polymerization of lactones, lactide and cyclic carbonates are well known to be degradable polymers. The new procedure has been elaborated in our laboratory in order to obtain biodegradable "tailor-made" polyesters with well-defined mechanical, physical and chemical properties including biodegradability. For this purpose new anionic initiators have been employed, capable of producing living homopolymers, block polymers or "star"-shaped polymers via "living" polymerization processes. The interdisciplinary approach has been adopted for this purpose which is based on the principles of supramolecular chemistry. New initiators and their combination with cation complexing reagents, as crown ethers and cryptands, are discussed. The utility of new initiator systems based on alkali metal supramolecular complexes, e.g. $K^+18C6 \cdot K^+$, $K18C6 \cdot Na^+$, $K^+15C5 \cdot K^+$, Na or K naphthalenides with crown ethers or cryptands and some new carbanions in the ring opening polymerization reactions is demonstrated.

Basic reactions to photodegradation of some important polymers

*Professor Bengt Rånby,
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It has been known for hundreds of years that polymeric materials like native textile fibres are degraded and lose strength on exposure to sunlight, e.g. in bleaching of cotton and linen fabrics. About 50 years ago it was reported that synthetic polymers such as plastics, rubber, fibres, paint and lacquers are also degraded on exposure to light.(1) Polymers show different inherent photostability and can be divided into three groups:(2):

Highly photostable polymers are commonly used without added photostabilizer.

Moderately photostable polymers can be used without added photostabilizer.

Poorly photostable polymers need extensive stabilization for outdoor use.

Systematic studies of photodegradation and photostabilization of polymers were started in the 1940s when it was observed that photo-initiated degradation in air also involved a simultaneous oxidation. The basic mechanism of photo-oxidation was established by Bolland and Gee.(3) It involves an initiation reaction of free radical formation by chain scission or other bond cleavage and a subsequent addition of molecular oxygen to form peroxy radicals which react further in various ways. Since the most important photodegradation of polymers is initiated by sunlight in air, the mechanism of Bolland and Gee has become the basis for extensive studies of photodegradation and photostabilization during the last 40 years. The propagation reaction of polymer peroxy radicals involve hydrogen abstraction to give hydroperoxide groups which decompose by photolysis to radicals, carbonyl, vinyl and vinylenic groups. Ketone groups on aliphatic chains absorb UV light quanta which causes chain scission by Norrish type I (to chain end radicals) and type II reactions (to methyl and vinyl end groups).

The chain termination reactions are due to radical combination to inactive products containing C-C bonds, peroxides, ketone and hydroxyl groups. Photodegradation of a polymer is usually related to sensitizers present in the form of impurities or modified groups which absorb light quanta and transfer the energy to cause polymer reactions. Commercial polymeric materials may contain such external and internal impurities from the manufacture, processing and

fabrication of the polymer and from environmental exposure.(4) Cellulose has a broad absorption peak at 265 nm with a shoulder into the UV of 300 to 400 nm which is assigned to the glycosidic bond of the chain and an overlapping absorption of aliphatic ketones formed during isolation and purification. In photolysis with near UV light the glycosidic bonds are broken and the radical on the 4th carbon adds molecular oxygen to a peroxy radical which is rapidly rearranged. Formyl radicals are also formed in photolysis of cellulose by splitting off CH_2OH groups (= the 6th carbon) and hydrogen radicals by abstraction.

Polyolefine and diene copolymers are photo-oxidized by very complex reactions which are being extensively investigated. A primary sensitized photoreaction of polyethylene is formation of a peroxy radical on a chain which may abstract hydrogen from another chain and form a hydroperoxyl group or split off as a hydroperoxy radical. The subsequent reaction offers many possibilities of chain scission, formation of ketone, hydroxyl, carboxyl and vinyl groups. Polypropylene is more sensitive to photo-oxidation than polyethylene, due to the tertiary bonded hydrogens along the chains which are easier to abstract than primary and secondary bonded hydrogens. The tertiary peroxy radicals may abstract hydrogen to hydroperoxyl groups which split off hydroxyl and methyl groups as radicals and leave a ketone group on the chain. Ethylene-propylene-diene copolymers are photodegraded by hydrogen abstraction from the diene residues giving allyl radicals which add molecular oxygen and form hydroperoxide groups. The further degradation reactions are well known from studies of other aliphatic polymers.

Polystyrene is produced commercially by free radical polymerization with residues of molecular oxygen present which is incorporated in the chains as peroxide groups by inadvertent copolymerization. Photolysis of these species by O-O splitting gives alkoxy radicals, tertiary carbon radicals by hydrogen abstraction, hydroperoxy and alkoxy radicals with subsequent chain scissions. The strong yellowing of polystyrene during UV irradiation is due to conjugated unsaturation and also ring-opening reactions to muconaldehyde structures.

Polyacrylates and polymethacrylates are photodegraded by the same mechanism. The main reactions are main-chain scissions and monomer formation ("unzipping") at the new chain ends. Also side chain scission occurs and the radicals formed abstract hydrogen and give methyl formate. Other low molecular weight compounds are also formed. The photolysis of polymethacrylates with near UV light give very little discolouration, which is important for commercial use of these materials as transparent sheets and domes.

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Radiation degradation of elastomers

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Radiation: High-energy irradiation produces changes in the properties of polymeric materials, which may be beneficial or deleterious, and may result from unavoidable exposure to radiation environments or by using radiation as a processing aid.

Molecular changes: When radiation is absorbed by a polymeric material, ionization and excitation of the polymer molecules occurs, followed by chemical reactions of ions, excited species and radicals. The molecular changes of these reactions can be classified as crosslinking, scission and structural modification of the molecules and formation of small molecules. The yields of crosslinking and scission can be determined from changes in molecular weight or solubility, but this provides no information on the actual reactions.

Radiation chemistry: The chemistry of the effects of radiation can be deduced from knowledge of the changes in molecular structure and of the reactive intermediate species. The aim of our research programme has been to investigate the chemistry of the degradation of polymers by high-energy radiation by determination of changes in chemical structure and observation of the formation and reaction of free radical intermediates.

Elastomers: Elastomers are an important class of polymeric materials and their elastomeric properties are

highly sensitive to irradiation. Depending on the molecular structure of the elastomer, either crosslinking or scission may be predominant. In this paper we report investigations of changes in the molecular structures of various elastomers by NMR spectroscopy, using solution and solid-state methods.

Polyolefins: Ethylene-propylene copolymer elastomers undergo both crosslinking and scission of the polymer molecules. The formation of methyl groups on new chain ends resulting from scission can be observed in solution NMR spectra at low radiation doses (below the gel dose - above this dose the proportion of soluble decreases with increasing dose) and in solid-state NMR spectra after higher doses.

Polydienes: Irradiation of poly(butadiene) and poly(isoprene) causes crosslinking with high yields and with high conversions of the C=C bonds to crosslinks. The disappearance of C=C bonds and the formation of crosslinks can be determined quantitatively from the solid-state ^{13}C NMR spectra. The radiation sensitivity is influenced by the molecular architecture of the polydiene molecules. Substitution with chlorine results in significant sensitization to radiation.

Polyisobutylene: Polyisobutylene provides some particular attractions for studies of the effects of radiation on molecular structure of polymers. Scission occurs with high yield and exclusively (without crosslinking). The ^{13}C NMR spectrum of the unirradiated polymer consists of three sharp resonances only. The polymer remains soluble after all doses of radiation. Many new resonances are observed, resulting from new structures in the polymer molecules. Identification of the structures which are formed from the chemical shifts of the new resonances and their quantitative measurement provides valuable information on the mechanism of the radiation-induced degradation.

Halogen sensitization: Substitution by chlorine or bromine in the structure of polyisobutylene containing small amounts of a copolymerized diene sensitizes the molecules to radiation and results in crosslinking becoming the main process at low doses. However the halogenated structures are rapidly consumed and the scission of the polyisobutylene structure becomes the main process.

Molecular structure: Thus, the different molecular structures of ethylene-propylene copolymers poly(diene)s and polyisobutylene result in different responses to high-energy radiation. The sensitivity and the predominant process is greatly affected by halogen substitution on the polymer molecule.

Environmental degradation of poly (ethylene terephthalate) by hydrolysis

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Mehrdad Mohammadian & Norman Allen*

Crystalline and amorphous poly(ethylene terephthalate) (PET) sheet have been exposed to both thermal and UV aging. Environmental breakdown has been emphasized by aging in dry and wet soils and at low and high humidities, in the absence and presence of UV irradiation. Degradation has been monitored by viscometric (chain scission) and density measurements. Results indicate that in both materials hydrolysis is the dominant mode of degradation at ambient temperatures. For highly oriented PET both chain-scission and cross-linking are evident. In the case of amorphous material crystallinity exhibits an initial increase due to plasticization and annealing. This is followed by rapid chain scission and thereafter degradation proceeds at a reduced rate with a combination of hydrolytic and oxidative mechanisms taking place. Density increases have not previously been attributed to hydrolytic annealing but rather considered to be due to a chemi-crystallization (1) process. The two processes are presented and discussed, with evidence for hydrolytic annealing being supported with data from thermal aging under dry conditions and UV irradiation. In view of the results obtained, current physico-chemical test techniques used for monitoring environmental breakdown of PET are evaluated.

Reference

(1) A. Ballara and J. Verdu, *Polym. Deg. Stabil.* 26(1989) 361.

Stability and degradation of polymethacrylates with controlled structure

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Polymethacrylates degrade relatively easily to allow molecular weight compounds or to monomers by heating or irradiation. This is often noticed on sheet extrusion of poly(methylmethacrylate) (PMMA). The decomposition or stability of methacrylate polymers strongly relates to the type of the ester group and of the end groups of the polymer, their molecular weight and molecular weight distribution, their stereoregularity and or copolymer composition. Isotactic and syndiotactic PMMAs have been prepared by living polymerization systems. Homo- and copolymers of various

methacrylates with carefully controlled structures have been synthesized.

The temperature of degradation and the mechanism of degradation of PMMA depends especially on the type of the end groups since the initiation usually starts from the chain ends. Radically prepared PMMA has some unsaturated end groups; the decomposition temperature of the polymers decreased with increasing amounts of these double bonds. Special techniques such as polymerization in the presence of transfer agent are utilized to prepare polymethacrylates of increased stability.

Tacticity of polymethacrylates strongly affects the degradation of polymethacrylates; isotactic polymers degrade faster than the syndiotactic polymers. An excellent example for the lower stability of isotactic polymethacrylates is their higher sensitivity as electron-beam or X-ray resist. Isotactic PMMA is also hydrolyzed more rapidly than syndiotactic PMMA. In methacrylate copolymers, the decomposition depends on the copolymer compositions. The thermal properties of the copolymers can be controlled by changing the copolymer composition. In some cases block copolymers have different decomposition temperatures than the corresponding homopolymers. With the advanced knowledge of the stereochemistry and the techniques of macromolecular engineering of stereospecific control and the control of copolymer composition for the synthesis of methacrylate polymers, we can now satisfactorily control the stability property relationship of polymethacrylates by tailor-making the structures of the polymers.

The effect of polymerization conditions on the degradability of polyamide 6

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It is well known that degradation of polymers initiated by heat or irradiation is strongly affected by traces of impurities. Besides dispersed molecular impurities having entered the polymer through impure reactants or by unsuitable processing, polymer stability is also affected by foreign structures in the macromolecule.

With polyamides, even end groups have to be regarded as active foreign structures. It has been found that with polycaprolactam (nylon 6), the most important representative of lactam-based polyamides, the velocity of thermo-oxidation can be changed by an order of magnitude by the proportion of the amine and carboxyl group concentrations.

In addition to the omnipresent end groups, in all lactam polymers exist irregular structures originating in unwelcome side reactions. These foreign structures positioned in the macromolecule's inner or chain ends, affect the degradability of the polyamide and can have positive or negative influences, depending on their structure.

The type and number of such foreign structures depends very much on the polymerization conditions. The more active the catalytic system, the more complicated are the side reactions leading to irregular structures. For example, rapid polymerization of lactams with anionic catalysts gives ketoamide derivatives, from which numerous side reactions result leading to several irregular structures. Even in polymerization with the mildest catalytic systems, unwelcome side reactions cannot be completely avoided.

It will be shown how particular polymerization methods (anionic, cationic, hydrolytic) and polymerization temperature influence the speed of the thermo-oxidation of nylon 6 and of other lactam polymers. Based on these correlations, polyamides of higher stability can be produced even without stabilizing additives, just by choosing such polymerization catalysts and conditions providing polyamides with optimized end groups and foreign structures.

Synthesis and degradation of polymers containing polyacetal segments

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Polyacetals are obtained by cationic ring-opening polymerization of cyclic acetals. Depending on the monomer structure, polymers with a wide variety of physical properties can be obtained. By proper choice of the initiator system and reaction conditions, "telechelic" polymers, i.e. polymers with functional end groups, can be synthesized. These telechelic polymers have been used to prepare block or graft copolymers and segmented polymer networks.

Many polyacetals are degradable when treated with cationic initiators, due to their low ceiling temperature. Acetal functions are also cleaved by acid-catalysed hydrolysis or alcoholysis. Consequently, linear or crosslinked polyacetals can be degraded to monomers (by depolymerization) or to mixtures of aldehyde and diol (by hydrolysis).

In segment copolymers (including segmented networks) the polyacetal segments can be degraded selectively, i.e. without affecting the second polymer

chain. This selective degradation provides information on the mechanism of network formation.

Organic solvent systems for cellulose as biodegradable polymer and their potential areas of application in cellulose spinning and derivatization

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Based on the realization that cellulose, being a reproductive material and a biodegradable polymer, will still be important in the future both as material and raw material for soluble process auxiliaries, this paper deals with a nowadays much-discussed possibility of better utilization of the potential of this polymer: the possibilities and limits of the use of organic cellulose solvents for fashioning and production of derivatives. From a chemical point of view, the organic cellulose solvents are subdivided into derivatizing and non-derivatizing systems. As demonstrated in detail by examples from the author's group, dissolution is achieved in the first case in connection with a covalent derivatization of the cellulose molecule to an instable cellulose ether, ester or acetal, whereas in the second case only intermolecular forces are active between polymer and solvent. While the chemical processes occurring during cellulose dissolution in the derivatizing systems known today are understood rather completely, many open questions still do exist regarding formation and structure of the intermolecular complexes formed in non-derivatizing systems.

The most important potential area of application of the organic solvent systems was and still is the transformation of cellulose pulp to threads and films within the context of searching for environmentally acceptable alternatives to the viscose process established now for a century. As shown by several research groups, cellulose filaments can be spun from a rather large number of derivatizing as well as non-derivatizing solvent systems, the choice is extremely limited though for economical, ecological and technological reasons. A current research problem is given today by the question whether or not in principle different physical structures exist in threads spun from derivatizing systems on the one hand and non-derivatizing systems on the other, resulting thus also in basic differences in macroscopic properties. In close connection with that there is the question how far high performance fibre polymers can be produced by jointly transforming cellulose and synthetic polymers.

Besides the new approaches to cellulose thread formation via the state of solution as the main area of application, the promotion of the organic chemistry of cellulose by employing organic solvent systems in

cellulose derivatization under homogeneous conditions must be mentioned. As demonstrated in a joint work with W. Wagenknecht, I. Nehls and M. Schnabelrauch on sulphation and phosphatization of cellulose in the N_2O_4 /DMF solvent system, regioselectivity with regard to the site of reaction within the anhydroglucose units can be obtained by proper choice of reaction conditions and acylating agent. The potential advantages and the limitations of these regioselective homogeneous reactions are discussed with regard to product properties. Finally, the problem of biodegradability of cellulose derivatives generally is discussed.

Biodegradable plastics based on cellulose acetate

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It is generally known that secondary cellulose acetate (with 53 to 56 per cent acetyl groups) is suitable for thermoplastic processing. With appropriate plasticizers a plastic material is obtained which excels in transparency and pleasant texture and is therefore often used for tool handles, combs, spectacle frames and the like.

Cellulose acetate with such a degree of substitution is in principle biodegradable, although degradation proceeds extremely slowly. However, when common plasticizers are substituted by specific esters and other low molecular components (at least 30 per cent by weight), the "plastic material" has still got the same thermoplastic properties but will decompose in soil or water within just a few years.

A cellulose acetate cup, for example, buried in sewage sludge lost more than 70 per cent of its original weight within about 18 months. In aqueous environment (Sturms's test) the decomposition amounted to more than 60 per cent. Under appropriate composting conditions or conditions of anaerobic fermentation, the degradation process is likely to be even faster.

However, the material can also be recycled or incinerated without residues.

The new kind of biodegradable plastics can be processed on conventional injection moulding machines or on extruders adapted to their specific processing properties. They can be turned into granular materials, strips and films and into injection moulded and extrusion blow moulded shapes.

The material properties are comparable to those of the known cellulose ester-based plastics: films and thin-walled hollow bodies are highly transparent. Mechanical properties compare well with those of conventional packaging materials. The thermal resistance is somewhat lower, but the permeability to steam and oxygen is

relatively high compared to that of standard plastics. The material is resistant to oils and fats and, for a short while, even to weak acids and alkalis.

PHB/V - A natural biodegradable thermoplastic polymer

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"Biopol" is ICI's trademark for a range of fully biodegradable thermoplastic polyesters produced from renewable raw materials. They are composed of hydroxybutyrate (HB) units with between 0 and 30 per cent of hydroxyvalerate (HV) units incorporated randomly throughout the polymer chain.

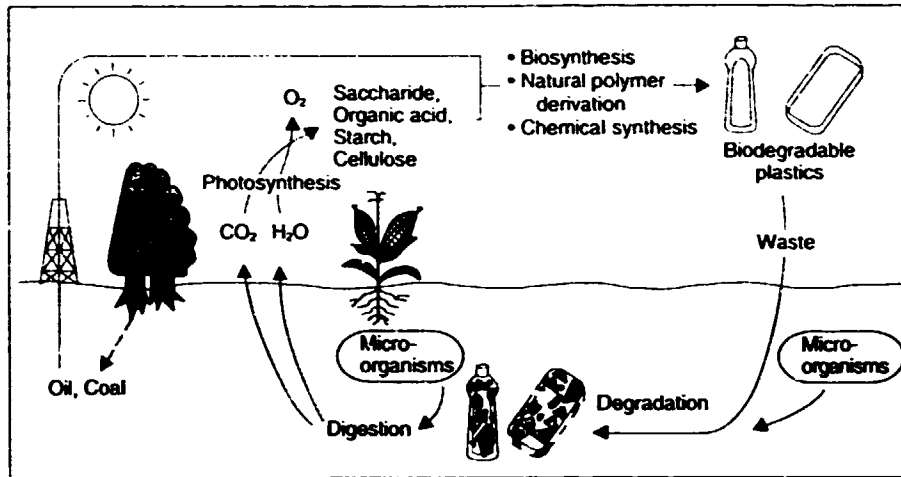
Sharing many of the properties of traditional plastics they can be processed on conventional equipment, using conventional technology, to produce moulding, containers, coatings, laminates, films and fibres. Just like conventional plastics, products produced from PHB/V are stable in use, durable and moisture resistant. They may be reused or recycled and upon incineration release only CO_2 and water. "Biopol" differs from traditional plastics in being naturally derived. The homopolymer PHB is found widely throughout nature where it is produced by micro-organisms as a carbon and energy store. PHB/V is recognized by the environment as a foodstuff and it is this recognition which confers true biodegradability to the entire polymer range.

The large-scale production of these polymers simply intensifies the natural process and is based on the fermentation of glucose from annually renewable agricultural feedstocks such as sugarbeet and cereals. In the future there is also the potential to use agricultural by-products such as molasses and whey. The process itself uses low temperatures and pressures generating no harmful gaseous, aqueous or solid effluents.

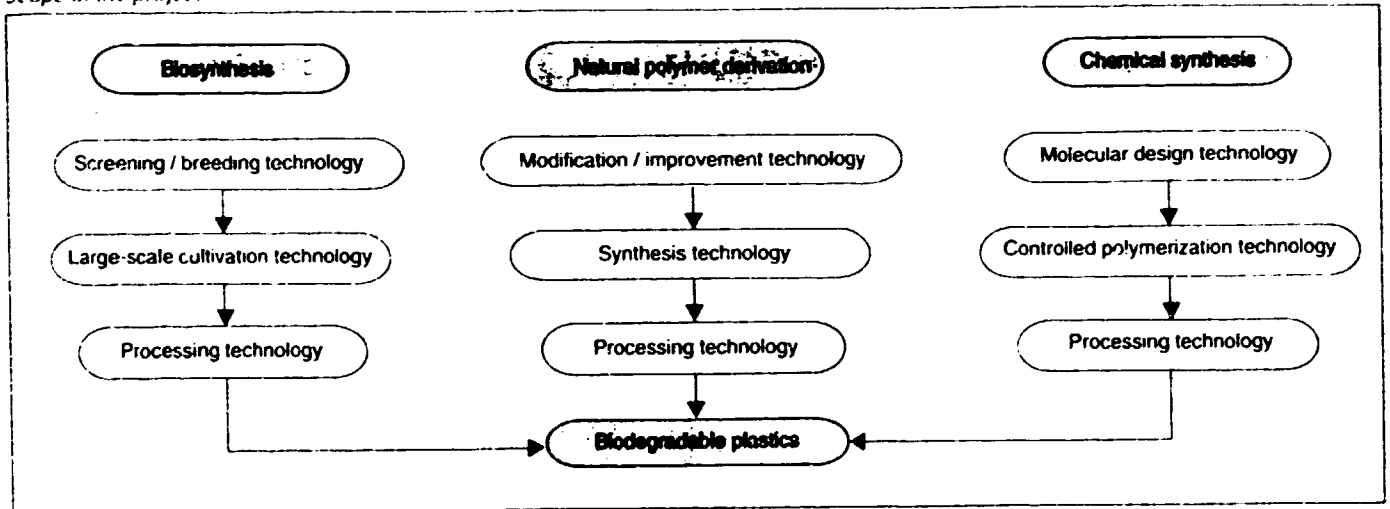
In addition, polyhydroxybutyrate is particularly compatible with mammalian tissue and blood. It is recognized by the human body where the monomer of polyhydroxybutyrate is itself a normal metabolite in mammalian blood.

PHB/V has the functionality of traditional plastics, is produced from sugar in a simple and safe fermentation process and is truly biodegradable. It answers the consumer's demand for natural products and the converter's need for performance. In addition, "Biopol" is compatible with all existing and developing waste management technologies and thus offers the security of environmentally responsible disposal. It is particularly suited to municipal composting, can be safely incinerated and can be recycled.

Objectives of the project



Scope of the project



(Research Institute of Innovative Technology for the Earth (RITE), Shin-Kyoto Center Bldg., Karasuma-nishiiru, Shiokoji-dori, Shimogyo-ku, Kyoto 600, Japan. Fax: +81 75 361 5607)

(Source: JETRO, April 1993)

3. APPLICATIONS

Biodegradable plastic with controlled degradation time

Professor M. Okada of the Faculty of Agriculture of Nagoya University, Dr. M. Atsumi of the Science Department, Tokyo Women's Christian University, and their research team have jointly developed a biodegradable plastic with freely controlled degradation. This plastic is a type of polyester and has a strength comparable to polypropylene now used for producing food containers.

Four raw materials (monomers) are used, and the degradation time can be controlled between one week and six months. The plastic is not decomposed completely into water and carbon dioxide, but the degradation performance is very high.

The research team synthesized a series of new degradable polyesters with main chains containing a cyclic ether, the basic structural unit in natural polymers such as nucleic acid and polysaccharide, and studied the correlation between polymer structure and degradability. The degradability can be controlled by various factors, such as the number of ring atoms in the cyclic ether, the bonding of main chains (acetalester type, ether-ester type), main chain bonding position (2,5-bonding and 2,6-bonding of the tetrahydropyran ring) and type of side chains.

The degradability of polyesters with tetrahydropyran rings as the main chains can be controlled by the type of side chains and composition. Even if the bonding positions on the tetrahydropyran rings differ, the degradability can be changed by the composition. Therefore, by controlling the molecular structure, it is possible to control the degradation rate.

The plastic developed with these properties is a substance with a structure resembling polyester. The degradation time can be changed by producing polymers based on four bicyclic oxalactone monomers with slightly different structures. Synthesis is by the same method used for ordinary plastics. By changing the ratios of the four monomers, the degradation time can be adjusted.

Degradation experiments were conducted in the soil and in faucet water (neutral phosphate buffer solution). The plastic was not degraded completely into water and carbon dioxide, but was reduced into shreds in one week to five months. Some of the polyesters degradation was faster in soil. According to experiments, the plastic degraded in about one week was fragile and impractical, but that degrading in one month or longer had about the same strength as polypropylene used for producing home dining ware. Also, when heated, the melting point for

commencement of degradation was as high as 150° C, so the plastic is of practical use. (Nagoya University, Faculty of Agriculture, Furo-cho, Chikusa-ku, Nagoya City, Aichi, Pref. 464-01, Japan. Tel.: +81-52-781-5111, Fax: +81-52-781-4447) (Source: *JETRO*, October 1992)

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Microbial degradation of poly(sodium acrylate)

Nippon Shokubai Co. Ltd., with the cooperation of Professor Y. Tani of the Faculty of Agriculture, Kyoto University, has announced that poly(sodium acrylate) can be degraded with ease by micro-organisms in the soil. The technology is expected to be applicable to the microbial degradation of paper diapers made of polyacrylate-based water absorbent polymers.

Studies on microbial degradation of synthetic polymer compound have discovered various micro-organisms capable of degrading polymers such as polyethylene glycol, polyvinyl alcohol, polyethylene adipate and polycaprolactone. Polyacrylate is a typical water-soluble polymer which is non-toxic, and used in various fields, but no detailed research on its biodegradability has been performed.

The research team screened soil micro-organisms capable of degrading poly(sodium acrylate), and studied the degradation activity and characteristics.

The company searched for micro-organisms primarily from the soil in the vicinity of the company's Tsukuba Research Laboratory and discovered that several strains of micro-organisms such as the *Arthrobacter* strain display the degradation activity. When two of these strains (strain L7-A and strain L7-B) are used in a mixture and cultured with a 0.2 per cent poly(sodium acrylate) nutrient source, polymers with molecular weights of less than 2,500 are degraded in about two weeks.

These strains cannot completely degrade the polymer independently, as one strain degrades high polymers of up to molecular weight 1,000 and the other strain degrades the polymers to lower molecular weight. The existence of an *Arthrobacter* sp. No. 18 has also been confirmed that degrades roughly 80 per cent of oligomers into CO₂ in several weeks, indicating that various strains of bacteria are involved in microbial degradation. (Nippon Shokubai Co. Ltd., Public Relations Section, 1-2-2, Uchisaiwai-cho, Chiyoda-ku, Tokyo 100, Japan. Tel.: +81-3-3506-7484, Fax: +81-3-3506-7598 (Source: *JETRO*, December 1992)

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A disappearing plastic pen

The first biodegradable plastic ballpoint pen. The Green Pen, was recently rolled out nationwide through Wal-Mart's and Sam's Wholesale Club by A&W Products, Port Jervis, N.Y., USA. Both the green body and yellow cap of the pen are moulded from Mater-Bi biodegradable corn-based plastic resin developed by Novamont, SpA, an affiliate of the Ferruzzi-Montedison Group. Novamont says the pen could disappear within two to three years in environments where both water and micro-organisms are present. Other applications being researched are composting and trash bags, diaper back sheets, tampon applicators and plastic cutlery. (Source: *Plastics World*, May 1993)

The first fully biodegradable bottle in the United States

Available through a retail department store is being used to package a new line of personal-care products. The container is made from Biopol resin, a line of fully biodegradable polymers developed and manufactured by Zeneca Bio Products (formerly ICI Bio Products), Wilmington, Del., USA. The polymer is produced through a natural fermentation process based on renewable agricultural feedstocks, such as sugar beets and cereal crops. (Source: *Plastics World*, May 1993)

Biodegradable plastic disposal razor

Kai Corp. will market two types of disposable razors, one the KII- β razor for men and the other the Fresh- β razor for women, both made of a biodegradable plastic Biopol.

The completely biodegradable plastic Biopol was developed by Imperial Chemical Industries PLC (UK), and is functionally the same as conventional plastics, but is produced by the fermentation process using glucose from corn, sugar cane or sugar beet as the raw material. When buried in the ground or cast into the sea after use, it starts decomposing after about three months by micro-organism action, and is completely decomposed into water and carbon dioxide within 2-3 years.

The biodegradable plastic is used on all parts other than the metal blade. The metal blade is oxidized and corroded in the natural environment, so the entire razor assembly will be completely returned to natural substances in the ground. Even when incinerated, it will be decomposed into carbon dioxide and water, so no toxic substance is left.

The biodegradable plastic developed jointly is a copolymer in which β -polyhydroxy butyrate and β -polyhydroxy valerate chains are bonded together. It

is produced by extracting the sugar content and converting into glucose, then fermenting the glucose with soil bacteria. The fermentation bacteria contain about 70 per cent of a polyester, which is refined to obtain the polymer. Since the polymer strength is inadequate for producing razors, clay is added to provide an adequate strength for making the razor. (Kai Corporation, 1-17-6, Higashi-Kanda, Chiyoda-ku, Tokyo 101, Japan. Tel.: +81-3-3862-6381, Fax: +81-3-3862-6382) (Source: *JETRO*, August 1992)

Biodegradable polypropylene strap

Sekisui Jushi Corp. and the Fermentation Research Institute of the Agency of Industrial Science and Technology have jointly developed a biodegradable polypropylene (PP) strap. The PP strap is produced by blending polycaprolactone and polyolefin, followed by the company's unique drawing technique.

During degradation, the polycaprolactone component, after the PP strap is discarded, is first decomposed by enzymes (lipase) in the micro-organisms in the soil, sea water or fresh water, followed by the degradation of the remaining polyolefin.

This biodegradable PP strap, when buried in the ground after use, undergoes volumetric reduction to enable effective use of waste sites, and does not pollute the ground. Even when left in the surrounding environment, it has much less influence on plants and animals compared with conventional plastics. In addition, the residual PP after degradation, in contrast to photodegradable plastics, does not undergo any change in molecular weight or chemical structure, and is therefore quite safe.

The company plans further research to elucidate the correlation between raw material blending and strength, and to commercialize the biodegradable PP strap. (Sekisui Jushi Corporation, R&D Plaza, Key Technology Center, 731-1-1, Kagami, Ryuo-cho, Gamou-gun, Shiga Pref. 520-25, Japan) Tel.: +81-748-58-2488, Fax: +81-748-58-2486) (Source: *JETRO*, August 1992)

Biodegradable plastic film

The Fermentation Research Institute and the Research Institute of Innovative Technology for the Earth (RITE) have jointly developed a new type of completely biodegradable plastic.

This plastic material is produced by dispersing a starch prepared in gelatinous form at high concentration into a biodegradable polycaprolactone (PCL) polyester, and was confirmed to have complete biodegradability in

the enzymatic evaluation method developed by the Fermentation Research Institute.

Biodegradable plastics which include a high concentration of gelatinized starch have already been developed in the United States and Italy, but lack water resistance and/or are not biodegraded completely.

The new biodegradable plastic material has complete degradability, and excellent water resistance. The plastic blended with gelatinized starch has a better flexibility than that blended with granular starch, making it easier to produce extra-fine films. Also, the material is cheaper since it uses starch in a high blend, and helps to conserve oil resources. The biodegradation speed is faster than that of PCL alone.

Biodegradable plastic decomposed by micro-organisms in nature is a means of solving the plastic disposal problem due to the many advantages such as ease of incineration, stabilization and prolongation of the service life of landfills, reducibility into compost for return into farmlands, and reduced influence on wild life due to refuse scattering, so research is intense in various countries for commercialization.

This research was conducted by RITE jointly with the Fermentation Research Institute under consignment by the New Energy and Industrial Technology Development Organization (NEDO). (Fermentation Research Institute, AIST, 1-1-3, Higashi, Tsukuba City, Ibaraki Pref. 305, Japan. Tel.: +81-298-54-6024, Fax: +81-298-54-6005) (Source: *JETRO*, March 1992)

Biodegradable plastic with elasticity

Kirin Brewery Co. Ltd. has developed technology for producing elastic biodegradable plastics by applying the fermentation process. The polymer obtained is poly(3-hydroxyalkanoate) (PHA).

The tremendous elongation is not possessed by biodegradable plastics developed up until now, and is controllable by mixing with other types of biodegradable plastics. *Pseudomonas* bacteria (G-1201 strain) was isolated from soil at a site in Gunma Prefecture and a method established for producing PHA. Firstly, this bacteria is cultured in bulk. The nutrient source is glucose or other saccharides as the carbon source for proliferating biomass, after which the bacteria are placed in a polymer culturing bed containing no nitrogen, which starts polymer storage inside the bacteria. Adding yeast extract to a concentration of 5 per cent causes the polymer productivity to be increased threefold. The existing productivity is 3.7 g/l, which will have to be improved further for commercialization, but can be increased to over 5 g by improving the bacteria and culturing conditions.

The polymer has a molecular weight of 50,000-100,000 and the melting point is as low as 50° C. The biodegradability in soil is expected to be around 2-3 weeks in summer and 2-3 months in winter. This polymer is sticky and elongated with ease simply by pulling, and a polymer 1 cm long can be elongated to 6 cm. By contrast, polyhydroxybutylate (PHB), a typical type of biodegradable plastic, has a high melting point, is hard and difficult to elongate, and is quite brittle at low temperatures.

The company blended both these materials and succeeded in increasing the PHB elongation to a significant practical level. The elongation ratio can be changed by regulating the ratios of PHB and PHA. Based on these results, the company is presently developing applications for using PHA independently or in a blend with PHB. It also plans to use cheaper nutrient sources such as waste molasses to lower the costs of these plastic materials to a practical level. (Kirin Brewery Co. Ltd., Public Relations Group, 6-26-1, Jingumae, Shibuya-ku, Tokyo 150, Japan. Tel.: +81-3-5485-6170, Fax: +81-3-3499-6190) (Source: *JETRO*, January 1993)

Biodegradable plastic alloy protects steel

A relatively low-cost biodegradable plastic has been developed by researchers from Sumitomo Metal Industries Ltd., Tokyo, Japan, and Tokyo Institute of Technology. The polymer alloy consists of about 40 per cent bacteria-based and 60 per cent synthetic-based polymers. Its strength and density are said to be similar to those of polyethylene. When buried in soil, however, it decomposes three to four times faster than conventional (and more costly) biodegradable plastics, which are 100 per cent bacteria-based. Sumitomo is developing the material as a "green" alternative to the plastics used to protect pipes, coated sheets, and other steel products from corrosion during sea voyages and damage during handling. (Source: *Advanced Materials & Processes*, December 1992)

Biodegradable synthetic fibre

Unitika Ltd. and Nippon Unicar Co. Ltd. have jointly developed a biodegradable synthetic fibre.

Synthetic fibres and plastics resist decomposition semi-permanently and are a major factor in environmental pollution, so the development of biodegradable synthetic fibres and plastics was required. Some degradable plastics are already being commercialized, such as the photodegradable type decomposed by light and the biodegradable type decomposed by micro-

organisms. The new synthetic fibre represents the first biodegradable synthetic fibre.

This new synthetic fibre consists of a synthetic polymer consisting primarily of high molecular weight polycaprolactone (PCL). It decomposes into fragments in two weeks to three months and ultimately completely into CO₂ and H₂O.

Polycaprolactone was known to be biodegradable, and attempts have been made to apply the material to disposable tableware. The companies discovered a polycaprolactone polymer with excellent strength and established spinning and drawing techniques, allowing the development of the new biodegradable synthetic fibre.

Conventional degradable fibres such as cotton and rayon are natural substances, so there are limits to processing methods and applications. Polycaprolactone is thermoplastic and hydrophobic, and has a broad range of applications in combination with conventional materials. Its strength depends on the degree of polymerization, and a polymer with a mean polymerization degree of 80,000 provides a fibre with a tensile strength of 5 g/denier, comparable to polyester. The fibre is available in thicknesses of 50-1,200 denier (0.08-0.38 mm), and can be used for producing fine threads for knitwear and fishing lines.

The biodegradability is being checked through experiments conducted underground, in activated sludge and in sea water, and biodegradation has been confirmed in all cases. Fabrics knitted with the new fibre are degraded so the original shapes cannot be recognized after about 120 days when buried.

The new fibre has a low melting point of 65° C, so may be unusable for apparel, but is usable for producing a wide variety of products such as agriculture/insect and weed control nets, disposable industrial materials, fishing lines, and disposable diapers and napkins. The price can be lowered by mass production to 1.5 times that of polyester fibres available on the market. (Unitika Ltd., Public Relations Section, 3-4-4, Nihonbashi Muro-machi, Chuo-ku, Tokyo 103, Japan. Tel.: +81-3-3246-7536, Fax: +81-3-3246-7538) (Source: *JETRO*, January 1992)

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Biodegradable plastic balloon

Chukoh Chemical Industries Ltd., a manufacturer of resins, and Maruto Sangyo Ltd., a packaging material manufacturer in Fukuoka Prefecture, have jointly commercialized and marketed a biodegradable plastic balloon that is degraded by micro-organisms in the natural environment to replace the rubber balloons less used in recent years due to the need for environmental preservation.

Chukoh Chemical Industries started research on plastic materials compatible with the environment eight years ago, but the major problem was the high cost of the products. The balloon was commercialized jointly with Maruto Sangyo that possesses advanced technologies for the manufacture of films.

The new balloon is made of a biodegradable plastic that chemically bonds starch and a special type of resin. Inflating the balloon with helium gas enables the balloon to float in a room for over two weeks. In the soil, it is decomposed by micro-organisms in about four months, and converted into carbon dioxide and water in about one year. Decomposition is faster in the sea. Also, when incinerated, the low calorific value does not damage furnaces or generate toxic gases, smoke and soot.

The balloon size, shape and colour can be determined flexibly, and the surface can be printed with characters and patterns. The companies are marketing balloons with a diameter of 45 cm at a price of ¥400 apiece in Japan. (Chukoh Chemical Industries Ltd., Product Development Center, 3-1-36, Watanabe-dori, Chuo-ku, Fukuoka City, Fukuoka Pref. 810, Japan. Tel: +092-724-1418, Fax: +092-724-1412) (Source: *JETRO*, January 1993)

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Biodegradable polyurethane from vegetable wastes

The National Institute of Materials and Chemical Research of the Agency of Industrial Science and Technology reports that its researchers have succeeded in synthesizing polyurethane with excellent biodegradability from vegetable waste. Apparently, the polyurethane has a mechanical strength surpassing that of ordinary polyurethane and a biodegradability compatible to wood such as cedar and beech.

Polyurethane is produced by polymerizing an isocyanate component and a polyol component. The new synthesis technique uses waste such as coffee grounds, sugar cane bagasse and molasses as the polyol component. In experiments, the waste-derived polyol component was mixed with petroleum-based polyols such as polyethylene glycol or polypropylene glycol. The petroleum-based polyol has the effect of making the polyurethane soft. The ratio of waste-derived polyol to petroleum-based polyol was 30:70 respectively.

The biodegradable polyurethane was synthesized in sheet form and foamed form. The sheet polyurethane had a strength 1.6-4.0 times that of polyurethane sheets of the same thickness containing no waste, while the polyurethane foam had double the compressive strength.

Fragments of polyurethane foam, cedar and beech were buried in the ground to confirm biodegradabilities. In three months, the weights of the cedar fragment and beech fragment were decreased by 1 per cent and 7.5 per

cent, respectively, while the polyurethane foam weight was decreased by 5 per cent and its mechanical strength halved during the 90-day period, indicating that biodegradation occurs. (The National Institute of Materials and Chemical Research, AIST, 1-1, Higashi, Tsukuba City, Ibaraki 305, Japan. Tel.: +81-298-54-6228, Fax: +81-298-54-6233) (Source: *Performance Materials Technology*, November 1993)

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Biodegradable fishing net

The Industrial Research Institute of Ishikawa and Chukoh Chemical Industries Ltd. have developed a prototype biodegradable fishing net. The fibre is decomposed by bacteria or other micro-organisms in soil and sea.

Conventional plastic fishing nets persist in soil and sea. After loss into the sea, they are disastrous to sea creatures, and devastate fishing grounds. The Institute has been investigating biodegradable plastics, which can be decomposed by micro-organisms, for use in biodegradable nets.

The fibre of the net is made of polymer extracted from micro-organisms such as hydrogen bacteria in soil

and sea. The polymer is formed by a spinner into fibre which is then drawn to increase the strength. While conventional biodegradable fibres easily break, the new fibre is as strong as rayon fibre because of the proprietary process of drawing. The new fibre can be mass produced. These features encouraged the developers to develop the fishing net.

The new net is decomposed by micro-organisms into carbon compounds, and the products of decomposition begin to circulate through the natural ecosystem. If the new net is lost at sea, it is decomposed with little impact on the environment. To demonstrate the degradability, the Institute buried the fibre in soil for half a year, and found that it was degraded to 60-70 per cent of the initial weight. The reduction will reduce the cost for burning or other disposal of waste nets.

The Institute is going to explore production processes for stronger fibre and to develop fibres with decomposition rates according to possible applications. (Industrial Research Institute of Ishikawa, Dept. of Textiles, Ro-1, Tomizu-machi, Kanazawa City, Ishikawa Pref. 920-02, Japan. Tel.: +81-762-67-8083, Fax: +81-762-67-8090) (Source: *JETRO*, August 1993)

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4. MARKETING

Degradable resin makers seek markets in Japan

Concrete plans for commercial and semi-commercial biodegradable resin plants in Japan have more to do with supplier optimism than user demand. Suppliers now believe they have the right combination of processability and physical properties to attract more users if they can offer their products less expensively.

While the market for biodegradable resins, mainly sample shipments, was valued at ¥400 million in 1992, think tank Nomura Research Institute of Tokyo forecasts plant start-ups will catapult this figure to ¥1.5 billion in 1993, ¥4.5 billion in 1995, and ¥11 billion in 1997.

Some suppliers say that the materials will overcome processor reluctance to use resins based on biodegradable starch or aliphatic polyester, if they can bring prices down from over \$7.70/kg (¥800) to around \$4.80/kg (¥500). (Extracted from *Modern Plastics International*, 1 October 1993)

Key market for degradable plastics: 1990-2000

(millions of pounds)

Application	1990	1995	2000
Trash bags	250	1 500	2 200
Agricultural	15	60	200
Food containers/utensils	-	200	400
One-way packaging	-	400	600
Food packaging	-	150	300
TOTAL	265	2 310	3 700

Trash bags: Polyethylene trash and garbage bags will constitute at least a 2.5 billion pound market in 1990, and one of every ten bags sold will be either starch-linked or photodegradable. Advertising biodegradability helps deflect criticism for solid waste problems from plastic fabricators. It also improves the attractiveness of the product to the consumer.

Agricultural: Economics favour degradable mulch film, which is laid over young crops to improve yield, lock in moisture and deter weed growth. The film can be used to form a mini-greenhouse so crops can be planted and harvested earlier to achieve the highest

prices. Since degradable film just disappears, there is no need for farmers to collect and dispose of it at costs up to \$150/acre.

Food containers/utensils: While MacDonalds has begun a pilot programme to recycle polystyrene containers and utensils at its New England outlets, other fast food companies lag far behind. Degradable cups and utensils may become the best solution in areas where an infrastructure for recycling has not yet been established. Degradability is also an attractive option for picnic plates, glasses, and utensils.

One-way packaging: Lots of packaging is used only once, then discarded. Applications for degradable polymers might range from glossy blister packs for toys or drugs to cigarette pack wrapping, tampon applicators and sanitary napkins, medical packaging, and grocery bags.

Food packaging: Starch-linked polymers are likely to meet Food and Drug Administration regulations because their key additive is a natural material, but this is not a likely market for photodegradable polymers, which contain more active chemicals, or water-soluble all-starch polymers, which might dissolve on the job. Unless they can be made transparent, starch-based polymers will not easily replace clear polyethylene and ethylene-vinyl acetate films now used to wrap meats. But they could be used to form meat trays and food containers. (Source: *High-Tech Materials Alert*®, 1990)

North American degradable plastics demand (in millions of lbs)

Type	1992	1997	Average annual growth (%)
All plastics	65,100	79,200	4.0
All degradable plastics	1,205	2,625	16.8
Biodegradable	490	1,025	15.9
Photo-degradable	420	825	14.5
Bio-photo-degradable	280	645	18.2
Other degradables	15	130	54.0

Source: The Freedonia Group (Cleveland)

(Excerpt from *Chemical Week*, 27 October 1993)

Water-resistant Novon polymers

Novon Polymers, a Warner-Lambert affiliate company, is stepping up the marketing of its bio-degradable starch-based polymers in Europe. The Swiss arm of the company last week unveiled new grades of product specifically designed to be water resistant.

One grade, *Novon M4900*, suitable for film extrusion, is targeted for the manufacture of bags to be used for the collection of compostable kitchen and garden waste. "As the compost bag is made from fully biodegradable *Novon*, it can be composted mutually with the bio-waste in the municipal composting facility", the company says. The bags are currently being tested at households in Hamburg, Germany.

A second grade, *Novon M1801*, is designed to be injection-moulded into cutlery items. The company claims this will allow for the first-time food residues and other biowaste to be composted together with disposable cutlery. A third new grade being introduced to Europe is *Novon M5600* for injection blow-moulded bottles for the vitamin, healthfood and pharmaceutical markets.

Novon estimates that by the mid-1990s half of the German and nearly all the Dutch and Austrian households will be connected to composting plants. The company anticipates similar developments in the Nordic countries. (Source: *European Chemical News*, 20 September 1993)

Technologies

Research into biodegradable materials runs the gamut from biopolymers produced by microbes, to synthetic petroleum-based polymers custom designed to biodegrade.

Lactic acid polymers or polylactic acid (PLA) represent one of the hottest areas of research today. PLA-materials process and perform like polyolefins but then can be broken down by common soil bacteria. Synthetic lactic acid is derived from hydrogen cyanide and acetaldehyde, by-products of the chemical industry. "Natural" lactic acid is produced by bacterial fermentation of sugars derived from corn, potatoes, grains and milk. According to Battelle Laboratories, Columbus, Ohio, USA, it is the optical isomers of lactic acid made through fermentation that are the most attractive from a polymerization point of view.

The optical isomer may offer other advantages as well. According to Argonne National Laboratory, Argonne, Ill., United States of America, researchers have found that short chains or oligomers of 2 to 10 units of the L-isomer may contain a plant-growth regulator (PGR). A PGR factor would enhance the attractiveness

of polylactides for agricultural applications. Agriculture - not packaging - is the real market niche for PLA-materials.

It is no surprise that Cargill and Ecochem also are working on "natural" PLA. As a major agri-processor, Cargill has a plentiful supply of corn dextrose from which to produce its lactic acid (see sidebar). And Ecochem, with its ConAgra connection, has a ready supply of whey, a natural by-product of cheese-making. Argonne manufactures its lactic acid from fermentation of potato waste.

But Battelle is less concerned about its lactic acid source. There are a couple of ways to look at the lactic acid polymers. One is to start with the rawest of raw materials and think about how to make useful packaging products from potato waste, for example. Or you can take advantage of the lactic acid capacity coming on line in the next two to three years and buy it. If you do that, you decouple the polymerization from the lactic acid production.

Argonne is offering its PLA technology for license. ARCH (Argonne Research Laboratory/University of Chicago) Development Corp., based at Argonne, recently signed a licensing agreement with a Japanese firm, Kyowa Hakko, USA, Inc. The project is still in an early stage and commercial production is not expected for at least two to three years.

Battelle is not licensing its PLA technology but has entered into an R&D joint venture with Golden Technologies Inc., Golden, Co., a subsidiary of ACX Technologies Inc. The company will be looking at the PLA-material for potential use in commercial packaging. At this point, however, there are no plans for commercialization.

IC - Biopol natural biopolymer is produced during fermentation by *Acaligenes eutrophus*, common soil bacteria. Biopol is a poly(L)-hydroxybutyrate-hydroxyvalerate (PHBV) copolymer. The bacteria feed on glucose and produce polyhydroxybutyrate (PHB). Add simple organic acids and the bacteria also produce the valerate component, which improves ductility of the material. At \$8-\$10/lb, Biopol is one of the most pricey biodegradable materials being offered today for packaging. Even if it drops to \$4/lb in 1996 when production capacity is expected to reach almost 10,000 metric tons/year, it will still be quite expensive.

Researchers at Michigan State University (MSU) are trying to address that by using plants to produce polyhydroxybutyrate (PHB). Reportedly, they have had some success in grafting three essential genes from *A. eutrophus* bacteria into experimental plants. Research is still in the early stage, but MSU researchers ultimately expect plants to be more efficient in producing PHB, resulting in a more cost-competitive product.

Starch-based biopolymers represent another significant group of biomaterials. Ecostar International offers an advancement over earlier starch master-batch technologies. Their product contains starch, but this is not the problem that it was in 1989. Starch got a bad name because many companies sold a material that had no mechanism for biodegradation of the accompanying polyethylene polymer. Ecostar has a proprietary catalyst technology that promotes the photo- and thermal oxidation of polyethylene.

Novamont, owned by the Italian conglomerate, Ferruzzi-Montedison, takes advantage of advances in both natural and synthetic biodegradable polymer technology. Like Ecochem, the Du Pont/ConAgra venture, Novamont has a strong agricultural base in Ferruzzi and a strong chemical base in Montedison. Novamont's Mater-Bi combines the starch and synthetic polymers to produce a biodegradable thermoplastic material.

Uni-Star, Canton, Ill., offers one of the most cost competitive products - a starch graft polymethylacrylate copolymer priced from \$0.75 to \$1.25/lb. The technology is licensed from the USDA. It is possible to regulate the water sensitivity of the material and delay the onset of dissolution or degradation for up to 12 hours.

As one would expect, synthetic materials are offered primarily by traditional plastics companies and/or those with a strong petrochemical base. For example, Union Carbide Corp., Danbury, Conn., and Air Products and Chemicals, Allentown, Pa., offer biodegradable polymers made from conventional petroleum-based sources. Union Carbide's polycaprolactone technology has been around since 1975 but only now promoted as biodegradable. Air Products' Vinex resins are based on polyvinyl alcohol (PVOH). According to Air Products, the Japanese are extremely interested in this kind of technology and have published extensively on biodegradation of PVOH.

Industry newcomer, San Diego-based Planet Technologies Inc., prides itself on its ability to design materials that degrade. They have a computer design program that allows them to make alloys and predict their performance beforehand. (Excerpt from *Plastics World*, March 1993)

Degradable plastics as problem-solvers

Increasing environmental awareness and the rapid growth in the volume of waste are the driving forces behind the expansion of the European degradable plastics market, which in 1991 accounted for \$25 million in Western Europe alone. According to surveys carried out by the British market research organization Frost & Sullivan, demand for these products will in the short term be maintained, since environmental issues are likely to dominate the headlines for some time to come.

However, experts are expressing doubt as to the validity of the dramatic surge forecast by Frost & Sullivan, with European sales of degradable polymers reaching \$172 million by 1995. The reason for this dampened enthusiasm lies both in the overbalance of imponderables contained in forthcoming pan-European legislation and also reservations as to whether degradable plastics really are the panacea as regards plastics disposal.

Shampoo in environment-friendly bottles

Finnuala Wynne,* scientific research assistance with Frankfurt-based Zeneca Bio Products, a subsidiary of the British ICI chemicals group, is convinced that for degradable plastics, the best is yet to come. It must be admitted that Ms. Wynne has a vested professional interest in maintaining an optimistic attitude. She is, after all, responsible for the development in Germany of "biopol", a biopolymer which ICI has been officially marketing for the last three years and which caused something of a stir in 1990. In the middle of that year, Wella AG, Darmstadt, decided to launch a pilot project using bottles made from this plastic, whose environment-friendly qualities are stressed by the manufacturers, for their "Sanara" shampoo. (Excerpt from *Popular Plastics & Packaging*, May 1993)

Biodegradable plastic based on lactic acid

Shimadzu Corp. has established manufacturing technology for inexpensive biodegradable plastic based on lactic acid. The company will construct a pilot plant at its Sanjo plant (in Kyoto City) in 1993 and complete a mass production facility with an annual production of 10,000 t before the end of 1995.

Environmental protection requires substitution of hard-to-degrade plastic based on petroleum products to more easily degradable plastic such as biodegradable plastic. Biodegradable plastic has already been merchandized elsewhere by the high cost of ¥800-¥2,000/kg due to the use of valeric acid for the material has hampered the transfer from conventional products.

The new plastic uses lactic acid as the material. This plastic decomposes completely to water and carbon dioxide in soil or water within one year. It does not generate hazardous nitrogen oxides when incinerated. Following success in making experimental pellets last year, Shimadzu decided to go into commercial production. According to the company, lactic acid-based plastic in film state has a strength of 20 kg/mm² or four times that of polyethylene, and is equivalent to or exceeds the petroleum type in both strength and transparency.

* Please note article PHB/V - A natural biodegradable thermoplastic polymer on page 19.

The company expects that the price will settle at around ¥800/kg when the mass production starts. (Shimadzu Corporation, Marketing Research and Planning Department, 1, Nishinokyo Kuwabara-cho, Nakagyo-ku, Kyoto 604, Japan. Tel.: +81 75-823-1110; Fax: +81 75-811-3188) (Source: *JETRO*, April 1993)

Biodegradable polymer

Biodegradable polymer can be processed on conventional polyolefin and polystyrene blow moulding and injection machines and extruders, its supplier says. Showa Highpolymer's Bionolle, an aliphatic polyester, has to be dried before processing because it absorbs air moisture, but the company says the material can be used for a number of applications in which polyethylene is currently employed. Potential applications include bags, food trays, diapers, blow-moulded bottles, cutlery, brush, combs and packaging.

The company says the material, which comes in homopolymer and copolymer grades, can be composted like paper or wood, and Showa plans to up Bionolle production to 3,000 tons/year. The material costs ¥800/kg (about \$7) in Japan. (Showa Highpolymer, Kanda Chuo Building, 320, Kanda Nishiki-cho, Chiyodaku, Tokyo 101, Japan) (Source: *Modern Plastics International*, June 1993)

Corn starch resin

A new corn starch-based resin that is water-resistant and can be completely decomposed by organic matter is to be developed by Amypol Co., a joint venture company formed by Japan Corn Starch Co. and Grand River Technology Inc. of the United States of America.

Water resistant and petrochemical free, the resin can be completely decomposed by micro organisms in soil or carbon dioxide in compost in just under a month. (Japan Corn Starch Co. Ltd., Nagoya Tokio Kaijo Bldg., 20-19 Marunouchi 2-chome, Naka-ku, Nagoya 460, Japan. Tel.: +81 52-211-2011; Fax: +81 52-231-2024) (Source: *Performance Materials Technology*, October 1993)

Biodegradable resins target packaging

Starch-based resins look set to find their niche in packaging applications in Japan. Nippon Synthetic's

grade of Mater-Bi currently carries a 50 to 80 per cent price premium over expandable polystyrene, although mass production is seen as a way to eliminate that. The material can be blown with water. The shipping arm of the Hitachi group, Hitachi Transport System, Tokyo, is considering switching from PS to Mater-bi for shipments of electrical appliances to Europe starting in November 1993.

Problems with starch-based biodegradables' low water resistance in such a humid country as Japan may preclude their use in more demanding applications. Here, polylactides and aliphatic polyesters are more suited.

Toppan Printing Co., Tokyo, will use Zeneca's Biopol resin in a prepaid card that will go commercial at the end of the year. The paper card is laminated with a 10-micron layer of the biodegradable resin. With such a thin laminate, the card is actually cheaper than its all-PET predecessor, even though Biopol sells for around \$30/kg. Some 424 companies using Biopol in such products as toiletry containers and disposable razors report disappointing sales due to consumer resistance to price and lack of environmental awareness.

Processability is a key concern to moulders and with some biodegradables, extreme care is necessary due to narrow processing windows. At present Shimadzu's polylactide has a high melting point of 170-180° C, while the resin begins to thermally degrade at 200° C. Zeneca got around a similar problem by offering copolymers with lower melting points, but some of its grades nevertheless have narrow processing windows and copolymers generally carry a heavier price tag than homopolymers.

Showa Highpolymer claims a wide processing window of 150-260° C for its Bionolle resin. The resin has the processability of PE and the mechanical properties of PET. Showa Highpolymer is still working on stretch blow moulding grades but once available, the resin would be competitive with PET if prices at \$4.80/kg. Besides the lack of stretch blow grades, another drawback of Bionolle is its low hardness. (Novamont SpA-Materials Division, Via Principe Eugenio 1/5, Milan, Italy. Shimadzu Corp., 1 Nishinokyo Kuwahara-cho, Chukyo-ku, Kyoto-shi 604, Japan. Showa Highpolymer Co., Kanda Chuo Bldg., 20 Kanda Nishikicho 3-Chome, Chiyoda-ku, Tokyo 101, Japan. Warner-Lambert, Novon Products Division, 182 Tabor Road, Morris Plains, NJ 07950, United States of America. Zeneca Specialties, P.O. Box 8, The Heath, Runcorn, Cheshire WA7 4QD, England) (Source: *Modern Plastics International*, 1 October 1993)

5. PUBLICATIONS

Plastics Euroguide 1993

A reference guide for anyone working in the plastics industry as a supplier, converter or end user, this book provides essential information on all major thermoplastics and thermosetting polymers, including prices, plastics recycling and plastics machinery sales. Priced at £150, it is available from IAL Consultants, 314 Harbour Yard, Chelsea Harbour, London SW10 OXD.

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Following five publications can be obtained through:

John Wiley & Sons Ltd., Baffins Lane, Chichester, West Sussex PO19 1UD, UK

The complete 19 volume set...:

Encyclopedia of Polymer Science and Engineering, Second Edition

Editorial Board: H. F. Mark, N. Bikales,
C. G. Overberger and G. Menges
Executive Editor: J. Kroschwitz

The entirely new second edition of the *Encyclopedia of Polymer, Science and Engineering* was completed by Spring 1990, with the publication of the final two volumes - a supplementary volume and the index, in February and April 1990.

This edition is completely rewritten and expanded to reflect the vast changes in polymer and plastics technology since the publication of the classic first edition over 20 years ago.

Coverage includes a 50 per cent increase in engineering and processing topics along with in-depth treatment of natural and synthetic polymers, plastics, fibres, elastomers, robotics, composites, and such computer topics as CAD/CAM (0471865192, 19 volume set, £2,500/\$3,950).

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High Resolution XPS of Organic Polymers The Scienta ESCA300 Database

G. Beamson and D. Briggs, ICI plc,
Wilton Research Centre, UK

This practical hand book contains a unique collection of high resolution XPS spectra of over one hundred organic polymers, recorded with the Scienta ESCA300, the world's best commercially available XPS spectrometer. An introductory section gives background material relevant to the database whilst the

database itself is presented in the form of easy to use double-page spreads of spectral data.

Special features include: a description of the ESCA300 spectrometer; experimental protocols used, including sample mounting methods, data acquisition, curve fitting and binding energy referencing; information on X-ray degradation of polymers; systematic reappraisal of polymer core level binding energies.

Contents: Introduction; description of the spectrometer; performance on conducting samples; performance on insulating samples; performance testing of the spectrometer; experimental protocol; curve fitting; line-shapes; shake-up structure; valence bands; impurities; X-ray degradation; organization of the database; list of polymers and acronyms; the database; appendices (0471935921, 306 pp., September 1992, £65.00, \$125.00).

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Principles of Polymerization Second Edition

G. Odian, College of Staten Island,
The City University, New York, USA

Describes the physical and organic chemistry of the reactions by which polymer molecules are synthesized. The book begins by introducing the characteristics which distinguish polymers from their much smaller sized homologs. It proceeds to a detailed study of three types of polymer structures, and the process conditions which are used to carry them out. Each chapter includes a selection of problems to aid learning and a solutions manual is available on request.

Contents: Step polymerization; radical chain polymerization; emulsion polymerization; chain co-polymerization; ionic chain polymerization; ring-opening polymerization; stereochemistry of polymerization; reactions of polymers (0471610208, 792 pp, 1991, £47.50/\$71.95).

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Introduction to Nonlinear Optical Effects in Molecules and Polymers

P. N. Prasad, State University of
New York, USA and D. J. Williams,
Eastman Kodak Company, New York,
USA

Written to be used as a reference book by researchers of varied backgrounds, this book minimizes detailed mathematical presentation and rather emphasizes concepts. This is the first book to comprehensively

focus on issues associated with development of new organic materials (0471515620, 320 pp., 1991, £49.95/\$75.95).

Introduction to Physical Polymer Science Second Edition

L. H. Sperling, Lehigh University,
Bethlehem, USA

Updated and revised, it focuses on the role of molecular conformation and configuration in determining the physical behaviour of polymers. New features include the macromolecular hypothesis and historical development of photophysics and fluorescences; the thermodynamics of blending polymers and polymer/polymer phase diagrams. Each chapter includes several classroom demonstrations and problem sets.

Contents: Introduction to polymer science; chain structure and configuration; molecular weights and sizes; concentrated solutions and phase separation behaviour; the amorphous state; the crystalline state; polymers in the liquid crystalline state; glass-rubber transition behaviour; cross-linked polymers and rubber elasticity; polymer viscoelasticity and rheology; mechanical behaviour of polymers; modern topics (0471530352, 624 pp., September 1992, £52.00/\$77.95).

Inorganic Polymers

By J. E. Mark, H. R. Allcock and R. West,
Prentice Hall, Englewood Cliffs, NJ.
1992, 272 pp., hardback, \$71.75,
ISBN 0-13-465881-7

This book is a must for scientists and engineers who are interested in knowing more about inorganic and organometallic polymers, an important emerging area of polymer science and technology. However, the title of this book can be misleading in the sense that a significant portion of the text covers mainly semi-inorganic or organometallic polymers.

The book begins with an introductory chapter, followed by a brief and well-written chapter on the characteristics and characterization of inorganic polymers. Topics covered in this discussion are: molecular weights, molecular weight distributions, chain statistics, solubility considerations, crystallinity, thermal transitions, spectroscopy and mechanical properties. These topics should provide the reader with an appreciation of the structure-property relationships of the polymers whose synthesis, reactions, molecular structure and uses are described in the next four chapters.

Three mature areas of inorganic polymers described by the authors include polyphosphazenes,

polysiloxanes (silicones) and polysilanes. The polyphosphazenes are the most versatile of the inorganic polymers and Professor Allcock, who I presume has written this chapter, has not only described the syntheses of these macromolecules, but has also provided insights into the mechanism of the ring opening and substitution of cyclophosphazenes. The structure-property relationships, so essential to the applications of polymers, have been dealt with adequately, and are followed by sections on applications. The chapter is rounded off by references to other newer types of polyphosphazenes, such as polycarbophosphazenes, polythiophosphazenes and liquid crystalline polyphosphazenes. A chapter on polysiloxanes and related polymers covers the chemistry and technology of these well tested and tried materials. An entire chapter is devoted to polysilanes, an important and relatively recent emerging area of inorganic polymers compared to the polysiloxanes. The syntheses, modifications and most important of all the unique and novel electronic and conformational properties of these materials are given. In all these chapters, some aspects of using these polymers as precursors for ceramics/inorganic materials have been included, although the coverage is rather cursory in nature. The final chapter, again rather superficially, examines other inorganic polymer systems containing boron, sulphur, selenium, tin, aluminum and transition metals.

Thermoplastic Aromatic Polymer Composites

By F. N. Cogswell, Butterworth-
Heinemann, Oxford 1992, 277 pp.,
hardcover. £45, ISBN 0-7506-1086-7.

This book is a detailed study of carbon fibre polyether-etherketone (PEEK) composites. Thermoplastic composites have received considerable attention for aerospace applications, primarily for their ease in processing, lower cycle time and damage tolerance characteristics. Carbon/PEEK composites offer excellent potential for aerospace applications in relation to common carbon/epoxy composites intended for service applications to 120° C. The book addresses several important areas such as microstructure of aromatic polymer composites, processing science and manufacturing technology and environmental resistance.

The first chapter provides an introduction to the subject, which is followed by detailed discussions of the constituents of these materials, how they are made into composites and their microstructure. A major chapter addresses how carbon/PEEK materials can be made into structural components. Some limited properties are given, and applications of these composites are also discussed. The final chapter considers the directions of research in this field and attempts to predict their influence. The book has considerable information on carbon fibre composites made from PEEK and can be used as a reference in many cases. Compilations of processing characteristics, material properties and

structural parts made from this class of composite materials are also presented in a fairly coherent manner. The chapter on processing is quite informative and is very well written. The references are extensive, although incomplete.

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Polymer solution thermodynamics

This handbook details up-to-date, easy-to-use methods for obtaining specific volumes of pure polymers, and phase-equilibrium data for design and research engineers working with polymers. It is available, priced at \$120, from the American Institute of Chemical Engineers, 345 East 47th Street, New York 10017, USA.

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Concise Encyclopedia of Polymer Processing and Applications

Edited by Patrick K. Corish, Pergamon, Oxford 1991, 772 pp., hardcover, £140, ISBN 0-08-037064-0.

A reader interested in information on polymers would usually be advised to consult one of the many-volume compendia, such as the *Encyclopedia of Polymer Science and Technology*, edited by H. F. Mark and N. M. Bikales and published by Wiley; or *Comprehensive Polymer Science*, edited by G. Allen and J. C. Bevington. In these, each entry is, in fact, a review article in the given field.

Sometimes a more condensed source of information is necessary, particularly for newcomers. The recently published *Concise Encyclopedia of Polymer Processing and Applications*, a volume of the series *Advances in Materials Science and Engineering*, will serve this purpose. The encyclopedia covers the applied part of polymer science more than the fundamental one. It contains 170 entries on over 700 pages, offering basic information on polymer materials: characterization of their main chemical (stability, ageing) and physical (processing, mechanical, adhesive, electric) properties and applications. Each entry is provided with cross-references and a bibliography.

Among polymer materials, more emphasis is given to, for example, elastomers (rubber processing, vulcanization recipes, radiation processing, liquid and powdered rubber processing, fillers, additives, blends, reclaiming and recycling, health hazards, fibres, coatings various applications) and adhesives (for wood, metals, in building, pressure-sensitive, for textiles, etc.) rather than to thermosets or protective coatings. Among characterization methods, rheology, mechanical properties and testing, and flammability issues are covered. The reader will find very little information on physico-chemical

methods of characterization of polymer materials (molecular masses, solution properties, solid-state structure, etc.). The encyclopedia is relatively strong in information on engineering operations and equipment (mixing, milling, extrusion, reaction injection moulding, melt delivery systems, etc.).

The *Concise Encyclopedia of Polymer Processing and Applications* can be recommended as a useful addition to libraries of institutions and individuals concerned with the processing, properties and applications of polymer materials.

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Polymer Characterization Physical Techniques

By D. Cambell and J. R. White, Chapman and Hall, London, 1989, viii, 362 pp., soft cover, £19.95, ISBN 0-412-27170-2.

This volume has been written for undergraduate majors in polymer and materials science and is a unique contribution in this field. The authors approach the subject from the perspective of materials scientists, rather than polymer or analytical chemists, making this book particularly useful. The focus is mainly on solid-state characterization techniques, rather than on chemical analysis or hydrodynamic properties of polymers. Each chapter deals with theory, instrumentation, and applications. Many of the chapters contain problems with answers.

Chapter 1 is a short introduction, emphasizing the need for, and importance of, polymer characterization in quality control, problem solving, and determining property-structure relationships. Approaches used for determining molecular weights and molecular weight distribution are reviewed in chapter 2. In the section on gel permeation chromatography, mention is made that pore size of packings range from "0.5 to 10^5 nm", it should, however, be closer to 5 to 3×10^2 nm. Also, in discussing universal calibration, the authors state that hydrodynamic volume is the product of intrinsic viscosity and "molar volume", rather than molecular weight.

Chapters 3-7 cover spectroscopic techniques: UV, Raman, IR, NMR and ESR. As compared to analytical chemistry instrumentation texts, treatment of these techniques is rather superficial and spectral interpretation is not stressed. However, specific techniques and applications to polymers are adequately discussed, for example, IR dichroism for studying polymer chain orientation. The NMR and ESR chapters were especially well-written, in particular the sections on the use of NMR for determining polymer microstructure and the application of ESR to follow polymerization reactions involving radical propagation, to study radiation effects in polymers, and polymer mechanical degradation. Chapter 8 on X-ray diffraction presented a good survey of the technique as applied to polymer crystallinity.

Microscopy is treated in chapters 9, 10 and 11 and includes transmission electron microscopy, electron diffraction, scanning electron microscopy, and light microscopy and related techniques (refractive index measurements and birefringence). Again, the application sections are especially informative. Thermal analysis methods are surveyed in chapter 12. In addition to the more common modes of thermal analysis, this chapter also covers thermomechanical analysis, dynamic mechanical analysis, and dielectric thermal analysis. Other techniques, such as density measurements, ESCA and neutron diffraction are briefly reviewed in chapter 13.

The last chapter discusses how these techniques are applied in solving a variety of practical problems. This chapter should prove highly useful to the student in that it demonstrates how results from various methodologies can be used to study and characterize polymers. (Extracted from *Advanced Materials*, March 1991)

Second Industry Workshop on Polymer Composite Processing

Prepared by C. Johnson, S. S. Chang and D. Hunston, is the report of a workshop held in 1990 at the National Institute of Standards and Technology (NIST) to address with industry the scientific and technical barriers to improving polymer processing within the next five to 15 years. Pressure moulding and liquid moulding were identified as the most important processing methods, followed by filament winding, thermoforming and pultrusion. The two technical barriers to the full exploitation of these processing methods singled out by the 24 industrial attendees are understanding and controlling resin flow and fibre orientation. While the majority of the attendees believed thermosets are still the dominant resin, all agreed that thermoplastics had significant potential and should be watched closely for future development. Liquid crystal polymers, molecular composites, smart materials and specialized polymer systems were also identified as having future potential. Seven performance issues selected as critical to the future, in order of priority, are impact, environmental attack, delamination, dimensional changes, thermal stability, fatigue and creep.

To obtain: Send a self-addressed mailing label to Dr. Donald Hunston, A209 Polymer Building, NIST, Gaithersburg, MD 20899, USA.

The Vibrational Spectroscopy of Polymers

D. I. Bower and W. F. Maddams,
Cambridge University Press, 1989,
300 pages, ISBN 0-521-24633-4.

Polymer characterization is an essential part of polymer science and technology, and this latest addition

to the Cambridge Solid State Science series makes an excellent contribution to an increasingly important and fashionable area of chemistry.

The 300-page book deals with the theory and practice of infrared and Raman spectroscopy as applied to the physical and chemical characteristics of synthetic polymers. It is written in a clear and concise style with a good selection of well-produced tables, figures and spectra. Its purpose is to give the new researcher in the field, with either a physics or a chemistry background, a firm foundation for the study of the more advanced literature. The authors assume no knowledge of either polymers or of vibrational spectroscopy, but undergraduate students and readers completely new to both areas will probably need to consult more elementary texts to supplement the present book.

The six chapters divide into two broad themes: the first four chapters, which comprise the first half of the book, provide the underlying theory and practice for polymer chemistry and vibrational spectroscopy, while the last two chapters deal with the spectroscopic analyses of polymer systems, using examples where the interpretation of the spectra is now generally accepted as established. Thus chapter 1 covers basic fundamentals of polymer types, as well as an introduction to vibrational spectroscopy, spectrometers and experimental methods. Chapter 2 comprises 40 pages on symmetry and normal modes of small molecules. Chapter 3 discusses the vibrational modes of polymer chains and crystals and chapter 4 is a semi-classical treatment of the origins of vibrational spectra, polarization effects, vibrational assignments, force fields and vibrational calculations. With the necessary background knowledge in place, the authors begin the detailed interpretation of polymer spectra using factor group analysis and group frequencies (chapter 5, 70 pages). This chapter also covers important aspects of quantitative analysis which is a topic often omitted from research texts.

Finally, chapter 6 (70 pages) is another substantial body of information on the microstructure of polymers, including topics such as the distribution of copolymerized units in the polymer chain, configurational and conformational isomerism, chain branching, hydrogen bonding, chain order and crystallinity.

Alternative books and reviews at the end of each of the first four chapters supplement the ideas covered. Key references given in chapters 5 and 6 to classic papers on the interpretation of polymer spectra are collected together at the end of the book.

Polymers and Complex Materials

Three books in the new series *Polymers and Complex Materials*, published by the American Institute of Physics (now the imprint AIP Press), are scheduled for release in 1994. *Statistical Physics of*

Macromolecules by Alexander Yu. Grosberg, *Design and Processing of Materials* by İlhan A. Aksay, and *Organic Molecular Crystals: Interaction, Localization and Transport Phenomena*, by Edgar A. Silinsh will commence the series. The aim of *Polymers and Complex Materials* is to offer volumes describing the molecular and supermolecular structure of materials such as polymeric liquids, solids, microemulsions and liquid crystals, as well as their macroscopic and processing characteristics.

For more information contact: American Institute of Physics, c/o AIDC, 64 Depot Road, Colchester, USA. Fax: +1-802-878-1102.

Polymers, Composites, Fatigue

The publishers of *Polymer*, Butterworth-Heinemann Ltd., are launching a new title, *Supramolecular Science*, in mid-1994. The new journal will contain original, refereed papers and has Dr. Wolfgang Knoll of the Max-Planck-Institut für Polymerforschung, Mainz, as its Editor-in-Chief. *Polymer* itself will expand again in size in 1994, with two extra issues per volume, taking its frequency up to 26 issues a year. *Composites* has continued to receive increased submissions and will increase in frequency for the second year in succession, giving ten issues a year in 1994.

For further details on any of these journals, please contact: Catriona Burns, Product Manager, Butterworth-Heinemann Ltd., Linacre House, Jordan Hill, Oxford OX2 8DP, UK. Tel.: +44 (0)865 310366. Fax: +44 (0)865 310898.

Materials Science and Technology

Publication of the VCH series *Materials Science and Technology - A Comprehensive Treatment*, edited by R. W. Cahn, P. Haasen and E. J. Kramer, has progressed further: *Volume 12, Structure and Properties of Polymers*, edited by E. L. Thomas, MIT, Cambridge, USA, and *Volume 13, Structure and Properties of Composites*, edited by T. W. Chou, University of Delaware, USA, appeared in 1993, as well as *Volume 11, Structure and Properties of Ceramics*, edited by M. Swain, University of Sydney, Australia; *Volume 2B, Characterization of Materials*, edited by E. Lifshin, General Electric Company, Schenectady, USA; and *Volume 3B, Electronic and Magnetic Properties of Metals and Ceramics*, edited by K. H. J. Buschow, Philips Research Laboratories, Eindhoven, the Netherlands. *Volume 10, Nuclear Materials*, edited by B. R. T. Frost is scheduled to appear early in 1994.

Also due to appear towards the end of 1993, is *Sensors 7: Mechanical sensors*.

For further information and sample chapters write to: VCH, P.O. Box 101161, D-69451 Weinheim, FRG. Fax: +49 (0)6201 606328.

Polymer Reaction Engineering is the first journal to combine the chemistry of polymerization and polymer reactions with the physical interactions of polymers, solvents and reaction equipment. The journal offers original basic and applied research articles that are mathematical in character and integrate theoretical treatments with experimental results, as well as short reports and letters to the editors. The subscription rate is \$97.50 for Volume 1 (4 issues).

For further details contact: Marcel Dekker, Inc., 270 Madison Avenue, New York, NY 10016, USA.

A new publication, *Chambers Materials Science and Technology Dictionary* aims to be the first affordable (priced at £9.99) comprehensive dictionary in this field for professionals, undergraduates and engineers. With accurate, up-to-date and clear definitions, it covers all areas of materials science, including metals and alloys, ceramics and glasses, natural materials, polymers, fibres, rubbers, advanced composites and electronic materials.

For further information please contact: Angela Robertson or Linda Orton, Chambers Harrap Publishers Ltd., 43-45 Annandale Street, Edinburgh EH7 4AZ, UK. Tel.: +44 (0)31-557 4571.

Photochemistry and Polymeric Systems, edited by J. M. Kelly *et al.*, from the Royal Society of Chemistry has brought together leading international researchers, from industry and academia, to consider the fundamental scientific principles and technological applications of the effects of light on polymers and polymer-based composites.

Also just published are *High Value Polymers*, edited by A. H. Fawcett, and *Essentials of Carbon-Carbon Composites*, edited by C. R. Thomas.

To obtain more information contact: The Royal Society of Chemistry, Sales & Promotion Department, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 4WF, UK. Fax: +44 (0)223 423623.

6. PAST EVENTS AND FUTURE MEETINGS

1993

- 8 July**
*ICI Runcorn Heath
Cheshire, UK* **Recent Developments in Polymer Characterization**
(The Polymer Centre, School of Physics and Materials, Lancaster University
Lancaster LA1 4YA, UK)
- 12-16 July**
Athens, Greece **19th International Conference in Organic Coatings Science and Technology**
(Institute in Materials Science, State University of New York at New Paltz, New Paltz,
NY 12561, USA. Fax: 914/255 0978)
- 15-20 August**
Beijing, China **34th IUPAC Congress**
(Professor Xingi Song, P.O. Box 2709, Beijing 100080, China, Fax: +86 1 256 8157)
- 22-27 August**
*Chicago,
Illinois, USA* **1993 Fall National ACS Meeting**
Subjects: advances in polarized polymers, rigid rod and oriented networks, macromolecular
metal complexes, advances in polyethers, characterization of polymer biomaterials surfaces,
polymer blends and alloys and fundamentals of adhesion and interfaces. (Eastman Kodak Co.,
Building 35, Kodak Park, Rochester, NY 14652-3701, USA. Fax: 716/722 7570)
- 7-11 September**
Oxford, UK **Second International Conference on Polymers for Advanced Technologies**
(PAT '93, Conf. Serv., P.O. Box 13, Kingswinford, West Midlands DY6 OHQ, UK.
Fax: (+44) 384 294 463)
- 8-10 September**
Bristol, UK **Polymers at Interfaces**
(School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK)
- 18-22 November**
*Cancun, Q.Roo,
Mexico* **International Symposium on Polymers**
(POLYMEX-93, Apartado Postal 86-144, Villa Coapa, Mexico, DF 14390. Fax: (5) 548 2703)
- 13-17 December**
*Queensland,
Australia* **Polymers - 3rd Pacific Conference**
(University of Queensland, Chemistry Department, Queensland, Brisbane, QLD 4072,
Australia. Fax: (+61) 7 365 3628)
- 20-22 December**
Leeds, UK **Condensed Matter and Materials Physics**
(Institute of Physics, 47 Belgrave Square, London SW1X 8QX. Fax: (+44) 71 259 6002)

1994

- 9 January**
*Cocoa Beach, FL,
USA* **Introduction to Bioceramics**
(Society for Biomaterials, 6518 Walker St., Suite 215, Minneapolis, MN 55426-4215.
Fax: (612) 927 8127)
- 12-19 February**
*Adelaide,
Australia* **8th International IACIS Conference on Colloid and Interface Science**
(School of Chemical Technology, S.A. Institute of Technology, P.O. Box 1, Ingle Farm,
S.A. 5098, Australia)
- 13-18 February**
Orlando, FL, USA **Smart Structures and Materials Conference**
(SPIE, European Office, Xantener Strasse 22, D-10707 Berlin, Germany or: SPIE,
P.O. Box 10, Bellingham, WA 98227, USA)
- 27 February -
3 March**
*San Francisco, CA,
USA* **Minerals, Metals and Materials Society, 94th Annual Meeting**
(Min., Met. and Mat. Society, Technical Programming Department, 420 Commonwealth Drive,
Warrendale, PA 15086, USA)

- 6-10 March**
Ventura, CA, USA **Chemistry of Electronic Materials Conference**
(Almaden Res. Center, IBM Res. Div., 650 Harry Road, San José, California 95120, USA)
- 13-18 March**
San Diego, CA, USA **1994 Spring National ACS Meeting**
Subjects: Polymer dynamics and thermodynamics in solution, dielectric properties of polymers, electronically conducting polymers, NMR spectroscopic characterization of polymers, polymers for the oil industry, transition-metal chemistry and polymerization, thermally stable polymers and industrial applications of biotechnology. (Chemistry Dept., Virginia Polytechnic Institute, Blacksburg, VA. 24061-0212, USA. Fax: (703)231 8517)
- 21-23 March**
Maastricht, The Netherlands **European Conference on Environment and Energy for the Ceramic Industry**
(Congrex Holland, Keizersgracht 782, 1017 EC Amsterdam, The Netherlands. Fax: 31/206 259 574)
- 21-16 March**
Utrecht, The Netherlands **Techni-Show 1994**
Biennial trade fair for industrial production techniques, processing and machining of metals and synthetics, accessories and fittings. (Techni-Show 94, Jaarbeursplein 6 3521 A1 Utrecht, P.O. Box 8500, 3503 RM Utrecht, The Netherlands. Fax: (31)30 961 660)
- 27-31 March**
Santa Barbara, CA, USA **Indium Phosphide and Related Materials, 6th International Conference**
(Institute of Electrical and Electronic Engineers, Inc. 345 E 47th Street, New York, NY 10017, USA)
- 4-9 April**
Vienna, Austria **High Temperature Materials Chemistry**
(Inst. f. Anorganische Chemie, Währinger Strasse 42, A-1090 Vienna, Austria. Fax: (+43)1 310 45 97)
- 5-7 April**
Nagoya, Japan **Ceramic Society of Japan - Annual Meeting**
(Ceramic Society of Japan, 22-17, Hyakunin-Cho, 2-Chome, Shinjuku-ku, Tokyo 169, Japan)
- 11-13 April**
Oxford, UK **Microscopy of Composite Materials II**
(Royal Microscopical Society, 37/38 St. Clements, Oxford OX4 1AJ, UK. Fax: (+44) 865 791237)
- 11-15 April**
Amsterdam The Netherlands **12th European Photovoltaic Solar Energy Conference and Exhibition.** (Fax: +49/89-720-1291)
- 11-15 April**
Birmingham, UK **Metalworking 94 International**
(FMJ Int. Publications Ltd., Queensway, Redhill, Surrey RH1 1QS, UK. Fax: (737)761 685)
- 12-14 April**
Loughborough, UK **Adhesion and Surface Analysis - 3rd International Conference**
(Inst. of Surface Science and Technology, University of Technology, Loughborough, Leics. LE11 3TU, UK. Fax: (+44)509 219702)
- 18-20 April**
Stuttgart, Germany **Semiconductor Processing and Characterization with Lasers - Applications in Photovoltaics**
(Inst. f. Technische Physik, DLR, Pfaffenwaldring 38-40, D-70569 Stuttgart, Germany)
- 16-19 May**
San Diego, CA, USA **High-Temperature Intermetallics - Int. Conf.**
(ASM International, Materials Park, OHIO 44073, USA, Fax: (+1)216 338 4634)
- 24-26 May**
? venue **International Conference on Superplasticity in Advanced Materials**
(The Management Academy, Moscow, Russia. For more information: University of Southern California, Materials Science & Engineering Dept., Los Angeles, CA 90080-0241. Fax: 213/740-7797)

- 24-27 May
Stuttgart,
Germany
German Materials Society (DGM) Annual General Meeting
(Deutsche Gesellschaft für Materialkunde e.V., Adenauerallee 21, D-61440 Oberursel, Germany)
- 26-28 May
Whistler, Canada
High-Tc Superconducting Electron Devices Conference
(Wksp Secr. FED, Fukide Bldg., No. 2, 4-1-21 Toranomom, Minato-ku, Tokyo 105, Japan)
- 30 May - 1 June
Balatonszeplak,
Hungary
Euromat 94
Combining the 15th Conference on Materials Testing in Metallurgy and the 11th Conference on Materials Testing. (Hungarian Mining and Metallurgical Society, H-1027 Budapest Fo u 68, Hungary. Fax: (36 1) 156 1215)
- 31 May - 3 June
Yokohama, Japan
Metal-Organic Vapor Phase Epitaxy (ICMOVPE), International Conference
(Business Centre for Academic Studies, 5-16-9 Honkomagome, Bunkyo-ku, Tokyo 113, Japan)
- 6-11 June
Varna, Bulgaria
Electron Beam Technologies Conference
(Bulgarian Academy of Sciences, Institute of Electronics, 72 Tzarigradsko Shose Blvde. 1784 Sofia, Bulgaria)
- 16-17 June
York, UK
Performance of Bolting Materials in High Temp. Plant Applications.
(The Institute of Materials, 1 Carlton House Terrace, London SW1Y 5DB, UK. Fax: 071-823 1638)
- 20-23 June
Albuquerque, NM,
USA
Magnetism and Magnetic Materials, 6th International Conference
(Courtesy Associates Inc., 655 15th St., NW, Suite 300, Washington D.C. 20005, USA)
- 22-23 June
Stratford-upon-
Avon, UK
Antiwear 2000
The Conference will be of practical value to those involved with: power generation and allied plant; prime movers, including engines, gas, and steam turbines; materials handling and transfer mechanisms, lubrication and condition monitoring; gear boxes, valves and control equipment; thermospraying, etc. (The Institute of Materials, 1 Carlton House Terrace, London SW1Y 5DB. Fax: 071-823 1636)
- 27 June - 1 July
Orlando, FL, USA
World Congress on Superconductivity, 4th International Conference
(World Congress on Superconductivity, P.O. Box 27805, Houston, TX 17227-7805, USA. Fax: (+1)713 469 5788)
- 27 June - 2 July
Tihany, Hungary
Olefin Metathesis and Polymerization, 10th International Symposium
(ISOM-10 Org. Committee, University of Veszprem, H-8201 Veszprem, P.O. Box 158, Hungary. Fax: (+36)802 6016)
- 29 June - 1 July
Southampton, UK
Computer Aided Design in Composite Material Technology
(Wessex Institute of Technology, Ashurst Lodge, Ashurst, Southampton SO4 2AA, UK. Fax: (+44)703 293 223)
- 29 June - 4 July
Florence, Italy
Ceramics (CIMTEC-8) - 8th World Congress
(8th CIMTEC Secretariat, P.O. Box 174, I-48018 Faenza, Italy. Fax: (+39)546 664 138)
- 1-4 July
Florence, Italy
Superconducting Materials Technology Conference
(World Ceramics Congress Secretariat, P.O. Box 174, I-48018 Faenza, Italy. Fax: (+39)546 664 138)
- 4-9 July
Grenoble, France
Materials and Mechanisms of Superconductivity/High-Tc Superconductors Conference
(CNRS, 25 ave. des Martyrs, F-38042 Grenoble Cedex, France)
- 5-8 July
Lyon, France
Defects in Insulating Materials, 7th European Conference
(LPCML, Bat. 205, 43 Blvd. du 11 Novembre 1918, F-69622 Villeurbanne, France)

- 10-14 July*
Worcester, MA,
USA **Inorganic Membranes, 3rd International Conference**
(Worcester Polytechnic Institute, Chemical Engineering Department, 100 Institute Road,
Worcester, MA 01609, USA)
- 17-22 July*
Kobe, Japan **Diamond Science and Technology, International Conference**
(ICNDST-4 Secr., c/o Japar Convention Serv., Inc., Osaka Branch, Sumitomo Seimei
Midousuji Bldg. 13F, 14-3, Nishitenma 4-chome, Kita-ku, Osaka 530, Japan. Fax:
(+81)6 311 2130)
- 17-22 July*
Pittsburg, PA, USA **Solid-to-Solid Phase Transformation in Inorganic Materials**
(The Minerals, Metals and Materials Society, 420 Commonwealth Drive, Warrendale,
PA 15086, USA)
- 24-29 July*
Seoul, Korea **Synthetic Metals (ICSM '94), International Conference**
(Department of Physics, Seoul National University, Secretary General of ICSM '94,
Seoul 151-742, Korea. Fax: (+82)(2)873-7037)
- 22-26 August*
Warsaw, Poland **Magnetism (ICM) - International Conference**
Polish Academy of Science, Institute of Molecular Physics, Smoluchowskieg 17/19,
PL-60 179 Poznan, Poland)
- 11-14 September*
Friedrichshafen,
Germany **Ceramic Processing Science and Technology, International Conference**
(Co-sponsored by the American Ceramic Society, European Ceramic Society and the Ceramic
Society of Japan. Deutsche Keramische Gesellschaft, Frankfurter Strasse 196,
D-5000 Köln 90, Germany. Fax: 02203/69301)
- 11-16 September*
Reading, UK **World Renewable Energy Congress II**
(Department of Engineering, University of Reading, Whiteknights, P.O. Box 225,
Reading RG6 2AY, UK. Fax: (734)313 835)
- 19-21 October*
Amsterdam,
The Netherlands **The Recycling of Metals**
(ASM European Office, rue de l'Orme, 75 Olmstraat, B-1040 Brussels, Belgium)

Advances in Materials Technology: Monitor

Reader Survey

The *Advances in Materials Technology: Monitor* has now been published since 1983. Although its mailing list is continuously updated as new requests for inclusion are received and changes of address are made as soon as notifications of such changes are received, I would be grateful if readers could reconfirm their interest in receiving this *Monitor*. Kindly, therefore, answer the questions below and mail this form to: Ms. A. Mannoia, Technology Development and Promotion Division, UNIDO, P.O. Box 300, A-1400 Vienna, Austria.

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