Biodegradable Materials – Present Situation and Future Perspectives

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Abstract: Biodegradable polymers constitute a loosely defined family of polymers that are designed to degrade through the action of living organisms. They offer a possible alternative to traditional non-biodegradable polymers if recycling is impractical or not economical. The main driving force behind this technology is the solid waste problem, particularly with regard to the decreasing availability of landfills, the litter problem and the pollution of marine environment by non-biodegradable plastics. Technologies like composting used for the disposal of food and yard waste are the most suitable for the disposal of biodegradable materials.

European Standardisation Committee (CEN), Organic Reclamation and Composting Association (ORCA) and German Institute for Standardisation (DIN) have already defined, at a draft level, the basic requirements for a product to be declared compostable. They are based on: complete biodegradability of the product in a time period compatible with composting, measured through respirometric tests (ASTM D5338-9, ISO/CD14855, etc); disintegration of the material during the fermentation phase; no negative effects on compost quality; checking of laboratory-scale results on pilot/full-scale composting plants. These requirements set forth a common base for a universal marking system to readily identify products to be composted.

Thermoplastic starch-based polymers and aliphatic polyesters are the two classes of biodegradable materials with the greatest near-term potential. This paper reviews a great variety of properties, structures and biodegradation behaviour of thermoplastic starch in combination with poly(vinyl alcohol) or some aliphatic polyesters like poly(hydroxybutyrate-*co*-hydroxyvalerate), poly(lactic acid), poly(ε-caprolactone) and poly(butanediyl succinate).

INTRODUCTION

The management of solid waste disposal with regard to the decreasing availability of landfills, the litter problem and the pollution of marine environment are becoming very urgent in the industrialized countries and the need for solution extends very quickly to the developing countries.

Common approach is the upvalueing of waste as a resource through its separation into specific fractions to be transformed in new products with a certain market value.

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

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Biodegradable polymers constitute a loosely defined family of polymers that are designed to degrade through the action of living organisms. They offer a possible alternative to traditional non-biodegradable polymers if recycling is impractical or not economical. Technologies like composting, used for the disposal of food and yard waste, accounting for 25-30 % of total municipal solid waste, are the most suitable for the disposal of biodegradable materials together with soiled or food-contaminated paper. International organizations such as the American Society for Testing and Materials (ASTM) in connection with the Institute for Standards Research (ISR), the European Standardisation Committee (CEN), the International Standardisation Organisation (ISO), the German Institute for Standardisation (DIN), the Italian Standardisation Agency (UNI), and the Organic Reclamation and Composting Association (ORCA), are all actively involved in developing definitions and tests for biodegradability in different environments and compostability [1,2].

Although a standard world-wide definition for biodegradable plastics has not been established, all the definitions already in place (ASTM, CEN, ISO) correlate the degradability of a material with a specific disposal environment and to a specific standard test method which simulates this environment in a time period which determines its classification.

According to this approach, CEN, ORCA, UNI and DIN have defined, at a draft level, the basic requirements for a product to be declared compostable, based on:

- Complete biodegradability of the product, measured through respirometric tests like ASTM D5338-92, ISO/CD14855 and CEN proposal xx1 or the modified Sturm test ASTM 5209, in a time period compatible with the composting technology (several months);
- Disintegration of the material during the fermentation phase;
- No negative effects on compost quality and, in particular, no toxic effects of the compost and leaches on the terrestrial and aquatic organisms;
- Testing of laboratory-scale results on pilot/full-scale composting plants.
- These requirements set forth a common base for a universal marking system to readily identify products to be composted.

An important driving force for the development of biodegradable materials and the related compostability label is the recently adopted European Directive 94/62/EC on packaging waste where composting of packaging waste is considered as a form of material recycling.

Cost is a major obstacle to the wide-scale use of biodegradable polymers.

Main classes of biodegradable materials under development are starch-based materials, polyesters, and natural products like proteins, chitin, and chitosan. The group of natural products other than starch is at a very early stage of development.

A short description of starch-based materials (Table 1) follows, which are either already on the market or at an advanced development stage.

STARCH-BASED MATERIALS

Starch is an inexpensive product available every year from corn and other crops, produced in excess of current market needs in the United States and Europe. It is totally biodegradable in a wide variety of environments and permits the development of totally degradable products for specific market demands.

Degradation or incineration of starch products recycles atmospheric CO_2 trapped by starch-producing plants and does not contribute to potential global warming.

All these reasons have aroused a renewed interest in starch-based plastics in the last years.

Table 1. STARCH-BASED MATERIALS ON THE MARKET

Material	Technology description	Patent situation	Company	Installed capacity ton/y	Market application
Mater-Bi	thermoplastic, blended, compatibilized, complexed starch with polyesters, vinyl alcohol copolymers, cellulose acetate and other thermoplastic polymers	dominating technology	Novamont	4000	composting bags, paper lamination, paper wrapping, cutlery, foams, cotton swabs, dog bones
Novon	thermoplastic, blended starch	technology acquired from W-L in 1995	Novon Int. (Ecostar) (before Warner-Lamber)	about 3000	?
Envirofil	thermoplastic starch	licence from W-L limited to loose fillers	Enpac (DuPont-Conagra joint venture)	5000 (through customers and sub-licensers)	loose fillers only
Ecofoam	thermoplastic high-amylose starch	niche technology with W-L licence	National Starch	5000 ?	loose fillers and other expanded materials
Chisso	as for Novon (limited to Japan)	W-L licence	Chisso	?	composting bags of old technology
Biopac	wafer technology	dominating niche technology	Haas	500 ?	food trays
Biotec	thermoplastic starch	acquisition of Fluntera patents	Melitta	pilot plant (1000?)	composting bags since 1995

Starch is constituted by two major components: amylose, a mostly linear $(1\rightarrow4)$-α-D-glucan and amylopectin, a $(1\rightarrow4)$-α-D-glucan which has $(1\rightarrow6)$ branches at the branch point. The linear amylose molecules has a molecular weight of 0.2-2 million, while the branched amylopectin has molecular weights as high as 100-400 million.

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

Crystalline starch

Crystalline starch beads can be used as a natural filler in traditional plastics [3]; they have been used particularly in polyolefins. When blended with starch beads, polyethylene films biodeteriorate on exposure to a soil environment. The microbial consumption of the starch component, in fact, leads to an increased porosity, void formation, and loss of integrity of the plastic matrix. Generally, starch is added at fairly low concentrations (6-15 %). However, the overall disintegration of these materials is achieved by transition metal compounds, soluble in the thermoplastic matrix, used as pro-oxidant additives to catalyze the photo- and thermo-oxidative processes [4]. These products rank among the first-generation degradable polymers which biodeteriorate more than mineralize to CO_2 and H_2O in a time period of some months.

Starch-filled polyethylenes containing pro-oxidants are commonly used in agricultural mulch films, bags, and egg packages.

Thermoplastic starch

Starch can be made thermoplastic using the extrusion cooking technology. Extrusion cooking and forming is characterized by sufficient work and heat being applied to a cereal-based product to cook or gelatinize completely all the ingredients. The equipment used for high-pressure extrusion heats materials during processing, and continually compresses them.

Gelatinized materials with different starch viscosity, water solubility and water absorption have been prepared by altering the moisture content of the raw material and the temperature or pressure in the extruder. An extrusion-cooked starch can be solubilized without any formation of maltodextrins, and the extent of solubilization depends on extrusion temperature, the moisture content of starch before extrusion and the amylose/amylopectin ratio [5-9] (Fig. 1).

Neat thermoplastic starch can be processed as a traditional plastic; its sensitivity to humidity, however, makes it unsuitable for most applications (Fig. 2).

Main use of neat thermoplastic starch is in soluble compostable foams (loose filler, etc.) as a replacement for polystyrene.

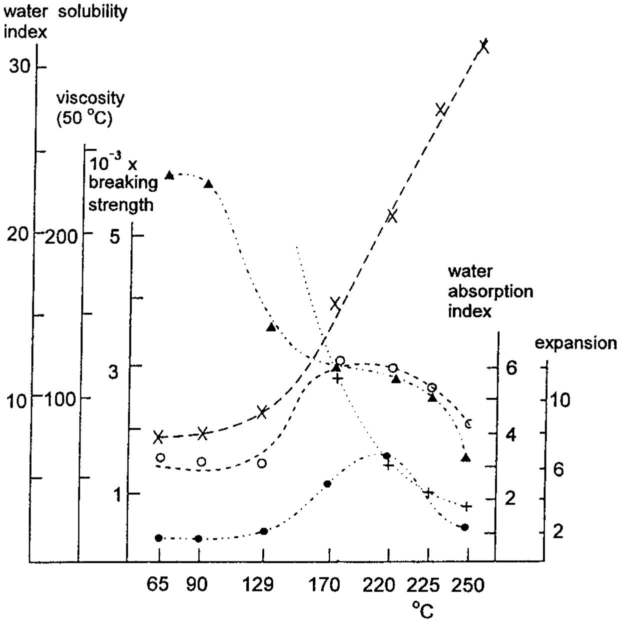


Fig. 1. Effect of extrusion temperature on expansion (●), breaking strength (+), viscosity at 50 °C (▲), water-absorption index (O), and water-solubility index (x) of extruded products from corn grits. Initial moisture content (before extrusion) was 18.2 wt.-%. (From [5].)

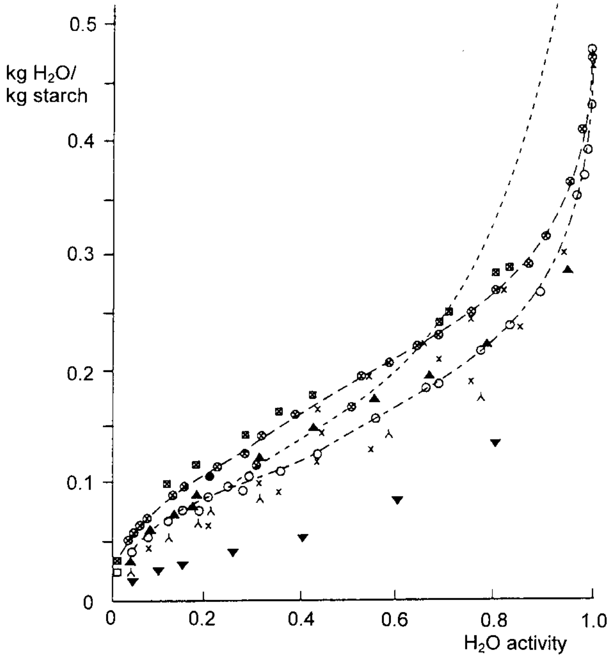


Fig. 2. Resorption-desorption isotherms of water vapour at 291-298 K on native potato starch as reported in the literature

Thermoplastic starch composites

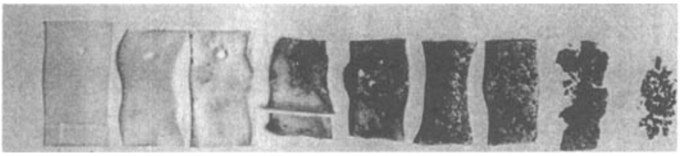
Starch can be destructurized in combination with various synthetic polymers to satisfy a broad spectrum of market needs. Thermoplastic starch composites can reach starch contents higher than 50 %.

As an example, starch/vinyl alcohol copolymer systems [10], depending on the processing conditions, on starch type and on copolymer composition, can generate a wide variety of morphologies and properties as a result of the extent of formation of a complex between amylose and the synthetic molecules.

A model has been proposed considering amylopectin macromolecules crosslinked at several points by hydrogen bonds and entanglements with amylose/vinyl alcohol copolymer complexes. This structure has been defined in the literature as "interpenetrated". The biodegradation rate of starch in these materials is inversely proportional to the content of amylose/vinyl alcohol copolymer complex.

As an example, the products based on starch/poly(ethylene-*co*-vinyl alcohol (EVOH) show mechanical properties good enough to meet the needs of specific industrial applications. Their moldability in film blowing, injection molding, blow molding, thermoforming, foaming, etc., is comparable with that of traditional plastics such as PS, ABS, LDPE [11]. Main limitations of these materials consist in the high sensitivity to low humidities, with consequent embrittlement.

The biodegradation of these composites has been demonstrated in different environments [12]. The degradation rate of 2-3 years in water environment is too slow for considering these materials compostable (Fig. 3).



Days	0	10	46	86	140	252	340	512	765
Weight loss (%)	0	16	23	36	47	48	50	65	92

Fig. 3. Weight loss of a molded part (thickness 0.5 mm) made of Mater-Bi AI05H (class) under semicontinuous activated sludge (SCAS) test conditions at 25 °C as a function of time

Starch can also be destructurized in presence of more hydrophobic polymers such as aliphatic polyesters [13].

It is known that aliphatic polyesters having low melting points are difficult to process by conventional techniques for thermoplastic materials, such as film blowing and blow molding. It has been found that their blending with starch allows to improve their processability and biodegradability. Especially suitable polyesters are poly(ε-caprolactone) and its higher-melting copolymers formed by the reaction of glycols such as butane-1,4-diol with succinic, sebacic, adipic, azelaic or brassylic acid. The presence of compatibilizers of starch and aliphatic polyesters, such as amylose complexed with EVOH [10], starch-grafted polyesters, chain extenders like diisocyanates, epoxides, etc., can improve properties of starch composites [13]. These types of materials are characterized by excellent compostability, excellent mechanical properties and reduced sensitivity to water.

Thermoplastic starch can also be blended with polyolefins, possibly in presence of a compatibilizer. Starch/cellulose derivative systems are also reported in the literature [12].

Combinations of starch with a soluble polymer such as poly(vinyl alcohol) (PVOH) and/or poly(alkylene glycol)s have been widely considered since 1970. In the last years, the system thermoplastic starch/PVOH has been mainly studied for producing starch-based loose fillers as a replacement for expanded polystyrene (Fig. 4).

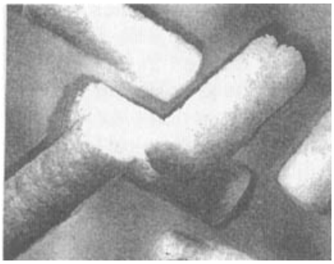


Fig. 4. Loose fillers made of Mater-Bi of class V (starch content higher than 85 %)

The results obtained using thermoplastic starch in combination with vinyl alcohol homo- or copolymers and with aliphatic polyesters and copolyesters in terms of biodegradation kinetics, mechanical properties and reduced sensitivity to humidity make these materials ready for a real industrial development starting from the film and foam applications. The present global market is around 12 000 ton/year. Main producers are Novamont with Mater-Bi trade-mark, ENPAC and National Starch.

The tensile properties of films made of two Novamont's Mater-Bi grades are reported in Table 2 in comparison with those of low-density polyethylene (LDPE).

Table 2. PROPERTIES OF STARCH / POLY(ε-CAPROLACTONE) COMPOSITES[a]

Property	Method	Mater-Bi ZF03U/A	Mater-Bi ZI01U	LDPE
Tensile breaking strength (MPa)	ASTM D682 (+)	30 (24)	15	16
Tensile elongation at break (%)	ASTM D (+)	800 (720)	850	873
Tensile modulus (MPa)	ASTM D852 (+)	296 (251)	150	191
Tear resistance (N/mm)	ASTM D1938 (+)	68 (84)	58 (65)	63
Elmendorf tear strength (N/mm)	TAPPI T414	20 (37)	18	22 (30)
Biodegradation in 60-day controlled composting (%)	ASTM D5338	100	100	0

[a] in longitudinal direction (the values for cross direction are in parentheses)

Figures 5 and 6 show applications of Mater-Bi starch-based materials currently on the market.

Fig. 5. Composting bag made of Mater-Bi of class Z (main components: thermoplastic starch and poly(ε-caprolactone))

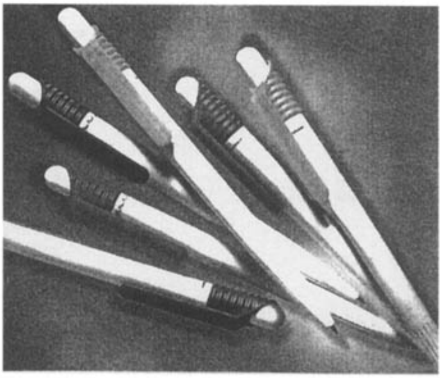


Fig. 6. Pens made of Mater-Bi of class Y (main components: thermoplastic starch and cellulose derivatives)

Figure 7 shows the biodegradability in composting environment of two Mater-Bi grades for bags containing thermoplastic starch and poly(ε-caprolactone).

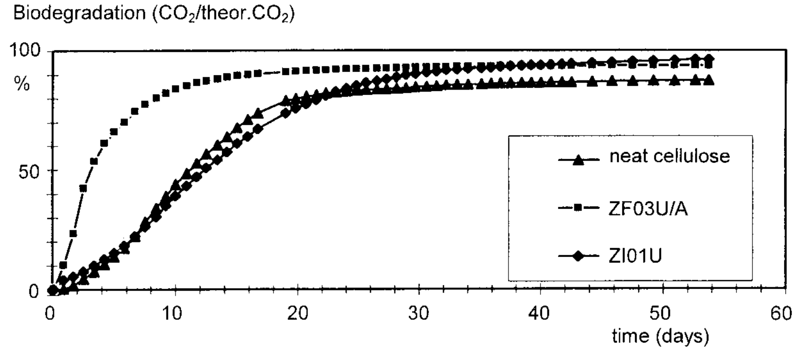


Fig. 7. Aerobic biodegradation under controlled composting conditions (ASTM D 5338-92)

POLYESTERS

A short description of polyesters (Table 3) follows, which are either already on the market or at an advanced development stage.

Table 3. BIODEGRADABLE POLYESTERS UNDER DEVELOPMENT

Material	Trademark	Company	Installed capacity ton/y	Market applications	Development stage
Poly(hydroxybutyrate-*co*-hydroxyvalerate)	Biopol	Monsanto	600	outdoor coatings, bottles, cutlery	development
Poly(ε-caprolactone)	Tone Placel Capa	Union Carbide Daicel Interox	> 5000	blends with starch	industrial
Poly(lactic acid)	Eco-Pla	Cargill Neste Chronopol Mitsui Toatsu	2000 - - -	thermoformed items, bottles, fibers, film	development
Poly(butanediyl succinate)	Bionolle Skygreen	Showa Denko Sunkyong	3000	fibers, film, bottles, cutlery	development
Poly(ester-amide)	Bak	Bayer	?	film, fibers	development
Poly(ethylene terephthalate; adipate)	-	Eastman BASF	-	film	research

Poly(hydroxyalkanoate)s

The bacterial poly(hydroxyalkanoate)s are aliphatic polyesters, homo- or copolymers of (*R*)-3-hydroxyalkanoic acids produced by microorganisms [14].

Prokaryotic organisms such as bacteria and cyanobacteria accumulate poly(3-hydroxybutyrate), as inclusion in the cytoplasmic fluid, amounting to 30-80 % of the cellular dry weight if their growth is limited by depletion of an essential nutrient such as nitrogen, oxygen, phosphorus, sulfur or magnesium. These microbial polyesters can be defined as intracellular storage products; their yield, composition, and molecular weight are influenced by the carbon source and nutrients.

Novel polymers have also been produced by the addition of appropriate substrates to the culture medium [15]. The polyesters obtained using this technology can be thermoplastic or elastomeric and those derived from valeric and butyric acids are mineralized.

Physical properties (Table 4) and biodegradability of microbial polyesters may be regulated by blending with synthetic or natural polymers. Their rate of hydrolytic degradation is dramatically affected by the presence of polysaccharides.

The mechanism of biodegradation of poly(3-hydroxybutyrate) involves the enzyme poly(3-hydroxybutyrate) depolymerase, which depolymerizes the polymer to the corresponding acid [16]. Recent efforts to express the copolymer in Escherichia coli and in plants [17] is drawing interest due to the possibility of reducing production costs and simplifying purification procedures.

High-molecular-weight poly(3-hydroxybutyrate) and its copolymers with 3-hydroxyvalerate can also be produced synthetically from racemic β-butyrolactone and β-valerolactone with an oligomeric aluminoxane catalyst.

The synthetic polyesters are less susceptible to enzymatic degradation than the bacterial polyesters due to the difference in structure: isotactic with random stereosequences for the bacterial copolyesters and with partially stereoregular blocks for the synthetic polyesters.

In this last case, the (*S*) units hinder the enzymatic degradation, making difficult for the depolymerase to penetrate into the surface and access the available (*R*) units.

Poly(hydroxybutyrate-*co*-valerate) is produced under the BIOPOL trade mark by Monsanto, with a production capacity of about 500 ton/year.

Poly(lactic acid), poly(glycolic acid)

Poly(lactic acid), a linear aliphatic polyester, is a thermoplastic polymer synthesized by polycondensation of the free acid or by catalytic ring-opening polymerization of lactide (cyclic dilactone of lactic acid) [18]. The enantiomeric monomers for the synthesis, L-lactic acid (naturally occurring) and D-lactic acid, can be produced by biological or chemical methods. The ester linkages in the polymer are sensitive to both enzymatic and chemical hydrolysis. Poly(lactic acid) is hydrolyzed by many enzymes including pronase, proteinase K, bromelain, ficin, esterase, and trypsin [19]. Biodegradable copolymers of glycine and DL-lactic acid have been synthesized.

In the past, poly(lactic acid) was primarily considered for medical implants and drug delivery, but wider applications in packaging and consumer goods are also targeted [18]. An attractive feature of this material is the potential relatively low cost of lactic acid, which can be derived from biomass (fermentation), coal, petroleum or natural gas.

Highly hydrophilic poly(ether-ester) block copolymers of ethylene oxide (molecular weight of blocks 600-6000) and poly(lactic acid) have also been synthesized. Copolymers of glycolide and L(-)-lactide, high-strength biodegradable thermoplastic materials, have been commercialized for biomedical applications. Homopolymers of glycolic acid and its copolymers with DL-lactides are presumed to be biodegradable, although the role of chemical hydrolysis vs. enzymatic depolymerization in this process remains open to debate.

Other materials with a possible future commercial interest are copolymers of lactic acid and ε-caprolactone.

The market for high polymers of lactic acid is still in its early stages. A large market growth for the polymer requires additional sources of lactic acid as a raw material. Cargill started a 10-million-lb/yr lactic acid/polylactide plant in 1994 and announced a large plant with a capacity as high as 250 million lb/year in the next years. Other producers of poly(lactic acid) are Mitsui Toatsu Chemical (which has developed a polycondensation process for lactic acid), Shimatzu, Dainipon Ink and Neste.
Mechanical properties of poly(lactic acid) are similar to those of polystyrene (Table 4). Problems still unsolved are the too low glass transition temperature, limited stability to hydrolysis and slow crystallization rate. Main applications at the development stage are in bottles, thermoformed containers for food, films and fibers.

Poly(ε-caprolactone)

Poly(ε-caprolactone) is a biodegradable aliphatic polyester made by ring-opening polymerization of ε-caprolactone. This polymer with molecular weight up to several thousands, is used in the form of a waxy solid or viscous liquid as polyurethane intermediate, reactive diluent for high-solid coatings or plasticizer for vinyl resins; with molecular weight higher than 20 000, it is used as a thermoplastic polymer with mechanical properties similar to polyethylene (Table 4).

Table 4. PROPERTIES OF SOME POLYESTERS UNDER DEVELOPMENT

Property	**PHB**[a] (Biopol)	**PHB-V**[b] (Biopol)	**PCL**[c] (Tone 787)	**PLA**[d] (Ecopia)	**PAS**[e] (Bionolle 1000)	**PAS**[e] (Bionolle 1000)	**PEA**[f] (BAK 1095)
Melting point (°C)	177	135	60	177-180	96	114	125
Tensile stress at break (MPa)	40	25	4	45	40	60	25
Elongation at break (%)	6	25	800-1000	3	600	800	400
Tensile modulus (MPa)	4000	1000	386	2800	300	500	180
Density (g/cm^3)	1.25	1.25	1.145	1.21	1.3	1.2	1.07
Biodegradability in 60-day controlled composting (ASTM 5338) (%)	100	100	100	100	20	90	100

[a] Poly(hydroxybutyrate); [b] poly(hydroxybutyrate-*co*-16% hydroxyvalerate); [c] poly(ε-caprolactone); [d] poly(lactic acid); [e] poly(alkylene succinate)s; [f] poly(ester-amide)s

A number of studies have clearly claimed biodegradability of poly(ε-caprolactone) [20]. The rates of hydrolysis and biodegradation depend on its molecular weight and degree of crystallinity. ε-Hydroxycaproic acid was detected as an intermediate in the degradation by *Penicillium sp.* [21].
Hydrolysis rate is very low for the homopolymer, particularly when compared with poly(glycolic acid) and poly(glycolic acid-*co*-lactic acid); the rate can be increased by copolymerization. Crosslinked poly(ε-caprolactone) films with a lower degree of crystallinity than the uncrosslinked material were also found to be biodegradable.

Union Carbide, Daicel and Interox are the three producers of poly(ε-caprolactone) worldwide. High-molecular-weight poly(ε-caprolactone) may be processed by a variety of techniques, including film blowing and slot casting. Main applications in the field of biodegradable plastics is in combination with thermoplastic starch in films, sheets and injection-molded parts.

POLYAMIDES

Recently, a bulk, low-cost synthesis of poly(amino acid)s such as poly(aspartic acid) in 95 % yield was demonstrated [22] The polymers are biodegradable and could replace poly(acrylic acid) as dispersants in paints, detergents, for scaling in piping, and absorbents in diapers and medical products.

Bayer has recently launched on the market a poly(ester-amide) constituted by poly(butanediyl adipate-*co*-ε-caprolactam); its properties are reported in Table 4.

Other approaches to the synthesis of poly(amino acid)s are possible, some of them being based on the use of trifunctional amino acids as starting materials. New biodegradable functional polymers will be forthcoming which may prove useful as fibers for rigid composites or compatibilizers. The costs associated with some of these processes will also have to be addressed.

MARKET POTENTIAL: CHALLENGES AND RISKS

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

Notwithstanding these positive results, thermoplastic starch-based materials are still at an early stage of development with many opportunities still to be taken.

Various aspects, such as the capability of recycling atmospheric CO_2 and a low energy content of renewable raw materials as well as the increased productivity of present crops due to more advanced agricultural technologies and improved genotypes, make their use as raw materials for biodegradable products very challenging, on the condition that possible chemical modification and purification steps will not significantly increase their energy content.

Polyesters are at an advanced stage of application development and are promising in the field of biodegradable fibres, thermoformed items, rigid films, etc.

A real growth of the market is associated with:

- compostability label to exclude not truly biodegradable materials;
- growth of separate collection of organic and yard waste and development of composting infrastructures;
- legislative attention to materials from natural sources;
- promotion of the concept that the disposal cost is an integral and relevant component of the product cost.

The sales volume of 1996 for biodegradable materials was less than 12 000 ton/year, mainly due to starch-based products. The reference price was between 3 and 10 DEM.

Whereas the possibilities offered by the market are very wide, including agricultural applications, packaging products with particular attention to expanded foams, fast-food items, composting bags, diaper backsheets, etc. and justify a potential market of about 500 000 tons, the absence of legislative attention could dramatically delay or even block the development of this business area. In the case of no significant changes in legislative, the forecast sales volume for the next four years in Europe will not considerably exceed 40 000 ton/year.

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