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USE OF BIOSYNTHETIC, BIODEGRADABLE THERMOPLASTICS AND ELASTOMERS FROM RENEWABLE RESOURCES: THE PROS AND CONS

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ABSTRACT

For several reasons, biodegradable polymers have recently attracted much public and industrial interest. This contribution focuses on microbial aspects of the biodegradability of polymeric materials in the environment. It provides an overview on biodegradability and the mechanisms of degradation of relevant natural and technical polymers. Almost all biosynthetic polymers, which are readily available from renewable resources, are biodegradable within a reasonable time scale. Many semibiosynthetic and even chemosynthetic polymers are also biodegradable if they contain chemical bonds which also occur in natural compounds. Only a few polymers are truly persistent. Arguments for and against the use of such polymers are summarized.

INTRODUCTION

Polymers represent the most abundant class of organic molecules of our biosphere [1]. Complex polymers like coal and lignin occur in amounts of approximately 835,000 × 10^6 and 700,000 × 10^6 tonnes, respectively. These polymers represent the largest fractions, and they were formed in the past or synthesis is still going on, respectively. Furthermore, approximately 40,000 × 10^6 tonnes cellulose and 20,000 × 10^6 tonnes lignin are currently synthesized each year. In contrast to these figures, the production of approximately 100 × 10^6 tonnes per annum of various plastic materials is rather low. However, although only comparably small amounts of plastics are produced, these materials are the source of rising problems since most of them are not used for long-lived materials but occur in waste, and communities in many countries have difficulty managing the problems resulting from continuously increasing amounts of plastic wastes.

Biodegradable polymers have recently attracted much public and industrial interest as a consequence of extensive discussions looking for better waste-management strategies. The use of biodegradable polymers allows composting as an additional way for waste disposal, which is currently done mostly by deposition in landfills or by incineration. Furthermore the use of biodegradable polymers opens several new applications in medicine, agriculture, and many other areas. Therefore, scientists and industry are intensively looking for polymers which are biodegradable in their respective habitats. On the other hand, biodegradability of a polymer may limit its use for long-lived materials, since the latter should not only be resistant to chemical degradation and physical disintegration but also to biodegradation.

CLASSIFICATION OF POLYMERS

Because of their chemical structure, polymers represent a rather complex class of molecules. Besides linear, branched, and crosslinked polymers, homopolymers, various kinds of copolymers (random, alternating, block, and grafted), as well as blends of various types can be distinguished (Fig. 1).

From their origin we can distinguish completely biosynthetic and completely chemosynthetic polymers (Table 1). In addition, many semibiosynthetic polymers are known; these polymers are obtained from chemical polymerization of precursors of which at least one results from biosynthesis. Also, many semichemosynthetic

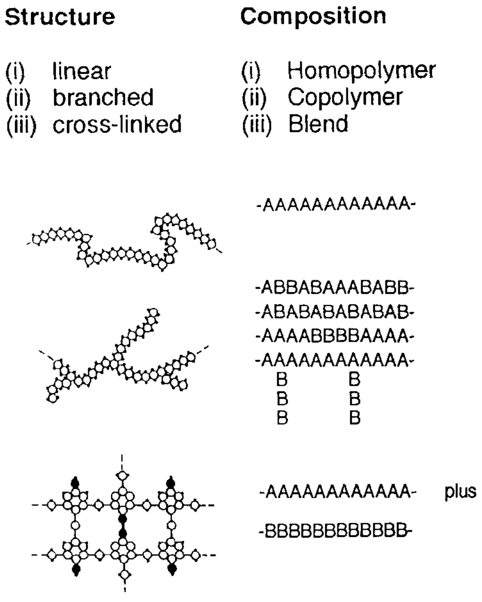

FIG. 1.

TABLE 1. Classification of Polymers (ii)

Completely biosynthetic [examples: proteins, polysaccharides, starch plastics, PHA]
Semibiosynthetic: Biosynthesis of at least one precursor and subsequent chemical polymerization [examples: polylactides, polyacrylamide, polyurethane, Bionolle (potentially), polymeric derivatives of the degradation of aromatic compounds]
Semichemosynthetic: Chemosynthesis of precursors and subsequent biological polymerization [example: PHF]
Biosynthetic but chemically modified [examples: casein plastics, cellulose nitrate, crosslinked PHA]
Chemosynthetic but biologically modified [?]
Completely chemosynthetic [examples: polyethylene, polyurethane, Bionolle]

polymers are known; these polymers are synthesized biologically from precursors which result from chemical synthesis. Furthermore, biosynthetic polymers which have been chemically modified upon biosynthesis are known.

BIODEGRADATION

Many organisms are able to degrade polymers which occur outside the cells. Among polymer degrading organisms, bacteria and fungi are the most abundant and exhibit the most flexible metabolism. Degradation of polymers—especially if plastic is degraded—often requires the disintegration of supramolecular structures (Step 1). Only after this first step will the backbone of the polymer become susceptible for cleavage by enzymes (Step 2). This step occurs mostly outside the cell by enzymes which are excreted into the medium. It has not yet been conclusively shown that polymers are taken into the cell prior to cleavage. Subsequently, monomeric or oligomeric cleavage products are transported into the cell (Step 3) and are degraded by catabolic enzymes (Step 4). With aerobic organisms, carbon dioxide and water may be the only degradation products of the polymer. With anaerobic organisms, fermentation products like organic acids and alcohols as well as methane may occur in addition to carbon dioxide [2].

Only the subsequent combination of all four steps will result in complete degradation of the polymer. If only Step 1 has occurred, the polymer may become invisible to the naked eye although the polymer molecules still exist and although degradation of the polymer has not occurred. This type of "biodegradation" often occurs with materials made from a blend of a persistent polymer and a biodegradable polymer; e.g., a blend of polyethylene and starch, respectively.

NATURALLY OCCURRING MECHANISMS FOR CLEAVAGE OF POLYMERS

Polymers represent major constituents of the living cells which are most important for the metabolism (enzyme proteins, storage compounds), the genetic information (nucleic acids), and the structure (cell wall constituents, proteins) of cells [2]. These polymers have to be degraded inside cells in order to be available for environmental changes and to other organisms upon cell lysis. It is therefore not surprising that organisms, during billions of years of evolution, have developed various mechanisms to degrade naturally occurring polymers. It is therefore also not surprising that all biosynthetic polymers, like all other natural products, are more or less readily degraded by organisms [3]. During the last hundred years the chemical industry has added many new polymers which are used as thermoplastics, elastomers, duroplasts, or many other applications. Most of these polymers are not, in general, persistent to biodegradation [4-6]. Only a few chemosynthetic polymers (e.g., polyethylene) are completely resistant to microbial degradation [7].

Since degradation of polymers occurs mostly outside cells, the number of mechanisms available for cleavage of the polymer backbone is limited ([6], Table 2). Glycosidic bonds as well as peptide bonds and most ester bonds (e.g., in proteins, nucleic acids, polysaccharides, and polyhydroxyalkanoic acids) are cleaved by hydrolysis. Some glycosidic bonds in polysaccharides are cleaved by a phosphorolytic mechanism; the enzymes cellobiose phosphorylase and α-1,4-glucanphosphorylase for the phosphorolytic cleavage of cellulose or starch, respectively, are examples. Lignin peroxidase catalyzes the cleavage of carbon—carbon bonds and of ether bonds in lignin. The enzyme has been studied in most detail in the fungus *Phanerochaete chrysosporium* [8]. Its unique radical mechanism seems to allow for attack on other molecules which are not readily degraded or which are not degraded at all. An oxidative mechanism catalyzed by polyethylene glycol dehydrogenase of various aerobic bacteria, which obviously depends on the presence of the artificial electron acceptor dichlorophenol indophenol, and a mechanism catalyzed by polyethylene glycol acetaldehyde lyase of various anaerobic bacteria employing rearrangements of carbon—carbon bonds and depending on cobalamin, were recently described for the degradation of water-soluble polyethylene glycols. From theoretical considerations and from experimental studies, evidence for an intracellular degradation of polyethylene glycol was obtained. How the polymer molecules pass the cell wall is, however, not known [6].

ARGUMENTS FOR THE USE OF BIOSYNTHETIC, BIODEGRADABLE POLYMERS FROM RENEWABLE RESOURCES

The use of thermoplastics and elastomers which are biotechnologically produced from renewable resources may offer several advantages as compared to the

TABLE 2. Mechanisms for Enzymatic Cleavage of the Backbones of Polymers

Mechanism	Cleavage of	Enzyme
Hydrolytic	Glycosidic bonds, ester bond, peptide bonds	E.g., proteases, nucleases, cellulases, muramidases
Phosphorolytic	Glycosidic bonds	E.g., cellobiose-phosphorylase
Radical	Carbon—carbon bonds, ether bonds	Lignin-peroxidase
Oxidative	Ether bonds	Monooxygenases, PEG-DH
Rearrangements	Carbon—carbon bonds	PEG-acetaldehyde lyase

use of conventional polymers. Production of these polymers is independent of fossil resources; fossil carbon sources are only required to support the growth (e.g., for the production of fertilizers and herbicides), and the harvest of plants provides the carbon sources that are offered to the bacteria in the bioreactor and the energy for the manufacture of materials from the polymer by, e.g., extrusion [9]. The carbon atoms of the polymer are derived from carbon dioxide in the atmosphere, and the synthesis of the renewable resource is driven by solar energy. The use of renewable resources will provide an alternative to the production of food for agriculture. At present, farmers in most developed countries produce agricultural surpluses. In addition, many regions are no longer suitable for the production of food since they were heavily polluted in the past. Land which is no longer required and which is not suitable for the production of food may therefore be used for the production of renewable resources. In addition, many interesting polymers could be produced from waste materials derived from food industry processes or from the paper manufacturing industry. In our laboratory, for example, recombinant strains of *Alcaligenes eutrophus* were obtained which utilize lactose (abundant in whey) as a carbon source for the production of polyhydroxylalkanoic acids [10]. Many more examples could be provided. Finally, and as outlined below, the use of some thermoplastics and elastomers may lead to many new applications.

One major argument for the use of these polymers is that waste can be directed to composting. Materials manufactured from these polymers must no longer be deposited in landfills, which are increasingly less available. In contrast to incineration, chemical reutilization, or recycling, composting can be achieved at comparably low capital costs, and it does not require extensive transportation. On the other hand, biodegradable materials disappear rather than being litter.

ARGUMENTS AGAINST THE USE OF BIOSYNTHETIC, BIODEGRADABLE POLYMERS FROM RENEWABLE RESOURCES

Despite the above-mentioned advantages, the use of biosynthetic, biodegradable polymers and their production from renewable resources is very controversial. The primary reason why biosynthetic polymers from renewable resources are not as widely used as chemosynthetically polymers produced from fossil resources is the high costs of these polymers. The price of Biopol, which is the trade name for a bacterial copolyester consisting of 3-hydroxybutyrate and 3-hydroxyvalerate, is approximately 15 to 20 US dollars per kilogram. This is much higher than the cost for conventional plastics used for the manufacture of packaging material. However, the price for Biopol will most likely drop to approximately 4 to 8 US dollars in large-scale production [11]. The situation is similar for other biosynthetic polymers.

Other concerns arise from the lack of evidence for a positive "Ökobilanz." It is doubted that the total input of energy is less and that all effects on the biosphere are less severe than for the production of polymers from petrochemicals. These complex effects have to be studied in detail. One has, however, to consider that the processes for the production of polymers from renewable resources may change drastically as a consequence of the increase of knowledge on the biosynthetic pathways and on the production organisms, and also due to the application of recombinant DNA technology. Many bacteria are able to synthesize large amounts of polyesters consisting of a wide range of hydroxyalkanoic acids [12, 13]. These polyesters have thermoplastic and elastomeric properties and are biodegradable. The polyhydroxyalkanoic acids biosynthesis genes from various bacteria have recently been cloned and analyzed at the molecular level [14]. For example, it was shown that it is possible to produce at least some polyhydroxyalkanoic acids in transgenic plants utilizing carbon dioxide and solar energy directly [15].

One other major and general concern on the use of biodegradable polymers is the possibility that greenhouse gases other than carbon dioxide are released into the atmosphere during the production and after the use of biodegradable polymers. Support of plant growth for the production of renewable resources by fertilizers may result in an increased release of NO_x gases. If biodegradable materials are deposited in landfills, the polymers will be at least partially converted to methane in anoxygenic areas by consortia of quite different organisms including methanogenic bacteria [2]. Methane, for example, exerts an approximately 20-fold higher greenhouse effect than does carbon dioxide.

The use of biodegradable polymers for recently developed plastics is further limited by the poor physical and technical properties of these materials. This is at present certainly true for many polymers and applications. However, one has to consider that such products as Biopol, Bionolle, and starch plastics were developed only recently, whereas most conventional plastics in wide use were developed over a period of several decades and were continuously improved. This will probably also occur in the future with the materials mentioned above. For example, the barrier properties of films manufactured from biodegradable polymers toward water vapor and molecular oxygen can be improved by metal vapor treatment as shown for PHA films treated with Al or SiO_x [16].

Certainly the use of biodegradable polymers will remain restricted to applications for short-lived applications. These polymers will probably not be useful for the outside parts of cars, for the construction of buildings, for the manufacture of pipelines, etc. Furthermore, the use of biodegradable materials for food packaging might cause hygienic problems under certain circumstances if the necessary precautions are not taken.

NEW APPLICATIONS FOR BIODEGRADABLE POLYMERS

Other applications of biodegradable polymers in the packaging industry focus on their use to improve the resistance to water and humidity of other materials. Plasticized starch has the disadvantage of not being waterproof. The use of blends of starch and water-insoluble PHA may overcome this problem. Water-sensitive materials can be also coated with PHA [17], allowing the replacement of barrier layers of aluminum or polyethylene in cardboard packages for soft drinks and mil, drinking cups, etc.

The uses of biodegradable polymers are not restricted to applications in the packaging industry which require large amounts of polymers produced at reasonable low costs. There are many other potential applications in other areas which require less material and for which the distinct properties of these polymers rather than their costs are important. Some of these applications will, of course, remain niche applications. For example, polyhydroxyalkanoic acids may be considered for many interesting applications in medicine, agriculture, and the food industry or to provide a source of interesting substrates for the chemical synthesis of enantiomeric pure chemicals [18]. Even applications for polyhydroxyalkanoic acids in photoelectrical apparatuses are possible. For example, nonbiodegradable thermoplasts are currently used in xerography where they function as carriers for the toner and cover a significant fraction of the surface of the principally biodegradable paper. This does not contribute to the biodegradability of paper during composting. Since the toner is tightly fixed to the paper surface, de-inking of the paper becomes a problem during recycling of used paper. It is currently being investigated whether biodegradable polyhydroxyalkanoic acids can be used instead of conventional nonbiodegradable thermoplastics.

CONCLUSIONS

The field of biosynthetic biodegradable polymeric materials has been largely developed in recent years, and many new polymers have been made available. Considering PHA, only poly(3-hydroxybutyrate) was known for almost six decades. Systematic feeding of precursor substrates to various bacteria, cultivation of the bacteria under appropriate conditions, and improved methods for the analysis of the accumulated polyesters have revealed approximately 80 different constituent hydroxyalkanoic acids of PHA. Most of these new PHAs have been detected in *Alcaligenes eutrophus* and *Pseudomonas oleovorans* only during the last 5 years [12, 13]. The PHA syntheses of both bacteria are distinguished by rather low substrate specificities. Furthermore, heterologous expression of PHA syntheses genes in other bacteria, which provide a suitable physiological background, resulted in additional new polymers [19-21]. In addition, biosynthetic polyhydroxyalkanoic acids can be modified by various measures after biosynthesis has been completed and after the polyesters have been isolated from cells. If polyhydroxyalkanoic acids consisting of medium-chain-length hydroxyalkanoic acids are exposed to irradiation, a rubberlike complex polymer is obtained which is still biodegradable [22]. The evaluation of the physical, technical, and biological properties of biosynthetic PHA is still at the very beginning, and analysis of the data will probably give hints for many new applications.

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