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DEGRADABLE POLYMERS

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ABSTRACT

Deterioration and degradation of organic polymeric structures are the basic mechanisms ensuring recycling of the elements of the biosphere. All organic polymers are, in principle, degradable, but even nature combines inert and degradable components in the same material, as, for example, in wood. Wood consists of degradable polysaccharides such as hemicelluloses and cellulose, and also rather inert substances such as lignin and smaller amounts of somewhat hydrophobic terpinoic molecules and waxes. The *total* degradation of wood in its natural environment takes a rather long time, suggesting that the rapid biodegradation of wood to carbon dioxide and water is not environmentally optimal. Thus, if we concede that the natural balance, as mentioned for wood, should be our model, then our synthetic polymers should emulate wood in their pattern of degradation. The idea that synthetic polymers should biodegrade totally in periods of a few months or less does not reflect how the natural environment functions.

INTRODUCTION

The interest in environmental issues is still growing and there are increasing demands to develop materials which do not burden the environment significantly. Awareness to the waste problem and its impact on the environment has awakened new interest in the area of degradable polymers [1]. To create materials that continue to have strength and functionality while in service but degrade after use is a rather novel concept in the development of materials. This new concept of "degradability" is now often demanded to be incorporated into the creation of new plastics products. At the same time, an additional demand is now widely requested that polymeric materials come from renewable resources instead of from petrochemical sources. A third demand is to save materials by improved product design and by recycling.

In nature the solution for used materials is their deterioration and degradation. The basic mechanisms ensure recycling of the chemical elements in the biosphere. This behavior has often been referred to as "biodegradation," but maybe it is better referred to as "environmental degradation." There are a large number of different degradation modes that synergistically combine to degrade polymers. Biodegradation might be better used as a term only when it specifically describes the action of living organisms. This allows that type of deterioration to be clearly distinguished from other degradation modes (e.g., photolysis, oxidation, hydrolysis).

Unfortunately, the term "biodegradation" is often used in contexts which clearly imply the meaning of "environmental degradation." The desire for the creation of artificial polymeric materials capable of undergoing degradation has increased all over the world as a consequence of ignoring the impact of introducing biologically refractory materials becomes apparent.

To recognize the importance of the problem of disposing of polymers by biological degradation, special organizations exist: a Biodegradable Plastics Society in Japan and a Bio/Environmentally Degradable Polymer Society in the USA. In Europe, there is a special committee charged with organizing the 2nd International Workshop on Biodegradable Polymers, but no specific society has been founded. The greatest demand for degradable polymers in Europe has been in Italy where, for a few years, a law existed requiring biodegradability for packaging materials. This no longer exists because a government decree was introduced which eliminated all the economically acceptable materials. The reason for this development was that they did not fit the arbitrary 30 days laboratory bacteriological test method (Sturm procedure) which uses sewage organisms at room temperature as a specification for the test procedure. In Germany, new government laws favor recycling. The new EC draft packaging directive also favors recycling but does not exclude the composting of organic waste. In the USA, some regulations have evolved on a state by state basis and require garden waste to be composted; in such cases, degradable plastic bags are acceptable in this usage. Some states also have regulations in place requiring the use of degradable plastics for the notorious rings for metal cans arranged as "six-packs."

Polymers accessible to degradative attack by living organisms are not directly related to their origin and only to some extent to their structure; all biopolymers are not truly biodegradable. Complex biological macromolecules, such as lignin, show great inertness, while synthetic polymers with a hydrolyzable polymer backbone chain, like aliphatic polyesters, can be biodegraded by esterases despite their usual enzymatic specificity.

The chemical structure of polymers is critically important in determining how easily they can be attacked by enzymes. However, it is probably not possible to create new enzymes for the degradation of polyethylene. Enzymatic induction is just a trigger for an existing gene to produce a number of molecules of the corresponding enzyme. Thus, a purely enzymatic degradation of a long, straight olefin chain dependent on enzymatic cleavage of the C—C bond can probably not be expected, since such an endoenzyme does not occur in nature. Oxidation, rather than enzymolysis, is the obvious and critical step for the degradation of many very inert hydrocarbon molecules.

POLYMERS WHICH DEGRADE OVER A LONG TIME PERIOD

The introduction of recalcitrant synthetic polymers into nature led to new problems. A controversy was inevitable because of the practical interest in the fate of industrial synthetic plastics and rubbers. This arose because durability is one of the general requirements for such materials in technological applications, and this conflicts with the need for them to enter into natural recycling degradative processes.

Recent trends in polymer research and more careful marketing studies point to an increasing demand for the development of a diversity of biodegradable polymer products with a predetermined lifetime in at least four main fields: for packaging materials, for mulching foils in agriculture, for disposable items located in garbage (litter) systems where they will be mineralized (totally degraded) saprophytically, and in medical applications, in vivo in the human or animal body, where degradation must proceed in a way resembling parasitic processes. With "programmed" degradation as a necessity, however, all significant deviations in the time schedule from a desired life span for these materials will be a nuisance.

Our early interest in the study of polymer biodegradation was focused on the question of the duration of structural integrity of the most inert polymeric products with respect to their anticipated chemical durability. In some cases this lifetime was guaranteed without actual long-time experience with such products.

Polyethylene is regarded as a chemically "inert" polymer, mainly due to its long degradation time. It is usually quite difficult to monitor slow changes in such polymers, but by using labeled materials and liquid scintillation counting it has been possible to study microbial and oxidative changes in the degradation of "almost inert" polyethylene [2]. The degradation rates are influenced by several factors such as irradiation [3, 4], by morphology and surface area [5, 6], by antioxidants [7], by additives [6, 7], and of course by molecular weight [3].

The very first study of polyethylene degradation in the Department of Polymer Technology (Stockholm) started in 1973, and measurements on the original series of samples still continues [8]. The most recent results show that the degradation of polyethylene proceeds. However, Scott had already concluded in 1975 that attack by microorganisms is a secondary process. The step which determines the rate at which degradable polyethylene is returned to the biological cycle appears to be the rate of the molecular oxidation process, which reduces the molecular weight of the molecule to the value required for biodegradation to occur. Even in the absence of any biodegradative attack, the carboxylic acids produced ultimately oxidize to carbon dioxide and water [9].

An improved mechanism for the biodegradation of polyethylene was recently presented [10], and it shows similarities with the typical β-oxidation of fatty acids and paraffins in man and animal. Initially, an abiotic step in the oxidation of the polymer chain is necessary. Once hydroperoxides have been introduced, a gradual increase in the amount of keto groups in the polymer is noticed, which is followed by a decrease in keto groups when short-chain carboxylic acids are released to the surroundings as degradation products [11].

The initial oxidation step should be compared with the initial step in the degradation of lignin and other rather inert natural products including natural rubber. It is also possible to compare this oxidation step with the degradation of lipids in the liver and with the oxidation process which occurs in a landfill.

Griffin [12] attempted to summarize the evidence for the breakdown of synthetic polymers in the natural environment, especially under the influence of living organisms. He reviewed the microbial and microbiotic impacts on both resistant and biosensitive polymers. He also presented and interpreted his own observations on the pictorial events of penetration of hyphae of filamentous fungi in polyurethane and in starch/EVA blends. The presentation is no doubt didactic as interdisciplinary information for nonmicrobiologists, but the biological principles quoted in this connection require some extension and explanation. Hyphal penetration in more or less solid structures is a common and generally known phenomenon both in soil colonization and in saprophytic decay processes as well as in parasitic growth on soft or hard tissues of plants or animals. Such hyphal penetration might deteriorate any solid structure by simple mechanical effects on a microscale and by the introduction of chemically active exudation products (mostly organic acids) from the microorganisms, especially filamentous fungi, myxomycetes, and such bacteria as actinomycetes, into high molecular weight polymers, with familiar manifestations such as the spreading of mildew on leather, textiles, fruit, and skin.

Astonishing in this connection is the purposeful partition of work between hundreds of specific enzymes and thousands of ubiquitous microorganisms in the recycling and mineralization processes. Still more peculiar is the fact that chemists have successfully produced organic materials in quantities which might become an environmental menace because of their stubborn resistance to microbial decomposition. Many synthetic polymers are biologically refractory, equaling mineral asphalts.

Without question, we must agree with the conclusions of Griffin [12] based on the definition of Hueck [13] and of Kaplan [14] that "polyethylene is not biodegradable because no laboratory has, so far, succeeded in demonstrating a high molecular weight hydrocarbon specific enzyme interaction of measurable rate with demonstrable metabolite production." There is no doubt this comment is true, and we fully agree that such enzymes probably do not exist in nature. It is understood that there is a wide variety of unsubstituted saturated hydrocarbon structures in different kinds of polyethylenes; each structure poses a different requirement for an enzyme's capability of nonterminal attack on the molecules.

The premises for the eternal resistance of polyethylenes are thus correctly specified but rather academic since these molecules are subject to different environmental influences with the passage of time and are certainly not stable enough to escape physical and chemical aging in the usual terrestrial or benthic environments. The onset of complex enzymatic fission effects on these molecules might be delayed but not stopped permanently since molecular rearrangements of autoxidation will follow the introduction of hydroperoxide, peroxides, and carbonyl groups and radicals. These functional groups will make the macromolecular structure accessible to the action of existing enzymes if they will be continuously exposed to support conditions suitable for maintaining these actions.

Hydrophobicity is often regarded as a major obstacle to microbial (biodegradation) attack on polymers. The addition of surfactants in degradation studies with polyethylene showed a considerable increase in the biodegradation rate compared with samples without surfactant [15]. Ongoing studies in which surfactants are incorporated in polyethylene show promising results as observed by ATR-FTIR, DSC, and SEM.

Even if very inert polyethylene is not attacked by enzymes as a first step, a clear influence of living organisms and their secretion products has been demonstrated and seems to be related to the sequence of chemical and biological actions.

MEDIUM LONG DEGRADATION TIMES

Several interesting solutions have made filled polyethylene degrade faster than previously observed. Incorporation of a chromophoric group, which increases the susceptibility of filled polyethylene toward photooxidation, is probably the method of choice. Metal salts are also useful and potent additives, and they give room for radical formation within the polymer chain and again increase the photooxidative behavior of these materials.

It is now widely accepted that the conservation of resources is most important. This demand has led to the use of renewable materials. Knowing that biopolymers usually degrade quickly by microbiological action has also led to the use of agricultural products as additives for synthetic polymers with the intention of producing a biodegradable polyethylene.

An interesting example studied [16] is the blend of polyethylene with starch. Starch is a polysaccharide and is most readily attacked by microorganisms. Griffin introduced the idea of mixing granular starch in its natural form with polyethylene [17]. The polyethylene/starch blend has been improved since the original development was made [18] by the addition of transition metal salts, unsaturated polymer, and a thermal stabilizer in a master batch.

The biodegradation step follows autoxidation of the polymer and is the initiation of total degradation by the consumption of the starch by microorganisms. The consequence of this combined activity is a brittle polyethylene-based material which is more susceptible to oxidation and continuing biological action.

Inclusion of starch alone in polyethylene does not improve the total degradation of polyethylene, as observed in photooxidation and thermal experiments [16]. Polyethylene with starch has been tested in several different environments (e.g., soil, refuse burial, anaerobic waste treatment, etc.) in which it was shown that starch is removed to varying extents in all exposure environments. Our studies showed that incorporation of starch alone does not improve the susceptibility toward irradiation and promotion of a hydroperoxide build-up. However, a combination as specified by Griffin [17, 19] made the material most susceptible to photooxidation and thus more prone to undergo biodegradation. A study of biodegradation of starch-filled polyethylene showed that a material designed with an induction time needs nearly 1 year in order to finish the induction period of a degradation starting at the polyethylene matrix [20, 21]. Using LSC of ^{14}C-labeled polyethylene with a masterbatch according to Griffin showed that initial heating of the materials at 100°C for 6 days led to the initial biodegradation of the polyethylene matrix. When the samples were not thermally pre-aged, they needed 1 year of exposure to the laboratory biodegradation environment before the induction time was concluded at lower temperatures than described above [22]. This induction time can be varied widely depending on the choice of the type of polymer, the antioxidants and autoxidation catalysts, and their concentrations.

POLYMERS WITH SHORT DEGRADATION TIMES

Polymers with hydrolyzable linkages in the backbone can also be used as environmentally adaptable polymers. So far, most of them are too expensive and do not have the desired or necessary mechanical and chemical properties. Well-known synthetic hydrolyzable polymers are polyesters, polycarbonates, polyanhydrides, polyamides and poly(amino acids) [23]. Hydrolyzable natural polymers may be cheaper and are believed to be representative for future development in degradable polymers. Many scientists today are looking for new possibilities using such traditional natural polymers as polysaccharides, proteins, and lipids. Special interest is focused on poly(β-hydroxybutyrate) and its copolymers. Well-known natural products such as Pullulan, cellulose acetate, and starch, as well as synthetic polyvinyl alcohol, are again being tested.

Polymers that can be hydrolyzed, such as polyesters, are often more prone to degradation but also less technically suitable in many applications than are the hydrophobic polymers.

Aliphatic homopolyesters, e.g., poly(tetramethylene adipate), and block copolymers, such as poly(ethylene succinate)-*b*-poly(ethylene glycol) and poly(ethylene succinate)-*b*-poly(tetramethylene glycol) [4], were synthesized and their degradation subsequently studied in a pseudoextracellular fluid buffered at pH 7.3 and maintained at 37°C [23]. The materials obtained showed the behavior of thermoplastic elastomers, and the degradation rate depended on the polyether composition. Poly(β-propiolactone) has been hydrolytically degraded in buffered salt solution (pH 7.2) at 37°C [24, 25].

Oriented and nonoriented fibers show different degradation properties, especially with regard to changes in mechanical properties. Changes in tensile strength were found to be slower for oriented materials than for nonoriented materials. The polymerization of 1,5-dioxepan-2-one gave a poly(ether ester) with amorphous properties, implying its usefulness as an amorphous block in copolymers possessing elastic properties [26].

Aliphatic polyanhydrides degrade within a few days while aromatic polyanhydrides are known to degrade slowly over a period of several years. Recently, a new synthetic route for the synthesis of linear poly(adipic anhydride) using ketene gas was described [27]. This synthetic route has the advantage of avoiding the formation of acetic acid, which could lead to the reverse reaction. Polyanhydrides are useful in biomedical applications because they can readily form fibers. An increase of the aliphatic chain length between the acid groups not only allows polymers with higher molecular weights to form but also substantially improves their hydrolytic stability

[28, 29]. Aliphatic polycarbonates are polymers derived from the polymerization of cyclic molecules; poly(1,3-propyl carbonate) is formed from 1,3-oxa-cyclohexaneone-2. Such a macromolecule can degrade to monomers at high temperature because of its relatively low ceiling temperature.

Poly(trimethylene carbonate) was synthesized using cationic and anionic initiators, giving a high molecular weight polymer which is rubbery at room temperature [30]. Since this polymer is an aliphatic polycarbonate, it could be useful as a biodegradable polymer for medical applications.

Polyanhydrides degrade in a short time period; aliphatic polycarbonates may take more than a year for complete degradation. Their chemical structure can be varied over rather wide limits, which allows the time of degradation to be widely regulated.

When designing new polymers, it is also important to take into account the degradation products and rate of decomposition without forgetting the need for maintaining mechanical and chemical properties as long as possible. The morphology of polymer samples also greatly affects the rates of biodegradation.

TOTAL BIODEGRADABILITY IS AGAINST NATURE

Nature combines polymers with short degradation times with polymers having long degradation times in an energy and material optimized process involving hierarchial systems. Sometimes a natural system of polymers has evolved to degrade in a month, sometimes in many years. Consider a tree consisting of three polymers: hemicellulose, cellulose, and lignin. Hemicellulose is water-soluble and has a short time of degradation, cellulose degrades at a medium rate, but lignin has a very long rate of degradation. All three polymer classes are needed in order for the tree to grow, survive, and ultimately to be disposed of in an orderly manner.

Oxidation is the initial step for all mechanisms of environmental degradation of polymers with long degradation times. Polyethylene starts to biodegrade when oxygen is incorporated in the polymer. Oxidation is also the initial step in lignin degradation.

Polymers with short degradation times, on the other hand, already have some oxygenated structures, which makes many of them hydrolyzable (e.g., polyesters, cellulose, hemicellulose).

The optimal use of degradable polymers confronts us with the requirement to formulate an appropriate list of characteristics which are necessary when degradation time is the central theme. The optimal goal is *not* 100% biodegradability within a few months. Controlled periods of biodegradation spanning from months to years, depending on the application, is a better choice.

CONCLUSION

For many inert polymers, oxidation is often the initial degradation mechanism before biodegradation based on the action of enzymes and microorganisms starts. 100% biodegradability within a few months may not be the most efficient way to decrease the amount of plastic waste and may constitute an extravagance when only finite resources are available. The unnatural character of such intensely biodegradable materials and the rapid development of anaerobic conditions could quickly lead to heavy BOD and destroy the natural balance that ensures an optimal, meaningful recycling of the elements of the biosphere.

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