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Dynamics in Prediction of Life-time of Environmental Adaptable Polymers

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ABSTRACT: Environmentally adaptable polymers are materials with well-defined life times made by tailoring the synthesis and creating a molecular architecture with precise functionality and morphology. Synthesis of such materials develops initiators/catalysts systems and enzymatic polymerisation while processing need to be adopted to the labile repeating units. The secondary structure of the environmentally adaptable polymers is susceptible to traditional processing introducing *e.g.* changes in the atomic positions of oxygen of poly(3-hydroxy-co-3-hydroxyvalerate). (Bio-) degradation of these materials is complex and difficult to predict. Modelling test-environments require an understanding of the many biological processes possible in nature. Many biodegradations require *e.g.* the co-operation of more than one microbial specium, which sometimes render standard biodegradation tests inadequate. The nonabsolute specificity of enzymes are probably responsible for the transformation of many of the novel molecules created in recent times, but it is wishful thinking to expect that every new compound has an enzyme able to catalyse its alteration.

INTRODUCTION

Environmentally adaptable polymers are those polymers where the degradation occurs predominantly by some process in the environment. The mechanisms are photolysis, oxidation, thermolysis and biological attack. Outdoors the most aggressive mechanisms are the photo-and thermo-oxidation, but depending on the functionality and morphology of the polymer in question, also biodegradation may be rapid. Synthetic polymers act in many respects as biopolymers during degradation. It is a dynamic system where several mechanisms cooperate in cumulative or synergistic mode. Many synthetic polymers are made inert by the inclusion of additives (*e.g.* antioxidants), while others are inert in themselves. In many applications, a shorter degradation time than that offered by traditional commodity plastics are asked for and means to achieve degradability is many.

The chemical functionality of synthetic and natural polymers influence the degradation time. Nature uses different functional groups depending on the application. Energy storing materials for biopolymers are *e.g.* glycogen in man which resembles amylopectine (polysaccharide formed in plants) but is more branched. Long-term energy-storing materials are lipids for higher organisms (humans, animals) while many micro-organisms use a polyester, polyhydroxybutyrate (PHB).

We proposed the biodegradation mechanisms of polyethylene where an abiotic oxidation initiates the subsequent biodegradation (1). Micro-organisms assimilate degradation products to various extent (2). In some cases this retard the overall degradation while in others it has only marginal influence. Fungi and bacteria in their metabolism use carboxylic acids formed in biodegraded polyethylene, but no effect is seen in the rate of the degradation of the polymeric matrix. On the other hand we have observed that lactic acid (LA) formed during

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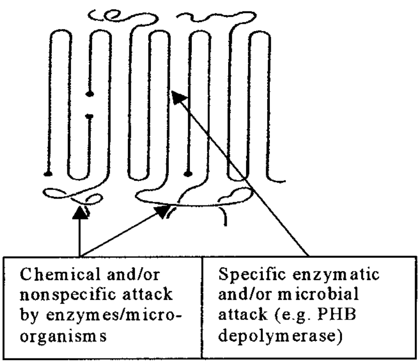
the bio-hydrolysis of PLA is used in preference to the material. This is explained as both an effects of crystallinity and availability. The bio-hydrolysis occurs mainly in the amorphous part of PLA, as the degradation continues less and less amorphous parts remain. Although the number of bacteria increases the LA is available as carbon source.

The role of micro-organisms in spoilage of solid materials and the development of protective chemical biocides initiated studies acquiring the title "biodegradation". Their status was recognised by the adoption of standard specifications. The term "biodegradation" previously adopted in connection with disposal of water-soluble materials such as surfactants, was used. Although many biodegradation tests are available, the lack of understanding how to choose microorganisms and test-environment lead to misinterpretation of rate of degradation of new environmentally adaptable polymers.

CHEMISTRY AND MORPHOLOGY

The oxidation of polyethylene starts in localised centres, leading to local variations in oxidation rate. The same is seen also for aliphatic polyesters such as polycaprolactone (PCL) and polylactide (PLA) although these are instead hydrolysable. Consequently the rate of biodegradation will differ in the materials; in addition, we also observe difference in rate of degradation between surface and bulk. The oxygen concentration is larger in the surface of PE as observed by FTIR and SEM (3). Chemiluminescence (CL) showed that early CL-signals were dependent on the traces of hydroperoxides present in the virgin PE. The amount of hydroperoxides were higher in PE degraded by fungi and bacterium (*Arthrobacter paraffineus* and *Verticillium lacanii* and *Verticillium niger*) than in abiotic environment (3). The CL intensity was almost proportional to sample thickness, indicating that it originates from both bulk and surface. X-ray diffraction (XRD) showed a decrease in lamella thickness for biodegraded LDPE while the corresponding samples in the abiotic environment instead showed constant or increased value (4). The crystallinity of the samples increased in value with prolonged degradation, where the increase is higher for abiotical than for biodegraded samples (4). In parallel we have observed increases in crystallinity during biodegradation of PLA and poly(1,5-dioxepan-2-one) PDXO (5, 6). This increase in crystallinity is due to a preference for assimilation and degradation of the amorphous parts of the polymer. The figure below illustrates how (bio-) hydrolysis occurs in environmentally adaptable polymers with a folded-chain structure.

Model of (bio-)degradation of semicrystalline environmentally adaptable polymer



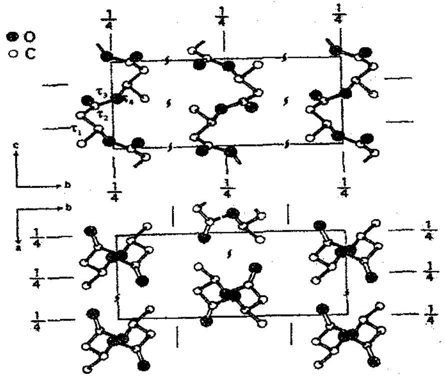
KINETICS OF BIODEGRADATION

Prediction of biodegradation of polymers is one part of the long-term properties of polymeric materials. Questions such as when do we expect biodegradation and if this is always a rapid process need careful analyses. A total conversion of the polymeric material to carbon dioxide and water is seldom seen and many biopolymers do not form end products such as these during a typical test-period of one month. The kinetics of polymer biodegradation is complex and a function of micro-organisms/enzymes, the polymer-structure relationship and the environment. The biodegradation kinetics is usually monitored by the disappearance of the polymer in question. Slow biodegradation is related to several factors with the respect to the polymer matrix while different sets of factors has more to do with the micro-organisms.

The fact that there are no micro-organisms capable to degrade the polymer is common, and if we still see biodegradation it often reflects the non-absolute specificity of enzymes. Many active enzymes are synthesised inside the cells and are thus not accessible. Often the foiling, coiling and high crystallinity of polymers results in inaccessible sites for enzymes in the polymeric molecule. Lack of induction of requisite enzymes is another cause of inertness to biodegradation. Environmental factors such as lack of nutrients, presence of toxins and traces of catalysts, initiators *etc.* inhibits many possible biodegradations.

The processing of environmentally adaptable polymers influences the structure-properties of polymers and gives changes in the biodegradation rate. We showed that high processing temperature and low screw speed causes changes in the atomic positioning of the oxygen atoms in poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (Poly(3HB-co-3-HV)) due to torsion of the main chain bonds (7). In addition, we observed that molecular weight or lamellar distribution (8) did not control the rate of biodegradation of Poly (3HB-co-3-HV). An increase in crystallinity reduced the biodegradation. A correlation was found between rate of biodegradation and intensities of the sharp X-ray reflection (020) and (110), which indicates that the positioning of the oxygen atoms affected the recognition of the extra-cellular enzyme (8). The unit cell dimensions are unaffected by the processing, the changes are instead due to small differences in the positioning of the atoms. The figure below shows the crystal structure of P(3HB-co-3HV) where the specific PHB-depolymerase fits. Polyhydroxyalkanoates (PHA) has a classical secondary structure of a helix, which reduces the possibility of non-specific enzymatic and/or chemical hydrolysis.

The crystal structure of P(3HB-co-3HV)



THE DYNAMICS OF POLYMERS IN ENVIRONMENTAL INTERACTION

It is a challenge and a necessity to model test-environments for polymer (bio-)degradation as it is not possible to have real-time tests. The dynamics of natural environmental degradation is usually far to complex to model. In catabolisms, biopolymers are degraded and building-blocks molecules are recycled to the biosynthesis of new structures. These mechanisms are initiated and inhibited by a series of low molecular weight compounds and enzymes. This is illustrated in the biodegradation of polylactides. Amorphous P(D,L-lactide) is rapidly hydrolysed while the semi-crystalline P(L-lactide) shows slower degradation rates. In biotic environment we also observe assimilation of LA in preference to the PLA matrix when the degree of crystallinity increases. LA is a natural metabolite and as such it fits into the catabolisms and may be used over and over again. The same is true for products of polyhydroxyalkanoates (PHA); β-hydroxybutyrate (HB) fits into the cycles of nature. Instead we should observe the degree of formation and the amount of formed products, and although LA and HB are natural metabolites the cycles of nature may be disturbed if too much of a certain compound is formed.

Oxidisable biopolymers such as lignin degrade to large amounts of different compounds, among these the humic substances are regarded as end products. During themochemolysis of humin and humic acids, hydrocarbons, methoxy alkanes and diesters were identified (9). Many of these substances resemble the functionality of polyethylene and its degradation product (10). Therefore also degradation products of hydrocarbon polymers fit into the cycles of nature. By analysing the total production of low molecular weight compounds continuously it is possible to predict the catabolism and biocycling of intermediates from polymer (bio)degradation. Already in the early 1980ths we used gas chromatography to show biodegradation of proteins (11). We identified two different GC-finger-prints from species of anaerobic bacteria, which indicate a variation in catabolism. In parallel, we now identify different chromatographic fingerprints of PCL, PLA and PHB hydrolysed in abiotic and biotic environment (12).

CONCLUSIONS

Proper tests are necessary for predicting the long-term properties of environmentally degradable polymers. The molecular architecture of synthetic and natural polymers determines the ease of (bio)degradation. We observe sequences of abiotic and biotic degradation mechanisms in nature. Polymer biodegradation is possible mostly due to the non-specificity of many enzymes to a range of substrates. Biodegradation is a process, which range in time between hours to hundreds of year depending on the polymeric structure and the molecular architecture.

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