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A Review of Biodegradable Polymers: Uses, Current Developments in the Synthesis and Characterization of Biodegradable Polyesters, Blends of Biodegradable Polymers and Recent Advances in Biodegradation Studies

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Abstract: This review considers the uses of biodegradable polymers in terms of their relevance within current plastic waste management of packaging materials, biomedical applications and other uses; research papers and patents are catalogued. The chemical synthesis of polyesters and the microbial production of poly(hydroxyalkanoate)s, including recent publications in these areas, are covered and methods of characterization and structural analysis are outlined. Current research into two- and three-component blends is reviewed as a method of reducing overall costs and modifying both properties and biodegradation rates of materials. Finally, there is a summary of degradation processes. Both abiotic and biotic reactions are discussed, together with the development of biodegradation test methods, particularly with respect to composting. © 1998 Society of Chemical Industry

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Key words: biodegradation; biodegradable polyesters; packaging; synthesis; characterization; blends

1 INTRODUCTION

Within this review, biodegradation will be defined as by Albertsson and Karlsson[1] as an event which takes place through the action of enzymes and/or chemical decom-

position associated with living organisms (bacteria, fungi, etc.) or their secretion products. However, it is necessary to consider abiotic reactions (e.g. photodegradation, oxidation and hydrolysis) that may also alter the polymer before, during or instead of biodegradation because of environmental factors. Albertsson and Karlsson[2] have also recognized that nature can be used

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as a model in the design of degradable polymeric materials, because it can combine polymeric materials with different degradation times into a hierarchical system that optimizes both energy and material properties. Naturally occurring biopolymers are susceptible to environmental degradation factors and their breakdown may be caused by a combination of these; for example, wood is both oxidized and hydrolysed. Tailoring the properties of polymers to a wide range of uses and developing a predetermined service life for the materials have become increasingly important and Albertsson and Karlsson suggest four different strategies:

(1) the use of cheap, synthetic, bulk polymers with the addition of a biodegradable or photo-oxidizable component;
(2) chemical modification of the main polymer chain of synthetic polymers by the introduction of hydrolysable or oxidizable groups;
(3) the use of biodegradable polymers and their derivatives, with poly(hydroxyalkanoate)s (PHAs) being the most studied;
(4) tailor make new hydrolysable structures, e.g. polyesters, polyanhydrides and polycarbonates.

All four approaches are considered within this review.

Current research interest in biodegradable polymers is connected with well-defined areas of use. Biodegradable plastics offer one solution to managing packaging waste. However, biomedical applications of biodegradable and biocompatible polymers generate an enormous amount of research and interest. Uses in this field range from wound dressings, drug delivery applications, surgical implants and other medical devices. There are also agricultural uses, e.g. for controlled release of fertilizers and pesticides, applications in the automotive industry and as surfactants.

As well as the uses of biodegradable polymers, this review will include sections on the chemical synthesis of polyesters, the microbial production of poly(hydroxyalkanoate)s (PHAs), blends of these biodegradable polymers, methods of characterization and structural analysis and, finally, recent research into the rates and mechanisms of the biodegradation of relevant polymeric materials. The latest published papers which have biomedical applications and relevant patents for the review are included as appendices.

2 USES OF BIODEGRADABLE POLYMERS

2.1 Biodegradable plastics for packaging

Synthetic polymers have become technologically significant since the 1940s and packaging is one industry that has been revolutionized by oil-based polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET) and poly(vinyl chloride) (PVC). Despite the major advances in the synthesis, manufacture and processing of these materials, two major problems still confront the industry: the use of non-renewable, oil-based chemicals for the manufacture of commodity polymers and the ultimate fate of the waste materials.

2.1.1 Plastic waste management. The need to confront the problem of recycling packaging material of all types is recognized by governments and the European Community Waste Management Legislation is the first attempt to unify the approach to the problem by all the member states. The targets from the EU directive are shown in Table 1.[3]

In the UK, overall recovery targets for all packaging waste have been set for each year (1998–2001) with the obligation from 2001 onwards of over 50% recovery, of which at least half must be met by recycling, and up to 16% of each material, e.g. plastics, must be recycled. It is estimated that 200 000 t of post-consumer plastic waste were recovered in 1997 by incineration for energy or by recycling; as the consumption of plastics for packaging in the UK is about 2×10^6 t year^{-1}, this represents only 10% recovery.

In the UK, Valuplast is the organization responsible for implementing industry's obligations under the new recycling legislation. The aim is to increase the annual recycling capacity from the current 100 000 to 300 000 t by 2001, with upwards of 500 000 t year^{-1} of post-use plastics being recycled by 2005. Many companies have registered with Valpak, an organization that has undertaken to manage their recycling responsibilities. The implications for raw material producers and converters as well as packagers and retailers is considerable and a review of the legislation seems inevitable.

'Plastics Recovery' examining data from 1995 is the most recent report available on plastic consumption and recovery in Western Europe.[4] It is produced by the Association of Plastics Manufacturers in Europe (APME) and this is the seventh year that data from manufacturers, trade associations, waste management organizations and government bodies have been analysed in this way. The UK is shown to be the fourth

TABLE 1. Targets for EC waste management legislation

1	By 30/6/2001, between 50% and 65% by weight of packaging waste will be recovered
2	Within this general target and within the same time limits, between 25% and 45% by weight of packaging materials in packaging waste will be recycled
3	Within 2 above, a minimum of 15% of each material must be recycled, e.g. plastic packaging

largest consumer of plastics in Western Europe, using $3·3 \times 10^6$ t in 1995 of the total $24·3 \times 10^6$ t demand (UK demand in 1997 was 4×10^6 t). The consumption of plastics for packaging between 1993 and 1995 remained at about 40% of the total. Despite the huge demand for plastics in this and other industries, polymers account for only 0·6% by weight of total waste. It has been estimated that plastics make up about 8% of municipal solid waste (MSW)[4] and this represents the ultimate fate of about 63% of all plastic waste. Removing plastics from packaging would create problems, not solve them, as a German study has estimated the dramatic increase in terms of weight and volume of using non-plastic packaging and also the additional energy consumption required.[5] However, total plastic waste in Europe in 1995 was estimated at 16×10^6 t and, because of its low density and hence large volume, it has considerable environmental impact. Table 2 shows the figures for different disposal methods.

The three main strategies available for the management of plastic waste are incineration, recycling and landfill. Over 25% of the 16×10^6 t of plastic waste was recovered in 1995 either as energy (~ 17%) or by recycling (>9%). Plastic waste disposal to landfill represented a 14% fall from the $13·3 \times 10^6$ t lost in 1994. Reviews of polymer waste management have been published by several authors.[6,7] The use of degradable plastics is, as yet, a minor factor in this overall strategy, but development of photo- and biodegradable polymers has considerable implications for medical, food and agricultural packaging.[8]

Incineration has the advantage that the plastics have high calorific value, but incineration plants have to be modified for efficient combustion of the polymers and regulation of the gas emissions to ensure that no toxic gases are released. Energy recovery through incineration is an essential part of an overall waste management scheme.

'In-house' recycling and interception of bulk waste at supermarkets, etc. are strategies that will have to be extended to meet the new British packaging regulations, which seek to double the amount of plastic packaging recycled by the year 2001, although a quadruple increase is more in line with EU targets. There are also emerging technologies for plastic feedstock recycling, which can take mixed plastic waste and turn it back into naphtha, monomers or other oil derivatives. A large-scale refinery-type operation is required to make these pyrolysis and hydrogenation procedures viable, but it is anticipated that the necessary economic climate will exist within the next 10 years.[9]

Some polymer manufacturers have their own recycling organizations, e.g. Petcore, the European PET container recycling organization. PET container collection for recycling in Europe has increased on average by 40% year-on-year from 13 000 t in 1991 to 86 000 t in 1997 although there has been a 10% annual growth in PET usage. However, the percentage increase in PET recycling in the UK was only 21% in 1997 and expected to be the same for 1998, because there is no funding mechanism to cover the cost of material collection as exists in other European countries. The new packaging legislation is bound to increase the UK totals, and recyclers are known to have excess capacity. However, the depressed price of virgin PET and all vinyl polymers makes it difficult for collectors and recyclers to run schemes profitably at the moment.

The non-statutory requirements given to local authorities by central government suggest a fivefold increase in materials collected from households in the next 4 years. Today about 40% of local authorities have packaging collection programmes, but it has been estimated that 80% of homes will have to participate in some form of kerbside collection by 2001. The two main challenges of plastic recycling are the separation and identification of the vast range of plastic items and the production of recycled material that has reproducible performance and is economically viable. The slight deterioration in the performance characteristics of a specific polymer only becomes significant after 5–8 cycles, but this closed loop recycling does not occur. Thus PET and PVC recyclates are used as fibres for thermal insulation (duvets, anoraks) and PS, PP and PE are reused for a range of office accessories, cassette cases, crates, pipes and refuse bags. Legislation prevents the use of recycled polymers in direct food contact packaging, and plastics with high technical specifications cannot be made from recyclates.

Plastic identification codes are one aid to separation that has been introduced, and mechanical sorting based on the specific gravity of the different polymers is well developed, although this will not effectively separate PVC and PET. Infrared technology is used to 'recognize' PVC from PET bottles, and both UV and surface dielectrics have been used to identify different polymers. Recently, Pira International has introduced a full-scale automated plant for the identification and separation of articles from mixed waste, using fluorescent tracers in

TABLE 2. European plastic waste disposal (1995)

Plastic fate	Amount (10^3 t)	%
Landfill	11354	70·7
Incineration without recovery	517	3·2
Waste exported from Western Europe for recovery	166	1·0
Energy recovery	2698	16·8
Feedstock recycling	99	0·6
Mechanical recycling	1222	7·6
Total	16056	100

various polymers which are then identified using ultraviolet light. Efficiencies of 95% have been achieved at sort speeds of six articles per second.

However, recycling from MSW is even more technically difficult and so far has proved uneconomic. Landfill sites are the main destination of plastic waste and the fate of even organic solids depends on the management of the site. The lack of air and water in the bulk of the material means that paper has been found intact even after 7 years. However, within these sites, temperatures up to 70°C can occur and anaerobic degradation can produce methane and other degradation products. Some bulk plastics undergo photochemical degradation, but most are not degraded.

Composting MSW has been attempted by some local authorities. This involves separating some of the landfill and, after preliminary screening, mechanically shredding the solid waste. The moisture content is then increased by the addition of sewage sludge and the mix is slowly agitated and aerated. After 5 days and screening, a large percentage of the material can be left to mature for use as compost. However, the plastic material is unchanged.

In the 1970s, work was started in the US and elsewhere to produce photodegradable and biodegradable plastics for the packaging industry. The requirements were:

(1) non-toxic materials with non-toxic degradation products that would not affect the drainage water from landfill sites;
(2) polymers with suitable mechanical properties for specific uses;
(3) economic viability;
(4) degradation control of the plastics via polymer modification;
(5) processability.

The source of these materials was of two main types: natural materials known to biodegrade and synthetic biodegradable polymers. Starch and cellulose are two natural materials that have been extensively investigated for use as packaging material and they have the added advantage of being renewable sources of polymeric material. The processability of the starch has been a major problem and the cellulose has to be significantly modified both to increase its biodegradability and to optimize its mechanical properties.

Poly(hydroxyalkanoate)s (PHAs), which are produced in plant cells and can be synthesized biochemically by fermentation, are another source of natural polymers. Poly(3-hydroxybutyrate) (PHB) and the copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) are produced commercially by Monsanto and sold as Biopol®. PHBV copolymers were first manufactured by ICI in 1983 (see Section 3)[10] and were originally intended as biodegradable substitutes for oil-based polyolefins in plastic containers, films and bottles.[11]

Their potential use was also seen for plastic items that could not easily be separated from other materials, e.g. nappies and sanitary towels. In 1990 the manufacture of blow-moulded bottles using Biopol for packaging shampoo was started in Germany by Wella AG, Darmstadt.[12] Hocking and Marchessault[13] have reviewed the actual and potential uses of PHB and PHBV for e.g. motor oil containers, film formation and paper-coating materials. The last two applications are based on biodegradable latex produced from PHAs with medium-length β-side chains.[14] The patents taken out over the last 10 years, which are summarized in Appendix II.1, give some indication of the range of possible uses.

Synthetic biodegradable poly(α-ester)s, e.g. poly(lactic acid) (PLA), poly(glycolic acid) (PGA) and copolymers of these, have been manufactured for biomedical uses since the 1970s. These and other polyesters known to biodegrade, e.g. poly(caprolactone) (PCL), have been investigated as packaging materials. In order to optimize the properties of all these biodegradable materials and reduce costs, different research strategies have been adopted. Block and statistical copolymers have been synthesized and blending studies have been carried out to obtain compatible mixtures of components which still biodegrade. The use of plasticizers to increase the flexibility of polymers and the use of fillers to reduce the cost are two advantages of the blending approach. A further bonus comes from components that are photo- or biodegradable and induce this behaviour in components that do not degrade as pure materials.

The main constraint on the use of biodegradable polymers for bulk packaging is the difference in the price of these polymers compared with that of bulk-produced, oil-based plastics. The current cost of Biopol® is approximately £8000 per tonne, compared with the current UK prices of commodity polymers of between £500 per tonne (PVC and PP) and £600 per tonne (HDPE and high-impact PS). Current low oil prices, increased recycling capacity and improved technologies for the separation of plastics and their reuse make the use of biodegradable polymers for most packaging requirements uneconomic.[9]

There are several problems besides cost associated with certain biodegradable polymers as packaging. PGA and PLA are highly susceptible to bulk hydrolysis, so this limits the range of contents for the packaging, and rigorous storage conditions must be used. Microbial polyesters are relatively resistant to chemical hydrolysis but are susceptible to bacteriological attack, which restricts their use as packing for foodstuff. However, PHBV has excellent gas barrier properties[15] and Scherzer[16] has recently reported the development of barrier layers against oxygen transmission using radiation-cured methacrylated gelatin. The layers showed extremely low oxygen permeability, high resistance against boiling water and good adhesion characteristics. It is postulated that, using substrate foils of

biodegradable polymers, the methacrylated gelatins would be suited as barrier adhesives in laminates for completely biodegradable food packaging.

Another recent paper by Suominen *et al.*[17] reports their investigation into the migration of microbes in food-packaging paper and board coated with PE, mineral pigment or a biodegradable polymer. Confocal laser-scanning microscopy was used to examine the spatial distribution of microscopically observable bacterial cells. The paper and paperboard studied were an efficient barrier against translocation of microbes and it was concluded that there was limited access to free water within the cellulose. However, there were relatively high concentrations of microbes residing between the paperboard and its polymer coating, which on the coating facing the food is a potential site for leakage into the food. The need for high-hygienic-quality surface-sizing chemicals was emphasized and mineral-coating pigments were found to be a source of microbes and thus to be discouraged.

The relative merits of the different methods of managing plastic waste materials are eventually related to cost and legislation. This paper will review the current situation in the development of biodegradable blends of materials for uses including packaging.

2.1.2 Use of renewable resources.
Renewable sources of polymeric materials offer an answer to maintaining sustainable development of economically and ecologically attractive technologies. The effect on the US economy of substituting production of corn-based polymer resins for petroleum-based polymers has been analysed by Beach *et al.*[18] and the use of agricultural materials and biomass has been reviewed by Mulhaupt.[19] Mulhaupt concluded that although Germany is at the forefront of green technology and a wide range of biodegradable pharmaceutical and novel surfactant materials can be made from renewable materials, it is only as components of packaging and as natural fibre composites that these materials are currently viable in terms of price and performance.

2.2 Biomedical uses

The most widely researched biodegradable polymers are the poly(α-ester)s (e.g. PLA, PGA) and the microbial poly(hydroxyalkanoate)s (e.g. P3HB, P3HV). These have been shown to be non-toxic and biocompatible both as polymers and as their degradation products, which in most cases occur naturally in the body. They have a range of pharmaceutical and biomedical uses based on these characteristics and their physicochemical properties.

The extremes of degradation rates between soluble macromolecules such as poly(vinyl alcohol) (PVA), which has a half-life of weight loss measured in hours, and the almost completely inert high-molecular-weight

homopolymers such as polystyrene are more correctly defined as a measure of hydrolytic attack. Biodegradation occurs through the action of or in association with living organisms and its measurement is based on standardized tests developed over the last 30 years. PLA and PGA, which are used as absorbable suture material, are hydrolysed *in vitro* and *in vivo* in days, while PHAs are broken down much more slowly. Holland[20] produced the hydrolysis data for these polymers using physiological conditions and on which Table 3 is based. The uses of these polymers would be extended considerably if a wider range of degradation profiles were available. PHAs have the most potential, because although their rate of abiotic hydrolysis is relatively slow, microbial hydrolysis is more rapid and can be manipulated by variations in processing techniques, molecular weight of the polymer, copolymer composition and blending.[21] Although there have been considerable advances in controlled synthesis, the chemical synthesis techniques for these polymers have not yet produced tailor-made biopolymers with the fine structure (e.g. chirality, monomer sequence, tacticity) necessary to match enzyme specificity in degradation reactions in different microbial environments.

2.2.1 Speciality packaging.
Speciality packing is potentially the largest use of biodegradable polymers. Polymeric materials and blends that have undergone toxicological and cytocompatibility testing for *in vivo* use and are biodegradable have obvious benefits as packaging materials for pharmaceutical products, drugs and wound dressings. The physiomechanical properties plus the gas and liquid barrier properties of these materials are obviously important, as is a knowledge of the conditions and rate of biodegradation. However, if processable biodegradable pure materials or blends could be manufactured, the economic imbalance between these materials and bulk-produced packaging materials would not be so great in this specialist packaging application.

2.2.2 Surgical fixation (*sutures, clips, bone pins and plates*).
The development of the uses of PGA, PLA and PGLAs for surgical fixation has been summarized by Holland and Tighe.[21] These materials have been used increasingly from the late 1960s as absorbable, synthetic sutures because they could be produced as strong filaments and were shown to degrade rapidly. The most widely used absorbable sutures are Dexon®, a multifilament PGA material, Vicryl®, a copolymer with composition PLLA (8%)-*co*-PGA (92%) and PDS®, poly(*p*-dioxanone).

The use of biodegradable implants for the fixation of fractured bones and joints has been reviewed by Hofmann[22] and contrasted with the use of metal pins and clips. About 40 different biodegradable polymers and copolymers are currently being used as alternatives

TABLE 3. Comparative weight loss for different biodegradable polymers, given as time for 10% weight loss at 37°C and pH 7·4

Polymer	t_{10} (h)
Vicryl® absorbable suture (PLLA (8%)-*co*-PGA (92%))	450 (18·8 days)
Dexon® (PGA suture material)	550 (22·9 days)
PDS® (poly(*p*-dioxanone) suture material)	1200 (50·0 days)
PHBV (20% HV) ($M_w = 3 \times 10^5$)	4·7%@5500 (229·1 days)
PHBV (12% HV) ($M_w = 3·5 \times 10^5$)	5·6%@5500 (229·1 days)
PHB (0% HV) ($M_w = 8 \times 10^5$)	18%@2500 (104·2 days)

to metal implants. The disadvantages of metal implants are cited as the need for 'stress protection', the sensitivity of patients to metals (particularly nickel) and the need for a removal operation. The use of self-reinforced PGA and polydioxanone, a polyester variation, as implants was also assessed and the main difficulties were listed as loss of stiffness in the material, in a time interval which is not long enough to guarantee bone healing, and the development of a sterile sinus over the implantation site. It is recognized that designs and assembling principles of metal implants in orthopaedic surgery cannot be directly transferred to biodegradable polymers. However, Hofmann states that these polymers can be used to treat osteochondral fractures and other defined injuries and a standard set of possible indicators for their use is given. Some specific examples

of their use are ligating clips and bone pins produced from Lactomer®, P(LLA/GA70/30), and from various polydioxanones and polyoxalates, and high-strength bone implants of PGA, PLA and PGLA. Tunc and co-workers[23,24] have published a series of papers on the use of an 'Orientrusion' process for realigning PLA molecules to create a strong matrix with a fivefold increase in tensile strength over unprocessed PLA.

PHBV has piezoelectric properties similar to those of natural bone.[25] Electric stimulation can be used to repair and strengthen bone and there is a potential use for reinforced PHB composites, with bone-matching mechanical properties, as fracture fixative plates. Theoretically, growth and healing of the bone can be stimulated as the polymer slowly degrades, with no need of a replacement operation. The most recent developments that have been reported on using biodegradable materials for surgical implants are summarized in Appendix I.1.

2.2.3 Controlled drug delivery. This is the most important and versatile application of these polymers. Controlled drug delivery has applications not only in medicine but also in veterinary and agrochemical fields. Active ingredients from pesticides to contraceptives can be delivered by sustained release with the ultimate biodegradation of the carrier medium.

Drug delivery profiles of the concentration of the drug in plasma against time can be used to compare traditional methods of drug delivery (oral, intravenous) and controlled release. Figure 1 is based on a figure from the review of Holland and Tighe[21] and illustrates typical drug delivery profiles, showing the advantages of controlled drug delivery.

The initial drug release systems involved incorporation of the active substance into a polymer matrix, which was implanted into the patient in various ways,
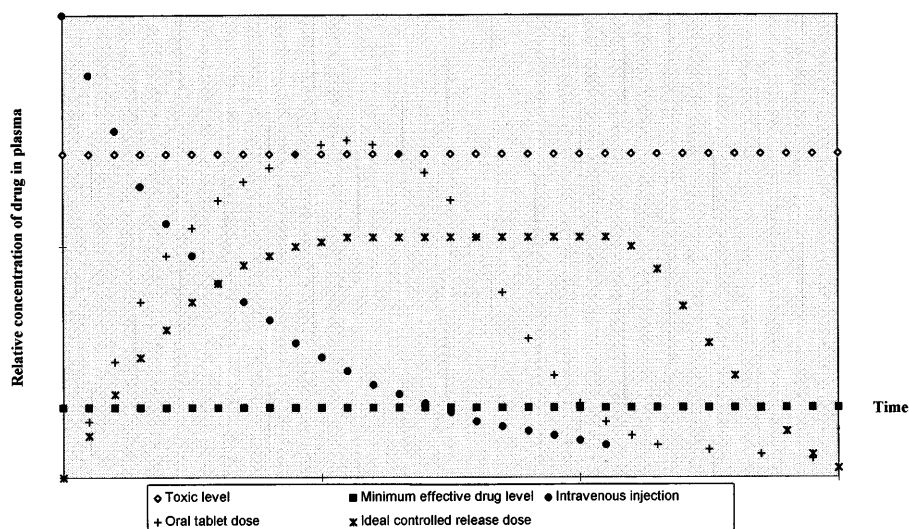
Fig. 1. Plasma–drug concentration profiles for various methods of administration.