

ENVIRONMENTALLY DEGRADABLE PLASTICS - PROSPECTIVES AND PROBLEMS

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SUMMARY

The perspectives of biodegradable plastics are discussed. The types of naturally occurring plastics as well as biodegradable synthetic plastics are shown; the advantages and drawbacks of the application of both are discussed. The possibilities and requirements are outlined for EPDs to be beneficial in plastics waste management. Polyhydroxybutyrate is discussed as a typical representative of biodegradable plastics; its advantages, drawbacks and the strategies for improvement are shown. Interesting phenomenon of extensive physical ageing is presented and discussed.

Keywords

Environmentally degradable plastics, renewable resources, standards, polyhydroxybutyrate, physical properties, physical ageing

1. INTRODUCTION

Biodegradable (BDPs) or in broader sense environmentally degradable plastics (EDPs) have been considered, synthesized, and tested in many laboratories all over the world. In the beginning, sometimes rather extreme opinions appeared in scientific community, from unrealistic expectations, suggesting that biodegradable plastics will be a final solution for the plastics waste in near future, up to scepticism claiming that it will never reach any significant application.

At present the expectations are much more realistic and the goals for EDPs can be seen in two directions : First, easy waste management after lifetime expiration is preferentially aimed, what needs a development of biodegradable plastics but not necessarily based on natural products. Another attitude is targeted to a production of plastics from natural, renewable resources, while biodegradability is advantageous but not necessary property.

2. DRIVERS FOR NEW MATERIALS / TECHNOLOGIES DEVELOPMENT

The time dependence of economic development is characterized typically by an S – shape curve, showing a slow acceptance of new technology or material by the market, followed by rapid expansion and growth and finally reaching the mature plateau phase [1]. Regarding plastics, three phases are observed, namely traditional materials, synthetic plastics, and environmentally friendly products which fit in a concept of sustainable development. The main features of the three groups of plastics are shown in Table 1.

Total carbon cycling can be taken as an important parameter indicating the general environmental acceptance of a material. The products should be CO₂ neutral, i.e. during the lifetime, including disposal, the total production of carbon dioxide should be the same as its consumption by formation of raw materials. Obviously, this condition is fulfilled if new materials are produced from biomass.

Table 1 Typical features for plastics materials of different age (according to [1]).

TRADITIONAL	SYNTHETIC	SUSTAINABLE
natural ingredients	cheap petroleum	renewable resources
labor-intensive	easy manufacture	energy efficient
attractive	low labor input	non-polluting
aesthetic	excellent functionality	recyclable or biodegradable
		tailored functionality

3. BIODEGRADABLE PLASTICS, OCCURRENCE AND STANDARDS

Many types of biodegradable plastics exist in nature, some of them are industrially important. Starch and cellulose may be given as examples. However, a broad substitution of synthetic plastics by natural products such as starch or cellulose is impossible, mainly because of unacceptable properties (e.g. brittleness and low water resistance) or difficult processing. Therefore the materials have to be modified physically or chemically and new technologies for processing have to be developed.

It has to be said that many products, which are claimed to be made of biodegradable plastics, are not really biodegradable. Companies, willing to demonstrate their “green” attitude toward environment, developed materials based on synthetic plastics filled with biodegradable fillers, especially starch. After biodecomposition of starch the material lost its mechanical properties and was mechanically easily destructed to small pieces or powder. Nevertheless this part does not undergo biodegradation. According to new standards (e.g. ASTM D 5338 or ISO 14 855) these materials cannot be claimed to be bio- or environmentally degradable, although they may be useful materials with applications in agriculture or elsewhere.

Biodegradable polymers are of various nature. The most important polymer groups with the examples of polymers are shown in Table 2

Table 2 The most important groups of environmentally degradable polymers

Naturally occurring
<ul style="list-style-type: none">• Polysaccharides : starch, cellulose, chitin/chitosan, pullulan, dextran• Proteins : Collagen / gelatin, casein, albumin, silk• Polyesters : Polyhydroxyalkanoates• Others : lignin, shellac, polyglutamic acid
Synthetic
<ul style="list-style-type: none">• Polylactic acid, polylactone• Poly(esters) : polycaprolactone, poly(amide-esters), poly(vinyl esters)• Poly(vinyl alcohol)• Polyanhydrides• Polyphosphazenes• Polyaspartic acid

Most of these materials are considered for certain applications and many research groups are involved in the R & D aimed to reveal the prospectives of the particular material. New biodegradable materials are searched and synthesized.

The main reason for relatively slow acceptance of EDPs consists in the fact that besides many obvious advantages, the materials suffer from several serious drawbacks which have to be dealt with before a significant part of plastics market can be overtaken by biodegradable plastic materials. The advantages and bottlenecks of EDPs are summarized in Table 3.

Table 3 Advantages and main problems related to high volume application of environmentally degradable plastics

ADVANTAGES

- CO₂ neutral, marginal impact on greenhouse effect
- Medium to long – term estimable prices
- High added value by using agricultural overproduction, revival of agriculture via industrial production
- Easy and conventional disposal by composting
- Almost unlimited raw material resources

BOTTLENECKS

- High prices due to high R&D cost and small production
 - Inferior properties compared to petrochemical plastics
 - Limited number of materials available
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At present, in spite of many problems, EDPs are starting to penetrate to the market. A number of companies are active in a production and processing of EDPs of different nature. These are large companies, where EDPs represent only small part of the total production (e.g. Solvay with production of caprolactone and polycaprolactone, BASF producing polyesters and polyaspartic acid) or small and medium enterprises producing special types or products in rather small quantities. Idroplast (polyvinyl-alcohol production), Biomer (polyhydroxy-alkanoates), Novamont (blends of polycaprolactone and starch), Biotec (extrudable starch materials) can be named just as few examples of European activities in the field. A number of companies are active in USA and Japan.

A production of polylactic acid by Cargil Dow should be mentioned, since with its present 20 kt production and 140 kt production unit ready to produce in near future it is the first really high volume production of biodegradable / renewable resources based industrially produced polymer.

4. MYTHS ABOUT BIODEGRADABLE PLASTICS

Two ideas, generally believed about EDPs should be cleared. First one is an opinion that BDPs will degrade anywhere and there is no need to care about plastic waste any more. This is completely wrong. The biodegradation of real EDPs starts only when it is placed in an appropriate environment, i.e. where bacteria can live and grow. Therefore even if the packages are made of EDPs, the waste has to be collected. The advantage is seen in much easier handling with collected plastics, since it is enough to deposit it in compostable conditions and the plastics will disappear within few weeks forming a compost suitable as fertilizer in agriculture.

Another incorrect idea is represented by a worry about a premature degradation before expiration of the service life. This is definitely not an issue. EDPs will not degrade unless they are attacked by bacteria in a proper warm and wet environment. If kept in dry environment where no extensive grow of bacteria can occur, EDPs will stay intact for almost as long as common synthetic plastics. EDPs will biodegrade rapidly only in specific conditions suitable for bacteria growth.

5. POLYHYDROXYBUTYRATE MODIFICATION, A CASE STUDY

Poly(3-hydroxybutyrate) (PHB) was chosen as an example to demonstrate the potential and problems connected with application of EDPs. PHB is the simplest member of the group of polyesters called polyhydroxy alcanoates (PHAs). PHAs comprise a group of biodegradable polyesters produced by bacteria. Their primary function is energy storage and they are used as an energy reserve for bacteria, similar to the role of polysaccharides or polyphosphates in living cells. PHAs can be produced by relative simple and efficient procedure based completely on biotechnology utilizing fully renewable resources. Among biodegradable plastics, PHB was considered to be a top favorite because of its excellent properties, similar to polypropylene, as seen in Table 4. A comparison with low-density

polyethylene is also shown, as a main competitor in packagings market.

Table 4 : A comparison of physical properties of PHB, polypropylene (PP), and low-density polyethylene (LDPE). Most data taken from [3].

	PHB	PP	LDPE
melting temperature, °C	175	176	110
glass transition temp., °C	4	-10	-30
crystallinity, %	60	50	50
density, g / cm ³	1,25	0,91	0,92
E modulus, MPa	3,5	1,5	0,2
tensile strength, MPa	40	38	10
elongation at break, %	5	400	600

Obviously, the properties of PHB are attractive enough to consider this polymer as a ecological plastics of the future. PHB is a completely biodegradable, highly hydrophobic thermo-plastics, containing almost 80 % crystallinity, with high melting temperature, resistant to organic solvents and possessing excellent mechanical strength and modulus resembling that of polypropylene [3]. In spite of excellent properties, especially strength parameters, an extensive application of this material in high volume range is hindered by several serious drawbacks so that at present PHB is used only exceptionally and in small quantities for special purposes. Very high brittleness, very low deformability (pronounced by an interesting phenomenon of extensive physical ageing), high susceptibility to a rapid thermal degradation, difficult processing by conventional thermoplastic technologies (mainly due to fast thermal degradation) and rather high price compared to other high volume plastics may be named as the major factors hindering a wider application of PHB. The factor of primary importance seems to be a low deformation at break, related to low film toughness and unacceptable rigidity and brittleness. The reason for the brittleness consists mainly in a presence of large crystals in the form of spherulites. Additional problems related to processing are connected mainly with low shear strength of the melt, which needs to be addressed if considering certain applications. All these problems are dealt with via either improving the biosynthetic routes of PHB production or modification of the material. Among the latters, blending with other biodegradable polymers, e.g. polycaprolactone or modification via crosslinking seems to be promising to get good properties. Mixing with inexpensive fillers is a way to reduce

the price, besides design of an efficient technology.

A very low resistance to thermal degradation seems to be a serious problem, too. Since the melting temperature of PHB is around 180 °C, the processing temperature should be at least 190 °C. At this temperature thermal degradation proceeds rapidly so that the acceptable residence time in the processing equipment is only few minutes. The principal mechanism was identified as hydrolysis under the high temperature conditions. However, free radical autoxidation process also occurs when aliphatic groups are present [4]. The phenomenon of an extensive physical ageing is an interesting feature of PHB behavior. It manifests itself in a substantial increase in E-modulus and tensile strength during storage. This effect is not accomplished in a short time period but can be observed over several months as demonstrated in Fig. 1.

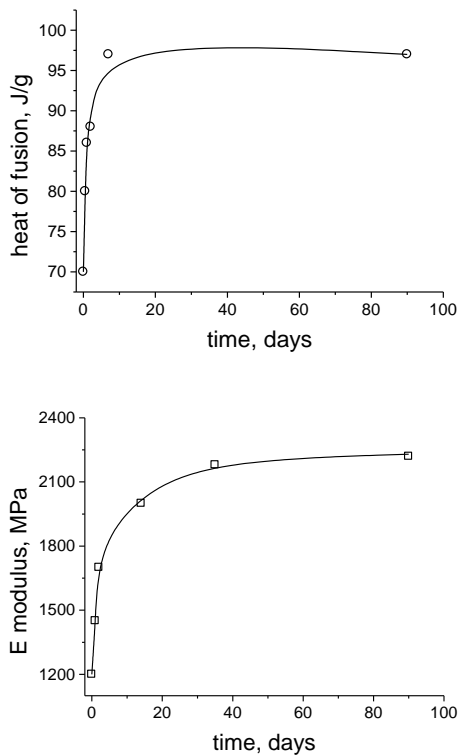


Fig. 1 Changes in heat of fusion and E-modulus of PHB due to the time of storing at room temperature.

The effect is generally ascribed to recrystallization leading to an increase in crystalline portion and consequently to the increase in E modulus and tensile or flexural

strength values. At the same time, a decrease in amorphous region results in a drop in ductility and enhanced brittleness of the material. However, as seen in Fig 1, the increase in crystallinity occurs much faster compared to the increase of stiffness, since the crystallinity, calculated from DSC heat of fusion, levels off after few days, when modulus has reached only about 70 % of its ultimate equilibrium value. This behavior, of course does not exclude the possibility of changing the crystalline structure while keeping the crystalline portion at the same level, but the extent of variation of strength indicates that some additional mechanism may be responsible for the phenomenon. A detailed study of the problem by de Koning et al [23] suggested a model explaining the process quantitatively. The model is based on a large specific crystalline–amorphous interface. Due to large interface area, subsequent crystal perfection during ageing results in a significant increase in a number of macromolecules in amorphous phase being under residual stress. Thus, relatively minor changes in the morphology of the crystalline part lead to much higher ageing effect compared to material with a lower crystalline–amorphous interface area, as is usual for the majority of synthetic polymers.

A detailed investigation of the ageing behavior of PHB containing 8 or 12 % of valerate as a comonomer has been described [24]. Both extruded and compression molded samples were investigated by DSC, DMTA, dielectric spectroscopy, and thermally stimulated discharge technique. Besides changes in the amorphous and crystalline phases, the authors considered the importance of the interphase region on the ageing process, consisting in relaxation above T_g due to morphological reorganization in the interphase [24]. This opinion is supported by fracture mechanics data indicating that the ageing process does not consist of a simple embrittlement but rather in a reduction of the energy dissipating properties of the material accompanied with the ability to survive high stress levels [6].

From this point of view, the changes in FTIR spectra of PHB during storage may be of interest. Two IR peaks have been found [25] to be sensitive to storage, namely 1685 cm^{-1} , and 3435 cm^{-1} , corresponding to carbonyl and hydroxyl stretch, respectively. Both peaks grow during storage with no leveling off after 14 days, indicating that some interactions between the functional groups of PHB may result from storage. It is not clear to what extent these interactions are related to the physical ageing.

Nevertheless, it is worth considering the importance of these effects in addition to changes in crystalline structure, especially in the interphase region.

Thus, both processing parameters and ultimate properties of PHB need to be modified if any application is considered. The main problem seems to be insufficient toughness, related to low deformability of the material. Various procedures have been tested to improve toughness. Among those, addition of plasticizers, cold rolling, solid state processing, crosslinking, and preparation of copolymers are those, which proved at least partial improvement. However, no final solution was found until now. The most promising procedure seems to be mixing with another biodegradable polymer. From this point of view, polyvinyl alcohol and polycaprolactone are of particular interest.

When dealing with polymer blends, the compatibility of the particular polymer pair is of primary importance regarding the ultimate properties. If the compatibility is insufficient, a compatibilization has to be achieved using compatibilizers. For the mixture of PHB and polycaprolactone, instead of addition of a compatibilizer, in situ compatibilization via cocrosslinking was tested. The deformation at break and consequently toughness could be substantially improved by such a way, as seen in Fig. 2. It is worth to mention that an increase in tensile strength is observed at medium degree of crosslinking.

It is believed that by combining several modes of PHB modification, the acceptable ultimate properties can be reached enabling the high volume application of the material, e.g. as packagings.

CONCLUSION

EDPs represent a viable option for plastic waste management since a simple composting can be used for substantial and fast reduction of the waste volume. EDPs must not be considered as a generally applicable remedy for dealing with plastic waste, but it is an alternative capable to take over a part of the market especially in packagings. In any case, collection cannot be avoided, while the availability of facilities for disposal (e.g. composting) is necessary condition for EDPs to be beneficial for environment.

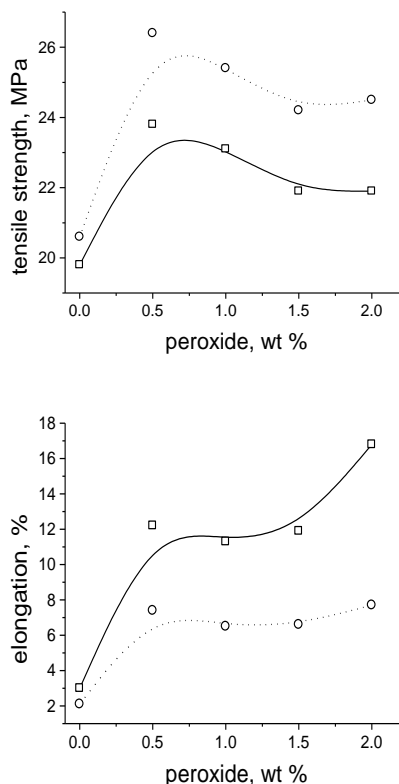


Fig. 6 The effect of crosslinking (degree given by content of decomposed peroxide) on mechanical properties of PHB / PCL blends. The effect of ageing is shown after 2 (full line) or 14 days (dashed line) after compression moulding.

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BIOGRAPHY

Ivan Chodák (59, PhD 1974, DSc 1997, associated professor 1999) is a senior scientist, Head of Department of Composite Thermoplastics at Polymer Institute of the Slovak Academy of Sciences in Bratislava. His scientific activities are aimed to the investigation of multiphase materials with thermoplastic matrix and the ways of tailoring the interface / interphase in polymer blends and composites by chemical modification initiated by free radicals. Main effort is aimed to biodegradable plastics and electroconductive polymeric materials.