

UDC 641.64:577.15.04

Biodegradable Synthetic Polymers

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(Received January 18, 2012; revised April 25, 2012)

Abstract

A brief review is presented concerning the methods for producing synthetic and composite polymer materials those can decompose under the influence of environmental factors. The advantage of these materials is demonstrated in comparison with the “classical” industrially produced petroleum-based polymers. Main ways and means are indicated to impart the biodegradable properties to polymeric materials.

Key words: biodegradation, polymer, biomass, polylactide, biodestruction, microorganisms, copolymer, polyester, polycondensation, compositions

INTRODUCTION

In connection with worsening the environmental situation all over the world, the term “biodegradable polymers” has become an integral part of the “green vocabulary”. Whereas earlier the idea of developing the synthetic polymers consisted in such a way as to obtain materials with a very high resistance with respect to environmental factors, today the urgent task consists in the development of polymeric materials those retain the properties only in the course of operation. Comprehensive solving the problem of environmental pollution by polymeric wastes (waste synthetic materials used as packaging and agricultural films, sanitation supplies, *etc.*) could be attained *via* making the polymers capable of undergoing the process of biodegradation [1–4]. From this standpoint, the development and industrial production of a wide range of biodegradable polymers is of particular urgency and relevance, which polymers could decompose under the influence of environmental factors to yield the components harmless with respect to the ani-

mate and inanimate nature, such as water, carbon dioxide, biomass, *etc.*

The biodegradation of a polymeric material could take place only when there are three main factors: corresponding environmental conditions, the presence of microorganisms those affect the polymeric material in a selective manner as well as certain chemical structure of the synthetic polymeric material. Otherwise this process cannot operate as an ecological idea.

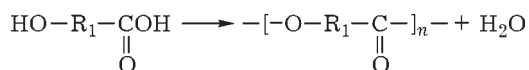
The analysis of data available from the literature allows one to distinguish two main directions of developing of scientific research and applied work in the field of synthesizing and mastering the biodegradable plastics such as synthetic (chemical and microbiological) of biodegradable polymers and biodegradable composites [5, 6].

BASIC METHODS FOR SYNTHESIZING BIODEGRADABLE POLYMERS

For the recent years, the production of biodegradable polyesters developed based on hydroxycarboxylic acids is under active develop-

ment, which is caused by decomposing them to produce CO_2 and H_2O due to the action of microorganisms [2–8, 10]. As early as in 1925 it was found that polyhydroxybutyric acid serves as a nutrient and a medium for storing various microorganisms. It should be noted that the researchers' interest is produced by statistical and block copolymers rather than by homopolymers. The synthesis of biodegradable polymers is carried out *via* polycondensation as well as *via* the polymerization of cyclic compounds and vinyl monomers.

The synthesis of biodegradable polyesters is carried *via* the homopolycondensation reaction of oxycarboxylic acids in the bulk of the reaction mixture in the presence of catalysts (Ti, Zn, Mn, Sb, Zr, Hf, and other metal compounds, *p*-toluenesulphonic acid):



$\text{R}_1 = -\text{CH}_2-; -\text{CH}(\text{CH}_3)- \dots$

as well as *via* the heteropolycondensation reaction between dicarboxylic acids and glycols (Scheme 1).

In the course of homopolycondensation reactions, mainly lactic and glycolic acids or a mixture thereof is used as a starting monomer for synthesizing biodegradable polyesters [11–13], whereas in the case of heteropolycondensation aliphatic dicarboxylic acids (succinic acid, azelaic acid, sebacic acid, tartaric acid) and various glycols are used [14–16].

One of the most promising biodegradable plastics used as packaging material is presented by polylactide, the condensation product of lactic acid [17, 18]. This is caused by the fact that lactide and polylactide derived synthetically or by enzymatic fermentation are renewable raw materials of biological origin. Polylactide represents a transparent, colourless thermoplastic polymer which is suitable for all the known methods of processing the thermoplastics. After an appropriate plasticizing, the polylactide acquires elasticity inherent in poly-

ethylene, polypropylene or plasticized polyvinyl chloride [19, 20]. Being in compost, the polylactide undergoes biodegradation for one month to be assimilated by sea water microbes [21, 22].

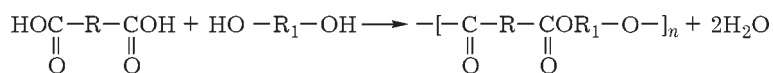
Despite the advantages, the polylactide is not widely used as a polymer for household and industrial purposes because of a low-productive technology of its obtaining and, as a consequence, a high cost of the product. In this regard, this time particular attention is focused on the development of high-productivity technological processes for obtaining biodegradable polymers as the most promising and environmentally safe materials [23, 24].

An active research work in this direction is under performing in the Cargill Company, Inc. (the USA) [25], where the production of biodegradable polymer Eco-Pla is mastered. The sheets of this material are comparable in the impact resistance to those of polystyrene, whereas coatings and films based on this material exhibit a high durability, transparency, gloss, an acceptable extrusion temperature (over 2000 °C) and a low coefficient of friction.

The Cargill Co., Inc. has also mastered the production of polylactide *via* the fermentation of corn dextrose with the productivity amounting up to 6 t/year. It is planned to increase the production up to 50–150 t/year and to reduce the cost of polylactide from 250 to 2.2 USD/kg. Japanese Mitsui Toatsu Chemical Inc. launched a pilot plant of one-stage process for obtaining the polylactide characterized by thermal stability and improved properties as to compare with the plastic obtained *via* a two-stage process. The material cost has amounted to 4.95 USD/kg [26].

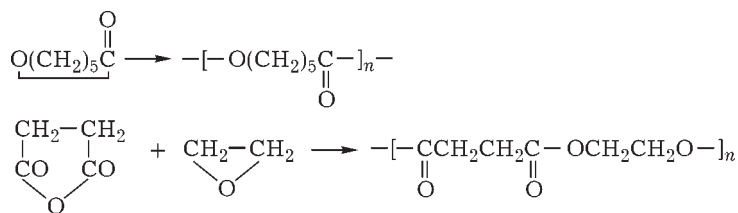
The development of the obtaining technology, the studies on physical and mechanical properties and the determination of the application areas of polylactide with the molecular mass ranging within 3000–10 000 is actively performed by the Negte Co. (Finland) [27].

Swiss DuPont Company is manufacturing hydro-biodegradable polyester whose cost price



where $\text{R} = \text{R}_1 = -\text{CH}_2-\text{CH}_2-; -(\text{CH}_2)_4-$

Scheme 1.



Scheme 2.

is slightly higher in comparison with the "petroleum" analog thereof.

Alongside with studying the polymers obtained basing on individual hydroxycarboxylic acids or their copolymers those exhibits guaranteed biological degradability, investigations are performed concerning polyhydroxycarboxylic acids in combination with various synthetic products [28, 29] and naturally occurring polymers as the initiators of biological degradability. This should provide the biological degradability and high physical and mechanical properties of the product, as well as reducing the cost thereof.

Another widely used method for the obtaining of biodegradable polyesters consists in the polymerization of cyclic compounds (lactides, lactones, cyclic anhydrides) with cyclic ethers in solution in the presence of Sn, Zn, La, K, Me, and other metal compounds. The synthesis of polyester by the example of caprolactone polymerization or a copolymerization reaction between succinic anhydride and ethylene is presented in Scheme 2.

For the synthesis of biodegradable polymers according to the above mentioned schemes, different cyclic compounds are used such as caprolactone, 3-butyrolactone, *L* and *D* isomers of lactide, propiolactone, or various mixtures

thereof, the mixtures of succinic anhydride with ethylene oxide and diepoxide [30–34].

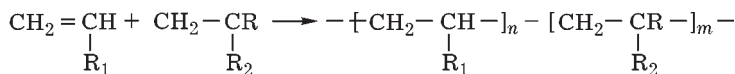
The reactions of ring-opening polymerization and lactide reesterification with aromatic polyesters based on isophthalic acid and aliphatic diols are used for the synthesis of biodegradable copolyester with a good moldability that can be applied for producing films and sheets.

The synthesis of biodegradable polymers containing ester groups in the side chains of macromolecules is carried out also *via* the copolymerization of vinyl monomers in the presence of initiators in the solution, emulsion or suspension. So, the copolymerization reaction between ethylene and vinyl acetate results in enhancing the biological degradability of polyethylene [35].

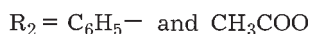
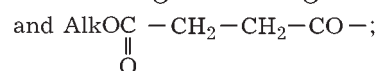
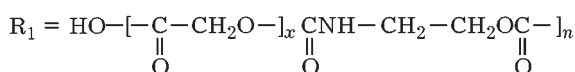
In general, the process of the copolymerization of vinyl monomers with the formation of biodegradable polyesters is presented in Scheme 3.

According to experts' judgments, there are the two materials most attractive from the economic standpoint. They are polylactic acid and aliphatic (aromatic) copolyester. According to the evaluations, within the coming years the use of biodegradable polyester only should exhibit a 70 % increase.

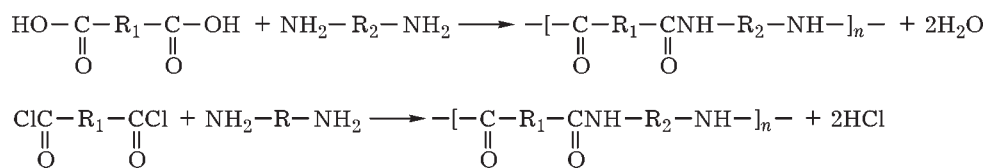
The next most well studied type of biodegradable polymers is presented by aliphatic polycaproadamides. Enhancing the biological de-



where R = CH₃— and H;



Scheme 3.



Scheme 4.

gradability of these compounds is provided either by the synthesis of copolyamides or by the obtaining of polymers based on α -amino acids. The synthesis of biodegradable polycapromides is performed *via* the reactions of low temperature polycondensation in solution or the reaction of high-temperature condensation in the bulk using different α -amino acids, diamines, dicarboxylic acids or derivatives thereof as a monomer [36–39] (Scheme 4).

Polycapromides based on benzylmalonic acid and hexamethylene diamine, polyene amino amides based on diketene and aliphatic diamines are characterized by a sufficiently high biological degradability [40, 41].

At the present time, there are two chemical giants such as companies BASF and BAYER AG those are actively working in the field of obtaining biodegradable synthetic polyester-based and polyester amide-based plastics [42, 43]. The BASF Co. as early as in 1995 had mastered the production of biodegradable plastic Ecofeek F based on polyester obtained *via* the condensation of aliphatic diols with organic dicarboxylic acids [44, 45]. This material is used for packaging foams.

The BAYER AG Co. basing on polyesteramide produces thermoplastics WAC-1095 and WAC-2195 biodegradable under aerobic conditions since the second half of the 90ths of the last century [46, 47]. Sacks mad of WAC-1095 used as water- and weatherproof packaging can be decomposed in compost under appropriate moistening within 10 days to yield biomass, carbon dioxide and water. Aliphatic polyesteramide WAC-2195 is recommended for the manufacture of flower vases and baskets, disposable utensils, hygiene items. These items after using can be rapidly degraded under the action of bacteria, fungi and mold within the ground in a wet environment [48].

A polyester film with the structure similar to polybutylene succinate, and the properties

close to those of films made of polyethylene or polypropylene was developed by Korean Sun Kyong Ind. Co. [49]. Skyprene polymer film made of the material with the mentioned composition exhibits degradation within 60 days in soil, fresh water or seawater.

A relatively novel direction in obtaining biodegradable polyesters is presented by microbiological method. The world's first biodegradable polymer Biopol was obtained in 1995 by the Zeneca Bioproducts PLC (UK) on the basis of 3-hydroxybutyric and 3-hydroxyvaleric acid in the course of the fermentation of polysaccharides under the action of bacteria *Alcaligenes eutrophys* [50–52].

The Biopol represents a thermoplastic which can be easily processed *via* blow molding, extrusion, and other traditional methods. The products made of this polymer within just a few weeks are decomposed by soil microorganisms to form CO_2 and H_2O .

WAYS TO OBTAIN COMPOSITE BIODEGRADABLE MATERIALS

Composite biodegradable materials represent a non-degradable polymer with special additives those are either can undergo biodegradation either themselves, or provide enhancing the destruction of the polymer under the influence of water, light and heat.

One of the most widely used methods for making biodegradable materials consists in imparting the biological degradability to synthetic polymers *via* introducing different filling agents into the polymer composition. At the same time, priority role is played by the ratio between the components which provides the system to be biologically degradable. In order to make biodegradable compositions consisting of synthetic and natural polymers, the natural polymer used is commonly presented by starch, whereas in

recent years it is presented by chitosan, a natural product of the alkaline hydrolysis of a nitrogen-containing polysaccharide such as chitin [52, 53]. The renewable resources of these waste products of plants (corn, rice, potatoes, etc.) and animal organisms (crustacean shells, covering tissue of arthropods, etc.) are vast.

The synthetic polymer in the structure of biodegradable composite materials determines the basic performance attributes of the material, whereas the natural polymer determines the ability of the material to biodegrade when buried in the soil or aquatic environment. Typically, in the course of making biodegradable compositions, as much as 20–30 mass % of a natural polymer is introduced as a filling agent or modifier.

The authors of [54–57] described the thermodynamics of the compatibility of components in the composite mixtures containing natural starch, amylose, methylcellulose, chitosan as a naturally occurring component of, synthetic polymers such as ternary copolyamide in formic acid, a copolymer of ethylene and vinyl acetate in chloroform or polyethylene oxide. It was demonstrated that in order to provide the compatibility of the components in the composition, there should be preferably introduced 10–30 mass % of polysaccharide matrix into the matrix of a synthetic polymer. The mentioned amount of a biodegradable component is sufficient for the efficient biodegradation of the systems obtained. There appeared that the composite mixtures based on ethylene vinyl acetate copolymer (EVAC-2.5) as well as on starch are the most reactive in the biodegradation process [58, 59].

Low copolyamide content in the copolyamide-chitosan system is thermodynamically favoured, whereas the introduction of small amounts of rigid-chain chitosan, on the contrary, is accompanied by an endothermic effect. This could be connected, to all appearance, with the energy required for the destruction of partially crystalline copolyamide structure when introduced to the amorphous (according to XRD data) chitosan [60, 61].

By the example of biodegradable systems based on crystalline polyethylene oxide (PEO) with different molecular mass and polysaccharides such as starch and chitosan those differ in the chain skeleton configuration (α - and β -configurations of 1,4-*D*-polyglucans, respectively) an effect exerted by the natural component

skeleton structure/configuration on the thermodynamics of mixing the substances [62–64]. It was demonstrated that polysaccharides have a significant impact on the sample of PEO with lower molecular mass, which promotes decreasing the melting point over a wide range of the compositions. At the same time, the melting point for of high molecular mass polymeric samples demonstrates only a 3–5 °C decrease.

The effect of starch in all the cases is exhibited in a wide range of compositions, whereas chitosan forms a compatible system only when the content thereof is small (10 %). This difference could be explained both by the formation of interchain hydrogen bonds such as OH–O in the system of starch-PEO, those are energetically more favourable as to compare with the NH₂–O hydrogen bonds in the system of chitosan-PEO, and by α -1,4-*D* configuration of the starch polymeric chain, favourably influencing the mixing of the components under investigation involved in the biodegradable compositions [65, 66].

A biodegradable composite material based on polyethylene was obtained by a joint introduction of modifying additives, inhomogeneous surface-active substances, in particular (20 OC-20) and lauryl-myristyl-7 (ALM-7), to the starch (made of maize and rice). It was demonstrated that the introduction of the mentioned substances in the PE-starch system causes increasing the ability of the composition with respect to the processing with improving the technological properties and biological degradability of the materials based on them [67–69].

On the basis of biodegradable compositions those contain polyesters of hydroxycarboxylic acids and starch one uses to obtain packaging materials [70, 71]. In particular, using the mixture of polyoxyalkylene glycol and starch esters results in obtaining resistant biodegradable polymers wherein the polyethylene glycol part is replaced by polyoxybutyrate with the molecular mass ranging within 1000–10 000 [72].

The hydrophilic composition based on destructed starch impregnated with a copolymer of ethylene with vinyl alcohol and aliphatic polyesters serves as a raw material for biodegradable diapers, sanitary pads [73].

At the Czech Fatra JSC there have been an Ecofol packaging film developed on the basis

of starch with polyolefin, which film decomposes in the course of composting for 3–4 months [74].

In the course of preparing biodegradable composite thermoplastic systems one uses, also other polysaccharides as natural components such as cellulose and chitin, cellulose and starch [75, 76]. The polymers obtained *via* the reaction between cellulose and an epoxy compound as well as dicarboxylic acid anhydrides, can be completely decomposed in compost for 4 weeks [77]. By means of forming the polymers, disposable utensils, bottles are made.

Particular developers' attention is attracted by the compositions containing chitosan and cellulose [78]. Biodegradable plastics and films containing 10–20 % of chitosan exhibit a good strength and water resistance; the thin film are degraded in soil for two months.

The application of natural polymers such as polysaccharides and proteins to create biodegradable materials is attractive first of all by the fact that the resources thereof are unlimited and constantly renewable.

An important role in scientific research concerning the creation of synthetic biodegradable compositions is played by the problem of imparting the biodegradation properties to commercial polymers produced on industrial scale such as polystyrene, polyethylene, polyvinyl chloride, *etc.*

For the last time, biodegradable compositions are under an active development containing the polyester/polyamide [79–81], urethane [82, 83], carbonate [84] groups, and, in particular, the fragments of hydroxycarboxylic acids [85]. Basing on these polymers one could obtain a wide range of biodegradable materials [86, 87] with useful physical and mechanical properties.

Introducing into the macrochain structure the molecules which contain functional groups those promote photodegradation provides polymeric material to be biodegradable. Such photodegradable polymers comprise copolymers obtained from the reaction between ethylene and carbon monoxide [88]. A photo initiator of the decomposition of polyethylene or polystyrene is presented by vinylketone monomers [89]. Introducing the mentioned substances as a comonomer to the macrochain in the amount of 2.5 % allows one to obtain plastics with the properties to similar polyethylene or polysty-

rene, however capable of decomposing under the action of ultraviolet radiation within the wavelength range of 290–320 nm.

Biodegradable polyolefin films can be obtained *via* introducing photosensitive additives in to the composition, such as ferrous and nickel dithiocarbamates [90] or corresponding peroxides [91].

In order to accelerate the photo- and biodegradation of the films based on polyethylene, polypropylene or polyethylene terephthalate the films are introduced with cellulose, alkylketones or fragments containing carbonyl groups [91–93].

The ability of the polymers to degrade and to be assimilated by microorganisms depends on several structural features, in particular on their chemical nature, molecular mass, the branching level of the macrochains and supramolecular polymer structure.

Synthetic polymers, as naturally occurring ones contain chemical bonds those could easily hydrolyzed and exhibit thus a high biological degradability level. Furthermore, the presence of substituents and side groups in the polymer macrochain often improves the biological degradability. The substitution level, the length of macrochain sites between functional groups, the flexibility of macromolecules also play a decisive role in the biological degradability of polymers.

The resistance of a polymer with respect to biodegradation is determined to a considerable extent by the size of the molecules thereof. Under the conditions when the monomers or oligomers could be affected by microorganisms, the polymers with high molecular mass appear to be more resistant with respect to biodegradation. In this case, the biodegradation of the most part of engineering polymers should be usually initiated by non-biological processes (thermal, photo-oxidation, and pyrolysis) or the polymers should be subjected to mechanical degradation. As the result, the molecular mass of the polymer is decreased to form low-molecular fragments with hydroxyl, carboxyl or carbonyl terminal groups prone to biological assimilation.

The biodegradation is also affected to a considerable extent by the molecular structure of synthetic polymers. The compact arrangement of the structural fragments of semicrystalline and crystalline polymers restricts the swelling thereof in water to prevent the penetration of enzymes in the polymeric matrix

and thereby hinders the biodegradation of macrochain [94].

The biological destruction of polymeric materials is mainly connected with the chemical composition, structure and properties of macromolecules. However, the resistivity of the polymers of the packaging destination with respect to biological degradability is to a great extent influenced by macrostructural characteristics such as porosity, the uniformity of additive distribution in the polymeric mixture, the features of product surface treatment and the technological parameters of manufacturing the material and the material processing into packaging.

A promising direction could be considered to consist in the use of nanomaterials based on biodegradable polymers and nanogammas those have better mechanical and thermal properties, which provides them to decompose faster at the expense of reducing the degree of the polymer crystallinity. In the course of the degradation the macromolecules first of all decompose to give smaller fragments (oligomers) those further are processed by bacteria.

Intense efforts are undertaken in order to develop and study the polymers those can decompose immediately under the action of microorganisms or suffer from rapid erosion in the environment followed by the further degradation due to microorganisms. In developed countries, the most part of disposable packaging materials is made of biodegradable matter. An example of one of these biodegradable polymers used could be presented by biosynthetic copolymer Biopol (ICI Co. Ltd., UK), polyhydroxybutyrate or polyhydroxyvalerate those completely meet the requirements for once or twice used packaging which can be easily decomposed within the range of 6–36 weeks under the action of biological factors under aerobic conditions or in anaerobic media (in the fields of irrigation or in water). Another example of a biodegradable polymer based on hydroxycarboxylic acids or lactide thereof could be presented by polymer Novon (Wamer-Lambert Co., the USA) that undergoes decomposition in the presence of moisture in the air as well as under anaerobic conditions.

It should be also mentioned that there is a packing material of a biodegradable polymer Biocell (France) created on the basis of cellulose

acetate, with the introduction of various additives and plasticizers which promote the decomposition of the material under the influence of environmental factors, including the solar radiation. When immersed in water, the material swells and could be decomposed by 40 % after 6 months, whereas the total decomposition thereof should happen during 18 months under the action of soil microorganisms.

The biodegradable material Mater-Bi (Italy) consists of a base polymer polyamide-6 (6.6), different additives of natural origin (60–90 %) and non-toxic biodegradable synthetic oligomers. The packaging made of this material can be almost completely decomposed without harming the environment. Basing on the Mater-Bi and non-toxic polyacetal, there are several compositions developed, too.

The Japanese Showa Corp. has developed a biodegradable organic polymer which exhibits high values of heat resistance, strength and elasticity; the material is able to be degraded in water and under the action of subsurface soil bacteria [95]. This material is proposed to use for the manufacture of outer casings of for TV sets and personal computers.

CONCLUSION

Despite the variety of biodegradable materials, the production and consumption thereof do not yet allow completely solving the problems of environmental pollution by spent and waste polymeric package. This is caused by the complexity of controlling the decomposition rate of the material in landfills under the influence of environmental factors, by a high cost of additives introduced, by the technological difficulties of production, etc. In this connection, great hopes are rested upon the developers of chemical technologies aimed at solving the mentioned problems.

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