

Biodegradable Polymer Composites Based on Synthetic and Natural Polymers of Various Classes

S. Z. Rogovina

Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow, 119991 Russia

e-mail: s.rogovina@mail.ru

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Abstract—The state-of-the-art in the field of polymeric materials that can degrade under environmental conditions into environmentally harmless compounds is reviewed. It is shown that the most efficient method for the production of such materials involves the creation of composites based on synthetic and natural polymers, in particular polysaccharides. Studies performed at the Semenov Institute of Chemical Physics, Russian Academy of Sciences, have demonstrated that biodegradable composites consisting of various polysaccharides with LDPE and polylactide may be obtained by an ecologically pure solid-phase method under the action of high-temperature shear deformation.

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INTRODUCTION

The constantly increasing environmental pollution by solid industrial and domestic wastes, mainly polymeric materials, is primarily connected with the continuous rise in the amount and types of articles based on various synthetic polymers; moreover, this trend will intensify in the 21st century. This circumstance and the necessity to gradually replace synthetic polymers derived from oil require the elaboration of effective methods for their processing and utilization, including the creation of polymeric materials that biodegrade under environmental conditions into environmentally harmless compounds [1–8]. Biodegradable polymers are usually split into two classes: natural polymers (e.g., polysaccharides) and synthetic biopolymers (polylactide, polyhydroxyalkanoates) obtained from natural monomers.

Today, there are three main directions in the design of biodegradable polymeric materials [9]: (i) synthesis of biodegradable polyesters of hydrocarboxylic acids, (ii) introduction of molecules carrying functional groups that promote the accelerated photodegradation into biodegradable polymers [10, 11]; and (iii) production of composites based on large-tonnage synthetic polymers and natural polymers.

Synthetic biodegradable polymers obtained from natural polymers chemically (polylactides) or micro-biologically (polyhydroxyalkanoates) feature high mechanical characteristics, but they are expensive. Therefore, they are less competitive than synthetic polymers. Even if their costs are comparable, synthetic polymers, especially polyolefins, will take leading positions in the production of plastics for a long time.

At present, one of the most promising biodegradable polymers is polylactide. This is a linear aliphatic polyester obtained by the polymerization of lactic acid that is formed during the fermentation of natural products (corn, sugar beets, potatoes, etc.) [12–17]. At the same time, the production of polyhydroxyalkanoates, that is, polymers based on hydroxycarboxylic acids (poly(3-hydroxybutyrate), copolyesters of 3-hydroxybutyrate and 3-hydroxyvalerate, etc.), which are set of biopolymers synthesized by different bacteria, has been actively developed in recent years [18].

Among photodegradable polymers are the copolymers of ethylene and carbon monoxide [19]. The photoinitiators of PE or PS decomposition are vinyl ketone monomers, whose introduction as comonomers of ethylene or styrene in an amount of 2–5% makes it possible to obtain plastics that have properties close to the properties of these polymers, but are photodegradable under UV light [20]. In addition, light-sensitive additives, such as iron and nickel dithiocarbamates [21] or the corresponding peroxides [22], are introduced into polyolefins.

BIODEGRADABLE COMPOSITES BASED ON POLYSACCHARIDES AND SYNTHETIC POLYMERS

Despite the active development of the two first directions, the most effective and economically profitable trend today is related to the design of composites based on synthetic large-tonnage polymers and natural polymers that serve as a nutrient medium for microorganisms initiating degradation of polymers under the action of the environment followed by for-

mation of environmentally harmless compounds (carbon dioxide and water). According to the predictions of IBAW analysts, in 2016, the output of biodegradable polymers will achieve \$4.14 billion, which corresponds to 714 thousand tons, and by 2020, the production of biodegradable plastics will be as high as \$38 billion [23]. Therefore, the development of new polymer composites degradable under environmental conditions, the improvement of the existing manufacturing procedures, and the elaboration of modern methods for analyzing the performance properties of the related materials have become important issues. In the creation of such composites, polysaccharides (cellulose; starch; chitin; and its deacetylated derivative, chitosan), which easily degrade under natural conditions under the action of microorganisms and natural-climatic factors (such as light, atmospheric oxygen, moisture, aggressive media, etc.), are constantly reproduced, and are an almost inexhaustible raw material, are of particular interest among natural polymers. Thus, the interest of researchers in composites based on natural polysaccharides is caused not only by their low cost but also by their availability and their biodegradability after their lifetimes.

Synthetic polymers have high mechanical characteristics, but are stable against the action of microorganisms, while the main disadvantage of polysaccharides that restricts their application is their high degradation rate and low mechanical characteristics, especially in the wet state, because of the hydrophilicity of their macromolecules. The production of blends based on these polymers is a simple and inexpensive method of their modification. The properties of blends (thermal, sorptive, strength) are determined by the type of bonds between components, their compatibility, and the character of the formed supramolecular structure.

The biodegradable composite materials based on synthetic and natural polymers have, as a rule, lower mechanical characteristics than those of the synthetic polymers. This situation has two main causes. The first is the incompatibility of polymer components that is related to the hydrophobic nature of a synthetic polymer matrix and the hydrophilic nature of a natural polymer. Their limited interaction generally leads to the formation of composites with worsened mechanical characteristics due to the ineffective stress distribution between the components. The second cause, which is related to the absorption of water by hydrophilic natural polymers, likewise promotes the deterioration of mechanical properties.

Polymer blends are usually produced by two main methods: mixing of components in softened or molten states and mixing of component solutions. The complexity of polysaccharide-based-material production is connected with the inability of polysaccharides to transform without decomposition into the viscoelastic state, where synthetic polymers are usually processed.

In this context, a promising method for production of polysaccharide-based blends is the solid-phase mixing of polymers under the high-temperature joint action of pressure and shear deformations, which makes it possible to obtain composites with more uniform component distributions than those attained by traditional methods. This method, which was developed at the Semenov Institute of Chemical Physics, Russian Academy of Sciences, is based on the work of Academician N.S. Enikolopov et al. [24–26]. It was shown that, at a certain combination of shear stress and temperature and with the use of a particular mixer, some polymers can transform into fine powders without any dispersers. It was assumed that, under the joint action of high pressure and shear deformation, the elastic energy accumulated in the solid polymer is released to form microcracks and leads to development of a new surface. The solid-phase mixing of polymers is usually performed in either single-screw or twin-screw extruders or in a Brabender mixer, where the above-mentioned principle (the joint action of high pressure and shear deformation on a material) is implemented.

The first biodegradable polymer composites with a natural polysaccharide as a biodegradable component were starch-based composites developed in the 1970s–1980s [27–30]. Nowadays starch remains the most-used polysaccharide in the creation of biodegradable packaging materials [31–38]. Along with the design of composites based on starch [39–41], a lot of companies use starch to produce materials for various applications. For example, Biotec GmbH obtained the molding bioplast in the form of granules to mold single-application articles and to produce compostable films and foam-materials for food packaging. High ecological compatibility and degradability in compost at 30°C for 2 months, accompanied by the formation of nontoxic degradation products, make it promising to use such materials in the household. Foam sheets and disposable ware are obtained from a composite consisting of granulated starch and aqueous solution of PVA [42]. Such composites degrade in soil for a week. Biodegradable diapers that well absorb liquids are manufactured from a hydrophilic composite consisting of destructed starch impregnated with a copolymer of ethylene with vinyl alcohol and aliphatic polyesters [43–45], while the films possessing high strength and preserving their properties at a temperature of 50°C for 3 months are used for mulching and as packaging materials.

Cellulose is the most widespread polysaccharide in nature; therefore, a lot of studies are dedicated to the investigation of composites based on this natural polymer. Because cellulose bears high-polarity hydroxyl groups, it can interact with synthetic polymers capable of forming hydrogen bonds, such as polyamides, polyesters, and many other vinyl polymers. The blends obtained from cellulose and the mentioned polymers must be compatible; however, other factors, for example, their tendency toward self-association, hindering

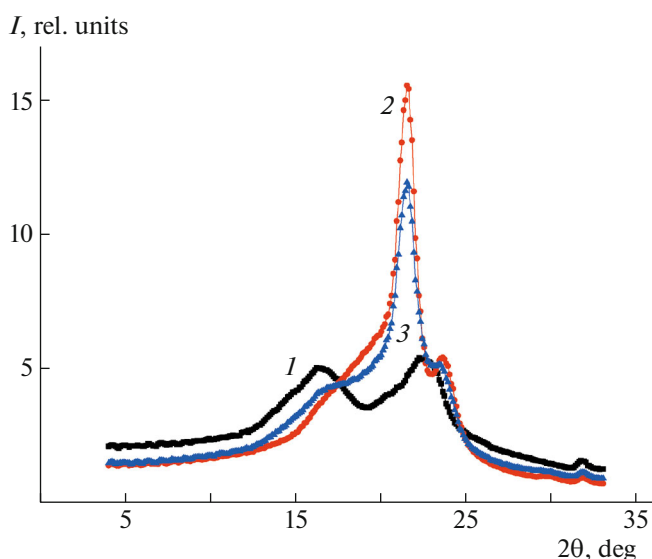


Fig. 1. X-Ray diffraction patterns of (1) cellulose, (2) LDPE, and (3) a cellulose–LDPE blend (30 : 70 wt %) obtained by mixing under high-temperature shear deformation.

the interaction of cellulose with a polymer, may be operative. The main problem arising during the creation of cellulose-based blends is related to selection of an appropriate solvent that can dissolve quite fast both cellulose and the second polymer. The blends of cellulose with PMMA [46, 47] and PVA [48] are of interest for practice. As was shown in [49], the composites formed by the interaction of cellulose hydroxyl groups with epoxy compounds and dicarboxylic acid anhydrides completely biodegrade in compost over four weeks. Bottles, disposable wares, and films for mulching are produced from them. Multilayered materials for food packaging that can be used in a wide temperature range are obtained from a cellulose film glued with starch and oil-resistant paper [50]. Many articles intended for various applications are molded from the composites of cellulose ester, aliphatic polyester, and microcrystalline cellulose [51]. Note that biodegradable plastics are produced not only from cellulose but also from lignin and lignin-containing compounds in combination with protein and other additives [52].

In recent years, the increasing interest in chitin and chitosan promoted the appearance of a large quantity of publications devoted to these natural polymers. The physicochemical characteristics of these polymers are relatively poor; therefore, it is important to obtain composites on their basis with the use of various methods. For example, the blends of chitosan as a filler with PA-6 were prepared by the method of polycondensation filling [53], and the blends with an epoxy resin, where chitosan serves as a curing agent due to the presence of amine groups, were prepared by cold and hot curing method [54]. The composites based on chitin and chitosan are most often manufactured as films

cast from solutions in a common solvent. It is natural that chitosan is easily mixed with water-soluble polymers, for example, PVA [55–58]. Such composites are used, in particular, to administer antibiotics into the stomach.

Because of biocompatibility with human tissues, low toxicity, the ability to amplify the regenerative processes during wound healing, and biodegradability, chitosan has found wide use in the manufacture of articles and medical preparations. The use of rigid-chain chitosan, which can form intermolecular ion–ion and ion–dipole bonds owing to the presence of ionogenic groups, as a component of the interpolymer complex provides improvement of the physicochemical properties of the films. These films can be successfully applied for pervaporation separation of aqueous–organic mixtures. For example, films based on the interpolymer complex chitosan–polyacrylic acid used for the pervaporation separation of an aqueous–isopropanol mixture are as good as the films based on traditional materials (cellulose acetate, PVA) in terms of transport characteristics and noticeably surpass them in selectivity [59, 60].

Depending on processing methods, the biodegradability of chitosan films changes significantly. The films based on acylated chitosan decompose in the medium of aerobic town compost faster than cellophane- or poly(hydroxybutyrate valerate)-based films [61].

Similar chemical structures and architectures of cellulose and chitosan make it possible to obtain homogeneous blends combining the unique properties of chitosan with the accessibility of cellulose. One of the promising directions of their combined practical application is the reprocessing of these polymer blends into films that exhibit not only high strength characteristics but also good biocompatibility, biodegradability, and hydrophilicity as well as high strength and water resistance at a chitosan content of 10–20%; they degrade in soil within 2 months [62]. On the basis of chitosan–microcellulose fiber–gelatin ternary composites, films with increased strength that degrade under the action of microorganisms during exposure in soil were prepared [63].

The production of blends based on polysaccharides in the solid phase makes it possible to avoid the use of solvents; as a result, the process becomes ecologically pure. Powder biodegradable composites of LDPE and some polysaccharides (cellulose, starch, chitin, chitosan, and ethyl cellulose) containing 20–50 wt % polysaccharide were obtained at the Semenov Institute of Chemical Physics, Russian Academy of Sciences, under the action of high-temperature shear deformation by the solid-phase method [64–68]. The polysaccharide was uniformly distributed in the synthetic polymer matrix in these composites, in contrast to the traditional mixing method, when polysaccharide occurs in the form of agglomerates and gathers in

Table 1. Effect of the compositions of polysaccharide–LDPE blends on their mechanical characteristics

Composites	Component ratio (wt %)	E , MPa	σ_b , MPa	ε_b , %
LDPE	—	200 ± 5	13.3 ± 0.2	460 ± 10
Cellulose–LDPE	20 : 80	390 ± 10	9.2 ± 0.1	16.5 ± 0.5
	30 : 70	660 ± 25	11.0 ± 0.2	5.5 ± 0.2
	40 : 60	720 ± 15	10.3 ± 0.1	4.6 ± 0.1
Ethyl cellulose–LDPE	20 : 80	240 ± 10	7.9 ± 0.2	130.0 ± 10
	30 : 70	350 ± 10	6.1 ± 0.2	7.2 ± 0.5
	50 : 50	510 ± 10	6.4 ± 0.4	2.3 ± 0.2
Starch–LDPE	20 : 80	220 ± 10	8.1 ± 0.1	105 ± 15
	30 : 70	290 ± 10	7.1 ± 0.2	105 ± 5
	50 : 50	255 ± 5	7.4 ± 0.2	85 ± 10
Chitin–LDPE	20 : 80	350 ± 6.74	9.2 ± 0.1	25.6 ± 1.6
	30 : 70	470 ± 20	9.8 ± 0.1	10.1 ± 0.4
	40 : 60	535 ± 25	10.3 ± 0.2	7.0 ± 0.2
	50 : 50	1270 ± 35	14.3 ± 0.4	2.5 ± 0.1
Chitosan–LDPE	20 : 80	185 ± 10	5.3 ± 0.15	25.3 ± 3.1
	30 : 70	370 ± 10	8.5 ± 0.25	13.6 ± 0.4
	50 : 50	740 ± 10	12.6 ± 0.15	5.4 ± 0.1

the least ordered regions of the polymer matrix. It was shown that, under the action of shear deformation, the polymers are ground and mixed at different structural levels and these processes are accompanied by amorphization of polymer components. For example, the X-ray diffraction pattern of the initial cellulose (Fig. 1, curve 1) show two crystalline reflections at angular positions of $2\theta = 16.4^\circ$ and 22.2° . A decrease in the first halo of cellulose after mixing performed under high-temperature shear deformation (Fig. 1, curve 3) is caused by a decrease in the crystalline fraction of cellulose as a result of its amorphization. Such changes are likewise characteristic for blends of other polysaccharides.

The mechanical tests of the pressed films showed that the addition of polysaccharides to LDPE leads to a significant reduction in elongation at break ε_b . This finding may be explained by the brittle fracture of the composites containing rigid polysaccharides and the absence (in contrast to polyolefins) of plastic flow during extension. A similar reduction is observed for ultimate tensile strength σ_b ; however, a change in the composition of the blend has almost no effect on σ_b , in contrast to ε_b . Because elastic moduli E of polysaccharides are higher than that of LDPE, the elastic modulus of the blend increases with an increase in the polysaccharide content (Table 1). Tests on fungus resistance performed for blends of different compositions showed that the intensity of mold fungus growth is maximum for starch–LDPE and chitin–LDPE composites. It seems that, because of the morphological

features of cellulose and chitosan, films based on their blends with LDPE are not easily accessible to microorganisms.

Biodegradability is one of the main factors characterizing these composites. Therefore, two approaches were proposed to improve this value and expand the possible application fields of these materials.

The first approach consisted in the introduction of poly(ethylene oxide) of various molecular masses that possesses proper biodegradability and is an efficient plasticizer as the third component into the polysaccharide–LDPE binary composition.

It was found that the introduction of PEO leads to improvement of composite biodegradability. The fungus resistance tests showed that the introduction of PEO into the system promotes the intensified development of mold fungi. For example, if, in the case of the cellulose–LDPE blend, the intensity of mold fungus growth was minimum, then the introduction of 20% PEO led to a sharp increase in this parameter (Fig. 2). Research into the influence PEO on the mechanical characteristics of the films showed that, in contrast to binary composites, ternary composites exhibit improved elastic moduli, while their tensile strengths and elongations at break decrease insignificantly (Fig. 3).

The second approach to increase biodegradability is based on introduction of one more polysaccharide as the third component into the polysaccharide–LDPE composite. Figure 4 illustrates the weight-loss curves for several binary and ternary composites after

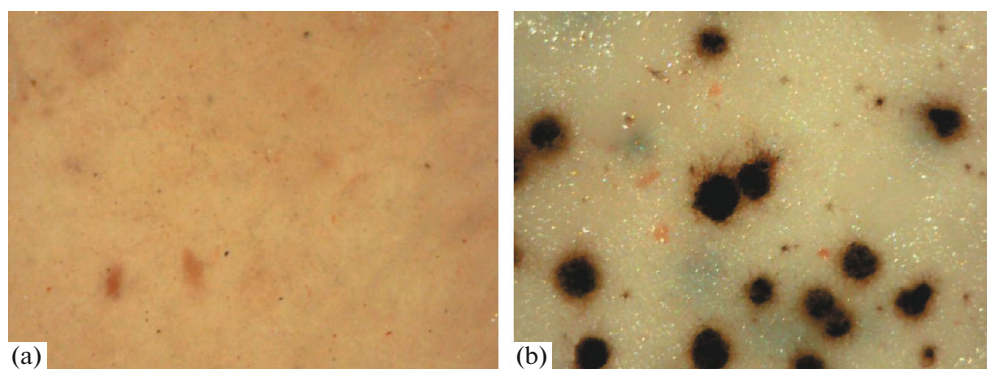


Fig. 2. Surface micrographs of (a) cellulose-LDPE and (b) cellulose-LDPE-PEO films infected with mold fungus spores. The component weight ratios are (a) 40 : 60 and (b) 40 : 40 : 20 (wt %).

their exposure in soil for 60 days. It is seen that the introduction of the second polysaccharide promotes a substantial gain in biodegradability. The most pronounced weight loss for the ternary composites occurs for the first 2 months. The maximum biodegradation rate was observed for the composites with starch and chitin having the maximum biodegradability. Figure 5 illustrates the SEM micrographs of the ternary composites before and after holding in soil for several months. The presence of holes in the polyethylene matrix testifies that not only polysaccharides but also the synthetic polymer degrades. This result is of principal importance, because it directly confirms that the synthetic polymer matrix degrades during biodegradation.

Introduction of the second polysaccharide leads to the appearance of a new fine fraction and an increase in the share of the fine fraction (Fig. 6). Thus, although, in the ternary composites, the fraction of infusible polysaccharides exceeds that in the binary systems and comprises 60%, the mentioned powder composites are more uniform and finely dispersed. This situation may be associated with the fact that the cogrinding of polymer component particles occurs simultaneously with mixing. Exactly this circumstance, namely, an increase in friction between the particles, makes it possible to explain the increased content of fine fractions in the composites containing a more rigid polysaccharide, cellulose.

BIODEGRADABLE COMPOSITES BASED ON POLYLACTIDE

Poly lactide obtained through the polymerization of the natural monomer lactic acid has good mechanical properties comparable to the properties of PS and PETP. Its main disadvantage is fragility; however, plasticization makes poly lactide elastic, and in terms of characteristics, it approaches PE, plasticized PVC, and PP [69–71].

The main advantage of poly lactide is that it is a transparent, colorless thermoplastic polymer that can

be processed by all methods used for the processing of known thermoplasts. Films, fibers, and food packaging can be obtained from poly lactide. Materials based on poly lactide are widely used in biomedicine and pharmaceuticals. Despite all the above-mentioned advantages of poly lactide, until recently, its wide application has been retarded by comparatively small production volumes; low productivity; and, as a result, by high cost. The production of poly lactide-based composites with various polymers makes it possible to impart new properties to poly lactide and to decrease the cost of poly lactide-based articles. Exactly this fact explains the sharply increasing interest of researchers in the design of poly lactide-based composites with both synthetic and natural polymers. For example, the blends of poly lactide with polybutylenecarbonate [72], with ethylene copolymers [73, 74], and with thermoplastic polyurethanes [75] were studied. It was shown that the mixing of poly lactide with a rubber leads to a substantial increase in elongation at break [76].

Although poly lactide is the product of polymerization of a natural monomer, it degrades well only in aggressive media: compost and sea water [77]. If the complete biodegradation of poly lactide-based materials in soil takes 20–30 months, then, in standard compost, they degrade over 30–40 days. (For comparison, cellulose materials in standard compost degrade over 15–20 days.) At the same time, it is known that, for poly lactide-based composite, biodegradability is higher than that for poly lactide [78]; therefore, its mixing with other natural biodegradable polymers makes it possible not only to increase biodegradability but also to affect its crystallinity and mechanical and thermal characteristics [79, 80].

To improve the processability, flexibility, and impact strength of poly lactide and to decrease its glass-transition temperature, plasticizers are often used [81]; of these, PEG is the most efficient [82]. Thanks to biodegradability, biocompatibility, and nontoxicity of PEG, its introduction into poly lactide improves the biodegradability and biocompatibility of

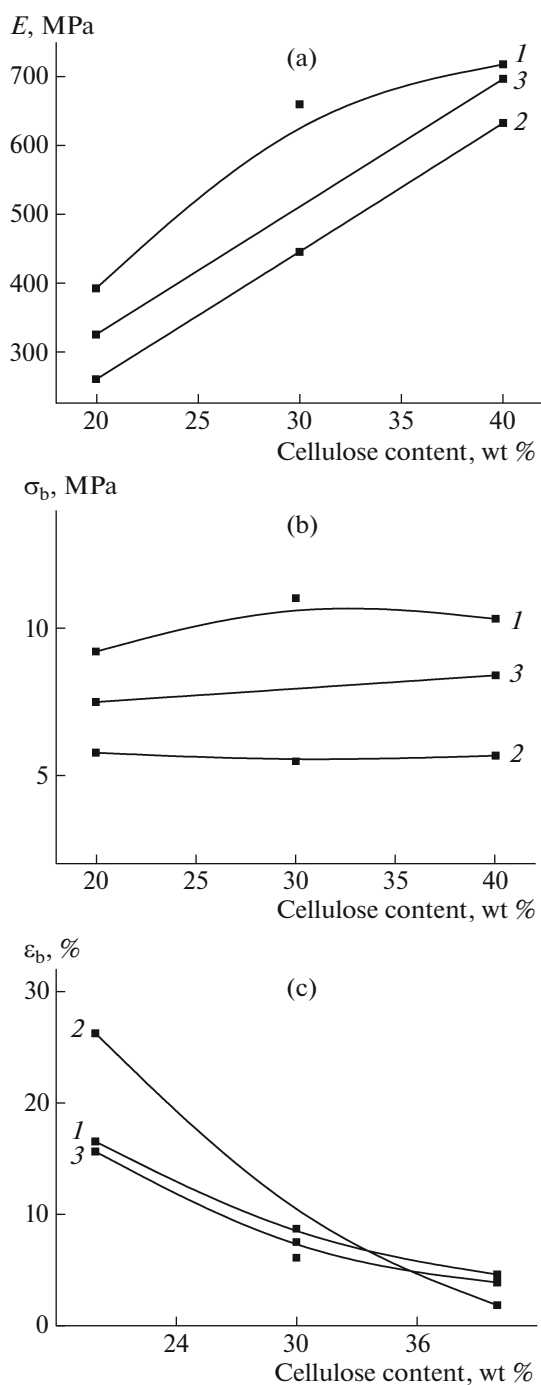


Fig. 3. Plots of (a) elastic modulus E , (b) tensile strength σ_b , and (c) elongation at break ϵ_b vs. cellulose content for (1) cellulose-LDPE and (2, 3) cellulose-LDPE-PEO blends. The PEO molecular masses are (2) 35×10^6 and (3) $(5-6) \times 10^6$.

the polylactide-based composites. The presence of end hydroxyl groups in PEG able to react with the carboxyl groups of polylactide molecules provides their good compatibility; in this case, the lower the molecular mass of PEG, the higher the compatibility of

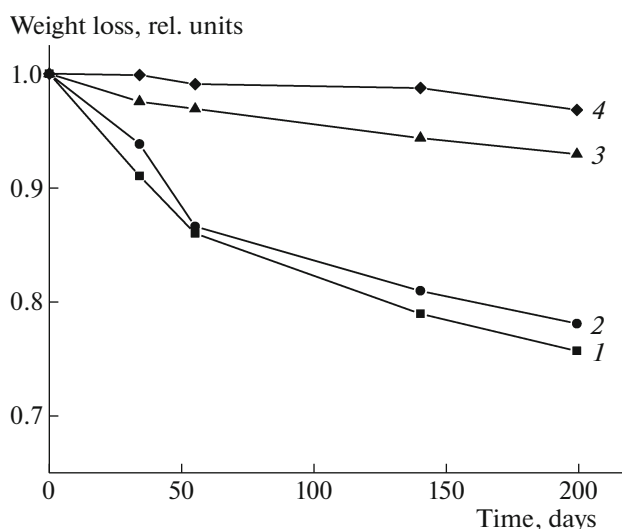


Fig. 4. Weight losses of (1) starch-LDPE-chitin, (2) starch-LDPE-chitosan, (3) cellulose-LDPE-chitin, and (4) cellulose-LDPE-chitosan. The component weight ratios are 30 : 40 : 30 (wt %).

PEG with the polylactide matrix [83]. The plasticization and solubility of PEG additionally depend on its molecular mass and increase as this value decreases [84, 85]. However, an increase in the content of PEG in the blend leads to a decrease in the glass-transition temperature of polylactide. The effect of PEG on the polylactide crystallinity was studied in [86]. It was shown that, in the presence of PEG, the mobility of polylactide polymer chains increases and thus promotes its crystallization. The presence of PEG improves the hydrophilicity, flexibility, and impact strength of polylactide and accelerates its degradation [87].

Among numerous polylactide-based composites of special interest are its blends with polysaccharides because these materials are obtained from renewable natural raw materials. The blends of polylactide with one of the cheapest polysaccharides, starch, are most often used [88–94]. The films based on blends of starch and polylactide degrade in compost at 40°C in seven days [95]. Using graphene oxides as an additive improving the compatibility of polylactide and starch made it possible to achieve good dispersion and strong surface adhesion of the resulting material; in addition, this composite has a higher yield point than the initial polylactide [96].

In [97], acrylic acid-grafted polylactide was mixed with corn starch. Thanks to good compatibility, these composites possessed improved mechanical characteristics relative to those of the polylactide-starch composite; they could be successfully used as materials for film packaging. The introduction of starch into polylactide deteriorates the water resistance and impact resistance of the composites [98].

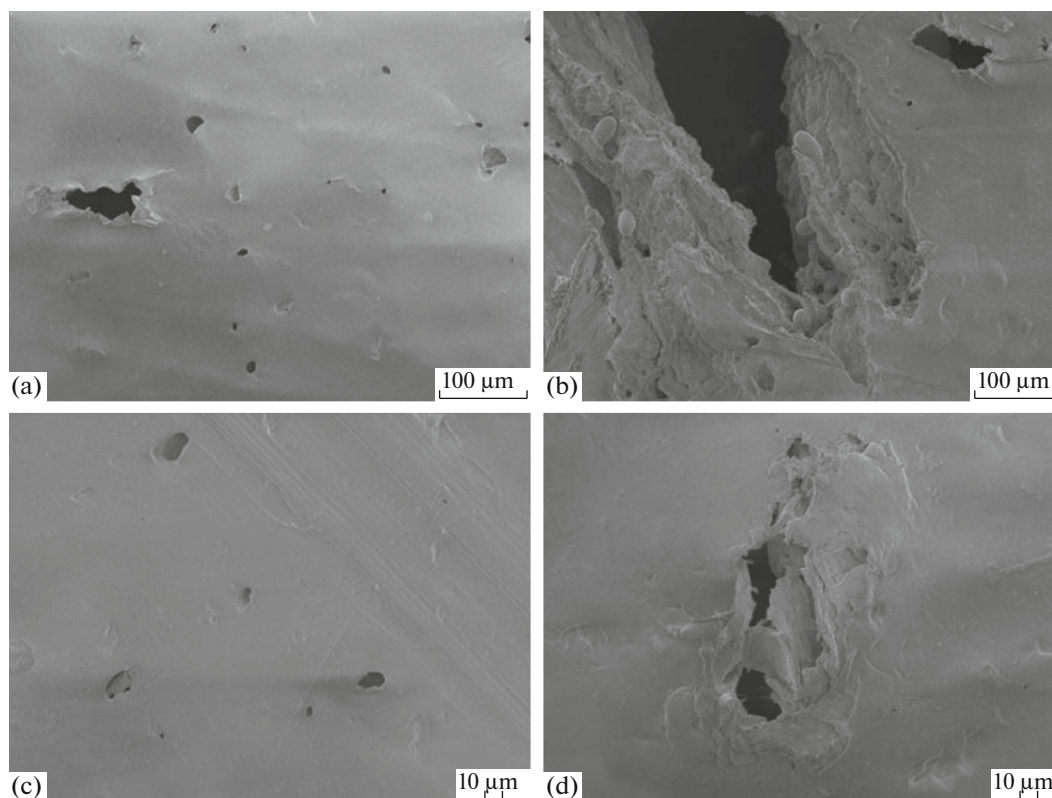


Fig. 5. Surface micrographs of the films based on (a, b) starch–LDPE–chitin and (c, d) cellulose–LDPE–chitin blends. The component weight ratio is 30 : 40 : 30 (wt %). The magnifications are (a, b) $\times 200$ and (c, d) $\times 300$.

The composites of polylactide with cellulose are produced with the use of wood and microcrystalline cellulose, viscose fibers, and nanocellulose whiskers obtained from lignocellulosic fibers of the plant origin. The introduction of cellulose promotes an increase in rigidity of composites because cellulose serves as a reinforcing filler. The mechanical properties of the polylactide-based composites with flax and wood cellulose used as natural cellulose fibers were improved in [99, 100] and [101, 102], respectively. On the whole, the rigidity of polylactide can be relatively easily improved by filling with natural fibers; however, it is quite difficult to improve such mechanical properties as tensile and bending strengths and impact strength. When the case in point is the production of films and packaging, it is optimal to use nanoscale cellulose. In this case, in order to improve the distribution of nanoparticles, plasticizers or surfactants are often introduced into composites. For example, in [103, 104] the addition of PEG made it possible to increase the elongation at break by 800%. The addition of 1% cellulose nanowhiskers and 20% glycerol triacetate as a plasticizer to polylactide improved the dispersion of nanofibers in the matrix and increased the elongation at break and impact strength [105]. The possibility to use PVA to improve the distribution of cellulose nanowhiskers in the polylactide matrix was

investigated [106]. It was shown that the nanowhiskers are mainly distributed in PVA and that only small part of them occur in polylactide; in this case, an insignificant increase in the mechanical characteristics was observed. In [107], cellulose nanowhiskers were impregnated with *tert*-butanol and a number of other surfactants to produce nanocomposites with polylactide.

Cellulose esters are one of the most important derivatives of cellulose important for industry. The blends based on thermoplastic cellulose esters and polylactide can be used in molding and casting of articles for various applications: spectacle frames, handles of instruments, toothbrushes, etc.

The materials based on compositions of polylactide with chitosan have found wide use. The combination of useful properties of both components determines the prospects to produce composites based on them and to obtain biomedical articles and preparations. Such materials can be obtained by both grafting block copolymerization and preparation of blend compositions [108, 109]. Specifically, fibers used as nerve conduits [110] and resorbable surgical sutures are produced on their basis. However, such articles have some disadvantages, among which the most substantial is unpredictable degradation in the body, which depends on the density, size, form, and porosity of the polymer

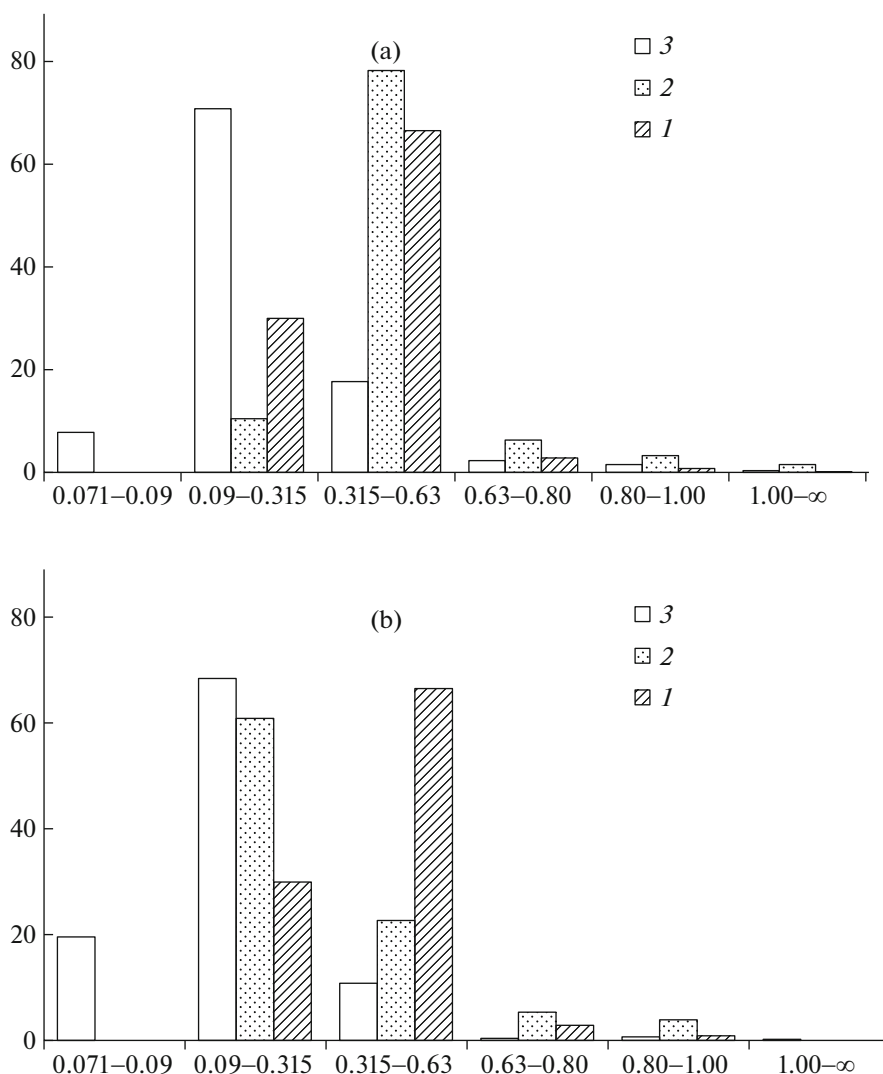


Fig. 6. Comparative histograms of particle distributions in (1, 2) binary and (3) ternary blends. (a) (1) chitin–LDPE (40 : 60, wt %), (2) starch–LDPE (50 : 50, wt %), and (3) starch–LDPE–chitin (30 : 40 : 30, wt %); (b) (1) chitin–LDPE (40 : 60, wt %), (2) cellulose–LDPE (30 : 70, wt %), and (3) cellulose–LDPE–chitin (30 : 40 : 30, wt %).

article and on the change in pH of the environment during suture biodegradation; these disadvantages restrict the fields of application of these materials as general-purpose biomedical materials [111]. The polylactide–chitosan composites are characterized by good antimicrobial properties, especially at small sizes of chitosan particles. The effect of polylactide additions to chitosan on barrier characteristics and water sensitivity was studied [112]. It was shown that, after the introduction of polylactide, these parameters increase; however, in this case, the ultimate tensile strength and the elastic modulus decrease simultaneously.

With the aim to impart new properties and to expand the possible application areas of polylactide-based biodegradable materials, the binary composites of polylactide with ethyl cellulose, chitosan, and cellu-

lose and their ternary composites with PEG of various molecular masses were obtained at the Semenov Institute of Chemical Physics, Russian Academy of Sciences, by solid-phase mixing of components under the conditions of shear deformation in a Brabender mixer [113–115]. The results of the mechanical tests of the resulting films are presented in Table 2. As is seen, the addition of polysaccharides to polylactide significantly decreases tensile strength σ_b and elongation at break ε_b . Elastic modulus E increases in the composites containing rigid chitosan and cellulose but remains almost the same in the ethyl cellulose-based composites. The addition of PEG leads to a noticeable increase in ε_b . For example, for the ternary composites with chitosan and 20 wt % PEG, the elongation at break increases up to 57.5%; for the composites with ethyl cellulose, the elongation at break increases up to 20.1%. After a fur-

Table 2. Influence of the compositions of blends based on polylactide and polysaccharide on their mechanical characteristics

Composite	Component ratio (wt %)	E , MPa	σ_b , MPa	ϵ_b , %
Polylactide	—	2625 ± 65	52 ± 1.0	4.70 ± 0.05
Polylactide–ethyl cellulose	70 : 30	2620 ± 89.4	32.7 ± 1.0	1.9 ± 0.13
Polylactide–chitosan	70 : 30	3110 ± 90	45.5 ± 2.20	2.5 ± 0.21
Polylactide–cellulose	70 : 30	3640 ± 111	40.6 ± 1.73	1.9 ± 0.03
Polylactide–ethyl cellulose–PEG ₆₀₀	60 : 30 : 10	1500 ± 74	12.9 ± 0.40	1.8 ± 0.13
	60 : 20 : 20	252 ± 17	4.9 ± 0.20	20.1 ± 1.60
Polylactide–chitosan–PEG ₆₀₀	60 : 30 : 10	1370 ± 61	17.6 ± 0.30	3.2 ± 0.23
	60 : 20 : 20	106 ± 11	8.9 ± 0.10	57.5 ± 2.0
	52 : 21 : 27	181 ± 28	3.6 ± 0.05	29.5 ± 2.20
Polylactide–cellulose–PEG ₆₀₀	60 : 30 : 10	2040 ± 42.1	19.4 ± 0.57	1.7 ± 0.05

ther increase in the amount of PEG, the elongation at break decreases; this finding may be explained by the crystallization of polylactide. Note that a similar effect was absent for the polylactide composites with cellulose. It seems that the presence of a rigid system of hydrogen bonds formed by cellulose hydroxyl groups hinders the penetration of PEG molecules between the polymer molecules; as a result, plasticization is absent.

The biodegradability levels of the films obtained from these composites were estimated from weight losses and changes in morphology of the samples by scanning electron microscopy after exposure in soil. Figure 7 shows the weight-loss curves for the initial polylactide, its binary composites with polysaccha-

rides, and their ternary composites with PEG after their holding in soil for several months. There is almost no weight loss for both polylactide and its composites with cellulose and ethyl cellulose. At the same time, the addition of PEG leads to an increase in biodegradability; in this case, the greatest weight loss is typical for the composites based on cellulose (24%). In this case, the character of the curves obtained for all the systems remains the almost the same and the main weight loss is observed for the first 3 months.

The photographs of the surfaces of the films after their holding in soil for several months are presented in Fig. 8. Here, as in the case of the ternary composites of LDPE with two polysaccharides, the film surface in the presence of PEG has microcracks and holes,

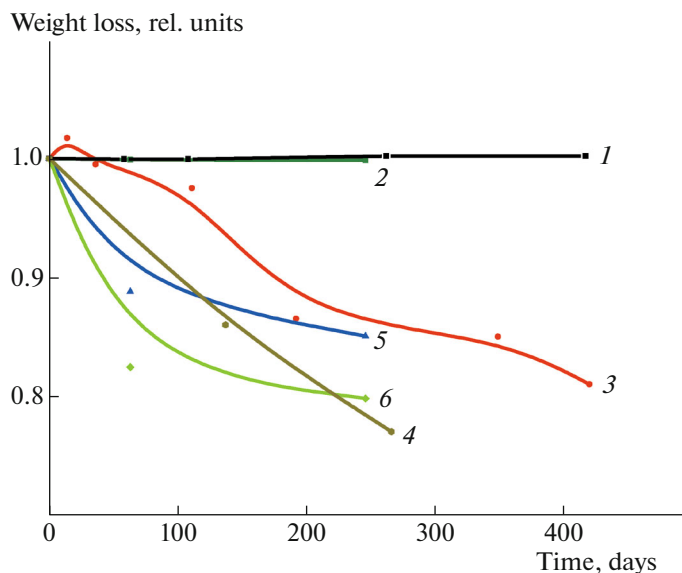


Fig. 7. Weight losses of samples after holding in soil: (1) polylactide, (2) polylactide–ethyl cellulose, (3) polylactide–chitosan, (4) polylactide–cellulose, (5) polylactide–chitosan–PEG, and (6) polylactide–ethyl cellulose–PEG. The component weight ratios are (2–4) 70 : 30 and (5, 6) 60 : 20 : 20 (wt %).

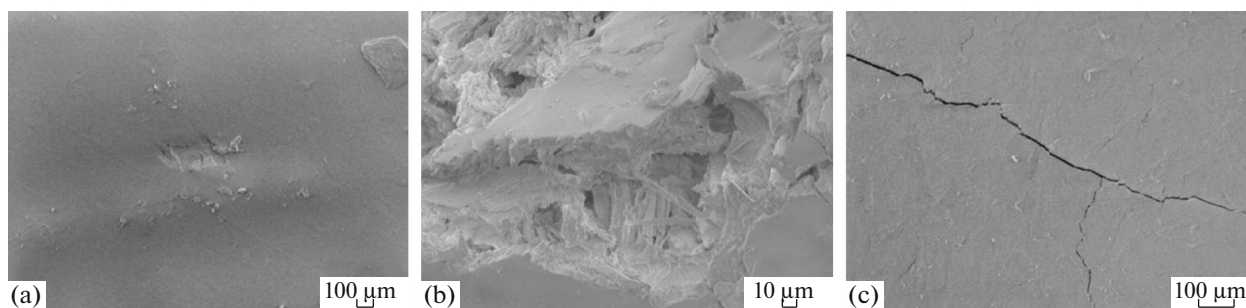


Fig. 8. SEM micrographs of surfaces of films based on (a) polylactide–ethyl cellulose, (b) polylactide–chitosan–PEG₆₀₀, and (c) polylactide–cellulose–PEG₄₀₀₀ composites after holding in soil for several months. The component weight ratios are (a) 70 : 30 and (b, c) 60 : 20 : 20 (wt %). The magnifications are (a) $\times 500$, (b) $\times 300$, and (c) $\times 100$.

which lead to the subsequent cracking and fragmentation of the materials. This circumstance points to the fact that biodegradation likewise involves the polylactide matrix. Moreover, Fig. 8a illustrates the formation of nodes on the film surface, which apparently are the microspores of fungi.

Thus, the results of studies performed at the Semenov Institute of Chemical Physics, Russian Academy of Sciences, on the biodegradability of the composites based on polymers of various classes show that the composites of polysaccharides with both synthetic polymers (LDPE) and polymers derived from natural monomers (polylactide) behave similarly during biodegradation. The presence of polysaccharide imparts biodegradability to the composites. Note that introduction of the PEG plasticizer accelerates the process; however, the mechanical characteristics usually become worse.

In summary of the above-mentioned evidence, it may be concluded that, despite their similarity to synthetic polymers that are obtained from oil, the polymers from renewable raw plant materials have found wide use in different fields and the creation of the composites based on them makes it possible to improve the characteristics of articles and to decrease their cost. Such new composite materials have expanded the application fields of the polymers based on natural raw materials and have increased their profitability.

The necessity to industrially produce biodegradable materials is becoming more apparent; therefore, the majority of advanced countries have passed laws restricting the application of synthetic polymers in the production of tare and packaging in effort to protect the environment.

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