Biodegradable Blends Based on Chitin and Chitosan: Production, Structure, and Properties

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ABSTRACT: Blends based on LDPE and chitin or chitosan were prepared under high-temperature shear deformations in a rotor disperser at different initial ratios of the components. Although one of the components is an infusible polymer (polysaccharide), the powder blends were obtained. The composition of the powder fractions was shown to be identical to the original blend composition. It was found that the addition of poly(ethylene oxide) to the mentioned blends improves the biodegradability of the polymer materials and extends their application areas.

Using various physicochemical methods, the structural and morphological changes in the polymer compositions under the action of shear deformations were examined, the mechanical characteristics of prepared films were determined, and also the features of their bio-, thermo-, and photo-oxidative degradation were studied. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1850–1859, 2011

Key words: biodegradable; blends; polysaccharides; polyethylene; mixing

INTRODUCTION

Because of constantly increasing production of polymers leading to environmental pollution, the problem of their utilization is becoming more and more urgent. This problem can be solved by creation of biodegradable polymer materials which can be decomposed under the environmental conditions to give harmless products. The most efficient and economically profitable research trend in this field appears to be the production of polymer materials via mixing the synthetic polymers with natural, biodegradable ones. This approach allows one to utilize large-tonnage industrial polymers, such as PE, PP, PVC, etc. The resulting materials combine good mechanical properties and processability with rather high biodegradability, i.e., meet both economical and ecological requirements.[1] Such composite materials can be successfully used to produce packaging materials, food films, articles for short-term use, etc.

The service life of most polymer products depends on the environmental impact involving chemical (atmospheric oxygen, water), physical (sunlight, heat), and biological (bacteria, fungi, yeast, insects) factors. As a result of their combined impact, the macromolecules of the natural origin are subjected to degradation with formation of pores and microcracks on the material surface. Such increase of

surface area promotes the intensive oxidation processes, which, in turn, lead to polymer fragmentation through the degradation and transformation into low-molecular compounds involved in the natural cycles of substances. A term "polymer biodegradation" actually means the deterioration of physical and chemical properties, a decrease in molecular weight of polymers up to formation of CO_2, H_2O, CH_4 and other low-molecular products under the action of microorganisms under aerobic and anaerobic conditions.[2] Among natural polymers a special attention should be drawn to a renewable and almost inexhaustible source of raw materials—polysaccharides, such as cellulose, starch, chitin, chitosan, easily degradable under natural conditions. On the one hand, synthetic polymers, for example, industrial large-tonnage polyolefins, have high mechanical and thermal characteristics, but are stable to the action of microorganisms, therefore, are not degradable. On the other hand, natural polysaccharides exhibiting high biodegradability have poor mechanical parameters. Thus, the production of the blends based on polysaccharides appears to be a simple and inexpensive method for modification of the initial polymers, which allows one to use the properties of each component in full measure.[3–5] Starch is a biodegradable polysaccharide most frequently used as an additive to synthetic polymers,[6,7] and the blends on its base are most extensively explored. The great interest to chitin and its deacetylated derivative—chitosan promoted the appearance of many works on production and investigation of the blends based on these polymers. Most works are

concerned with chitosan blends. However, nowadays chitin and its blends are extensively used in production of various medical products. For example, chitin blends with copolymer of polylactic and polyglycolic acids were used to produce the microspheres for pharmaceutics.[8] The chitin blends with PVA and polyurethane were studied in detail.[9,10]

A wide variety of unique properties, the most important of which are the chemical and radiation resistance, bactericidal action, and high sorption capacity, along with the presence of polar groups responsible for an additional reactivity (OH and NH_2 groups forming hydrogen bonds with other polymers) afford a great diversity of chitosan applications.[11] At present among them the most promising are the pharmaceutical and biological products, and to a lesser extent the cosmetic one.[12–16] In this context the blends of chitosan with collagen,[17] poly-(hydroxybutyrate),[18] polylactic acid,[19] and starch[20] should be noted. As chitosan is a polymer soluble in water-acid media, so to produce its blends with synthetic polymers the water-soluble ones, such as polyvinyl alcohol,[21–23] PEG,[24,25] polyvinyl pyrrolidone,[26] etc., are mainly used. The compositions based on chitosan are of practical interest as ion exchangers, separation membranes, film and spongy dressing materials, carriers for drugs, textile fibers, and also as antibacterial materials.[27]

At the same time in literature there are no works concerning chitin/chitosan blends with polyethylene, although such systems are of interest for construction of biodegradable composites on the base of large-tonnage polyethylene. Earlier by authors of this work the binary blends of low-density polyethylene (LDPE) with some natural polysaccharides and their derivatives were prepared and comparative study of their structure and properties was made.[28]

The goal of present work is a further study of binary systems on the base of chitin and chitosan with LDPE, as well as their ternary blends with polyethylene oxide (PEO) under conditions of intensive high-temperature shear deformations and investigation of their properties.

EXPERIMENTAL

Materials

In experiments, chitin containing 87.2% basic substance with deacetylation degree of 0.045 and chitosan with deacetylation degree of 0.87 and molecular weight 4.4×10^5 (Bioprogress, Russia) were used. LDPE used in this work has the following characteristics: $T_m = 108°C$, $M_n = 23000$, MFI = 2 g/10 min. Low-molecular poly(ethylene oxide) (PEO) with $M = 35,000$ and high-molecular PEO with $M = 5 \div 6 \times 10^6$ were used.
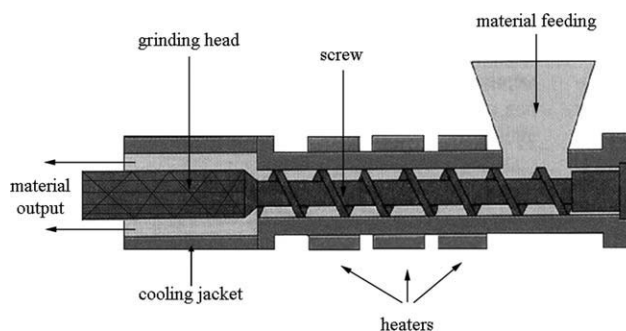

Figure 1 Principle diagram of a rotor disperser.

Blend preparation

The mixing of polysaccharides with LDPE was carried out by a single pass of the components through a rotor disperser, during which the material was subjected to high-intensive shear deformations. To create the intensive shear deformations, the rotor disperser, differing from extruder, has a grinding head designed as a cam element rotating inside a channeled cylinder and equipped with a cooling jacket (Fig. 1). Temperatures in different zones were 120 and 150°C. The feeding was carried out with certain time intervals at 130–150°C. The residence time of the material at every pass was about 5 min.

Fractionation

For fractionation of the blends, the sieve analysis based on the mechanical separation of the particles by their size was used. Mesh sizes were 1, 0.80, 0.63, 0.315, 0.09, and 0.071 mm. By passing the material through a set of sieves, the probe was separated into several fractions. The particle sizes of these fractions were limited by the hole sizes used in the sieve analysis.

Laboratory tests on fungus resistance

The laboratory test on fungus resistance is based on the exposition of the materials infected with fungus spores under the optimum conditions for their growth with the following estimation of fungus resistance by the degree of the fungus growth.

In this work, the estimation of the degree of the microscopic fungus growth was carried out under the conditions imitating mineral impurities, for which purpose the material was infected with fungus spores in an aqueous solution of mineral salts. Fungi grew at the cost of salts of mineral medium and nutrients contained in a sample. In the tests, the fungi from the All-Russia Collection of Microorganisms were used. The concentration of different fungus spores in the suspension comprised 1–2 billion/cm³.

The samples under investigation shaped as plates 50×50 mm^2 were placed in exsiccators containing water at the bottom. The distance between the samples was not less than 10 mm. The sample surface was uniformly infected with the suspension of fungus spores. Then the samples were exposed in a box at 25°C to drop drying. The tests were carried out at 29°C and relative humidity 90% without the influence of natural and artificial lighting. The tests for determining the degree of fungus growth were performed within 28 days with intermediate inspection within 14 days. The samples were examined by naked eye in scattered light at the illumination of 2000–3000 lux and zooming of 56–60. The fungus resistance in terms of the intensity of fungus growth on the samples was evaluated according to a six-number scale.

Pressing

For the mechanical tests and laboratory tests on fungus resistance the film samples 0.18–0.25 mm thick were prepared at 160°C and 10 MPa for 10 min with the following cooling under the same pressure at the rate of ~ 15 K/min. The obtained probes were shaped as dumbbell with the size of gauge of 35×5 mm^2.

Mechanical tests

The mechanical tests were performed on an Instron-1122 tensile test machine in tension mode at the rate of the upper traverse of 50 mm/min at room temperature. Based on the stress (σ), elongation (ε) diagrams, the initial elastic modulus E, ultimate tensile strength σ_b, and elongation at break ε_b were calculated. The results were averaged for 10–14 samples.

X-ray diffraction analysis

The X-ray diffraction analysis of powder samples was performed on a Rigaku RU-200 Rotaflex diffractometer (Japan) with a 12-kW generator and a rotating copper anode in the transmission mode (40 kV, 140 mA). CuK_α radiation with wavelength $\lambda = 0.1542$ nm was used. The 2D wide-angle diffraction patterns were obtained on a two-coordinate position-sensitive Bruker AXS GADDS detector with a plane graphite monochromator positioned in the primary beam (Germany). The collimator was 0.5 mm in diameter.

Differential scanning calorimetry

The thermophysical parameters of the samples were determined via DSC on a DSM-10 m calorimeter (Russia). The weight of the samples was in the range of 2–6 mg, the heating rate was 16 K/min. The calorimeter was calibrated relative to indium, tin, and

zinc. The melting enthalpies of individual LDPE and the blends were calculated per unit mass of LDPE in the blend.

Thermogravimetric analysis

The analysis of thermal stability of the individual polymers and their blends was carried out on a synchronic thermal analyzer STA 449 F3 Jupiter (NETSCH, Germany) over the temperature range of 30–560°C with the rate of temperature change of 10 K/min under argon atmosphere. The weight of the samples was 5–8 mg, the rate of gas consumption was 40 mL/min.

Photooxidation

The samples were photooxidized according to ISO 4892-1. The equipment for exposure and light source consisted of a xenotest 150°C with a tube-type xenon lamp Xe 1501, light filters for correction of IR radiation of xenon lamp, and an UV filter. The intensity of the incident light in UV region was 69 W/m^2, while the intensity of the total radiation in UV, visible and IR region was 1610 W/m^2. The total time of irradiation was 165 h. To control the light intensity during the tests, a RADIOLUX type radiometer was used.

Biodegradability under the natural conditions

The biodegradability of polymer compositions was studied by modeling the processes occurring under the natural conditions. For this purpose, the samples under investigation were placed into a container with wet soil (pH 7.5) meant for plant growing. The containers were kept in a thermostat at 30°C during five months. The rate of biodegradation was controlled by the weight losses of sample measured with regular time intervals.

RESULTS AND DISCUSSION

Preparation and fractionation of binary blends based on LDPE and polysaccharides

The blends of chitin and chitosan with LDPE were prepared in a rotor disperser with the content of polysaccharides varied from 20 to 50 wt %. When passing through the rotor disperser, the polymers undergo the joint action of pressure and shear deformations. The method is based on the physical principle that the energy accumulated in the sample after the application of pressure is consumed on forming of new surface under the influence of shear deformations that allows one to obtain highly dispersed powders. Although the initial polysaccharides, in contrast to LDPE, are infusible polymers, the polymer blends after passing through the rotor disperser
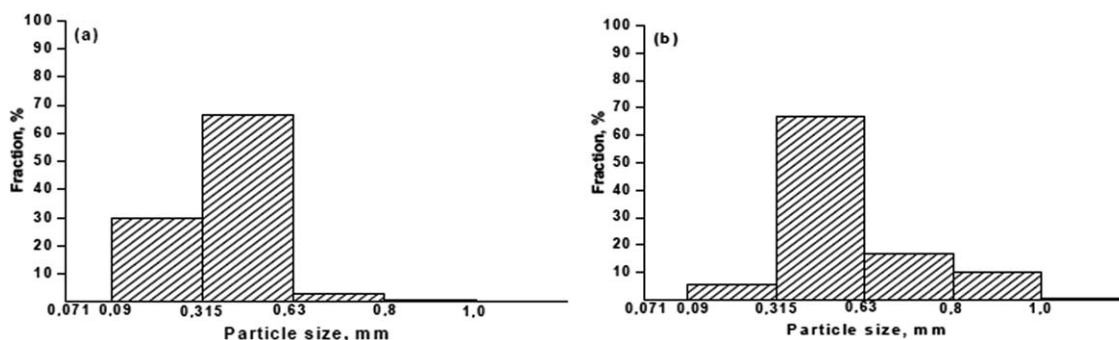
Figure 2 Histograms of particle size distribution for blends: (a) chitin–LDPE (40 : 60 wt %), (b) chitosan–LDPE (50 : 50 wt %).

become fine powders, which can be easily fractionated. Figure 2 shows the typical histograms of the obtained blends. It is evident that the basic fraction (about 50% for all component ratios) is composed of particles 0.315–0.63 mm in size.

The chitin and chitosan content in various fractions of the obtained blends was determined by DSC. As is seen from Figure 3, the melting curve of LDPE displays one peak. At the same time, there is no endo or exo peak on the DSC curves obtained for chitin and chitosan; i.e., the DSC curves for all blends of these polysaccharides with LDPE show a single peak typical for LDPE, and its position corresponds to T_m of LDPE independently of the polysaccharide nature (Fig. 3). As the change of melting enthalpies of LDPE depends not only on amorphization, which is constant for each blend, but also on the content of the second component, the polysaccharide content in composition can be calculated. The results of the fractionation of the obtained blends at various component ratios are presented in Table I. It follows from Table I that the composition of the fractions is rather similar to the initial component ratio in the blend.

Thus, DSC can serve as the additional method for determination of the polysaccharide content in the blends with LDPE.

Mechanical characteristics of the obtained blends

The results of the mechanical tests are given in Table II. Since the elastic modulus E of polysaccharides is higher than that of LDPE, the elastic modulus of the blends increases with the polysaccharide content in composition. The highest E values were obtained for chitin–LDPE blends, since E is determined by the structural features of polysaccharide and grows with its rigidity.

The introduction of polysaccharides also influences on the values of ultimate tensile strength σ_b for their blends with LDPE. The ultimate tensile strength σ_b for these blends first drops, and then increases up to comparable values, and, for a chitin–LDPE blend (50 : 50 wt %), even exceeding σ_b for LDPE (σ_b for the blend

and LDPE are equal to 14.3 and 13.3 MPa, respectively). These differences in σ_b behavior can be explained by a higher rigidity of chitin compared to chitosan and the inversion of the polymer matrix, which probably takes place at the chitin content of 50%.

The addition of polysaccharides to LDPE results in a significant decrease of the elongation at break ε_b that is connected with an increase in the system rigidity occurring as the polysaccharide content in the blend increases. Hence, a change in the mechanical characteristics of the blends of polysaccharides with LDPE depends both on the blend composition and the polysaccharide nature.

Figures 4 and 5 show the X-ray diffraction patterns of the individual components and their blends prepared via mixing under shear deformations at the component ratio of 30 : 70 wt %.

The X-ray pattern of the original chitin (Fig. 4, Curve 1) displays several crystalline reflections with the angular positions $2\theta = 9.3°, 12.6°, 19.1°,$ and $26.2°$. The observed decrease of their intensity and also the decrease of the characteristic reflection of LDPE (Curve 2) after mixing (Curve 3) under the action of shear deformations is related to the decrease of the crystallinity degree of polymer owing to its amorphization.
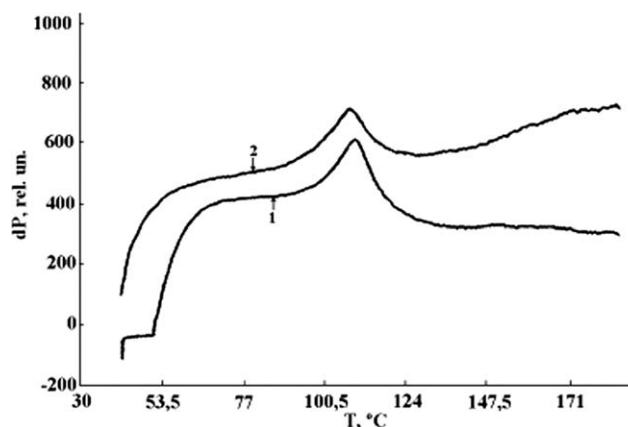

Figure 3 DSC curves of individual LDPE (1) and blend chitin–LDPE (30 : 70 wt %) (2).

TABLE I
Fractional Composition of Polysaccharide–LDPE Blends by DSC Data

Blend composition	Polysaccharide–LDPE (wt %)	Particle size (mm)	Enthalpy ΔH_{exp} (mJ)	Fractional composition (%)	
				Polysaccharide	LDPE
Chitin–LDPE	30 : 70	0.09–0.315	131	26.5	73.5
		0.315–0.63	123	30.8	69.2
	40 : 60	0.315–0.63	111	37.6	62.4
	20 : 80	0.09–0.315	139	22	78
		0.315–0.63	145	18.5	81.5
Chitosan–LDPE	30 : 70	0.315–0.63	129	27.5	72.5
		0.63–0.80	125	29.8	70.2
	50 : 50	0.09–0.315	92	48.3	51.7
		0.315–0.63	94	47.2	52.8
		0.63–0.80	93	47.8	52.2

The X-ray pattern of chitosan (Fig. 5, Curve 1) is characterized by several crystalline reflections with the angular positions $2\theta = 9.7°$, $19.8°$, and $29°$. As is seen from the X-ray pattern of chitosan–LDPE blend (Curve 3) obtained via mixing under the action of high-temperature shear deformations, the intensity of the reflections considerably decreases after treatment of the polymer blend in the rotor disperser.

Therefore, under the action of shear deformations, the significant change of the polysaccharide structure due to a decrease of degree of crystallinity is observed.

Investigation of blend biodegradability

The tests on the fungus resistance were performed with the films obtained from the chitin–LDPE and chitosan–LDPE blends (50 : 50). Upon microscopic examination of the films obtained from chitosan–LDPE blend, only separate sprouted spores and a weakly developed mycelium are observed, thus the intensity of fungus growth was measured at 1, and the investigated material was considered as funginert, i.e., this blend contains nutrients in the amount providing an insignificant fungus growth. At the same time, for the films obtained from the chitin–

LDPE blends, the growth of fungi covering more than 90% of surface is clearly seen by the naked eye, consequently, the intensity of fungus growth in this case was measured at 5. The films of the latter blend have no fungus resistance and contain nutrients providing fungus growth in the presence of mineral pollutants, i.e., they are not considered as funginert.

Such effect may be explained as by fungicidal properties of chitosan due to the presence of amino groups[29] so by morphology peculiarities the films obtained from its blend with LDPE are hard-to-reach for action of microorganisms.

Changes occurred in the samples after holding in soil at 30°C during 5 months were investigated by determining their weight losses and changes of mechanical properties. The curves of weight loss for the samples placed in soil are given in Figure 6. As illustrated in this figure, the character of the curves for all explored systems remains rather unchanged, and the weight loss occurs mainly during first 2 months. In this case, the microcracks and spots can be clearly seen, and especially great changes are observed for the samples containing chitosan. Moreover, the investigated samples become notably more fragile. The similar character of weight loss for blends based on chitin and chitosan shows that the

TABLE II
Influence of Polysaccharide–LDPE Blend Composition on Their Mechanical Characteristics

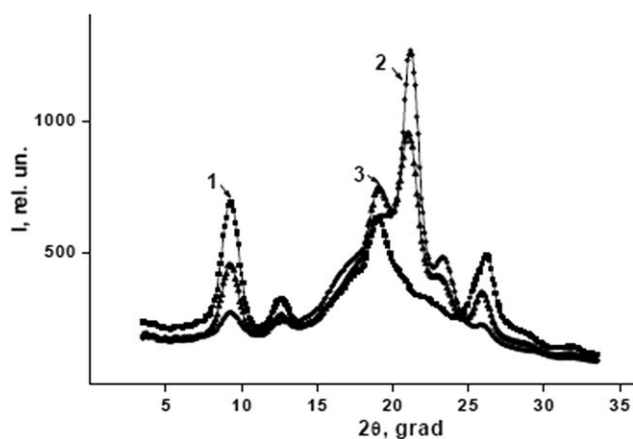| Polysaccharide– LDPE	Polysaccharide– LDPE ratio (wt %)	E (MPa)	σ_b (MPa)	ε_b (%)
LDPE	–	200 ± 5	13.3 ± 0.2	460 ± 10
Chitin–LDPE	20 : 80	350 ± 6.74	9.2 ± 0.1	25.,6 ± 1.6
	30 : 70	470 ± 20	9.8 ± 0.1	10.1 ± 0.4
	40 : 60	535 ± 25	10.3 ± 0.2	7.0 ± 0.2
	50 : 50	1270 ± 35	14.3 ± 0.4	2.5 ± 0.1
Chitosan–LDPE	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

Figure 4 X-ray patterns of chitin (1), LDPE (2), and their blend chitin–LDPE (30 : 70 wt %), prepared via extrusion mixing (3).

action of chitosan on soil microorganisms is not the same as on the fungus and obviously in the common case depends on origin of microorganisms.

The results of the investigation on mechanical characteristics of the samples after holding in soil during 5 months are presented in Table III. The obtained data testify an insignificant decrease of elastic modulus and elongation at break while ultimate tensile strength is practically unchanged.

Preparation and investigation of polysaccharide–LDPE–PEO ternary blends

To increase the biodegradability of the obtained compositions, the third component, namely, PEO of various molecular weight (low-molecular, $M = 35,000$ and high-molecular, $M = 5 \div 6 \times 10^6$) was added to the system consisting of synthetic and natural polymers. PEO exhibits low toxicity, therefore, the compositions on its base can be used for preparation of medical products.
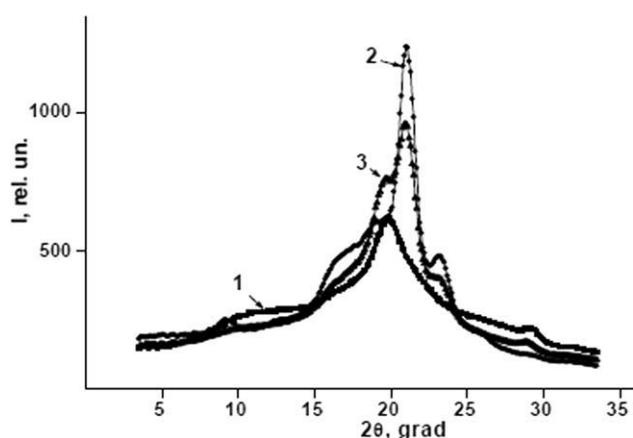

Figure 5 X-ray patterns of chitosan (1), LDPE (2), and their blend chitosan–LDPE (30 : 70 wt %), prepared via extrusion mixing (3).
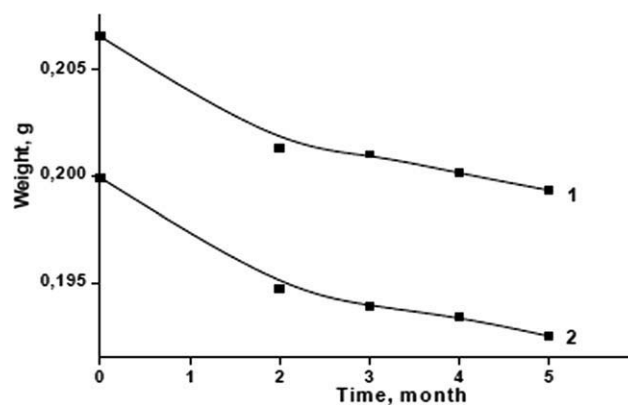

Figure 6 Weight loss of films from blends: (1) chitin–LDPE (50 : 50 wt %), (2) chitosan–LDPE (50 : 50 wt %).

Preparation and fractionation of polysaccharide–LDPE–PEO ternary blends

The polysaccharide–LDPE–PEO ternary blends were also prepared in the rotor disperser. At that, the content of polysaccharides varied from 20 to 40 wt %, while the content of PEO in all blends was as high as 20 wt %.

The process was carried out via feeding a polymer blend into the disperser at intervals at 130°C.

Fractionation of chitin–LDPE–PEO and chitosan–LDPE–PEO compositions was carried out using the same set of sieves as for fractionation of the binary blends. Figure 7 shows the histograms of the polysaccharide–LDPE–PEO blends at the ratio of the components 30 : 50 : 20 wt %. As compared to the binary blends, the increase of the system dispersity is observed due to the appearance of the fractions with more coarse particles. Moreover, the ratio of the basic fractions is changed. Thus, for a chitin–LDPE–PEO blend, the basic fraction (almost 50%) contains particles 0.09–0.315 mm in size, and the content of fraction with particles 0.315–0.63 mm in size is about 30%, whereas, for chitosan–LDPE–PEO blend, the ratio of the fractions with particles 0.09–0.315 and 0.315–0.63 mm in size is approximately the same ($\sim$ 30%).

TABLE III
Change of Weight and Mechanical Characteristics of Blends after Holding in Soil during Five Months

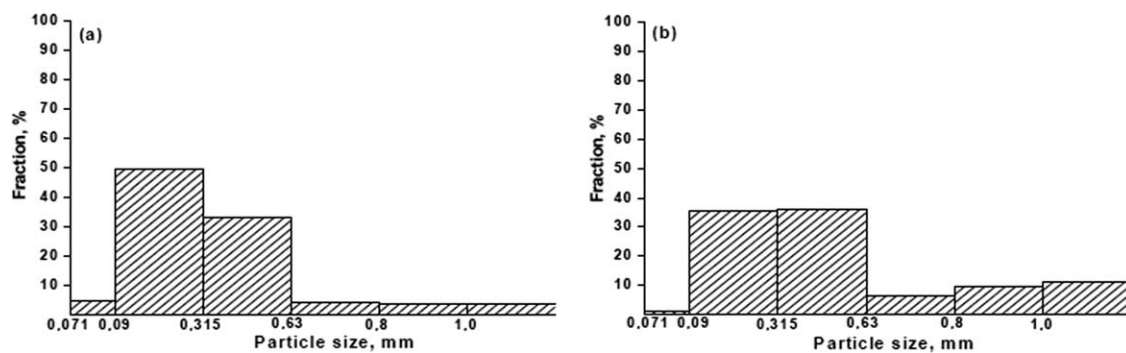| Composition	Weight loss (%)	Change of mechanical characteristics (%)	
		E	ε_b
Chitin–LDPE (50 : 50 wt %)	3.5	−1.6	−8
Chitosan–LDPE (50 : 50 wt %)	3.5	−4.9	−14.8

Figure 7 Histograms of particle size distribution for blends: (a) chitin–LDPE–PEO (30 : 50 : 20 wt %), (b) chitosan–LDPE–PEO (30 : 50 : 20 wt %) (M_{PEO} = 35,000).

Determination of the component ratio in polysaccharide–LDPE–PEO ternary blends

To establish whether the composition of the obtained blends is identical to the initial ratio of the components and determine their real ratio in the ternary blends after passing through a disperser the DSC method was used. All melting curves of the ternary blends display only two peaks with positions corresponding to melting temperatures of PEO ($T_m \approx$ 66–68°C) and LDPE ($T_m \approx$ 108–110°C), since polysaccharides are infusible compounds as it has already been mentioned. Changes in melting enthalpies of LDPE and PEO, besides the change of enthalpy owing to amorphization, which is constant for all blends, also depend on the content of components. Thus, the polysaccharide and synthetic polymer contents in composition can be calculated by the difference between the melting enthalpies of pure PEO and LDPE and the enthalpies of the blends (Table IV).

As is seen from Table IV, where the characteristics of the ternary blends with low-molecular PEO are presented, the obtained values are close to the initial component ratio. The same results were also obtained for the blends containing high-molecular PEO. Therefore, DSC can be considered as an additional method for calculation of the polysaccharide content in the ternary blends with synthetic polymers.

Investigation of mechanical characteristics and structure of polysaccharide–LDPE–PEO ternary blends

Table V lists the mechanical characteristics of the films obtained from the polysaccharide–LDPE–high-molecular PEO ternary systems. Figure 8 shows their dependences from the content of polysaccharides in the ternary blends with low-molecular PEO.

By comparing data presented in Tables II and V, it can be concluded that the addition of the third component to chitin–LDPE and chitosan–LDPE binary blends leads to an insignificant decrease in elastic modulus. However, the ultimate tensile strength σ_b both for the binary and ternary blends slightly depends on the content of the polysaccharides.

The values of elongation at break ε_b decrease with addition of the third component to the binary system. As the polysaccharide content in the blends increases, the values of elongation at break become almost the same for all compositions.

Figure 8(a) shows the dependence of elastic modulus from the polysaccharide content in the ternary blends with low-molecular PEO. As is seen from the presented data, for both films an increase of the polysaccharide content leads to an increase of elastic modulus E. The highest values of E were obtained for the films from the blends containing chitin that is caused by its higher rigidity compared to chitosan.

TABLE IV
Determination of Composition of Polysaccharide–LDPE–PEO Blends (M = 35,000) via DSC Method

Blend composition	Polysaccharide–LDPE–PEO ratio (wt %)	ΔH (LDPE) (J/g)	ΔH (PEO) (J/g)	Determined component content		
				Polysaccharide	LDPE	PEO
Chitin–LDPE–PEO	20 : 60 : 20	29.8	25.875	27	53.3	19.7
	30 : 50 : 20	25.823	33.081	28.7	46.1	25.2
	40 : 40 : 20	21.3	24.9	41.3	38.1	18.9
Chitosan–LDPE–PEO	20 : 60 : 20	32.61	26.9	21.3	58.2	20.5
	30 : 50 : 20	27.65	28.84	28.7	49.4	21.9
	40 : 40 : 20	24.99	25.94	35.6	44.7	19.7

TABLE V
Mechanical Characteristics of Films Obtained from Blends of Polysaccharides with
Synthetic Polymers at Various Component Ratios

Blend composition	Component ratio (wt %)	E (MPa)	σ_b (MPa)	ε_b (%)
LDPE	–	200 ± 5	13.3 ± 0.2	460 ± 10
Chitin–LDPE–PEO[a]	20 : 60 : 20	390 ± 8.1	7.03 ± 0.2	9.5 ± 2.1
	40 : 40 : 20	838 ± 18.5	8.9 ± 0.1	2.6 ± 0.1
Chitosan–LDPE–PEO[a]	20 : 60 : 20	325 ± 9.32	7.7 ± 0.1	16.8 ± 0.8
	40 : 40 : 20	587 ± 25.6	8.4 ± 0.15	3.9 ± 0.1

[a] $M_{PEO} = 5 \div 6 \times 10^6$

The values of ultimate tensile strength σ_b for the systems under investigation are close to each other and change insignificantly as the polysaccharide content in the blend increases [Fig. 8(b)].

Figure 8(c) exhibits changes of elongation at break ε_b of films from the blends of the investigated polysaccharides. As is seen from figure, the lowest values of ε_b are observed for the films with chitin at all component ratios. As the polysaccharide content in the blends increases, the values of elongation at break still decrease. Apparently, the observed differences are connected both with the morphology features of the investigated systems and the influence of the polysaccharides on the polymer matrix structure. Previously we have studied similar systems with LDPE and PEO based on cellulose, ethylcellulose, and starch.[30] As chitin and chitosan are more rigid polysaccharides than abovementioned ones, elastic modulus, tensile strength, and elongation at break of systems on their base are higher, but the dependence of the mechanical parameters of these blends from polysaccharide content is similar.

TGA measurements

To establish the influence of synthetic polymers on the thermostability of chitin and chitosan, we studied the thermal degradation of their blends with LDPE.
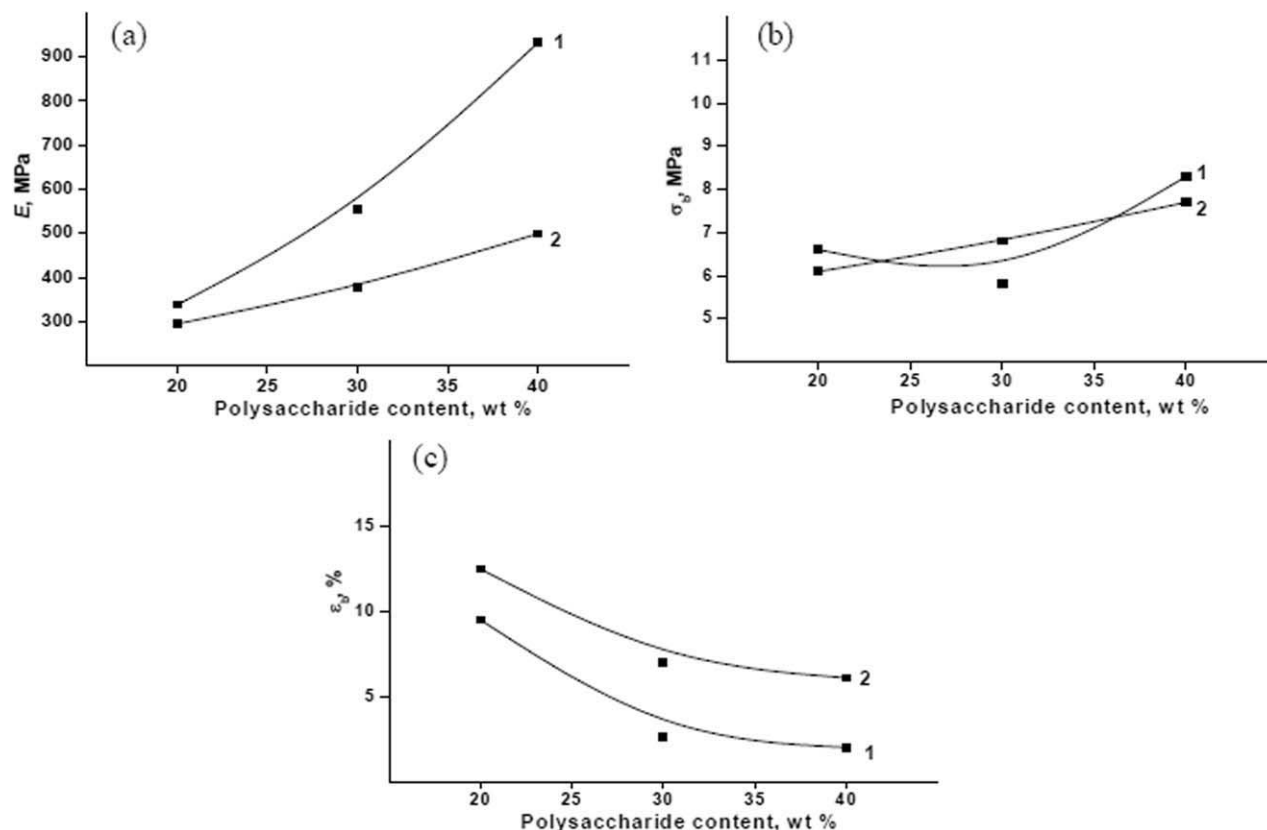

Figure 8 Dependence of mechanical characteristics of films from chitin–LDPE–PEO (1) and chitosan–LDPE–PEO (2) blends from polysaccharide content ($M_{PEO} = 35,000$, PEO content for all blends—20 wt %): (a) elastic modulus E, (b) ultimate tensile strength σ_b, (c) elongation at break ε_b.
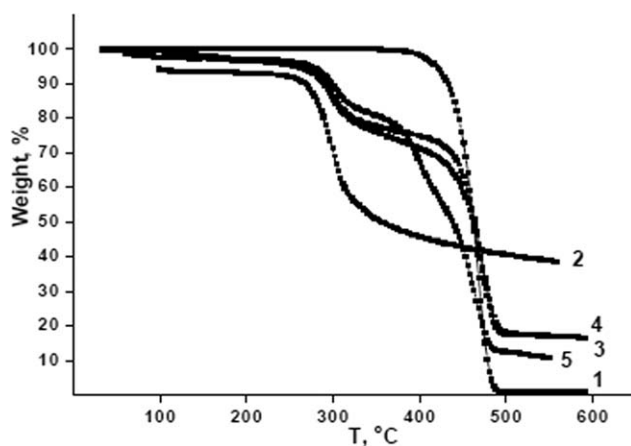
Figure 9 TGA curves of LDPE (1), chitosan (2), blend chitosan–LDPE (50 : 50 wt %) before (3) and after (4) irradiation and blend chitosan–LDPE–PEO (40 : 40 : 20 wt %, M_{PEO} = 35,000) (5), obtained in an argon atmosphere.

The investigation of the thermal properties of the individual components and polysaccharide–LDPE blends via TGA showed that the temperature of thermal decomposition of the systems, i.e., the onset of the blend degradation occurs at temperatures higher than for the individual polysaccharides. The presence of LDPE raises the decomposition temperature of the system compared to the initial chitosan that improves the thermal stability of the compositions (Fig. 9).

Table VI presents some characteristics of the thermal degradation process of LDPE and the individual polysaccharides under argon atmosphere. The initial temperature of degradation was determined using the standard procedure by the point of intersection of tangents of the thermogravimetric curves. The maximum yield of the volatile products was observed during the LDPE degradation. Thus, if LDPE is decomposed almost completely with formation of volatile products, chitin is decomposed by 70%, and chitosan only by 54% leading to formation of coke. The character of the curves is indicative of

TABLE VI
Parameters of Thermal Degradation of LDPE and Polysaccharides

Polymer	Temperature of degradation onset by ISO 7111	Maximum rate of degradation (%/min)	Temperature corresponding to maximum rate of degradation (°C)	Weight loss (%)
LDPE	443.4	−25.14	465.5	98
Chitin	218	−9.11	373.5	70.2
Chitosan	276.2	−8.92	298.6	54.09

the different rates of degradation and, consequently, of various contents of the forming products.

It is known that one of the important factors characterizing the influence on the thermal stability of the polymer materials is an intensive photooxidation under natural conditions. To investigate the influence of photooxidation on the stability of the studied compositions, the blends of LDPE with chitin and chitosan were subjected to photooxidation using a xenon lamp for 168 h, after that their thermal stability was examined. It was found that the effect of photooxidation for the blends of LDPE with chitosan appears to be more significant than for LDPE–chitin blends.

Figure 9 shows the TGA curves of LDPE, chitosan and their binary blends before and after photooxidation as well as a ternary blend with low-molecular PEO. As is seen from this figure, the temperature of the degradation onset for the irradiated blend is lower than for the blend before photooxidation that testifies the changes in the polymer structure during photooxidation. The addition of the third component (PEO) leads to a decrease of the system thermal stability compared to the binary systems approximately to the same extent, which is observed under the influence of photooxidation. Nevertheless, the degradation temperatures are somewhat higher than those for the polysaccharides, i.e., the operating properties of such systems are not deteriorated.
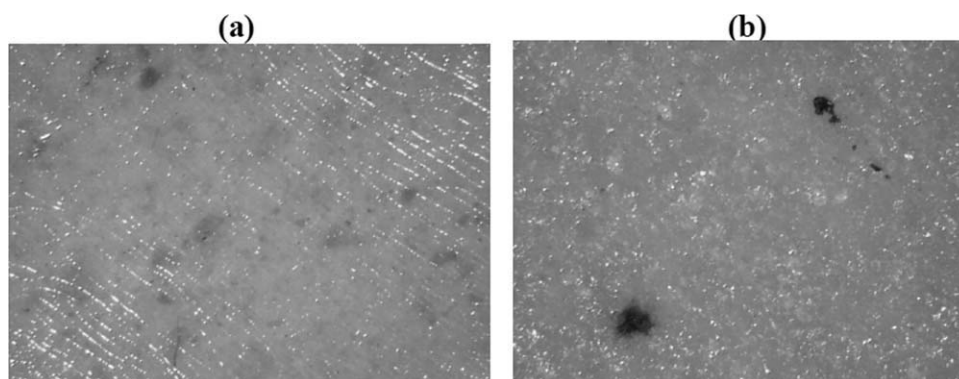

Figure 10 Micrographs of surface of films, infected with fungus spores for 28 days, from blends: chitosan–LDPE (50 : 50 wt %) (a) and chitosan–LDPE–PEO (40 : 40 : 20 wt %, M_{PEO} = 35,000) (b).

Study of biodegradation of ternary blends

The tests on the fungus resistance performed with films obtained from the blends of various compositions showed that the introduction of PEO into the system promotes the fungus growth. Hence, while for the films obtained from the chitosan–LDPE (50 : 50 wt %) blend the maximal intensity of fungus growth corresponds to 1, the addition of 20% PEO ($M = 35,000$) significantly increases the fungus amount and they can be clearly seen by the naked eye (Fig. 10). The estimation in this case corresponds to 5 for the composition of chitosan–LDPE–PEO film of 40 : 40 : 20 wt %, i.e., the addition of the third component leads to the significant increase of biodegradability. So in the presence of PEO chitosan does not show the fungicidal properties.

CONCLUSIONS

By summing the results on mixing chitin and chitosan with LDPE under the action of high-temperature shear deformations, although the initial polysaccharides are the infusible compounds, the powders are formed. In this case, a partial degradation of the crystalline structure of the polymers is observed.

The investigation of biodegradability of the obtained compositions showed that the blends based on chitin are characterized by a higher biodegradability. To increase the biodegradability of the blends containing chitosan, PEO of different molecular weight was added to the composition with the intensity of fungus growth increasing to the maximal level.

The study of thermooxidative degradation of chitin, chitosan, and their blends revealed that the LDPE presence promotes the increase of thermal stability of the composition, whereas the PEO introduction and prior photooxidation lead to a decrease of the initial temperature of the blend degradation.

The determination of the mechanical characteristics of the binary blends of chitin and chitosan with LDPE and the ternary blends chitin (chitosan)–LDPE–PEO showed that the introduction of PEO results in a slight deterioration of the mechanical properties, which, nevertheless, are still sufficient for creation of materials for different purposes including medical application.

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