NATURAL POLYMERS

Biodegradable Polymer Composites Based on Polylactide and Cellulose

**S. Z. Rogovina[a],*, K. V. Aleksanyan[a], A. A. Kosarev[a],
N. E. Ivanushkina[b], E. V. Prut[a], and A. A. Berlin[a]**

[a]Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, 119991 Russia
[b]Skryabin Institute of Biochemistry and Physiology of Microorganisms,
Russian Academy of Sciences, pr. Nauki 5, Pushchino, Moscow oblast, 142290 Russia
*e-mail: s.rogovina@mail.ru
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Abstract—Blends of polylactide with microcrystalline cellulose are obtained under high-temperature shear deformation. In order to improve plasticity and biodegradability of the system, low-molecular-mass poly(ethylene glycols) of various molecular masses are introduced into the composites. The mechanical and thermophysical properties of these composites, as well as their water and moisture absorptions, are studied. The morphology and biodegradability of the samples are investigated with the use of various physicochemical and biological methods.

Biodegradable polymers based on renewable raw-material resources are attracting attention from a growing amount of researchers, a circumstance that is connected with both existing ecological problems and the inevitability of the depletion of oil reserves [1−3]. Among the polymers based on natural raw materials, a special place is occupied by polylactide—a linear aliphatic polyester that is formed via the polymerization of the lactic acid resulting from the fermentation of renewable natural products (corn, sugar beet, potato, etc.).

Polylactide has good mechanical properties; however its main disadvantage is brittleness. Nevertheless, during proper plasticization, polylactide becomes elastic and approaches polypropylene and poly(ethylene terephthalate) in terms of characteristics [4−6]. Despite the fact that polylactide is produced via polymerization of a natural monomer, it rapidly biodegrades only in compost and sea water [7]. At the same time, it is known that the biodegradability of polylactide-based composites is higher than that of the pure polymer [8]; therefore its mixing with other natural biodegradable polymers makes it possible, on the one hand, to increase biodegradability and, on the other hand, to impart new properties to the composites. Exactly this fact determines the abundant quantity of studies dedicated to the investigation of polylactide blends with various polysaccharides, for example, starch [9, 10] and chitosan [11−13]. Disadvantages inherent in natural polysaccharides, such as low mechanical characteristics, poor water resistance, and difficult processability, restrict their wide application in the production of materials based on them. The creation of composites based on polylactide and natural polysaccharides promotes elimination of these disadvantages and allows one to obtain the materials with improved properties and increased biodegradability.

Of unconditional interest are biodegradable composites based on polylactide and cellulose, the most abundant polysaccharide in nature. Such composites are produced with the use of wood cellulose, microcrystalline cellulose (MCC), nanocellulose whiskers obtained from lignocellulose fibers of the plant origin, and viscous fibers. The addition of cellulose, which in this case serves as a reinforcing filler, makes it possible to improve the properties of polylactide, thereby affecting its crystallinity and mechanical and thermal properties [14, 15], and, in addition, to decrease the cost of the related articles and to simultaneously impart new properties to them.

Improvement of the mechanical properties of the composites based on polylactide in which flax and wood cellulose are used as cellulose natural fibers was reported in [16, 17] and [18, 19], respectively. On the whole, the rigidity of polylactide may be increased relatively easily via its filling with natural fibers; however, the improvement of such mechanical properties as tensile and bending strengths, as well as impact strength, is a complex task.

Nanoscale cellulose is best suited to the production of films and packages; in this case, plasticizers or surfactants are often introduced into composites in order to improve the distribution of nanoparticles. For

example, MCC and cellulose nanowhiskers were introduced into polylactide [20, 21]. The nanowhiskers were obtained from MCC through its mixing with *N,N*-dimethylacetamide containing LiCl and then, in the form of a suspension, were added in the polylactide melt during extrusion. The application of poly(ethylene glycol) as a plasticizer made it possible to improve the mechanical properties of the composite: for example, the tensile elongation increased 800%. As was shown in [22], the introduction of 1% cellulose nanowhiskers and 20% glycerin triacetate as a plasticizer into polylactide improves the dispersion of nanofibers in the matrix and increases the elongation at break and viscosity.

The authors of [23] used PVA to improve the distribution of cellulose nanowhiskers in the polylactide matrix [23]. It was shown that nanowhiskers are mainly distributed in PVA, while only a small portion is in polylactide. In this case, the mechanical characteristics improve insignificantly. In the production of nanocomposites with polylactide, cellulose nanowhiskers were impregnated with *tert*-butanol or a number of other surfactants [24]. The SEM investigation of the morphology of films showed that the untreated cellulose nanowhiskers have the form of flakes, while their treatment with *tert*-butanol yields network structures. On the basis of TEM data, it was found that the surfactant-treated nanowhiskers are uniformly distributed in the composite. TGA studies revealed that the obtained materials are stable in a wide temperature interval, and the results of dynamic mechanical thermal analysis made it possible to conclude that both initial and *tert*-butanol-impregnated nanowhiskers increase the dynamic elastic modulus of polylactide at high temperatures.

However, the blends of polylactide with MCC prepared in the absence of the plasticizer additionally feature high mechanical characteristics that increase with an increase in the MCC content [25].

As is known, cellulose poorly dissolves in the majority of organic solvents and requires the use of specific complex solvents. Because of the absence of common solvent for cellulose and polylactide, the obtainment of their composites from solutions presents a problem; therefore, they are usually produced via blending of a polylactide melt with cellulose.

The method of solid-phase blending under the high-temperature joint action of pressure and shear deformation shows promise for the production of cellulose blends. This method provides a way to obtain composites with a more uniform distribution of the components than that attained via traditional methods of blending.

EXPERIMENTAL

The objects of research were Biopolymer 4032D polylactide (Ingeo, T_m = 155–170°C, a transparency of 2.1%), powder MCC (MP Biomedicals, France), and low-molecular-mass PEG (Sigma, Germany; M_w = 600, 1000, and 4000).

The MCC and PEG were blended with polylactide in a Brabender Plastograph EC mixer (Germany) at 160°C for 10 min. The components were gradually added to the polylactide melt.

For mechanical tests, tests on fungus resistance, and investigations of biodegradability under conditions imitating the environment, the samples were pressed into 0.2-mm-thick films at a temperature of 160°C and a pressure of 10 MPa for 10 min and then were cooled under pressure at a rate of ~15 K/min. Dumbbell-shaped samples with a test area of 35 mm × 5 mm were cut from plates.

The mechanical tests were performed at room temperature on an Instron-1122 tensile testing machine in the stretching mode at a constant rate of upper traverse displacement of 50 mm/min. The results were averaged over six to seven samples.

The thermal stability of the composites was analyzed on an STA 449 F3 Jupiter synchronic thermal analyzer (Netzsch, Germany) over the temperature range 30–560°C in air. Temperature was changed at a rate of 10 K/min; the sample mass was approximately 10 mg.

Water absorption was measured according to the following procedure (GOST 4650-80): the film samples placed in water were allowed to stay in a thermostat at 30°C and were weighed at certain time intervals.

The laboratory tests on fungus resistance were performed according to GOST (State Standard) 9.049-91, which makes it possible to estimate the degree of fungus growth in the absence of mineral and organic pollutants. The method is based on the exposure of materials infected with an aqueous suspension of fungus spores under conditions optimum for their growth followed by estimation of the degree of fungus growth. Testing was performed with the use of test organisms from the All-Russia Collection of Microorganisms: *Aspergillus brasiliensis* Varga et al. 2007 ARCM F-1119, *Aspergillus terreus* Thom 1918 ARCM F-1025, *Aspergillus oryzae* (Ahlburg 1878) E. Cohn 1884 ARCM F-2096, *Chaetomium globosum* Kunze 1817 ARCM F-109, *Paecilomyces variotii* Bainier 1907 ARCM F-378, *Penicillium chrysogenum* Thom 1910 ARCM F-245, *Penicillium aurantiogriseum* Dierckx 1901 ARCM F-265, *Penicillium pinophilum* Thom 1910 ARCM F-1115, and *Trichoderma virens* J. Sheldon 1904 ARCM F-1117. The tests were performed for 45 days with an intermediate inspection at 21 days. The fungus resistance in terms of the intensity of fungus growth on the samples was evaluated according to the six-number scale.

The biodegradability of the polymer composites was studied via modeling processes occurring in the environment. For this purpose, the samples were placed in containers with wet soil at pH 7 meant for

Table 1. Influence of blend composition on the mechanical and thermal characteristics of the related films

Composite	Blend composition	Component ratio, wt %	E, MPa	σ_b, MPa	ε_b, %	Onset temperature of MCC degradation, °C
1	Polylactide	–	2625 ± 65	52.0 ± 1.0	4.7 ± 0.05	–
2	Polylactide–MCC	70 : 30	3640 ± 111	40.6 ± 1.73	1.9 ± 0.03	–
3	Polylactide–MCC	60 : 40	3900 ± 106	34.5 ± 1.76	1.5 ± 0.1	282.5
4	Polylactide–MCC–PEG$_{600}$	60 : 30 : 10	2040 ± 42.1	19.4 ± 0.57	1.7 ± 0.05	–
5	Polylactide–MCC–PEG$_{600}$	60 : 20 : 20	–	–	–	214.7
6	Polylactide–MCC–PEG$_{1000}$	60 : 30 : 10	1890 ± 79.1	19.0 ± 0.76	1.8 ± 0.10	–
7	Polylactide–MCC–PEG$_{1000}$	60 : 20 : 20	1150 ± 29.7	7.0 ± 0.5	0.9 ± 0.05	219.2
8	Polylactide–MCC–PEG$_{4000}$	60 : 30 : 10	1910 ± 24.1	21.0 ± 0.6	1.75 ± 0.1	252.8
9	Polylactide–MCC–PEG$_{4000}$	60 : 20 : 20	1400 ± 47	9.0 ± 0.5	1.0 ± 0.1	248.9

plant growth and were held in a thermostat at 30°C. The rate of biodegradation was monitored via measurement of mass losses of the samples at regular time intervals.

The morphology of the samples before and after exposure in soil for several months was investigated via SEM. For this purpose, the cross-sections of the initial films were prepared in liquid nitrogen; in addition, the surfaces of the films were studied. The tests were performed with an SEM JEOL SM-70001 F scanning electron microscope (Japan).

RESULTS AND DISCUSSION

MCC and polylactide were blended under conditions of high-temperature shear deformation in a Brabender mixer at 160°C; the MCC contents in the compositions were 30 and 40 wt %. Previously, the blends of polylactide with chitosan and ethyl cellulose were obtained under the same conditions and their mechanical and thermophysical properties and biodegradability were examined [26, 27].

In order to improve the plasticity of composites and to improve their biodegradability, low-molecular-mass PEG (M_w = 600, 1000, and 4000) was added as a plasticizer to the blend. In this case, blending was performed as follows. PEG was introduced into the polylactide melt in the Brabender mixer to attain a more uniform distribution of the components, and MCC was slowly added in small portions. The content of the plasticizer was varied from 10 to 20%. The results of the mechanical testing of the pressed films are listed in Table 1.

As is seen from the table, the addition of MCC to polylactide leads to an increase in elastic modulus E and a decrease in breaking strength σ_b and in elongation at break ε_b. For example, for the composites containing 30 and 40 wt % MCC, the values of strength and elongation at break decrease from 40.6 to 34.5 and from 1.9 to 1.5, respectively.

For the plasticizer-containing composites, the content of MCC was varied from 20 to 30 wt % in the blend and the content of PEG was varied from 10 to 20 wt %, while the content of polylactide remained constant and equal to 60 wt %.

It was found the introduction of PEG of various molecular masses into the composites leads to a decrease in the elastic modulus and tensile strength and weakly affects the elongation at break, an outcome that is apparently associated with poor compatibility of PEG with the blend components.

At the same time, the mechanical characteristics of the composites are affected not only by the molecular mass of PEG but also by its amount. For example, increases in the contents of both PEG$_{1000}$ and PEG$_{4000}$ lead to worsening of all mechanical parameters of the composites (Table 1). It should be emphasized that the use of PEG$_{600}$ in an amount of 20 wt % makes the samples so brittle that they go to pieces in one's hands; therefore, their mechanical characteristics cannot be determined.

The TGA study of the thermal behavior of polylactide–MCC and polylactide–MCC–PEG composites showed that there is almost no mass loss (only water removal) for any of composites in the 50–200°C range. In the absence of PEG, the MCC begins to degrade at 300°C; however, after the addition of PEG of various molecular masses, degradation begins as early as at 200–250°C. The onset temperature of composite degradation depends on the molecular mass of PEG and falls with its decrease. The onset temperatures of the degradation of MCC in the blends containing PEG of various molecular masses are presented in Table 1 and Fig. 1.

Water absorption is an indirect characteristic of biodegradability of a material because the presence of moisture is needed for the growth of microorganisms. The data on water absorption of the polylactide–MCC and polylactide–MCC–PEG composites mea-
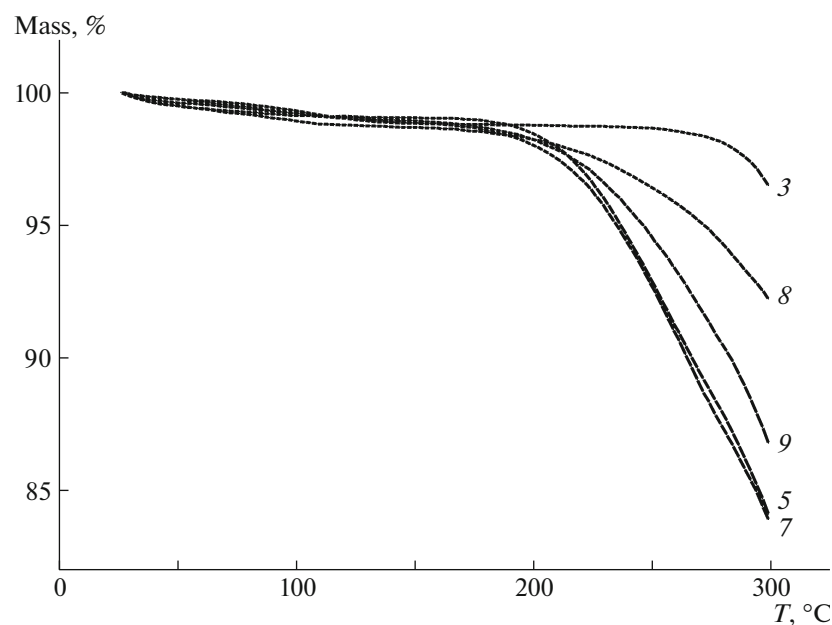
Fig. 1. TGA curves. Here and in Figs. 2−6, curve numbers correspond to the composite numbers in Table 1.

sured at various component ratios are presented in Table 2 and Fig. 2.

As is seen, the highest level (about 9%) of water absorption was observed for the polylactide−MCC−PEG_{600} (60 : 20 : 20 wt %) composite after a 15-day exposure in water, whereupon the system became equilibrated and no further increase in water absorption was observed. For the remaining composites, the maximum water absorption was observed as early as after 6−7 days exposure in water, whereupon the values of water absorption changed insignificantly. The lowest values (2−3 wt %) were observed for the polylactide−MCC−PEG_{4000} (60 : 20 : 20 wt %) composite. These results may be explained by the fact that water absorption of the composites depends on both the content of the hydrophilic cellulose polymer and the

molecular mass of PEG, because, a lower molecular mass of PEG results in a greater amount of its hydroxyl groups that can bind water. Exactly this fact determines the location of water-absorption curves relative to each other when the polylactide−MCC−PEG_{600} (60 : 20 : 20 wt %) composite absorbs a higher amount of water than the polylactide−MCC (60 : 40 wt %) binary composites, for which water absorption, in turn, is higher than that of the polylactide−MCC−PEG_{600} (60 : 30 : 10 wt %) ternary composite.

Because PEG incorporated into the composites is a water-soluble oligomer, its washout from the samples was studied as depending on its molecular mass and content in the composites. It was impossible to allow for the factor of washout of the filler from the samples at every weighing, because drying of a sample

Table 2. Water absorption and washout of PEG in relation to the blend composition

| Composite	Blend composition	Component ratio, wt %	Water absorption, ±0.5 wt %, days					PEG washed out, wt %
			2	6	14	28	5	
2	Polylactide−MCC	70 : 30	4.0	8.0	6.0	6.1	4.7	−
3	Polylactide−MCC	60 : 40	5.0	6.0	7.0	7.6	7.6	−
4	Polylactide−MCC−PEG_{600}	60 : 30 : 10	4.0	5.0	5.5	6.8	3.9	5
5	Polylactide−MCC−PEG_{600}	60 : 20 : 20	3.8	4.6	9.5	9.3	9.7	14
6	Polylactide−MCC−PEG_{1000}	60 : 30 : 10	5.9	7.1	6.7	6.7	6.2	4
7	Polylactide−MCC−PEG_{1000}	60 : 20 : 20	2.8	3.9	3.3	3.4	3.6	18
8	Polylactide−MCC−PEG_{4000}	60 : 30 : 10	6.2	8.4	7.0	7.7	6.4	5
9	Polylactide−MCC−PEG_{4000}	60 : 20 : 20	2.6	2.8	2.6	2.2	2.6	17
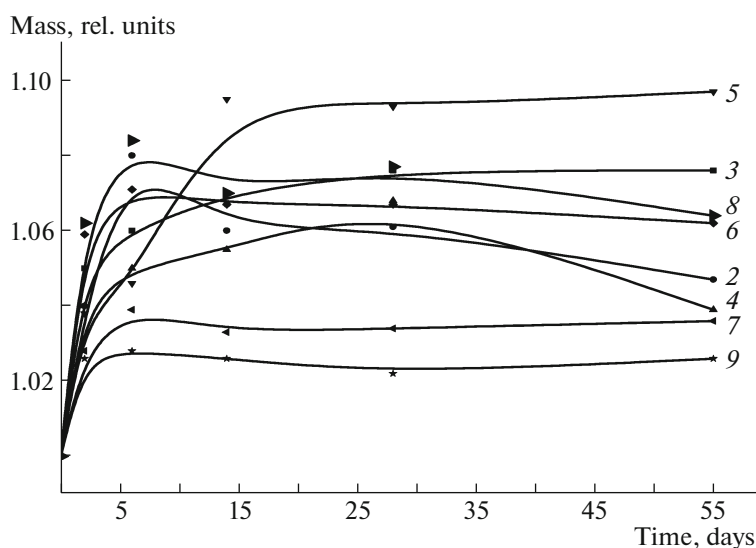
Fig. 2. Water absorption of composites vs. time of exposure in water.

to a constant mass was required; therefore, only the masses of the initial samples and the masses of the same samples during the last weighing, after 55 days, were compared. The difference in the masses of the initial and dried samples taken relative to the initial sample made it possible to calculate the amount of the washed-out PEG. The results are summarized in Table 2.

As is seen, the most intense washout of PEG was attained for the composite containing 20 wt % plasticizer. In this case, almost all PEG was washed out from the composites (14−18%). In the composites containing 10 wt % PEG, almost half of it was washed out. Such behavior can be explained by the looseness of the composite's structure, which increases with an increase in the amount of PEG and thus facilitates its subsequent washout during contact with water. Note that, in this case, the molecular mass of PEG does not affect its washout.

The presence of hydrophilic PEG in the samples imparts the ability to absorb moisture from air into them. Measurements of film sample mass after exposure in the drying chamber to a constant mass at 100°C and exposure in air for several days showed that the samples absorbed about 1 wt % moisture without direct contact with water.

During fungus-resistance tests of the samples, the samples were held in a nutrient medium for 45 days to obtain the maximum reliable results. These tests were performed for the polylactide−MCC (60 : 40 wt %) composite and the polylactide−MCC−PEG_{600}, polylactide−MCC−PEG_{1000}, and polylactide−MCC−PEG_{4000} (60 : 20 : 20 wt %) composites.

For the films obtained from the polylactide−MCC (60 : 40 wt %) blend, the intensity of growth after incubation for 45 days is demonstrated only by single

microcolonies typical for fungi belonging to the genus *Aspergillus* (Figs. 3a, 3b); that is, the tested samples are sufficiently stable against the action of the mold fungi. Therefore, the intensity of their growth was estimated as 2 points.

The growth of fungi on the films containing PEG is illustrated by the polylactide−MCC−PEG_{1000} (60 : 20 : 20 wt %) composite. After incubation for 21 days, the growth of fungi was insignificant. At a 50-fold magnification, they appeared as point microcolonies in the form of small dark dots (Figs. 3c, 3d); at a greater magnification (×200), they are similar to the conidial heads of fungi (Fig. 3e), looking like those of the genus *Aspergillus* fungi. After incubation for 45 days, the character of the microcolonies changed slightly; at a ×200 magnification, the conidial structures typical for the genus *Penicillium* fungi were distinguished (Fig. 3f).

Similar features are observed for the composites containing PEG_{600} and PEG_{4000}.

Thus, despite the fact that, after testing for 45 days, the growth of fungi (mycelium growth and weak sporulation observable under the microscope) is detected for all samples, these systems are highly stable against the action of fungi. It appears that the biodegradability of the MCC-containing composites significantly depends on the type of second component.

Changes that occurred in the samples after their exposure in soil at 30°C for 266 days were investigated through mass-loss measurements. As is seen from Fig. 4, there is no mass loss for the polylactide−MCC composite throughout its exposure; however, the addition of 10 wt % PEG leads to a substantial mass loss. The greatest mass loss (24%) was found for the sample containing 10 wt % PEG_{600}, while for the sample containing PEG_{4000}, the mass loss was about 15%;
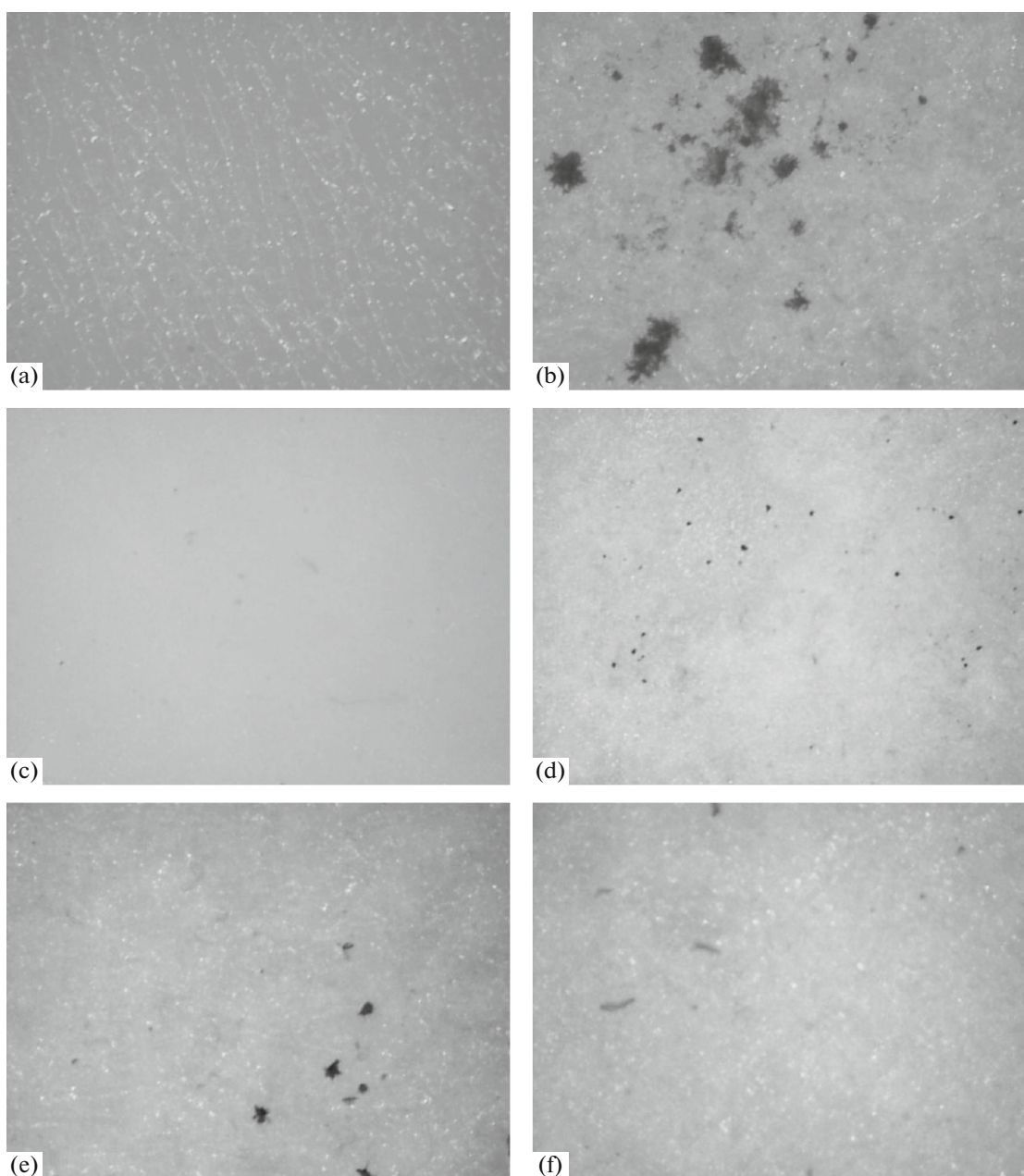
Fig. 3. Micrographs of films obtained from composites (a, b) 3 and (c–f) 7 (a, c) before and (b, d–f) after fungus-resistance tests. The test durations are (b, f) 45 and 21 (d, e) days. The magnification factors are (a, b, e, f) 200 and (c, d) 50.

that is, the mass loss of the composite depends on the molecular mass of the plasticizer.

The structure of the samples was studied via SEM. Figure 5 shows the micrographs of the initial polylactide–MCC (Figs. 5a, 5b) and polylactide–MCC–PEG (Figs. 5c, 5d) composites at various magnifications.

Figures 5a and 5b clearly show the MCC microfibrils located in the polylactide matrix. The introduction of PEG into the system promotes the formation of more pronounced and ordered polymer structures (Figs. 5c, 5d).

The surface micrographs of the polylactide–MCC–PEG$_{4000}$ film after exposure in soil for 137 days are presented in Fig. 6. In this case, a film cross-section cannot be obtained, owing to its high brittleness. At ×100 magnification (Fig. 6a), a deep crack and branches emanating from it are clearly seen. This result is evidence that degradation of the sample occurs during exposure in soil. As is seen in Fig. 6b,
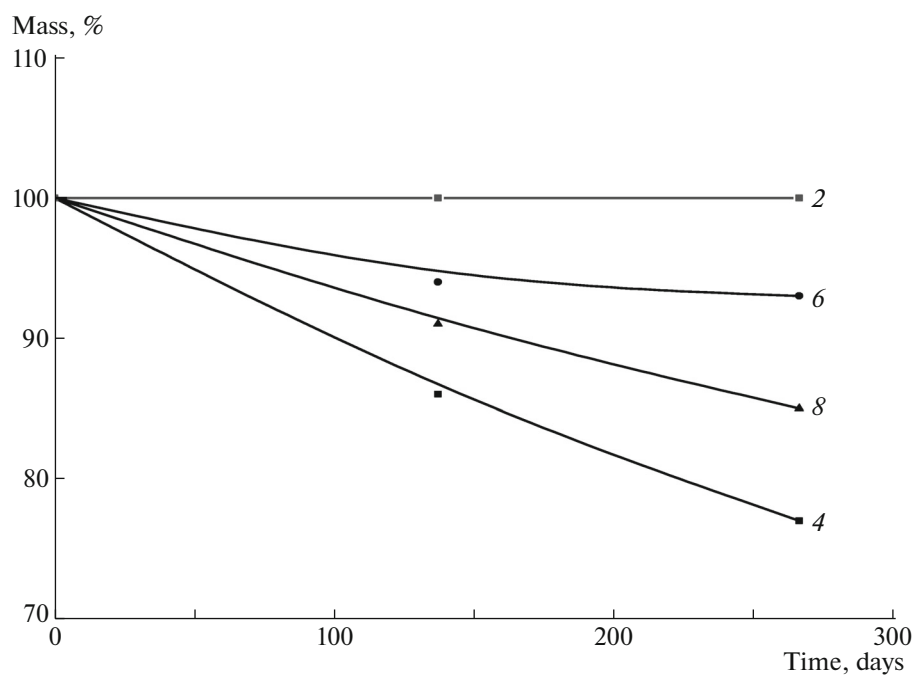
Fig. 4. Curves of mass loss for samples after exposure in soil.
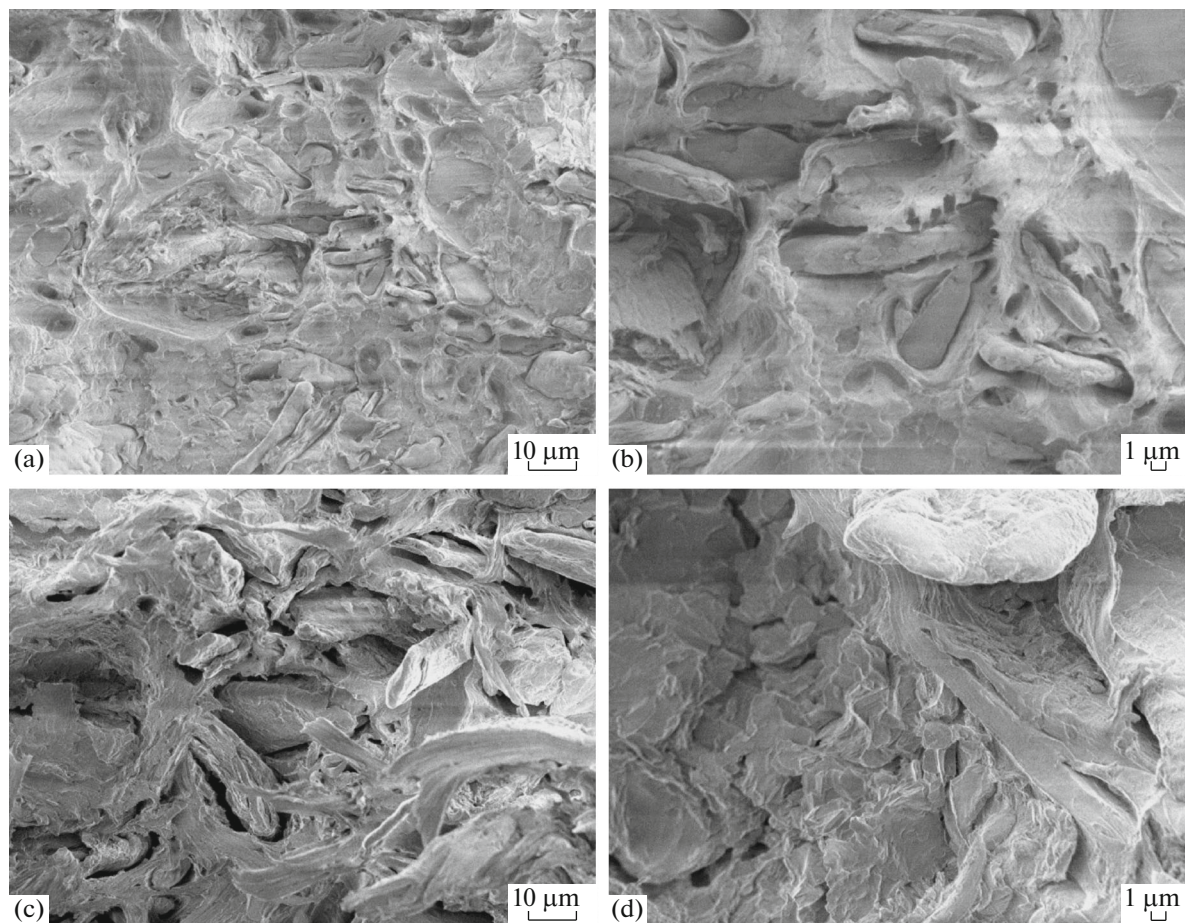

Fig. 5. SEM micrographs of film cross-sections obtained from composites (a, b) 2 and (c, d) 9. The magnification factors are (a, c) 1000 and (b, d) 3000.
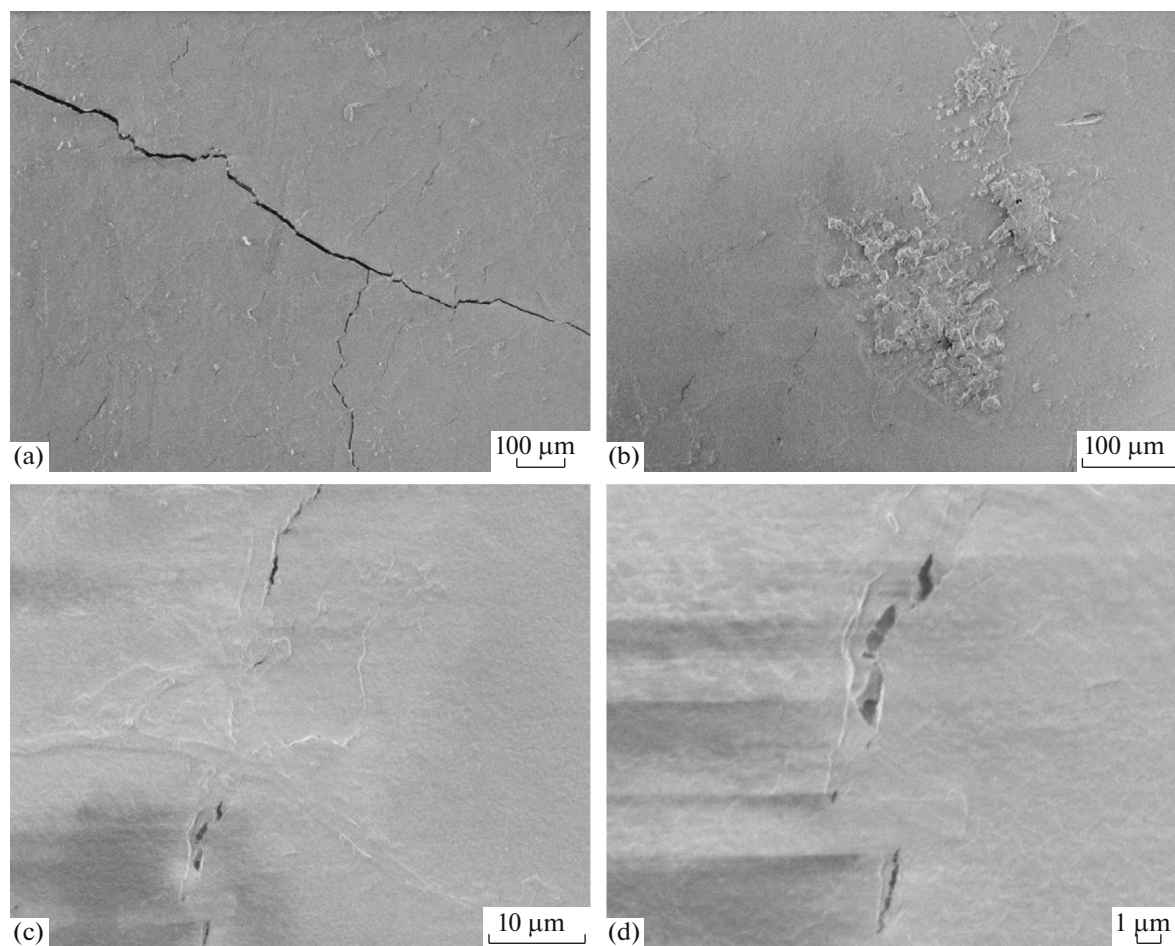
Fig. 6. SEM micrographs of the surfaces of films obtained from composite 9 after exposure in soil for 137 days. The magnification factors are (a) 100, (b) 200, (c) 2000, and (d) 5000.

scabs, which are apparently microspores of the solid fungi, form on the film surface.

Figures 6c and 6d illustrate the micrographs of the same film at greater magnifications. In this case, holes are clearly seen on the micrographs at ×2000 and ×5000 magnifications on the surfaces of the films. This finding is indicative of the initial stage of fragmentation of the samples, which leads to their subsequent degradation related to the process of biodegradation.

Thus, the polylactide−MCC and polylactide−MCC−low-molecular-mass PEG (M = 600, 1000, and 4000) composites have been prepared in a Brabender mixer at elevated temperatures under shear deformation. The addition of PEG weakly affects the mechanical characteristics of the composites, but decreases the initial temperatures of their thermal degradation and promotes biodegradation during exposure in soil. The SEM study of film morphology after exposure in soil makes it possible to ascertain the presence of structural defects that form as a result of sample biodegradation and lead to their subsequent fragmentation and destruction.

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