

## Investigation of biodegradability of composites based on polyethylene and polysaccharides by independent methods

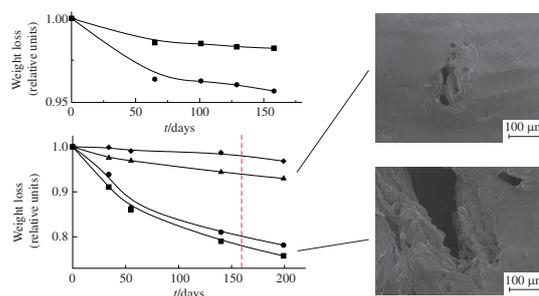
Svetlana Z. Rogovina,<sup>\*a</sup> Kristine V. Aleksanyan,<sup>a</sup> Arkadii Ya. Gorenberg,<sup>a</sup>  
Natalya E. Ivanushkina,<sup>b</sup> Eduard V. Prut<sup>a</sup> and Alexander A. Berlin<sup>a</sup>

<sup>a</sup> N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 137 8284; e-mail: s.rogovina@mail.ru

<sup>b</sup> G. K. Skryabin Institute of Biochemistry and Physiology of Microorganisms, Russian Academy of Sciences, 142290 Pushchino, Moscow Region, Russian Federation

DOI: 10.1016/j.mencom.2018.01.036

The biodegradability of the binary polymer composites containing a polysaccharide and low density polyethylene was improved *via* addition of a second polysaccharide as a third component. It has been studied by three independent methods, *viz.*, the measurement of the sample weight loss after exposure in soil, tests on fungus resistance, and the examination of the changes in the sample morphology by SEM. The composite biodegradability was shown to depend on the component ratio and the polysaccharide nature.



Among different factors causing the increase in environmental pollution, one of the most significant is the abundance of the synthetic polymer wastes. Polyethylene, especially low density polyethylene (LDPE), belongs to the most widespread synthetic polymers and its fraction in the solid wastes approximates 8–10%.<sup>1</sup> As the synthetic polymers are stable to the biological degradation, the creation of new biodegradable composite polymer materials on the basis of synthetic and natural polymers is of great importance.<sup>2–6</sup> Being synthesized from the lactic acid as the monomer of natural origin and having the properties comparable to those of the synthetic polymers, polylactide is widely used for production of new biodegradable composites.<sup>7–9</sup> Generally, the biodegradable composites may be produced *via* the blending of different synthetic polymers or polylactide and natural polymers, especially, nature polysaccharides, which present a nutrient medium for microorganisms initiating the polymer degradation. Thus, the synthetic polymer is responsible for the basic properties of material while the natural additives provide the biodegradability. The obtained materials may be successfully used in food industry, packaging production, *etc.*

According to the existing concept, the first stage of the degradation of the polymer composites with natural polymers under environmental conditions is the biodestruction of the natural component. The appearing cracks propagation is accompanied by formation of free radicals on the material surface. The forming free radicals initiate the oxidation reactions leading to further destruction of the material. Thus, the synthetic polymer matrix is involved into the biodegradation reactions and, hence, the fragmentation of composite materials takes place.

The increase in the biodegradability of the composites based on synthetic and natural polymers can be achieved by the addition of another biodegradable component (for example, a second polysaccharide) to the system. Although numerous studies on the biodegradability of the polysaccharide-based composites have been documented, the biodegradation of the ternary composites

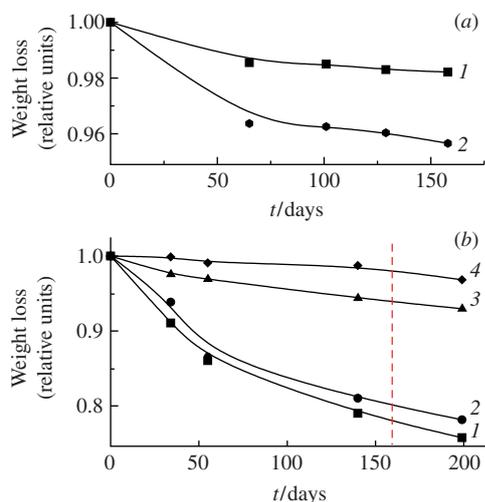
containing two different polysaccharides has not been investigated so far.

In our previous works, the composites of LDPE with different polysaccharides were obtained by mixing the components in a rotor disperser under the action of shear deformation and their properties were studied.<sup>10,11</sup>

Here, we report the results of comparative study of the biodegradability of the binary (starch–LDPE, cellulose–LDPE) and ternary composites (starch–LDPE–chitosan, starch–LDPE–chitin, starch–LDPE–chitosan, cellulose–LDPE–chitin, and cellulose–LDPE–chitosan) by three independent methods, *viz.*, the measurement of the sample weight loss after exposure in soil, tests on fungus resistance, and the examination of the sample morphology by SEM before and after tests on fungus resistance and exposure in soil.

To study the biodegradability under environmental conditions, the samples of binary blends and ternary blends were placed in the soil for plant growing at room temperature for several months. The rate of biodegradation was estimated by the weight loss of samples measured at time intervals (Figure 1). The weight loss of the binary composites starch–LDPE proceeds more intensively than that of the cellulose–LDPE composite [Figure 1(a)]. The corresponding values obtained after 160 days are 4.5 and 1.8%, respectively. At the same time, the addition of chitin or chitosan as second polysaccharide leads to more significant weight loss [Figure 1(b)] of 20% for starch–LDPE–chitosan, 22% for starch–LDPE–chitin, 2.5% for cellulose–LDPE–chitosan, and 6.5% for cellulose–LDPE–chitin. Thus, the starch-based composites are more strongly subjected to destruction than the cellulose-based ones. In both cases, the addition of chitin favors a more intensive decrease in the weight loss of composite as compared to the chitosan addition. Note that the most intensive weight loss of ternary composites occurs mainly within the first two months.

The tests on fungus resistance were performed as follows. The materials infected with fungus spores from the All-Russian Collection of Microorganisms (VKM) were incubated under the



**Figure 1** Weight loss after exposure in soil for films of (a): (1) cellulose-LDPE and (2) starch-LDPE (30:70 wt%); (b): (1) starch-LDPE-chitin, (2) starch-LDPE-chitosan, (3) cellulose-LDPE-chitin, and (4) cellulose-LDPE-chitosan (30:40:30 wt%).

optimum conditions of their growth and then the degree of fungus growth (from 0 up to 5) was estimated by a digital microscope. It was established that only binary systems of LDPE with starch and chitin contained the significant amount of nutrients favouring the intensive fungus growth. In this case, the fungi covering more than 90% of the surface are clearly seen with the naked eye. At the same time, the degree of fungus growth for chitosan-LDPE and cellulose-LDPE blends with the same component ratio was evaluated as 1, since the microscopic examination showed only separate sprouted spores and a weakly developed mycelium.<sup>10</sup> However, the introduction of second polysaccharide promotes more intensive fungus growth.

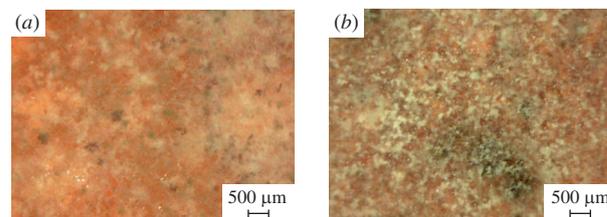
For the starch-based composites containing two polysaccharides, the fungus growth on the surface was clearly seen by the naked eye and exceeded 25%, which corresponds to the maximal point 5 and implies the minimal fungus resistance of these materials (Table 1). The additions of chitin or chitosan as the second polysaccharide have different effects on the fungus growth: the total surface area infected by fungus was larger for starch-LDPE-chitosan composite compared to that for the composite involving starch and chitin (Figure 2, Table 1), *viz.*, 100 and 85%, respectively. Moreover, the weight loss of the samples in 84 days, determined after the fungus removal from the surface, was also higher in the case of starch-LDPE-chitosan than for the starch-LDPE-chitin system: 9.1 and 7.7%, respectively. Thus, these values correlate with each other and allow one to quantitatively evaluate the biodegradation.

The cellulose-based composites demonstrated a greater stability to the action of fungi as compared to the starch-based systems. Despite the fact that the cellulose-LDPE-chitin sample also showed the maximal degree of the fungus development, the total

**Table 1** Parameters of fungus resistance evaluation.

Composite <sup>a</sup>	Parameter, test duration		
	Fungus resistance, 28 days	Fungus infected area, 28 days (%)	Weight loss, 84 days (wt%)
Starch-LDPE-chitosan	5	100	9.1
Starch-LDPE-chitin	5	85	7.7
Cellulose-LDPE-chitin	5	50	1.5
Cellulose-LDPE-chitosan	3	15	0

<sup>a</sup>Component ratio for all composites was 30:40:30 wt%.



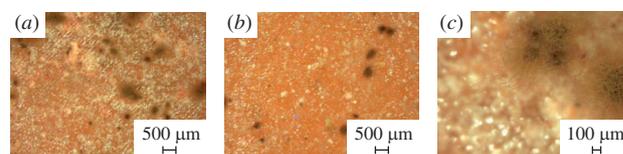
**Figure 2** Micrographs of film surfaces infected by fungus spores in 84 days: (a) starch-LDPE-chitin and (b) starch-LDPE-chitosan (30:40:30 wt%).

infected area did not exceed 50%, the weight loss was as low as 1.5%. At the same time, the cellulose-LDPE-chitosan composite may be considered as fungus resistant, since the fungus growth was poorly visible with the naked eye, but was clearly seen through the microscope, which corresponds to the degree of fungus growth of 3; in this case, the fungus infected area did not exceed 15%, and no weight loss was observed (Figure 3).

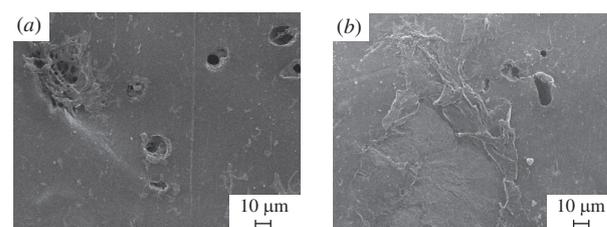
The first colonizer for all composites was *Chaetomium globosum*, which forms clear distinguishable black fruiting bodies on the substrate even in 14 days [Figure 3(c)]. This organism primarily known as an active cellulolytic fungus<sup>12</sup> dominates in the cellulose-based samples for 84 days. For the starch-based systems, within 28 days of observation, one can reveal other dominating fungi known as producers of amylase and chitinase: *Aspergillus terreus*, *Paecilomyces variotti* (starch-LDPE-chitosan), *Penicillium spp.*, *Trichoderma virens* (starch-LDPE-chitin).<sup>13,14</sup>

The SEM images of the surfaces of the starch- and cellulose-containing composite films after tests on fungus resistance are presented in Figure 4. The investigation of the film cross-section was impossible because of the film high fragility. The SEM results confirm the obtained regularities of the fungus resistance. The destruction of the samples resulting in formation of holes was more intensive in the starch-based composites [Figure 4(a)] as compared to the cellulose-based ones [Figure 4(b)].

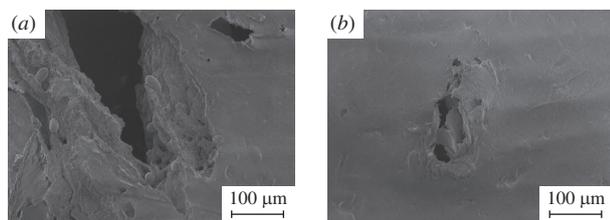
The SEM study of the morphology of films prepared from the ternary composites after exposure in soil shows the presence of structural defects resulted from the sample biodegradation leading to formation of holes in the polyethylene matrix followed by fragmentation and destruction of the sample (Figure 5). This fact testifies that not only the polysaccharide participates in the biodegradation but also the synthetic polymer matrix is subjected to degradation. The similar data for starch-LDPE composite were obtained previously;<sup>15</sup> moreover, with the use of SEM and optical microscopy, it was shown that the commercial LDPE lost the integrity in 22 months under generally favorable conditions.<sup>16</sup>



**Figure 3** Micrographs of film surface infected by fungus spores in 84 days: (a, c) cellulose-LDPE-chitin and (b) cellulose-LDPE-chitosan (30:40:30 wt%). (c) Fruiting bodies of *Chaetomium globosum*.



**Figure 4** SEM images of the surface for (a) starch-LDPE-chitin and (b) cellulose-LDPE-chitin films (30:40:30 wt%) after tests on fungus resistance.



**Figure 5** SEM images of the surface for (a) starch-LDPE-chitin and (b) cellulose-LDPE-chitin films (30:40:30 wt %) after exposure in soil.

Note that the film surface before exposure is smooth and uniform, whereas after exposure the test samples become significantly more fragile.

Apparently, the microcracks and spots are more visible in the SEM images of starch-LDPE-chitin films compared to cellulose-LDPE-chitin ones that is indicative of a more intensive biodestruction of the starch-based composites (Figure 5). These data correlate with the results of the SEM examination of the samples after tests on fungus resistance and the corresponding weight loss of the studied systems.

The obtained results are confirmed by the data of FTIR spectroscopy.<sup>17,18</sup> Previously,<sup>19</sup> we also showed, using FTIR spectra of the films obtained from ternary composites before and after exposure in soil during six months, that crystallinity of LDPE after exposure in soil changes. Being calculated from the intensity ratio of rocking vibrations of the CH<sub>2</sub> group D<sub>730</sub>/D<sub>720</sub> (or 730 and 720 cm<sup>-1</sup>), the degree of crystallinity of LDPE appears to be increased in ~5%. The observed decrease in the content of the amorphous phase seems to be related to the degradation of LDPE that correlates with the SEM data.

Moreover, the comparison of IR spectra of starch-LDPE composite before and after its exposure in water considered as the action of the groundwater on the films for several weeks allows one to reveal the IR bands characteristic of starch on the film surface. Being absent on the initial film surface, these bands are attributed to the degradation of LDPE. As the investigated composites represent the polysaccharide encapsulated in the LDPE matrix, the latter is mechanically destructed as long as the starch swells in water and the radicals for initiating the process of LDPE degradation are formed. The presence of starch on the film surface after exposure in water was also confirmed by the characteristic iodine reaction resulting in the surface colouring blue.

Thus, the study of biodegradability of the binary and ternary polysaccharide-based composites by three independent methods showed that the process generally depends on the nature of the polysaccharides used and the ratio of components. The addition of second polysaccharide (chitin or chitosan) as the third component

to cellulose-LDPE and starch-LDPE composites results in an increase both in the rate and in the degree of biodegradation. All obtained results agree with the existing concepts on biodegradation of the polymer composites containing polymer of natural origin (polysaccharide) described above.

The application of the proposed complex of methods allowed one to follow the versatile changes proceeding in the polysaccharide-based materials during the biodegradation under various conditions.

This work was supported by the Russian Science Foundation (grant no. 14-13-00803).

## References

- 1 T. Ojeda, A. Freitas, K. Birck, E. Dalmolin, R. Jacques, F. Bento and F. Camargo, *Polym. Degrad. Stab.*, 2011, **96**, 703.
- 2 A. Clarinval and J. Halleux, in *Biodegradable Polymers for Industrial Applications*, ed. R. Smith, Woodhead, London, 2005, pp. 3–31.
- 3 J.-M. Raquez, R. Narayan and P. Dubois, *Macromol. Mater. Eng.*, 2008, **293**, 447.
- 4 M. Rinaudo, *Prog. Polym. Sci.*, 2006, **31**, 603.
- 5 S. Z. Rogovina, *Polym. Sci., Ser. C*, 2016, **58**, 62 (*Vysokomol. Soedin., Ser. C*, 2016, **58**, 68).
- 6 F. Xie, E. Pollet, P. J. Halley and L. Avérous, *Prog. Polym. Sci.*, 2013, **38**, 1590.
- 7 S. Z. Rogovina, K. V. Aleksanyan, A. V. Grachev, A. A. Berlin and E. V. Prut, *Mendelev Comm.*, 2015, **25**, 361.
- 8 K. Oksman, A. P. Mathew, D. Bondeson and I. Kvien, *Compos. Sci. Technol.*, 2006, **66**, 2776.
- 9 M. A. Huneault and H. Li, *Polymer*, 2007, **48**, 270.
- 10 S. Z. Rogovina, K. V. Aleksanyan, D. D. Novikov, E. V. Prut and A. V. Rebrov, *Polym. Sci., Ser. A*, 2009, **51**, 554 (*Vysokomol. Soedin., Ser. A*, 2009, **51**, 813).
- 11 S. Z. Rogovina, K. V. Aleksanyan, E. V. Prut and A. Ya. Gorenberg, *Eur. Polym. J.*, 2013, **49**, 194.
- 12 K. H. Domsch, W. Gams and T.-H. Anderson, *Compendium of Soil Fungi*, IHW-Verlag, Eching, 2007.
- 13 G. H. Dar, A. N. Kamili, R. Nazir, S. A. Bandh and T. A. Malik, *Int. J. Biotechnol. Mol. Biol. Res.*, 2014, **5**, 35.
- 14 A. A. Shubakov and P. S. Kucheryavykh, *Appl. Biochem. Microbiol.*, 2004, **40**, 445.
- 15 H. V. Ruiz, E. S. M. Martinez and M. Á. A. Méndez, *Starch*, 2011, **63**, 42.
- 16 T. Mumtaz, M. R. Khan and M. A. Hassan, *Micron*, 2010, **41**, 430.
- 17 S. M. Goheen and R. P. Wool, *J. Appl. Polym. Sci.*, 1991, **42**, 2691.
- 18 S. Djellali, N. Benmahmoud and T. Sadoun, *Ann. Chim. Sci. Mat.*, 2009, **34**, 41.
- 19 S. Z. Rogovina, K. V. Aleksanyan, L. V. Vladimirov, E. V. Prut and A. A. Berlin, *Dokl. Phys. Chem.*, 2015, **465**, 270 (*Dokl. Akad. Nauk*, 2015, **465**, 58).

Received: 15th May 2017; Com. 17/5249