Oxidation and biodegradation of polymeric composites based on polylactide: structure and properties

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Abstract. Polymer blends of polyethylene – polylactide of different composition were obtained and studied. Thermal degradation was investigated in the temperature range from 20 to 700 °C. It is shown that the polyethylene more resistant to the effects of temperature (peak of destruction - 414 °C) than polylactide (peak degradation – 364 °C). In blends with increasing polyethylene content in the matrix increases the maximum temperature of thermal degradation. The process of thermal oxidation carried out at temperatures of 80, 90, 110 °C and a pressure of 300 Torr. Binary polylactide–low-density polyethylene blends of various compositions were prepared, and their biodegradability in soil. The weight loss is higher upon incubation in laboratory soil compared to open soil.

1. Introduction
Polymer blends are systems, made through mixing of two or more polymers. In most cases polymer mixing is a process of mutual dispersion, possibly combined with further mutual solution of two or more liquids of higher viscoelasticity. Within such a system, inter-phase dispersability, morphology and adhesion largely depend upon interfacial energies that are of paramount importance for formation of a level of performance properties. In this connection, research of blends, their structures and properties is important for analysis of their performance.

A great number of scientific papers are dedicated to compositions based upon biodegradable polymers. The most popular biodegradable polymers: polylactide (PLA), polycaprolactone (PCL), polyhydroxyalcanoates (PHB, PHV) [1-7].

It is thought that PLA made with use of natural raw materials, such as corn, grain and other agricultural crops can partially replace polymers, being products of petrochemicals synthesis. PLA exhibits optimal mechanical properties, but shows a not high value of elongation per unit length and thermal stability [8].

That way, research works by various authors are mainly focused on improvement of PLA physical and mechanical properties. Extensive works were performed with purpose of manufacture of PLA blends with biodegradable, synthetic and secondary polymers. One of the benefits of PLA is its degradability under the influence of a number of various factors. Therefore, more extensive research is required to enable assessment of degradability of PLA and its compositions in a variety of conditions [9, 10].
2. Experimental
Blends of LDPE (TM 15803-020 from Neftekhimsevilen, OJSC, Russia) with PLA (4032D from Nature works, USA) in a wide range of compositions were studied. The PLA content in the polymer matrix was 20, 30, 50, 70, 80 wt% and pure polymers PLA and LDPE. There were also made three triple blends with 10, 20, 30 wt% of LDPEa (LDPE held in air, in an open vessel, at a temperature of 90°C for 250 hours, TM 15803-020 from Neftekhimsevilen OJSC, Russia) to neat LDPE respectively and 30 wt% of PLA[7].

The degree of crystallinity and melting temperature of the samples were studied with differential scanning calorimeter DSC 214 Polyma (Netzsch, Germany) at a heating rate of 10K/min and a sample weight of 5±0.1 mg. The experiment on thermal oxidation was performed in a static manometric installation at 80, 90, 110 °C and oxygen pressure of 300 Torr with the absorption of gaseous reaction products by solid KOH [7].

Thermogravimetric analysis using NETZSCH Tg 209 F1 Iris derivatograph (Germany) was carried out to study the thermal resistance of polymers. The heating rate was 20 °C / min, the analyzed temperature range was 25-700 °C.

The infrared spectra of the samples were recorded on the FT-IR spectrometer Perkin Elmer Spectrum 100 at T = 23 ± 2 °C in the wave number range 4600 ≤ ν ≤ 450 cm⁻¹ in transmitted light [7]. For a complex study of the biodegradation of the materials, we performed a soil test on restored soil. The restored soil prepared according to GOST (State Standard) 9.060 simulates the real soil, leveling off the difference between various types of soils and ensuring high reproducibility of the results [11].

3. Results and discussion
As demonstrated in article [12], blend components are crystallizing polymers, and it makes the nature of their molecular level interaction more complex. According to numerous studies, the introduction of a high-molecular second component into a polymer matrix can ambiguously affect its molecular structure, material properties, and resistance to aggressive media.

Introduction of rigid-chain polymers into PE is, as a rule, accompanied by a lower elongation per unit length. In these PLA:LDPE compositions, a trend as follows is seen: higher PLA contents result in higher strength of the material. This is due to a rather high value of tensile strength of pure PLA, which ranges from 56 to 63 MPa.

In this paper, we studied the process of solid-phase oxidation of low-density polyethylene and polylactide blends at a temperature of 80, 90, and 110°C (figure 1).

![Figure 1. Oxygen uptake kinetic curves for various blends:](image-url)

(1) 30PLA:40LDPE:30LDPEa and (2) 30 PLA:70LDPE at 110°C; (3) 30PLA:40LDPE:30 LDPEa and (4) 30PLA:70LDPE at 90°C; (5) 30PLA:40LDPE:30LDPEa and (6) 30PLA:70LDPE at 80°C.
The influence of temperature on the process of thermal oxidation is confirmed by the calculation of the oxidation rate of the compositions. The obtained dependence is shown in figure 2. It is noted that the oxidation rate increases with increasing temperature and content of LDPE in the blends.

![Figure 2. Dependence of the oxidation rate of PLA:LDPE blends on the content of LDPE in the blends at a temperature of (1) 80°C, (2) 90°C and (3) 110°C and an oxygen pressure of 300 Torr.](image)

It should be noted that LDPEag oxidized faster than the original polyethylene, although according to the DSC melting point it is higher than the original LDPE. The above fact is confirmed by thermogravimetric analysis (TGA) (figure 3). It is shown that the polyethylene more resistant to the effects of temperature (peak of destruction - 414 °C) than polylactide (peak degradation – 364 °C).

![Figure 3. DSC (a) melting thermograms: 1 – 100LDPE, 2 – 100LDPEag and TGA curves (b) of compositions PLA: LDPE: 1 – 100PLA, 2 – 70PLA:30 LDPE, 3 – 30PLA:70 LDPE, 4 – 100 LDPE, 5 – 100 LDPEag.](image)

An important aspect of present-day polymer materials is their biodegradability under the influence of such a factor as soil microorganisms. In the paper [13], dedicated to research of PLA incubation in soils under normal conditions, it was found that it undergoes slow destruction, and degradation begins in several months. Other papers [14, 15] reveal that the number of PLA-decomposing microorganisms is considerably lower than that of those able to degrade PHB and PCL. On the other hand, PLA degradation can be accelerated by composting, where PLA hydrolysis leads to formation of smaller molecules (oligomers, dimers and monomers) in 45 – 60 days within a temperature range of 50–60 °C and then to formation of CO₂ and H₂O due to presence of microorganisms in compost. The
experiments on degradation of the materials in soil allowed prediction of their behavior upon disposal in dumps. The main experiment was performed at constant temperature and moisture content (laboratory soil), and field tests were also performed for comparison. The weight loss $\Delta m$ (%), changes in the specimen appearance, and intensity of the development of microorganisms on the specimen surface upon exposure to soil were used as the main parameters characterizing the degradation of the materials. After incubation of specimens in restored soil for 12 months, the largest weight loss, 18%, is observed for the 50 PLA:50 LDPE blend. For the other compositions, $\Delta m$ is 5–10% [11].

In parallel to that laboratory test one conducted a 24-month outdoor research of PLA:LDPE binary mixtures. Figure 4 shows images of film samples of PLA:LDPE compositions upon exposure of materials to natural conditions within 24 months. The figure illustrates pores, cracks and blush. The latter is the most pronounced in samples of higher PLA contents, exposed to hydrolytic degradation.

After exposing the materials under natural environmental conditions, numerous mechanical damages are observed. It is important that some PLA:LDPE blends, e.g., those with 30, 50, and 100 wt. % polylactide content, undergo biofouling under field conditions more intensely compared to the materials subjected to laboratory tests. This fact can be attributed to higher concentration of microorganisms in soil on the test site. In laboratory soil, the concentration of microorganisms can decrease with time (figure 5). An average weight loss in the compositions upon natural tests comes to about 7 – 10% [11].

**Figure 4.** Photographs of specimens of PLA:LDPE blends. PLA content of the polymer matrix, wt %: (a) 30, (b) 70, (c) 100 after 24-month exposure to natural environmental conditions.

**Figure 5.** Photomicrographs of specimens of PLA–LDPE blends after exposure to soil under field conditions for 24 months. PLA content of the matrix, wt %: (a) 30, (b) 70, (c) 100.
To control the structure upon exposure in soils, one used IR spectroscopy and differential scanning calorimetry (DSC) methods. For PLA:LDPE samples subject to outdoor conditions within 24 months a ratio of crystal-phase optical densities $755\ cm^{-1}$ to amorph-phase ones $870\ cm^{-1}$ was calculated ($D_{755}/D_{870}$). An increase of this ratio is observed, which illustrates amorph phase destruction processes.

Research results of thermal and physical characteristics of the compositions upon outdoor exposure within 24 months are presented in Table 1, which shows that a degree of crystallinity is decreased by 5–15%, suggesting material destruction processes in progress.

Table 1. Thermal and physical characteristics of PLA:LDPE compositions after 24 months in soils.

| Blends PLA:LDPE, wt.% | $T_m,^\circ C$ | $T_m,^\circ C$ after 24m soil | $\chi$, % | $\chi$, % after 24m soil |
|-----------------------|---------------|-------------------------------|-----------|--------------------------|
| 100:0                 | 165           | 163                           | 45        | 40                       |
| 70:30                 | 163:103       | 161:103                       | 39:17     | 35:15                    |
| 50:50                 | 164:103       | 162:102                       | 53:19     | 35:16                    |
| 30:70                 | 164:104       | 162:103                       | 52:17     | 37:16                    |
| 0:100                 | 105           | 104                           | 25        | 24                       |

The results obtained enable to draw a conclusion that in a laboratory environment, subject to a constant temperature and contents of moisture, weight loss processes carry more actively than in soils. Analysis of the band intensity ratio ($755\ cm^{-1}/870\ cm^{-1}$) and DCS data reveals that destruction processes carry both in amorph- and crystalline-phases of PLA matrix.

4. Conclusion

The present study enables the conclusion that the process of oxygen uptake depends on the blend composition, i.e., on the content of PLA, as a component with a high degree of crystallinity. The addition of LDPE, to the compositions containing 30 wt % PLA, accelerates the thermal oxidation of blends at all examined temperatures.

Upon incubation of the specimens in laboratory soil for 12 months, the weight loss is 5–10% (the largest weight loss, 18%, was observed for the 50:50 wt % blend), and after 24-month field tests the weight loss is 2–6% depending on the composition, with the largest weight loss observed for the 20:80 (about 11%) and 50:50 wt % (8%) blends. The weight loss in open soil is smaller than in the laboratory soil. This fact is associated with temperature fluctuations in the open soil and with the concomitant decreases in the microorganism activity. The most intense development of mycelial fungi in open soil was observed for the blends containing 30, 50, and 100 wt % polylactide.

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References

[1] Farah S, Anderson D G and Langer R 2016 Adv. Drug Deliv. Rev. 107 pp 367–392
[2] Peelman N, Ragaert P, Ragaert K, Meulenaer B D, Devlieghere F and Cardon L 2015 J. Appl. Polym. Sci. 132 pp 42305
[3] Ni J and Abe H 2015 Polym. 60 p 260
[4] Arrieta I P, Lopez J, Hernández A and Rayon E 2014 Eur. Polym. J. 50 p 255
[5] Tertyshnaya Yu V and Podzorova M V 2018 Russ. J. Appl. Chem. 91 p 417
[6] Zhang X, Espiritu M, Bilyak A and Kurniawan L 2008 Polym. Degrad. Stab. 93(10) pp 1964–1970
[7] Podzorova M V, Tertyshnaya Yu V, Karpova S G and Popov A A 2019 IOP Conf. Ser. Mater. Sci. Eng. 525 012043
[8] Bobel A, Lohfeld S, Shirazi R N and McHugh P E 2016 Polym. Test. 54 p 150
[9] Kim Y F, Choi C N, Kim Y D, Lee K Y and Lee M S 2004 Fibers and Polym. 5 pp 270-274
[10] Ploypetchara N, Suppakul P, Atong D and Pechyen C 2016 Energy Procedia 56 pp 201-210
[11] Tertyshnaya Yu V and Podzorova M V 2019 Rus. J. Appl. Chem. 92(6) pp 737–744
[12] Tertyshnaya Yu V, Podzorova M V, Monakhova T V and Popov A A 2016 Rus. J. Phys. Chem. B 10(5) pp. 825–829
[13] Ohkita T and Lee S H 2006 J. Appl. Polym. Sci. 100 pp 3009-3017
[14] Pranamuda H, Tokiwa Y and Tanaka H 1997 Appl. Environ. Microbiol. 63 pp 1637-1640
[15] Tokiwa Y and Calabia B P 2007 J. Polym. Environ. 15 pp. 259-267