Biodegradable materials containing recycled polymers

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Abstract. The work is devoted to study the effects of different environmental factors such as water, oxygen and, light composition based on polylactide and polyethylene of low density with the addition of oxidized polyethylene, as an analog of recycled materials. Established that in the composition polylactide – polyethylene at the first stage the significant impact of moisture and UV light. The influence of UV radiation on polylactide destruction was proved by differential scanning calorimetry (DSC). It is found that polylactic acid is oxidized slower than polyethylene.

1. Introduction
At the present time, the effect of temperature, water, oxygen, light, microorganisms on biodegradable polymers such as polylactide [1-4], polyhydroxybutyrate [5-7], polycaprolactone and composites on their basis are studied intensively. Polylactide or polylactic acid (PLA) is the polyester with a good range of physical and mechanical properties, biocompatibility with the human body, as well as the ability to biodegrade in the environment [4]. At low temperature, microbiological degradation of PLA is strongly retarded [8].

The main problem for those blends is the low compatibility between systems. The idea of using highly degraded polyethylene as a compatibilizer has good prospects [9]. In this study highly oxidated low density polyethylene (LDPEox) was used as a model of recycled polyethylene. The idea was to improve adhesion between PLA and neat low density polyethylene (LDPE) by the addition of LDPEox. Furthermore, the obtained triple blends, made of PLA, LDPE, LDPEox should be more prone to biodegradation than the double ones, made of PLA and LDPE. The influence of the environmental factors on the polymeric materials is extremely important [10-12]. That is why it is important to determine the influence of ultraviolet radiation, water absorption and thermal oxidation on the polymer degradation.

2. Experimental
In this study the authors evaluated the influence of ultraviolet radiation, incubation in the soil, and water absorption of double blends made of PLA and LDPE, and triple blends made of PLA, LDPE and oxidized LDPE. Different methods were used in this study: differential scanning calorimetry (DSC), thermal oxidation, influence of ultraviolet and water absorption.

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 0, 20, 30, 50, 70, 80, 100 wt%. There were also made three triple blends with 10, 20, 30 wt% of LDPEox (LDPE held in air, in an open vessel, at a temperature of 90°C for 250 hours, TM 15803-020 from Neftekhimsevilen OJSC, Russia) added to 60, 50, 40 wt% of neat LDPE respectively and 30 wt% of PLA. The blends were prepared by the Plasticorder PLD-651 (Brabender) at a temperature of 180°C for 6 minutes. After cooling, the samples of the obtained material were milled using a knife mill RM-120 and then compressed in a manual hydraulic press PRG-10 at 180°C under a load of 7 kN followed by rapid cooling. As a result, film round samples with a diameter of 8 cm and thickness of 100±10 μm were obtained.

The degree of crystallinity of polymers in the blends was studied using a differential scanning calorimeter Netzsch DSC 214 Polyma at a heating rate of 8 K/min and sample weight of 10±0.1 mg. The temperature scale was calibrated against the indium standard (Tm = 156.6°C, ΔH = 28.44 J/g). The water absorption degree was determined in distilled water at 25°C according to DIN EN ISO 62:2008-05.

The influence of ultraviolet on the obtained samples was studied by a lamp Vilber Lourmat VL-6.LC at λ=254 nm for 100 hours. The experiment on thermal oxidation was performed in a static manometric installation at 110°C and oxygen pressure of 300 mm Hg with absorption of gaseous reaction products by solid KOH.

The mechanical properties were examined by a tensile compression testing machine Devotrans DVT GP UG 5 (Turkey) according to ISO 527-1:2012. The tensile strength and elongation at break were determined. The data were averaged by six samples.

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3. Results and discussion
It was found that the addition of a small amount of LDPEox to the blend of PLA and LDPE does not influence their melting temperatures (method DSC) but decreases the crystallinity degree of LDPE and slightly increases the crystallinity of PLA (Table 1).

| Blends PLA/LDPE, wt.% | Tm, °C | ΔHm, J/g | χcr, % |
|-----------------------|--------|----------|--------|
| 0/100                 | 103    | 61       | 21     |
| 30/70                 | 164/105| 49/46    | 52/16  |
| 100/0                 | 165    | 42       | 45     |

| Blends PLA/LDPE/LDPEox, wt.% | Tm, °C | ΔHm, J/g | χcr, % |
|-----------------------------|--------|----------|--------|
| 30/60/10                    | 165/104| 47/40    | 50/14  |
| 30/50/20                    | 165/104| 44/41    | 47/14  |
| 30/40/30                    | 165/104| 41/47    | 45/16  |

It has been established that at the initial stage of LDPE-PLA blends biodegradation two factors have the main influence: water and ultraviolet radiation. Water absorption of LDPE-PLA blends is rather low, but it is enhanced with the addition of oxidized LDPE to the blend (figure. 1). The maximum degree of water absorption is observed for the mixture containing 30% PLA, 40% LDPE and 30% recycled LDPE. But nevertheless the composition can be attributed to the hydrophobic materials, since the degree of water absorption is less than 10%.
During the experiment, ultraviolet radiation does not affect the structure of PE but has a strong influence on the structure of LA that was confirmed visually by samples cracking (figure 2) and by DSC – melting temperature decreases after radiation (figures 3-6). It is observed that compositions without oxidized LDPE are more resistant to UV radiation than compositions with oxidized LDPE.

Thermophysical parameters of PLA before and after UV treatment are studied. The change in the degree of crystallinity after exposure to UV radiation has been determined (figure 3). It is shown at the Figure 1 that as the time of exposure to UV radiation increases, the degree of crystallinity decreases. After 100 hours, this value drops by half, from 45 to 24%.
In the process of UV degradation the PLA melting temperature changes significantly. Under the action of UV radiation (wavelength of 254 nm) $T_m$ decreases from 163 to 152 °C after 50 hours, and to 135 °C after 100 hours (figure 6). The decrease in the melting temperature is explained by the shortening of macrochains due to oxidative degradation.

Figure 3. Degree of crystallinity of PLA after UV radiation.

Figure 4. PLA melting temperature before (black) and after (grey) ultraviolet radiation.

Figure 5. PLA crystallinity degree before (black) and after (grey) ultraviolet radiation.

Figure 6. Change in the melting temperature of PLA: 1 – initial sample, 2 – after 25 hours, 3 – after 50 hours, 4 – after 100 hours of UV radiation.
It was also found that PLA had a lower oxidation rate than LDPE. Triple blends (with oxidized LDPE) had a higher rate of oxidation than the double ones (without oxidized LDPE) (figure 7). PLA has a fairly high crystallinity and is probably dense amorphous phase, low permeability for oxygen. If the temperature of the experiment increases, the oxidation process is rapidly moving to destruction.

![Figure 7. Kinetic curves of thermal oxidation of blends (1 - LDPE, 2 – 30PLA/40LDPE/30LDPE\textsubscript{ox}, 3 - 30PLA/50LDPE/20LDPE\textsubscript{ox}, 4 - 30PLA/60LDPE/10LDPE\textsubscript{ox}, 5 – 30PLA/70LDPE, 6 – 50PLA/50LDPE, 7 – PLA).](image)

The mechanical characteristics of the PLA after UV exposure reduced significantly. It was found that after 10 hours of UV exposure, the mechanical parameters of the PLA fell dramatically, it became fragile, and therefore the study after 25 hours of exposure was impossible to occur (figure 8).

![Figure 8. Mechanical characteristics of PLA in dependence to the time of exposure.](image)
4. Conclusion
PLA becomes brittle after 50 hours of exposure to UV radiation. After 100 hours of photo-oxidation, cracking of all samples was noted, as well as the sharp decrease in the melting temperature (from 163 to 135 °C) and the degree of crystallinity (from 45 to 24%).

The tensile strength and the elongation at break of the PLA after 25 hours of exposure to UV radiation was sharply reduced.

At the infrared spectrum before and after 50 hours of UV irradiation, the optical density of the characteristic regions and PLA bands was changed. It indicates the oxidation and destruction of the material.

It is possible to deduce that all the double (LDPE-PLA) and triple (LDPE-PLA-LDPEox) blends satisfy the technological requirements and are suitable for producing goods. The addition of oxidized LDPE into PLA/LDPE blends changes their properties significantly. Blends with oxidized LDPE degrade easier because they are less stable to oxidation, more prone to water absorption and LDPE in such blends has a less degree of crystallinity. In order to accelerate the process of biodegradation in the environment, it is possible to radiate these blends by ultraviolet at the initial stage.

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