Impact of UV treatment on polylactide–polyethylene film properties

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Abstract. Influence of different environmental factors on the degradation of film samples based on polyactic acid and low density polyethylene with the addition of aged polyethylene was studied in this work. The article presents data after 100 hours influence of UV irradiation (λ=254 nm) obtained by differential scanning calorimetry (DSC) and electronic paramagnetic resonance (EPR). It was found that polylactide is more prone to UV degradation than polyethylene. It is shown that the effect of UV radiation for 100 hours reduces the melting point of polylactide from 165 to 135 °C, while the thermal characteristics of polyethylene vary slightly. There is a decrease in the melting temperature of the polylactide by 10-30 °C in all compositions. In the compositions with the content of PLA is more than 50 wt. % correlation time after UV exposure is significantly reduced.

Introduction

Creation of blends based on polylactide (PLA) with other materials is perspective for adjusting its properties and extend the range of possible applications [1]. Blends based on biodegradable polymers with the addition of synthetic polymers are the most perspective and in the focus of the researchers all over the world [2-4].

Biodegradable materials do not pollute the environment after using. Under the influence of ultraviolet, heat and air soil microorganisms they degrade to low molecular compounds and easily assimilate in soil, being included in closed ecological circuit [2]. The most popular biodegradable polymers: polylactide (PLA), polycaprolactone (PCL), polyhydroxyalkanoates (PHB, PHV) [5-10]. The problem is the high price of these polymers. That is why they are widely used in medicine but still unavailable for packaging industry.

In [11] it is noted that blends of polylactide – polyethylene in the first stage has a significant impact of moisture and ultraviolet light. Photodegradation of polymers is influenced by light rays that can be absorbed by the polymer. The absorbing centres are most often carbonyl and other oxygen-containing groups. In the presence of oxygen, UV light initiates a chain oxidation reaction. The number of CO-groups in the polymer increases sharply during photo-oxidation.
It is possible to produce thin transparent films with sufficient mechanical properties from the blends of biodegradable polymers with polyolefins. Such blends are cheaper than pure biodegradable polymers, that is why they may be used in a wide range of applications including packaging.

**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. The blends were prepared by mixing for 6 minutes at Plasticorder PLD-651 (Brabender, Germany) with a temperature of 180°C. After cooling the samples of the obtained material were milled using a knife mill RM-120 (Vibrotechnik, Russia) and then compressed in a manual hydraulic press PRG-10 (VNIR, Russia) 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 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 temperature scale was calibrated against an indium standard (Tm = 156.6°C, ΔH = 28.44 J/g). The influence of ultraviolet on the obtained samples was studied with a lamp Vilber Lourmat VL-6.LC at λ=254 nm for 100 hours. Electron paramagnetic resonance (EPR) was studied by EPR spectrometer EPR-V (N.N. Semenov Institute of Chemical Physics, Russia). Stable nitroxide radical (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO-1) was impregnated into films from the fumes at 30°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. The software ACDlabs was applied for the mathematical processing of the obtained data.

**Results and discussion**

The research demonstrated that in binary blends of PLA and LDPE the ratio of polymers did not have an influence to their melting temperatures for the initial blend (Table 1). But, after UV irradiation melting temperature of PLA decreased more in the blends with low amount of PLA. Evidently, if PLA does not form its own phase, it is more prone to UV degradation. The blend 50_PLA:50_LDPE has the highest crystallinity degree for both polymers, apparently it would have the best mechanical and barrier properties. The crystallinity degree of both polymers fell significantly after UV irradiation, but in the blend 50:50 χcr of LDPE had the highest value, it looks that in this blend both polymers are the most stable to UV degradation.

It was found that the addition of LDPEag to the blend of PLA and LDPE does not influence their melting temperatures (method DSC), but decreases the crystallinity degree of LDPE and PLA, if to compare with binary blend 30_PLA:70_LDPE (Table 1). In triple blends, containing LDPEag, melting temperature and crystallinity degree of PLA reduced after the influence of UV irradiation as well. It was stated that the addition of 30 mas. % of LDPEag led to dramatic decline of these parameters in PLA: PLA melting temperature decreased from 165 to 135 °C, and PLA crystallinity degree fell from 45 to 16%. Three initial blends with 10, 20, 30% of LDPEag had the same melting temperatures and similar crystallinity, but after UV irradiation their characteristics differed from each other strongly.

The study of amorphous phase of PLA and LDPE in blends was made by EPR-spectroscopy with paramagnetic sonde. Nitroxide radical – tetramethylpiperidine oxide, has dual nature (polar and nonpolar parts), for that reason, it is usually concentrated in interphase regions of polymer blends. Segmental mobility in amorphous regions of blends was evaluated by rotation velocity of radical-sonde (rotational correlation time) and shape of EPR-spectra.
Table 1. Thermophysical characteristics of PLA/LDPE and PLA/LDPE/LDPE ag blends.

| Blends PLA:LDPE, wt.% | $T_m, \degree C$ | $T_m, \degree C$ after 100h UV | $\chi, \%$ after 100h UV |
|----------------------|-----------------|-------------------------------|-------------------------|
| 100:0                | 165             | 135                           | 45                      | 20                      |
| 80:20                | 164:104         | 135:103                       | 40:17                   | 24:15                   |
| 70:30                | 163:105         | 137:102                       | 39:15                   | 24:14                   |
| 50:50                | 164:103         | 149:102                       | 53:19                   | 23:17                   |
| 30:70                | 164:104         | 151:103                       | 52:16                   | 24:17                   |
| 20:80                | 163:104         | 155:103                       | 40:18                   | 22:18                   |
| 0:100                | 103             | 102                           | 23                      | 18                      |

| Blends PLA:LDPE:LDPEag, wt.% | $T_m, \degree C$ | $T_m, \degree C$ after 100h UV | $\chi, \%$ after 100h UV |
|-----------------------------|-----------------|-------------------------------|-------------------------|
| 30:60:10                    | 165:104         | 150:102                       | 50:14                   | 34:12                   |
| 30:50:20                    | 165:104         | 148:103                       | 47:14                   | 20:13                   |
| 30:40:30                    | 165:104         | 135:102                       | 45:16                   | 16:13                   |

Figure 1 presents EPR spectra of PLA:LDPE blends. Blends with high content of PLA have complicated shape of spectra. For the blends with the low (<30%) and high (>50%) content of PLA shape of triplets are different. Apparently, PLA form its own phase in blends just from the concentration of 50%.

Figure 1. EPR spectra of nitroxide radical–sonde of double blends PLA:LDPE with the content of LDPE 100 (1), 80 (2), 70 (3), 50 (4), 30 (5), 20 (6), 0 (7) mass. %.
The correlation time ($\tau_c$) for compositions of various compositions is calculated. The values of the rotation correlation time of the radical probe in PLA are much higher than in HDPE. First of all, this is due to the supramolecular structure of the blend components. In PLA, the degree of crystallinity is almost 2 times higher than that of LDPE, therefore, the PLA is less permeable for radicals.

![Figure 2](image-url). Change in correlation time 1- initial, 2-after 100 hours of UV.

From figure 2 shows that in the compositions of PLA:LDPE with a PLA content of more than 50 wt. % correlation time decreases after UV exposure within 100 hours. The observed regularities can be explained from the position of inhomogeneity of mixtures.

Table 2 presents correlation time data of compositions containing aged polyethylene in the matrix.

| Blends PLA:LDPE:LDPEa, wt.% | $\tau_c \times 10^{10}$, c$^{-1}$ | $\tau_c \times 10^{10}$, c$^{-1}$ after 100h UV |
|-----------------------------|-----------------------------------|---------------------------------------------|
| 30:60:10                    | 4.7                               | 3.7                                         |
| 30:50:20                    | 4.8                               | 4.4                                         |
| 30:40:30                    | 5.1                               | 4.6                                         |

It can be seen from figures 3 and 4 that after exposure to UV radiation there is a change in the spectra, therefore, changes in segmental mobility and changes in the structure of the samples. No significant changes were found in the EPR spectra of the samples with aged polyethylene after UV.

The characteristic region for PLA is 1400-1000 cm$^{-1}$, which characterizes the stretching vibrations of C-O in esters. Also a band of 870 cm$^{-1}$ is responsible for valence symmetrical and asymmetric oscillations in the C-O-C group.

As it can be seen at the figure 5, after 50 hours, the changes occur in the characteristic areas and bands of the PLA. Thus, the optical density of the 870 cm$^{-1}$ band increases from 1.34 to 1.62, which indicates the oxidation and destruction of PLA under the influence of UV. Absorption at a frequency of 1160 cm$^{-1}$ that appears after radiation, refers to the vibrations of C-O groups in carboxylic acid anhydrides formed during the oxidation of the polymer.
**Figure 3.** EPR spectra before (solid) and after (stroke) UV irradiation (100 hours $\lambda=254$ nm) PLA:LDPE: 30PLA:70LDPE (1), 50PLA:50LDPE (2), 70PLA:30LDPE (3), 100PLA (4) mass. %.

**Figure 4.** EPR spectra before (solid) and after (stroke) UV irradiation (100 hours $\lambda=254$ nm) 30PLA:60LDPE:10LDPEag (1), 30PLA:50LDPE:20LDPEag (2), 30PLA:40LDPE:30LDPEag (3) mass. %.

**Figure 5.** IR spectrum of the initial PLA (1) and after (2) 50 hours of UV radiation.
In our study, after 50 hours of exposure to UV radiation there is a peak of low intensity at 1654 cm\(^{-1}\), which refers to the oscillations of the vinyl group [12], so the degradation of PLA occurs with the formation of C=C bond. In mixtures UV absorption center is PLA, which due to occurs fragmentation of PLA: LDPE blends.

**Conclusion**

In blends made of polyethylene and polylactide more stable to UV degradation is polyethylene. Melting temperature and crystallinity degree of polyethylene was more stable after degradation than polylactide. Under the influence of UV irradiation aged polyethylene accelerates physical degradation of polylactide in triple blends. Therefore, polyethylene waste is a good additive to PLA:LDPE blends focused on rapid biodegradation. By EPR spectroscopy it was found that PLA do not form its own phase when its content in blend is less than 50%. PLA parts are encapsulated in polyethylene matrix and nitroxide radical is unable to penetrate into PLA in that case. When studying the effect of ultraviolet radiation at \(\lambda = 254\) nm on the above samples by IR spectroscopy method was found that the PLA decay proceeds with the formation of C=C bond.

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