

Effect of UV-Irradiation and Ozone Exposure on Thermal and Mechanical Properties of PLA/LDPE Films

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Abstract. The mechanical properties of polymer composites based on polylactide vary significantly over a wide range of values. It has been established that photodegradation of low-density polyethylene – polylactide blends occurs both in the amorphous and in the crystalline phase of the PLA matrix, which leads to deterioration of the mechanical properties of the studied mixtures. Ozonolysis affects the strength parameters of polylactide-polyethylene samples as well as photodegradation. By the differential scanning calorimetry it is determined that the melting point of polylactide decreases by 2-4 °C, the glass transition temperature - by 1-3 °C, while the degree of crystallinity increases by 3-6%. In the process of ozonolysis, the thermophysical characteristics of PLA/LDPE have changed.

Introduction

Biodegradable composite materials are obtained from a combination of synthetic polymers with the addition of natural additives that are susceptible to biodegradation. Among biodegradable polymers, a special place is occupied by polylactide (polylactic acid, PLA). One of the disadvantages of polylactide is its relatively high fragility. Unfortunately, not all materials currently being developed are able to meet all the necessary technological requirements for full use (mechanical characteristics, biodegradability).

A semi-crystalline PLA is preferable to an amorphous polymer when higher mechanical properties are required. In turn, it is worth noting that the main feature of the PLA is strength and toughness, and the development of mixed materials based on polymers that differ in their mechanical characteristics is relevant, since it is possible to create a material with specified properties [1-4].

It is also important to study changes in the structure and physico-mechanical characteristics of the resulting blends when exposed to environmental factors, for example, ultraviolet radiation. Earlier in [5, 6] it was shown that UV- radiation affects the structure and crystallinity of PLA. Some researchers suggest compositions based on boards with components that increase its resistance to UV-radiation [7-9].

The urgency of the problem of giving biodegradability properties to well-mastered multi-tonnage industrial polymers (polyethylene, polypropylene, polyethylene terephthalate, etc.) is explained by the fact that currently the share of biodegradable plastics in the global consumption

of polymer materials does not exceed 2-3%, and in the foreseeable future it is not expected to overcome the threshold of 5-7%.

The effect of ultraviolet on the mechanical properties of PLA/LDPE film samples has been studied. It is shown that changes in thermophysical characteristics are observed both in the polylactide phase and in the polyethylene phase [7, 10-12].

Several degradation studies have shown that ultraviolet irradiation of polyethylene demonstrates a decrease in elongation due to embrittlement. It is known that embrittlement in semi-crystalline polymers is caused by a decrease in molecular weight as a result of the chain splitting process [13, 14].

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 30, 50, 70 wt % and pure polymers PLA and LDPE. The blends were prepared by mixing at Plasticorder PLD-651 (Brabender, Germany) for 5 minutes at 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. As a result, film round samples with a diameter of 7 cm and thickness of 100±10 µm were obtained [15].

The degree of crystallinity of polymers in the blends was studied using differential scanning calorimeter Netzsch DSC 214 Polyma at the heating rate of 8K/min and sample weight of 10±0.1 mg. The temperature scale was calibrated against an indium standard ($T_m = 156.6^\circ\text{C}$, $\Delta H = 28.44$ J/g). The value of the degree of crystallinity χ_c was calculated by the formula (1):

$$\chi_c (\%) = 100 \times \Delta H_0 / \Delta H_i, \quad (1)$$

χ_c - degree of crystallinity, the heat of melting of an ideal crystal PLA $\Delta H_0 = 93,1$ J/g [16], PE $\Delta H_i = 293$ J/g [17].

Mechanical properties were examined by 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.

The influence of ultraviolet on the obtained samples was studied by the lamp Vilber Lourmat VL-6.LC at $\lambda=254$ nm for 5 -100 hours.

Ozonolysis of film samples for 8 and 16 hours was carried out at atmospheric pressure and $T = (20 \pm 2)^\circ\text{C}$ in an atmosphere of an ozone-oxygen mixture with a partial concentration of ozone equal to 5.0×10^{-5} mol/L.

Results and discussion

Under ultraviolet irradiation, degradation processes occur differently in the thickness of the material, demonstrating changes in the deep profiles of the carbonyl index of polymers, which can lead to various changes in mechanical properties.

In this paper, changes in the mechanical characteristics of mixed compositions based on polylactide during exposure to UV radiation $\lambda = 254$ nm are investigated. Due to the interest in research of this kind, this wavelength is often used as an accelerated test method [6]. In composite materials, there is a decrease in thermal and mechanical characteristics after exposure to UV radiation. The melting point T_m of PLA decreased by 12°C after exposure to UV radiation for 25 and 50 h and by 30°C after exposure for 100 h. Mechanical characteristics are represented in Figure 1.

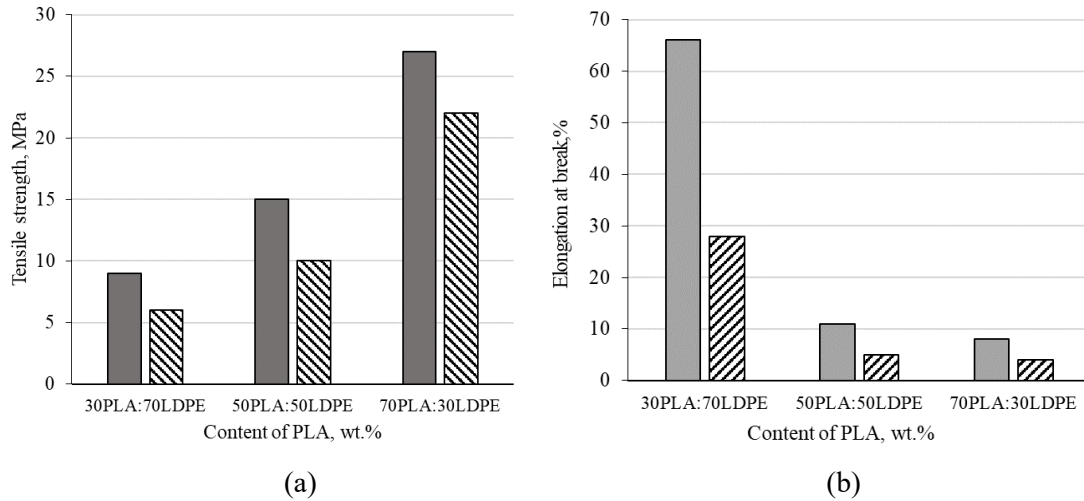


Fig. 1. Mechanical characteristics of PLA after 5 hours of exposure to UV radiation: a – Tensile strength, b – Elongation at break (gray – before UV radiation; dashed line – after UV radiation).

Tests have shown that ultraviolet radiation affects the polylactide, after 5 hours of exposure $\lambda=254$ nm, the tensile strength and elongation at break of the PLA decrease. These results are also confirmed by literature data, in [10] it was shown that after exposure to this wave for 12 hours, the strength of the polylactide decreases by 5 times.

It is known that photodegradation begins with an attack of the radical of the macromolecular chain of the PLA. By the same mechanism, ozone oxidation of polylactide occurs, only the activator of the process is an O[•]-radical formed as a result of the decomposition of an ozone molecule.

In the case of polymers, ozone treatment of the surface layer improves its adhesive properties, and also allows to insert some specific functional components into the polymer [18-20], due to which the latter acquires new properties. The degradation process initiated by ozone was considered in [18, 21] in relation to various types of polymers.

Table 1. Thermophysical characteristics of samples of PLA /LDPE blends – initial and after their ozonation for 8 and 16 hours

Composition [wt. %] PLA/LDPE	T _m [°C] ±0,5 °C			χ _c [%] ±0,5%		
	Initial	After 8 h ozon.	After 16 h ozon.	Initial	After 8 h ozon.	After 16 h ozon.
100/0	165	165	164	45	47	50
70/30	163/103	161/102	160/101	39/17	43/14	45/13
50/50	164/103	162/102	160/100	51/19	53/17	56/16
30/70	164/104	162/103	160/99	50/16	52/14	56/12
0/100	104	102	100	21	17	14

When ozone acts on a polymer material, many characteristics of the polymer matrix can change, ranging from thermophysical to visible surface defects (submicro- and microcracks) with deep degrees of destructive processes. In amorphous-crystalline polymers, as is known, the degradation

process begins in the amorphous phase. The disintegration of the amorphous and crystalline phases leads to a decrease in the strength of the material, a change in mechanical properties.

To control the thermophysical characteristics of PLA/LDPE mixture samples: was used the DSC method. After an 8-hour action of ozone, a decrease of 1-3 °C in the melting point of PLA for mixtures is observed, while for pure PLA, the T_m does not change (Table 1). After ozonolysis for 16 hours, the tendency to increase the degree of crystallinity (χ_{cr}) of polylactide persists. Melting temperatures in blends of PLA/LDPE decrease.

Along with the degradation of the amorphous phase, exposure to ozone may contribute to the continuation of crystallization due to the rupture of strained flow chains, therefore, the degree of crystallinity of polylactide increases. In turn, the χ_{cr} of pure LDPE is reduced by 5%, and mixtures are slightly less, which may be caused by the course of an oxidative destructive process, which also leads to deterioration of mechanical properties.

Conclusion

This study examined the processes of photodegradation and ozonolysis of PLA/LDPE films. Thus, the effect of both UV radiation and ozone affects the structural characteristics of the components of the mixture and reduces the mechanical properties of PLA/LDPE samples.

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