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VIII ВСЕРОССИЙСКАЯ НАУЧНО-ПРАКТИЧЕСКАЯ КОНФЕРЕНЦИЯ С МЕЖДУНАРОДНЫМ УЧАСТИЕМ, ПОСВЯЩЕННАЯ 50-ЛЕТИЮ ОСНОВАНИЯ ИНСТИТУТА ХИМИИ НЕФТИ

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THE DEGREE OF POLYMER OXIDATION AND ITS EFFECT ON STRUCTURE AND PROPERTIES OF LDPE FILMS

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Low density polyethylene (LDPE) is the most commonly used polymer material. It has many advantages, such as low cost, good moisture and chemical resistance, availability of grades, which are permitted for food packaging and etc. Nevertheless, the biggest disadvantage of LDPE usage is its high stability to environmental degradation, which is the main reason of increasing polymer wastes.

Polymeric materials released into environmental media (soil or water) can be degraded under following factors: air, temperature, moisture, light (photo degradation), high energy, microorganisms and insects. These factors can influence on structure and properties of LDPE solely or as a combination.

The process of biodegradation consists of two or more consecutive stages. Firstly, abiotic (photo or thermo) oxidation takes place, then microbial biodegradation occurs. Initial abiotic oxidation is an important stage as it determines the rate of the entire process. In this first period, oxygen consumption by the carbon backbone influences on the formation of functional groups, such as carboxylic acids, esters, or aldehydes and alcohols as well. The hydrocarbon polymers change their behavior from hydrophobic to hydrophilic, and chain scission can be provoked. In the second stage, these fragments can be degraded by microorganisms′ enzymes in soil or during composting.

The aim of the study was to examine how the degree of oxidation influenced on structure and properties of LDPE films and how it correlated with biodegradation process of composites on its basis.

Low-density polyethylene (LDPE) 15803-020 produced according to GOST 16337-77 by Neftekhimsevilen, LLC in Kazan, Russia was used for the study. The properties are as follows: density 0.919 ± 0.002 g/cm^3, melting temperature 107 °C, $\chi = 26 \pm 1\%$, $M_w = 1.0 \times 10^5$.

The films were pressed by a manual hydraulic press VNIR PRG-1–10 at 135 °C under 7 kN for 3 min followed by rapid cooling.

The temperature was set at 85 °C for LDPE in order to accelerate the oxidation process and examine the polymer stability in the solid phase, below the melting point. Samples of material were placed in the vessels in which the oxygen was under the pressure of 66 kPa. The vessels were placed in thermostat heated to a specific temperature. The intensity of the oxygen absorption by material was fixed during a certain time interval. Based on the data the kinetic curves of oxygen absorption were plotted. Volatile components were captured by potassium hydroxide. The experiment was carried out for 50, 100, 200, 300 and 400 hours respectively. As a reference, the other range of polyethylene samples was prepared. The hold up time was the same, but films were annealed at 85 °C in argon and under the pressure of 500 mm Hg in order to establish the impact of annealing on LDPE structure and properties.

X-ray diffraction measurements at wide angles were made on an HZG4 modernized X-ray diffractometer (Freiberger Präzisionsmechanik, Germany) in the Bragg–Brentano configuration, with a scintillation X-ray detector and a diffracted beam graphite monochromator (Cu*K*α radiation). The average crystallite sizes were calculated from the width of diffraction lines by the Selyakov–Scherrer formula on making a correction for the instrumental line broadening.

Thermophysical parameters (polyethylene melting temperature and degree of crystallinity) were examined by differential scanning calorimeter Netzsch 214 Polyma (Germany). The temperature and melting enthalpy were calibrated with an indium standard. The mass of all samples encapsulated into aluminum flat pans was kept about 7 mg.

The kinetic curves of oxygen absorption of LDPE samples were obtained. There were 6 similar samples of pure LDPE held in the same conditions for different time intervals. The overlay of kinetic curves shows high capability of reproducing. In addition, there was no change in oxygen absorption for annealed PE in argon atmosphere.

In order to characterize the specifics of mechanism of thermal oxidation the anamorphosis of LDPE kinetic curve was plotted. The linear character of anamorphosis indicated that termination step was followed by quadratic chain-breaking process. In other words, the rate of chain-breaking process was corresponded to squared root from initiation stage rate.

To examine the changes in structure of crystallites in the LDPE samples, the method of X-ray diffraction (XRD) analysis was used. The diffraction pattern of LDPE had at wide X-ray scattering angles distinct diffraction lines corresponding to the crystalline phase of this polymer with an orthorhombic unit cell.

The crystallinity degree and average crystallite sizes were calculated from the width of (110) diffraction line. Crystallinity degree of oxidized LDPE increased with hold-up time. The values of crystallinity degree of annealed LDPE at first increased, but then varied in margin error. It can be explained by both annealing of amorphous areas and ordering of paracrystalline areas in polymer. It was concluded that the influence of oxygen on increase in crystallinity degree of LDPE was caused mainly by temperature factor. The average crystallite sizes of annealed and oxidized LDPE samples changed in margin error. The more exposure time was, the more average crystallite sizes were.

In order to establish the impact of oxygen and temperature factors on thermophysical properties of LDPE samples the differential scanning calometry in non-isothermal mode was applied.

It was found, that as oxidation time increased, crystallinity degree of oxidized LDPE samples rose. This increase can be attributed mainly to ordering of amorphous regions of polymer. The values of annealed PE samples varied insignificantly in dependence to annealing time.