The degradation of materials based on low-density polyethylene and natural fillers

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SUMMARY
An investigation was made of the process of thermal degradation of blended composites based on low-density polyethylene with different natural fillers. The different effects of additives of dissimilar nature on the kinetic parameters of thermal oxidation, the deformation, the thermal degradation, and the water absorption of composites were established.

Traditional synthetic polymeric materials possess a collection of unique properties that has enabled them to occupy an important niche in the demand structure. However, some of their properties may be both useful and harmful, depending on the specific application. For example, the bioresistance of synthetic polymers is a useful property for structural materials; however, for materials with a short application cycle, this property is harmful. Packaging materials generally land up at refuse dumps only 2–6 months after their production. The biodegradation period of materials of this kind under natural conditions takes several decades. In order to improve the ecology in the vicinity of large towns by saving substantial areas from dumped polymer refuse, scientists throughout the world are creating biodegradable polymeric materials. In performance properties, such materials are on a par with normal polymers, but, when discarded, and under natural conditions, they are completely absorbed by soil microorganisms. The principal problem of most biodegradable polymeric materials is their high cost [1].

The high cost of most biodegradable polymers is due to the method of their production, as they are all synthesised from expensive organic raw material. This problem is solved by using composite materials containing both traditional synthetic polymers and natural biodegradable fillers [2].

The aim of the present work was to assess the service and processing properties of the materials. Among the service properties, the mechanical characteristics are critical. And, as articles of polyethylene-based composite materials are manufactured in the temperature range 125–160°C, it was important to study their resistance to thermal and thermo-oxidative degradation.

METHODS AND MATERIALS
In the present work an investigation was made of blended composites based on low-density polyethylene (LDPE) of grade 15803-020 with natural fillers. As the fillers, use was made of waste of different industries: flax shive (referred to below as “shive”) – textile production waste; sunflower husks (“husks”) – vegetable oil production waste; banana skins – food production waste; birch leaves (“leaves”); cereal chaff (“chaff”). The blends contained 30 wt% filler, ground to <200 µm fraction, and 70 wt% LDPE. The components were mixed in a mill at a temperature of 160°C for 5 min. Film specimens were obtained by pressing on a laboratory press at a temperature of 160°C for 2 min with subsequent rapid cooling to room temperature.

The size and shape of the filler particles in the polymer matrix were assessed by transmission optical microscopy. Specimens were investigated using an Olympus CX41 microscope in transmitted light with a 100x magnification.
The mechanical characteristics of the specimens were determined on an RM-10 tensile testing machine designed for determining the quality of film and roll materials at a rate of 50 mm/s. The length of the specimens was 50 mm, and their width 10 mm.

The kinetics of oxidation was investigated on a manometric unit with absorption of volatile oxidation products by solid KOH [3]. The experiment was conducted under two temperature regimes at 90°C and at 130°C and an oxygen pressure of 500 mmHg.

Investigation of the thermophysical characteristics of specimens was conducted using a DSM-10M differential scanning microcalorimeter. The scanning rate was 8°C/min, and the specimen weighed 10 mg. As the standard, use was made of indium (\(T_m = 156.6°C\), specific enthalpy of melting 28.4419 J/g).

The kinetics of water absorption was studied by a procedure described in the GOST 4650-80 standard. Film specimens were placed in test tubes with distilled water. The test tubes were placed in an oven heated to 30°C. The weight of specimens was measured before and after their immersion in water, and the percentage water absorption was calculated from the difference between the two weights.

RESULTS AND DISCUSSION

The distribution of fillers in the polymer was of interest, and the size and shape of the filler particles were assessed. To this end, all specimens were investigated by optical microscopy.

Photographs of films are presented in Figure 1. It can be seen that the fillers are fairly well distributed in the polymer matrix. The filler particles had different shapes. The shive and chaff have a long drawn-out shape, the husk particles are slightly broader and shorter, and the leaf and banana skin fragments are spherical in shape.

The introduction into the hydrophobic polymer of a hydrophilic filler generally is accompanied with a reduction in the mechanical properties of the polymer. The elasticity of the material will be reduced most significantly, by a factor of 20–50. The strength of the materials in relation to polyethylene does not decrease so significantly, by 8–30%. A behaviour pattern is observed, according to which there is a balance between elasticity and strength: the higher the value of one of these properties, the lower the value of the other. Thus, specimens with banana skin possess the best elasticity but the lowest strength, and specimens with chaff possess the best strength but the lowest elasticity (Table 1). The strength of materials with fibrous fillers (shive, hay) is high, while the strength of materials with spherical particles (banana, leaves) is lower.

The question as to how necessary a high elasticity is to packaging materials is debatable. For example, paper is not an elastic material, but it is actively used for packaging. The same packaging materials are manufactured from paper as from polymers, and this has no effect on their performance properties. With regard to strength, composite materials are not significantly inferior to polyethylene and can be used as packaging materials, replacing the traditional polyolefins.

All materials coming into contact with air oxygen undergo oxidation to some degree, especially at processing temperatures.

An experiment on thermal oxidation was conducted at temperatures above (130°C) and below (90°C) the melting temperature.

Figure 2 presents the kinetic curves of oxygen absorption by composites at 130°C and an oxygen pressure of 500 mmHg. It can be seen that the fillers affect the oxidation process in different ways. Banana skin has practically no effect on the oxidation of pure LDPE. Additions of husks and shive accelerate the oxidation of the polymer more intensely. Increase in the oxidation rate of composites with husks and shive may be due both to the influence of these additives on the packing

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<th>Table 1. Mechanical characteristics of specimens</th>
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Figure 1. (a) Photograph of LDPE/shive film; (b) micrograph of LDPE/shive film (100x); (c) photograph of LDPE/leaves film; (d) micrograph of LDPE/leaves film (100x)
of macromolecules, leading to increased mobility in the amorphous phase, and to the composition of the additives themselves: the content in them of traces of flaxseed oil, sunflower oil, and variable-valency metals.

The nature of the effect of the additives on the oxidation rate of composites in the solid state (at 90°C) is similar to the dependence at 130°C. Composites with sunflower husks and flax shive are oxidised at greater rates than polyethylene. When leaves are introduced into a composite with LDPE, a material resistant to thermo-oxidative degradation is produced.

The use of husks and shive yields a material that will oxidise much more rapidly than the initial LDPE. On the basis of the data obtained it can be asserted that, for biodegradable materials with a short application cycle, it is desirable to use shive or husks. For materials that must be exposed to air for a certain time without failure, it is better to use leaves.

The thermal stability of the obtained composite materials was investigated using the DSC method. Figure 3 gives DSC curves of the materials. In the work, it was of special interest to study materials in the temperature range 125–160°C, as it is at these temperatures that the processes of mixing of the components and the manufacture of articles take place.

The calculated values of the average change in heat flux in the investigated temperature range for composites are given in Table 2. For polyethylene and blends of polyethylene with chaff and with leaves there is a small change in the heat effect with increase in temperature. For polyethylene with shive and husks, the rate of change in the heat flux with temperature increases considerably. The parameter characterises the initial stage of the exothermic process of breakdown of the polymer. Taking into account that the additives themselves are stable in this temperature range, the additives initiate the breakdown of polyethylene, leading during subsequent heating to the crosslinking of macromolecules (a considerable exothermic effect).

For additional characterisation of the materials, their water absorption was investigated. Data on the equilibrium water absorption of specimens for a 40 day period are presented in Figure 4. From the figure it can be seen that composite materials with husks and shive possess the greatest water absorption, and composite materials with chaff the lowest.

Table 2. Average magnitude of change in the heat flux in the temperature range 125–160°C for composites of polyethylene with different additives (DSC method)

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<th>Specimen</th>
<th>PE/shive</th>
<th>PE/husks</th>
<th>PE/banana skin</th>
<th>PE/chaff</th>
<th>PE</th>
<th>PE/leaves</th>
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<tr>
<td>ΔdH/dt/ΔT</td>
<td>-54.2</td>
<td>-36.7</td>
<td>-17.8</td>
<td>-7.3</td>
<td>-7.1</td>
<td>-3.6</td>
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The data of this experiment confirm the assumption that the polyethylene matrix is looser in materials with husks and shive and is most susceptible to different effects (oxygen, temperature, water).

Thus, when different natural fillers are introduced into a composite with LDPE, a material is obtained with different degrees of resistance to thermo-oxidative degradation. The use of sunflower husks and flax shive yields a material that will oxidise much more rapidly than the initial LDPE. The obtained composite materials can be used for the manufacture of different articles for which the elasticity parameter is not critical. The shape of the filler particles affects the mechanical characteristics of the material. Fibrous filler particles create high strength and low elasticity in the material, whereas spherical filler particles in the material are able to stretch fairly well and do not readily rupture.

REFERENCES


