Degradation kinetics of ethylene-octene copolymer/wood flour biocomposites in dependence to filler content

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Abstract. This article is focused on thermal oxidative degradation and biodegradation in soil of biocomposites based on ethylene-octene copolymer (EOC), filled by wood flour (from 30 to 70% wt.), in dependence to the filler content. The study of oxidative degradation of composites was carried out at two temperatures (80 and 130°C respectively). The induction period and the rates of oxidation were determined. It was concluded that as filler content raises, the induction period increases. It can be explained by the higher specific area of composites in comparison with pure EOC. However, high filled composites (60 and 70 % of the filler) are oxidized with a huge induction period because polyphenols in the filler inhibit the oxidation process. Biodegradation test under laboratory conditions was carried out to investigate the biodegradability of the material. Composites with lower filler content have lower weight loss rate. Small particles are capsulated by polymer and are isolated from moisture and microorganisms. On the other hand, at a high filling of the composite small particles stick together and act as large ones. Such filler agglomerates are connected with each other and allow microorganisms to penetrate into the composite. It was concluded as filler content raises the mass loss increases.

1. Introduction
New environmental legislation all over the world and a growing ecological awareness led to the development of eco-friendly composites – hybrid materials. It can be degraded in different natural medias, such as sea water [1] and soil [2] without environmental contamination. The total world production of plastics in 2004-2014 has changed from 225 m. tones to 311 m. tones and has a tendency to increase [3]. In Europe the total amount of polymer output for the same period has changed insignificantly from 60 m. tons to 59 m. tons. According to the new law [4], France banned the usage of fully plastic bags and serviceware. The authorities expect the reduction by 50% of waste in landfills by 2025.

Researches all over the world have been developing new types of materials, which have the same or better mechanical properties than common used polyolefins [5-6].

Biocomposites based on polyolefins and natural fillers are commonly used in different areas of economy, mainly in automotive (interior door linings and paneling, seat backrests) and construction industries (light structural walls, insulation materials, floor and wall coverings, geotextiles, thatch.
roofing) [7]. Biocomposites should have reduced price and can be partly or fully degraded in soil without harm to ecology.

Wood flour is widely used in composite engineering. This type of filler has several advantages such as high production output (>1.5 m. tons) [8] and low cost (0.2-0.4$/kg). A relatively high thermal stability (180-200°C) [9] allows compounding with traditional thermoplastics polyethylene (PE), polypropylene (PP), poly styrene (PS), polyvinyl chloride (PVC).

Synthetic biodegradable polymers such as polylactide acid (PLA) [10], polycaprolactone (PCL), polyhydroxybutyrate (PHB) [11], and polyhydroxyvalerate (PHV) can be used as polymer matrix in fully biodegradable biocomposites. However, they are still very expensive in comparison with the traditional polymers. Polyolefins such as polyethylene [12] and polypropylene [13] are widely used for partially biodegradable composites.

Some other polymer matrices are also examined for biocomposites development. For example, polyolefin elastomers (POEs), such as ethylene–octene copolymer (EOC) can be used as the polymer matrix in composites. Few studies have investigated the properties of composites based on POE. Most of these papers consider the mechanical, thermal and rheological [14] properties of EOC–modified corn starch blends [15]. EOCs are known to have higher filler loading capacity than polyolefins. Some manufacturers (Ultrasoft Plastic LLC, Alexandrov, Vladimir region, Russia and Polymer Alliance LLC, Khimki, Moscow region, Russia) produce highly filled composites based on EOC.

There are a lot of methods, which examined the oxidative stability of polymers and composites, such as thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), isothermogravimetric analysis (IGA), thermal volatilization analysis (TVA), accelerated aging tests [16-17].

The objective of this study is to investigate the thermal oxidative degradation and biodegradation in soil of biocomposites based on EOC, filled by wood flour, in dependence to the filler content.

2. Materials and methods
Ethylene–octene copolymer (EOC) of Lucene 670 trademark manufactured by LG Chem (South Korea) was chosen as the polymer matrix. The properties of considered polymer, provided by LG Chem, are as follows: 1-octene content 35 % mol, melting point 57°C, density 0.870 g/cm³, MFI (melt flow index) at 190°C 5 g/10 min, Mn/Mw = 32000/75000.

Birch wood flour (WF) was selected as the filler for the biocomposites. WF was produced according to GOST 16361-87 and referred to trademark № 120. WF was provided by «Novotop» Ltd. (Russia, Moscow). The chemical composition of the filler is presented in Table 1.

| Filler            | Cellulose | Lignin | Hemicellulose | Proteins | Fats | Ash | References |
|-------------------|-----------|--------|---------------|----------|------|-----|------------|
| Birch wood flour  | 37–56     | 18–22  | 25–40         | 0.3      | 0.4  | 0.4 | [18-19]    |

The wood flour was sieved by a sieve set. The fraction 0–200 µm was chosen for the biocomposites preparation.

The components of the biocomposites were mixed in following proportions (pure EOC and wood flour respectively): 100/0, 70/30, 60/40, 50/50, 40/60, 30/70 (% wt.).

The compositions were mixed by stirred mixing rolls UBL-6175BL (China) at T ≈ 160°C for 5 min.

The mixtures were pressed by the manual hydraulic press VNIR PRG-1–10 (Russia) at 135°C under a load of 7 kN for 3 min with subsequent quick cooling. The obtained films were round, with a diameter of 7 cm. The thickness of the films varied from 100 µm for composites with 30% of the filler to 1000 µm for composites with 70% of the filler.

The study of oxidative degradation of composites was carried out at 80°C and 130°C and under the oxygen pressure of 500 mmHg in the system described and developed in Semenov Institute of
Chemical Physics of Russian Academy of Sciences [20]. This method simulates the process taking place in natural conditions during material degradation in the environment. Samples were placed in the vessels in which the oxygen is under the pressure. The vessels are placed in thermostat heated to a specific temperature. The intensity of the oxygen absorption by the material was measured in fixed intervals. Based on the data the kinetic curves of oxidation were plotted. According to the results, the influence of a filler (or compatibilizer) on oxidation rate can be seen. The total time of exposure at 80°C and 130°C was 1000 hours and 30 hours respectively. The rates and induction period of considered processes were determined for both temperatures. The rates were presented by two values. First value is characterized as the time (hours) for which the composite absorbs fixed amount of oxygen. The second value determines average rate of oxidation and was measured in mol/kg·s. It should be noted that the filler itself is oxidized insignificantly in compare with composite.

The biodegradation test under laboratory conditions was carried out in accordance with ASTM D 5988-96 [21] to investigate the biodegradability of the material. The soil was made of sand, garden soil, and horse manure taken in equal amounts. The resulting soil was held for 2 months at 20 ± 5°C with daily stirring and humidity maintained at 60%. The same soil was used in previous studies [22, 12, 23]. The film samples were immersed vertically in the prepared soil and held for 12 months. The samples were cleaned and dried to the constant mass. The difference in mass of the composites was measured.

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3. Results and discussion

Figure 1 shows the kinetic curves of oxygen absorption of pure EOC and composites based on EOC and WF.

![Kinetics of thermal oxidation of composites at 80°C (a) and at 130°C (b).](image)

It is known that thermal-oxidative degradation of polyolefins in air is autocatalytic, i.e., the rate is slow at first but gradually accelerates to a constant value. [17, 20, 24]. The reactions are presented below according to the source [25].

The initiation steps in the radical-chain oxidation process are

\[ RH \rightarrow R^\cdot + H^\cdot \]  \hspace{1cm} (1)

\[ RH + O_2 \rightarrow R^\cdot + HOO^\cdot \]  \hspace{1cm} (2)

\[ 2RH + O_2 \rightarrow 2R^\cdot + H_2O_2 \]  \hspace{1cm} (3)

The chain propagation steps are
The chain-branching steps are
\[
ROOH \rightarrow ROO^· + OH
\]  
(6)
\[
ROOH + RH \rightarrow RO + R^· + H_2O
\]  
(7)
\[
2ROOH \rightarrow ROO^· + RO + H_2O
\]  
(8)

The chain termination steps are
\[
2R \rightarrow R_2
\]  
(9)
\[
R^· + ROO^· \rightarrow ROOR
\]  
(10)
\[
2ROO \rightarrow ROOR + O_2
\]  
(11)

EOC and composites based on EOC are oxidized with the induction period. It can be explained by high amount of polyphenols in WF. It was concluded that as filler content raises, the induction period increases. It should be noted that the role of antioxidant added during polymerization at the factory is insignificant, because the content of antioxidant in polymer is constant.

The rate of oxidation and induction period was determined. The results are presented in Table 3. According to the results, it was found that pure EOC has lower rate of oxidation than composites based on EOC. It can be explained by the higher specific area of composites in comparison with pure EOC. The comparison of pure EOC rate and oxidation rate of composites is not correct, because pure EOC is homogeneous system, and oxidation occurs only on the surface of polymer. Hence, composites are heterogeneous and have large (developed) interfacial contact area. A specific area of particles correlates with the interfacial contact area between the filler and EOC matrix, which is mostly prone to oxygen absorption. It was concluded that as filler content rises, the oxidation rate decreases.

Table 2. Oxidation rate and induction period of composites at 80 and 130°C and oxygen pressure 500 mmHg.

| Composite   | Oxidation rate, hours | Induction period, hours | Oxidation rate, mol/kg*s |
|-------------|-----------------------|-------------------------|--------------------------|
|             | 80°C (0.2mol) | 130°C (0.3mol) | 80°C | 130°C | 80°C | 130°C |
| 100EOC      | 287          | 3            | 163  | 0.2   | 5.97*10⁻⁷ | 2.76*10⁻⁵ |
| 70EOC/30WF  | 287          | 4            | 163  | 0.2   | 2.44*10⁻⁶ | 5.19*10⁻⁵ |
| 60EOC/40WF  | -            | 6            | -    | 0.5   | -       | 1.3*10⁴  |
| 50EOC/50WF  | 380          | 11           | 311  | 1     | 3.43*10⁻⁶ | 4.8*10⁻⁵ |
| 40EOC/60WF  | 1000         | 20           | 717  | More than 25 | -       | -       |
| 30EOC/70WF  | 1000         | 25           | 717  | More than 30 | -       | -       |

According to the results of biodegradation test under laboratory conditions (Figure 2), composites with lower filler content have lower weight loss. Pure EOC did not change its mass and it was concluded that pure EOC is not biodegradable polymer. Small particles in composites are capsulated by polymer and unavailable for penetration by microorganisms. On the other hand, large and long particles are connected with each other and allow microorganisms to penetrate into the composite. At a low filling of the composite the particles are separated and capsulated by polymer. At a high filling the
small particles have the tendency to agglomerate and act as large ones or even as a network. It was concluded as filler content raises the mass loss increases. It is well correlates with previous studies [23]. At the initial stage of biodegradation there is no difference between composites with 60 and 70% of wood flour. Apparently, the quantity of wood flour at the surface is the same in these two composites, it should differ into the volume and it would be observed at the next stages of biodegradation process.

![Kinetic curves of biodegradation of composites on recovered soil.](image.png)

**Figure 2.** Kinetic curves of biodegradation of composites on recovered soil.

### 4. Conclusion

Biocomposites based on EOC and WF were investigated by two methods defining their degradation in the environment. At first stage of biodegradation process, high weight loss is observed cause of filler degradation at the composite surface. Later, when the microorganisms’ enzymes have an effect on the composite surface, the microbial waste products initiate the oxidation. According to the data of thermal oxidation, it can be concluded that the addition of WF to the EOC matrix lead to the accelerated oxidative degradation of EOC in the composite. Thus, EOC in composite is stable on the air for some period of time (when it is used by consumer) but it degrades rather quickly after the induction period (when it is thrown out). Biodegradation test showed that WF biodegrades easily and makes composite partially biodegradable. Filler content in biocomposite correlates with the mass loss. Obtained materials are promising because they are much cheaper than fully biodegradable biocomposites but they have a good potential for degradation in the environment by both mechanisms – oxidative and biological degradation.

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