Investigation of the structure and thermal properties of composites based on polyethylene terephthalate and organoclay

Kh.M. Berbekov Kabardino-Balkarian State University, Nal’chik

In this work, a study was made of the thermophysical properties and structure of layered silicate composites based on polyethylene terephthalate (PET) and organoclay modified with surface-active substances of different nature.

The investigation was conducted on a copolymer of polyethylene terephthalate with isophthalic acid of grade SPET 8200 L, produced by OAO Mogilevkhimvolokno, and montmorillonite modified with Katapav (alkylbenzyldimethylammonium chloride) and caprolactam (cyclic amine (lactam) of ε-aminocaproic acid). Composites were obtained by melt mixing of PET with organoclay on a twin-screw extruder with six heating zones, with a screw diameter of 20 mm and a ratio of screw length to screw diameter $L/D = 36$. The processing temperature was 230–265°C, and the screw rotational speed was 190–210 rev/min.

The thermophysical parameters of the nanocomposites were determined by differential scanning calorimetry (DSC) on a DSC 4000 instrument, and thermogravimetric analysis (TGA) was conducted on a TGA 4000 instrument (PerkinElmer, USA). The heating rate of specimens in air amounted to 10°C/min. Investigation by scanning electron microscopy was conducted on a Vega 3 microscope (Tescan, Czech Republic).

To compare the effect of montmorillonite modified with Karapav (OMMT-Katapav) and caprolactam (OMMT-caprolactam) on the thermophysical transformations of PET, composites with a content of 1 and 2 wt% of each organoclay were obtained.

The composites obtained were investigated by DSC under the following conditions:
1. holding at 30°C for 1 min;
2. heating from 30 to 280°C at a rate of 10°C/min;
3. holding at 280°C for 1 min.

As can be seen from Table 1, when organoclay is introduced, no significant changes in melting or glass transition temperature of the initial polymer is observed. Increase in the enthalpy of melting of nanocomposites indicates the effect of montmorillonite on the crystallisation processes of PET, where organoclay particles act as centres of crystallisation and lead to an increase in the degree of crystallinity of the polymer [5–7]. Increase in the degree of crystallinity may be a positive factor in relation to the barrier properties, as the crystallites are largely impermeable for gases [8].

Here, it is important to note that the increase in the degree of crystallinity of PET in the process of modification with layered silicate fillers should not have any significant effect on its service characteristics, as the degree of crystallinity of extruded PET and PET/organoclay nanocomposites lie in the range 10–20%, whereas it was established that embrittlement of PET begins with degrees of crystallinity of 30% and above [9].

Subsequent investigation of the obtained nanocomposites by DSC was directed towards studying crystallisation processes. The experiment included the following stages:

1. holding at 30°C for 1 min;
2. heating from 30 to 280°C at a rate of 10°C/min;
3. holding at 280°C for 1 min (in order to minimise the influence of the thermal prehistory);
4. cooling from 280 to 30°C at 10°C/min;
5. holding at 30°C for 1 min;
6. heating from 30 to 280°C at a rate of 10°C/min;
7. holding at 280°C for 1 min;
8. cooling from 280 to 30°C at 10°C/min.

The most important in the above stages of the experiment are stages 4 and 6. During stage 4, the polymer melt is cooled to 30°C, in the course of which its crystallisation occurs. During stage 6, melting peaks of the crystallites formed at stage 4 appear on the thermograms. This makes it possible to calculate more accurately and correctly the heat of melting without the influence of the thermal prehistory of the specimen.

Figure 1 gives DSC thermograms obtained in the course of stage 4.

The main indices of crystallisation and melting of nanocomposites based on PET and organoclay are given in Table 2.

To determine half the crystallisation time (t_{1/2}), i.e. the time necessary to achieve a 50% relative degree of crystallinity, use was made of the formula [10]:

\[
X_{cr} = \frac{\Delta H_m - \Delta H_{cr}}{\Delta H_{m0}} \times 100
\]

where \(\Delta H_m\) is the enthalpy of melting, \(\Delta H_{cr}\) is the enthalpy of crystallisation, and \(\Delta H_{m0}\) is the enthalpy of melting of PET in an absolutely crystalline state (135 J/g).

### Table 1. DSC results for PET/OMMT nanocomposites

<table>
<thead>
<tr>
<th>Composition</th>
<th>T_{g}, °C</th>
<th>T_{cr}, °C</th>
<th>T_{m}, °C</th>
<th>\Delta K_{cr}, J/g</th>
<th>\Delta H_{m}, J/g</th>
<th>X_{cr}, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET_{extrud}</td>
<td>82.0</td>
<td>124.5</td>
<td>250.0</td>
<td>28.5</td>
<td>42.0</td>
<td>10.0</td>
</tr>
<tr>
<td>OMMT-cap</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1%</td>
<td>80.0</td>
<td>126.0</td>
<td>251.0</td>
<td>29.0</td>
<td>48.0</td>
<td>14.0</td>
</tr>
<tr>
<td>2%</td>
<td>79.0</td>
<td>123.5</td>
<td>250.0</td>
<td>26.5</td>
<td>42.5</td>
<td>12.0</td>
</tr>
<tr>
<td>OMMT-Kat</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1%</td>
<td>80.5</td>
<td>125.5</td>
<td>250.5</td>
<td>23.0</td>
<td>37.0</td>
<td>10.5</td>
</tr>
<tr>
<td>2%</td>
<td>80.0</td>
<td>121.5</td>
<td>250.5</td>
<td>25.5</td>
<td>50.0</td>
<td>18.0</td>
</tr>
</tbody>
</table>

a The degree of crystallinity of PET and of PET-based nanocomposites was calculated by means of the formula:

\[
X_{cr} = \frac{\Delta H_m - \Delta H_{cr}}{\Delta H_{m0}} \times 100
\]

### Table 2. DSC investigation of PET/OMMT composites

<table>
<thead>
<tr>
<th>Composition</th>
<th>Melting</th>
<th>Cooling</th>
<th>ΔT_{m - cr}, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_{m0}, °C</td>
<td>T_{cr}, °C</td>
<td>ΔH_{m0}, J/g</td>
</tr>
<tr>
<td>PET_{extrud}</td>
<td>216</td>
<td>250</td>
<td>40</td>
</tr>
<tr>
<td>OMMT-caprolactam</td>
<td>1%</td>
<td>226</td>
<td>250</td>
</tr>
<tr>
<td>2%</td>
<td>223</td>
<td>250</td>
<td>39</td>
</tr>
<tr>
<td>OMMT-Katapav</td>
<td>1%</td>
<td>221</td>
<td>250.5</td>
</tr>
<tr>
<td>2%</td>
<td>223</td>
<td>251</td>
<td>37</td>
</tr>
</tbody>
</table>
where \( T_{st.cr} \) is the temperature of the start of crystallisation, \( T_{c.r} \) is the peak crystallisation temperature, and \( \chi \) is the cooling rate.

However, it must be noted that the given formula is valid for symmetrical heat effects of crystallisation, and the exothermic peak of PET\(_{extrud}\) is not a symmetrical effect (Figure 1). For the latter, the average \( t_{1/2} \) was calculated by means of the formula

\[
t_{1/2} = \frac{(T_{st.cr} - T_{c.r})}{2 \chi}
\]

where \( T_{st.cr} \) is the initial crystallisation temperature, \( T_{e.cr} \) is the end crystallisation temperature, and \( \chi \) is the cooling rate.

From Table 2 it can be seen that, at a specified cooling rate, for all composites the value of \( t_{1/2} \) is lower than for PET\(_{extrud}\). This confirms that clay particles are crystallisation nucleators. The crystallisation rates, defined as the ratio of \( \Delta H_{c.r} \) to the time from the start to the end of crystallisation, indicate that their values for PET/organoclay composites are roughly 3 times greater than the values for the initial PET\(_{extrud}\). The highest crystallisation rates are characteristic of nanocomposites containing 2% organoclay, which confirms the increase in the amount of nucleators. Increase in the total crystallisation rate is also confirmed by a reduction in the value of \( DT = T_m - T_{c.r} \), which is 7–9°C lower than for PET\(_{extrud}\). Here, no significant differences were found in the behaviour between the two modifications of organoclay relative to the given characteristics.

In a number of studies [11, 12] it is asserted that, when organoclay tactoids are present in the nanocomposite, and also in the case of the formation of an intercalated structure, there is an increase in the crystallisation rate and enthalpy, whereas with the formation of an exfoliated structure, lamellar particles limit the movement of macromolecules and inhibit the reorientation of chains for crystallisation [13, 14]. However, Gong et al. [15] point out that significant nucleating action may also appear in the process of formation of exfoliated structures of nanocomposites. In our case, it is more likely that the nanocomposites have a partially intercalated structure with the inclusion of tactoids, as there is a considerable increase in the crystallisation rate. At the same time, there is only a small change in the enthalpy of crystallisation (\( \Delta H_{c.r} \)) relative to PET\(_{extrud}\), which indicates the formation of finer imperfect crystallites.

The given assumptions confirm the results of DSC of nanocomposites, which are given in Figure 2. As can be seen from the figure, the endotherms of melting of PET\(_{extrud}\) and nanocomposites are characterised by dual heat effects. It is known [16–18] that PET can have two morphological structures of crystals. It is assumed that form I, to which correspond a higher-temperature endothermic melting peak, has a folded structure with highly organised crystals, while form II with a lower-temperature peak possesses an imperfect crystalline structure of more extended chains [19].

As can be seen from Figure 2, PET\(_{extrud}\) is characterised largely by morphological structure I, i.e. possesses a more perfect spherulite structure. However, there is a weak peak corresponding to form II in the region of 238°C. The introduction of organoclay leads to strengthening of the melting peak of the crystalline structure of form II and to displacement towards higher temperatures (~5°C). This probably indicates the appearance of a large amount of imperfect extended crystallites in connection with the presence of tactoids and the partial intercalation of PET chains into the interlayer spaces of the organoclays.
The results of thermogravimetric analysis of the obtained nanocomposites are given in Figure 3.

It must be noted that the introduction of organoclay into PET has practically no effect on the temperature of the start of degradation of the polymer; however, there is an increase in the temperatures of 10 and 50% weight loss (Table 3). Here, in the case of the use of OMMT-Katapav, the values of the heat resistance are slightly higher. The given organoclay is evidently dispersed better in the polymer matrix, with the formation of an intercalated structure where the clay particles inhibit the diffusion of oxygen towards the macromolecule chain [20, 21].

As shown by data of X-ray diffraction studies, in the case of the modification of montmorillonite with caprolactam, the thickness of each aluminosilicate layer of MMT in the process of organomodification hardly changes. This means that the process of penetration of caprolactam into the interplanar spaces of MMT occurs owing to the formation of bridge bonds between the hydroxyl groups of the surface of aluminosilicate and the amino groups of caprolactam.

In the case of the use of cation-active Katapav, a reaction occurs between quaternary ammonium cations of the modifier and interlayer ions of sodium, and the distance between the silicate plates of MMT increases from 1.2 nm in the initial MMT to 1.9 nm, promoting easier penetration between the silicate plates of polyethylene terephthalate [22].

Here, as shown by the TGA data, both of the modifiers used hydrophobise MMT fairly effectively, replacing the water molecules coordinated around the exchange cations of the mineral. However, the heat resistance of OMMT-Katapav is slightly higher, which possibly plays a decisive role in its distribution (Figure 4).

*Figure 4. Thermogravimetric curves of MMT (1), OMMT-Katapav (2), and OMMT-caprolactam (3)*

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*Figure 3. TGA curves of PET composites containing 1 and 2% organoclays modified with Katapav and caprolactam*

<table>
<thead>
<tr>
<th>Composition</th>
<th>T_{init},°C</th>
<th>T_{10%},°C</th>
<th>T_{20%},°C</th>
<th>T_{50%},°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET_{extrud}</td>
<td>393</td>
<td>410</td>
<td>422</td>
<td>440</td>
</tr>
<tr>
<td>OMMT-caprolactam</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1%</td>
<td>393</td>
<td>416</td>
<td>427</td>
<td>444</td>
</tr>
<tr>
<td>2%</td>
<td>394</td>
<td>415</td>
<td>426</td>
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<td>OMMT-Katapav</td>
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<tr>
<td>1%</td>
<td>394</td>
<td>414</td>
<td>425</td>
<td>442</td>
</tr>
<tr>
<td>2%</td>
<td>394</td>
<td>417</td>
<td>430</td>
<td>445</td>
</tr>
</tbody>
</table>
Investigations of PET/organoclay nanocomposites by scanning electron microscopy (SEM) showed that in the PET matrix there are coarse aggregates of organoclay (0.3 µm). Here, it is possible to see particles with a size of up to 100 nm (Figure 5). As assumed above, the composites have a mainly intercalated structure with the presence of tactoids and agglomerates.

CONCLUSIONS

It can be concluded that optimisation of the properties of PET is possible by its modification with small (up to 2 wt%) amounts of nanosilicate. It was established that the introduction of different organoclays entails structural changes in PET, which in turn is accompanied with appreciable changes in its thermophysical and thermal properties.

ACKNOWLEDGEMENTS

This study was conducted using equipment of TsKD RDM of the Kh.M. Berbekov Kabardino-Balkarian State University.

REFERENCES


