INNOVATIVE PRODUCTION OF NANOCOMPOSITES ON THE BASIS OF THERMOPLASTICS AND MONTMORILLONITE MODIFIED BY POLYVINYL PYRROLIDONE

Volodymyr Krasinskyi, Oleh Suberlyak, Yurii Klym, Ivan Gajdos

Abstract
A new method of layered silicate (montmorillonite) intercalation by polyvinylpyrrolidone in the solution under ultrasonic treatment is described in this work. The structure and thermophysical properties of the developed nanomodifier and the components rational ratio have been investigated. The effect of intercalated montmorillonite on physico-mechanical, thermophysical and insulating properties of polycaproamide PA-6 has been determined.

Key words
montmorillonite-polyvinylpyrrolidone mixture, nanocomposite, intercalation, crystal structure, sol-fraction, physico-mechanical properties.

Introduction
Today in the field of development of layered silicate polymeric nanocomposites the main attention is focused on the achievement of high level of nanoparticles exfoliation in the polymeric matrix that specifies high operational characteristics. Thus the choice of effective organic modifiers of layered silicate is an urgent problem because the modifier ensures high adhesion of the filler with polymeric matrix. From this point of view the study of effect of organic clay on the structure and properties of obtained nanocomposites with unknown nature is of great interest. The determination of mentioned regularities will give the possibility to control the structure and predict the properties of the composites based on organic clay.

One of the approaches used to improve thermodynamic compatibility of non-polar polymer with layered silicates is the introduction of polymeric polar modifier.

Therefore the aims of the work are:

- development of method for compatibility of montmorillonite (MMT) with water-soluble polymer – polyvinylpyrrolidone (PVP) – in order to use the obtained mixture for the modification of polar and non-polar polymers;
- investigation of structure and thermo-physical properties of montmorillonite-polyvinylpyrrolidone mixture (MPM), as well as efficiency of MMT intercalation;
- determination of modified montmorillonite effect on physico-mechanical, thermo-physical and insulating properties of polycaproamide PA-6.

Results and Discussion
To obtain MPM we used polyvinylpyrrolidone with molecular weight of 12600±2700 and “Fluka” montmorillonite supplied by Sigma-Aldrich firm. PVP and MMT solutions were prepared in water with corresponding concentrations to obtain the following PVP:MMT ratios (w/w): 7:1; 5:1; 3:1; 1:1 and 1:2. Before mixing with PVP the colloid solutions of MMT were pretreated by ultrasonic waves with the frequency of 22 kHz for 3 min using apparatus “Volna UZTA-0.4/22-OM”. Then PVP and MMT solutions were mixed using a mechanical
stirrer and the obtained solution was treated by ultrasound for 15 min. Ultrasonic waves set in motion a limited volume of treated solution and carry out the local effects with ultrasonic frequencies ensuring high rate and efficiency of mixing. Then mixtures were dried under vacuum at 80°C and obtained films were grinded in agate mortar till fine-dispersed powder was obtained.

While mixing MPM with PA-6 in the melt in plunger-capillary plasticator at 230°C and loading of 5 kg we obtained granulated concentrate based on PA-6 polyamide with MPM content corresponding to 7 wt% of montmorillonite. Then we mixed the concentrate with pure PA-6 and obtained composites with different content of MMT.

Plasticization of obtained composites was carried out using injection machine Kuasy 32/25 and samples were casted as standard blades. Injection moulding parameters are:

1) Temperatures of the zones of injection machine material cylinder – 215, 230 and 245°C;
2) Temperature of the mold – 18°C;
3) Moulding pressure – 100 MPa;
4) Exposing time under pressure – 10 s;
5) Exposing time for cooling – 15 s.

To determine the structure of the obtained composites based on PVP with MMT the samples were investigated using X-ray, differential-thermal and thermogravimetric analyses. X-ray photographs of pure MMT (Fig. 1a) demonstrate clear reflexes typical of clay aluminosilicates crystal structure [1, 2]. Two wide plateaus typical of polymer amorphous structure are observed at PVP roentgenogram (Fig. 1c). X-ray photograph of the composite with the ratio MMT:PVP = 2:1 (Fig. 1b) is similar to that of pure MMT. The reason is a great amount of MMT in the composite but intensity of peaks is less and they are wider. It means that PVP chains get into interlayer space of MMT. X-ray photographs of the samples with the ratio MMT:PVP = 1:3 and 1:5 (Figs. 1d and 1e) are similar to those of pure PVP. The difference is the appearance of shifted and less intensive (compared with MMT) peaks at the angles 2θ = 26.77° and 2θ = 34.66° for MMT:PVP = 1:5 and 2θ = 26.47° and 2θ = 34.80° for MMT:PVP = 1:3 typical of reflexes for pure MMT (for MMT – 2θ = 26.57° and 2θ = 35.03°, respectively).

At the same time the intensive peak at 2θ = 45.57° (typical of pure MMT) disappears at the roentgenogram of the sample with MMT:PVP = 1:5. For the sample with MMT:PVP = 1:3 this peak is low-intensive and shifted to 2θ = 45.99°. Moreover, for these samples the view of amorphous plateau differs from that of PVP. The obtained results reveal the formation of fluctuation net between PVP and MMT macromolecules and new partially crystal structure with increased softening temperature (compared with pure PVP). The most complete physical interaction between PVP and MMT occurs at the ratio MMT:PVP = 1:5 because peaks typical of pure MMT are almost absence at X-ray photograph due to the high level of exfoliation.

The results of DTA (Fig. 2) and TG analyses also indicate the presence of physical interaction between PVP and MMT macromolecules. For the studies we used MPM samples with the ratio MMT:PVP = 1:7, 1:3 and pure PVP.

Thus, according to the data of thermal analysis the composite with MMT:PVP = 1:7 has higher thermal stability compared with PVP and composite with MMT:PVP = 1:3. The beginning of thermal destruction of the composite with MMT:PVP = 1:7 is shifted toward the
area of higher temperatures (260°C). At the same time thermal destruction begins at 200°C for PVP and 220°C – for the composite with MMT:PVP = 1:3.

The developed MPM may be used as a modifier for polar and non-polar polymers. From the economic and technological points of view the composite with MMT:PVP = 1:5 is the most profitable one, therefore it is interesting to study its effect on the properties of thermoplastic polymers.

To demonstrate the effect of MPM on the structure and properties of nanocomposite based on it we selected the most used and popular commercial polymer – polyamide-6. The development of new layered-silicate nanocomposites based on polyamide-6 should extend the areas of their application as the construction materials due to their improved physico-chemical characteristics and fire resistance.

Fig. 1. X-ray photographs of MPM and pure compounds:
a) MMT; b) MMT:PVP = 2:1; c) PVP; d) MMT:PVP = 1:3; e) MMT:PVP = 1:5
Fig. 2. Differential thermal analysis of MPM: 1 – PVP; 2 - MMT:PVP = 1:7; 3 - MMT:PVP = 1:3

The pure PA-6 has the greatest value of elongation at tension and the smallest breaking strength (Table 1). The increase of MPM content in the composite decreases the elongation and increases breaking force. For the sample with MMT content of 7 wt% it is higher by 17 MPa than that of pure PA-6. At MMT content in the composite of more than 5 wt% the elongation at tension decreases threefold.

Young’s modulus (elastic modulus of the first order) has the similar dependence on MMT content in the composite based on PA-6: with the increase of MMT content Young’s modulus increases but more sharply than the increase of breaking force (Table 1). At MMT content of 2.5wt% it is higher by 40% compared with pure PA-6, and at the content of 7 wt% it is higher by 60%. The breaking force of the composite with MMT content of 7wt% is higher by 45% than that of pure PA-6.

The introduction of MPM into PA-6 increases tensile strength of the samples, as well as hardness and bending strength (Table 2). At MPM content corresponding to 2.5% of MMT in PA-6 bending strength and elasticity modulus at bending are increased twice and at MMT content of 5-7% – bending strength increases by more than threefold (Table 2).

**Table 1 Effect of MMT content in MPM on physic-mechanical properties of PA-6 at tension**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameter</th>
<th>PA-6</th>
<th>PA-6 / 2.5% MMT</th>
<th>PA-6 / 5.0% MMT</th>
<th>PA-6 / 7.0% MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_{\text{break}}$, MPa</td>
<td>38</td>
<td>45</td>
<td>49</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>$\sigma_{\text{max}}$, MPa</td>
<td>40</td>
<td>48</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon$, %</td>
<td>60</td>
<td>36</td>
<td>21</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>$E$, MPa</td>
<td>1160</td>
<td>1602</td>
<td>1685</td>
<td>1810</td>
</tr>
</tbody>
</table>

$MPM - MMT:PVP = 1:5$ where $\sigma_{\text{break}}$ – breaking strength, MPa; $\sigma_{\text{max}}$ – maximum tensile strength, MPa; $\varepsilon$ – elongation at break, %; $E$ – Young’s modulus, MPa.
Table 2  Effect of MPM content on PA-6 physico-mechanical properties at bending

<table>
<thead>
<tr>
<th>Sample Parameter</th>
<th>PA-6</th>
<th>PA-6 / 2.5% MMT</th>
<th>PA-6 / 5.0% MMT</th>
<th>PA-6 / 7.0% MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma_{\text{bend}}), MPa</td>
<td>16.5</td>
<td>33.0</td>
<td>54.0</td>
<td>55.5</td>
</tr>
<tr>
<td>(E_{\text{bend}}), MPa</td>
<td>1050</td>
<td>2020</td>
<td>2580</td>
<td>2600</td>
</tr>
<tr>
<td>(H_{\text{B}}), MPa</td>
<td>47.7</td>
<td>77.4</td>
<td>119.2</td>
<td>135.4</td>
</tr>
</tbody>
</table>

MPM – MMT: PVP = 1:5

where \(\sigma_{\text{bend}}\) – bending strength at flexure of 10 mm, MPa;
\(H_{\text{B}}\) – Brinell hardness, MPa;
\(E_{\text{bend}}\) – elasticity modulus at bending, MPa.

Brinell hardness of the samples also depends on MPM content – the increase of MMT amount in the composite its hardness constantly increases. MMT content of 2.5 wt% increases the hardness by 60% and 7 wt% of MMT – by 180%.

Improvement of PA-6 physico-mechanical properties while introducing MPM into it is a result of effective exfoliation of modified montmorillonite particles in polyamide, nanosilicate separation into layers, and likely formation of high-crystalline materials based on PA-6 and MMT.

Introducing MPM to PA-6 we improve the heat resistance and insulating properties of the obtained composites but the value of water absorption is constant (Table 3). The composite with MPM content corresponding to 2.5 wt% of MMT has the best insulation properties. The increase in conductivity of the samples with MMT content of more than 2.5 wt% may be explained by the increase of hygroscopic MPM amount in the composite. The investigation results concerning water absorption of such composites confirm this fact. The increase in MPM content increases water absorption.

The introduction of MPM into PA-6 also increases its heat stability according to Vicat and melting point. The increase of MMT content in the composites increases both values. At MMT content of 5-7 wt% heat stability according to Vicat and melting point of polyamide increase by more than 20°C.

The experimental results represented in Table 5 additionally confirm the effect of developed nanomodifier – MPM – on the processing and operational properties of polyamide.

Table 3  Effect of MPM content on the operational properties of PA-6

<table>
<thead>
<tr>
<th>Sample Parameter</th>
<th>PA-6</th>
<th>PA-6 / 2.5% MMT</th>
<th>PA-6 / 5.0% MMT</th>
<th>PA-6 / 7.0% MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\rho_{\text{e}} \times 10^{10}, \text{Ohm} \cdot \text{m})</td>
<td>1.4</td>
<td>17.4</td>
<td>12.6</td>
<td>10.0</td>
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<td></td>
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<td>------</td>
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<tr>
<td>TV, °C</td>
<td>190</td>
<td>205</td>
<td>212</td>
<td>215</td>
</tr>
<tr>
<td>Tmelt, °C</td>
<td>205</td>
<td>220</td>
<td>224</td>
<td>228</td>
</tr>
<tr>
<td>Water sorption for 24 hrs, %</td>
<td>2,22</td>
<td>1,98</td>
<td>2,12</td>
<td>2,31</td>
</tr>
</tbody>
</table>

where $\rho_v$ – specific volume electrical resistance, Ohm·m;
$TV, T_{melt}$ – heat stability according to Vicat and melting point of the composites, °C.

Conclusion
Thus, the experimental results confirm the positive effect of MPM in the composite with PA-6, allow to determine the rational composition of nanomodifier for polymers based on montmorillonite modified by polyvinylpyrrolidone at PVP:MMT ratio of 5:1 and confirm its efficiency while obtaining composites on the basis of polyamide-6 and MPM in the melt. The introduction of the developed MPM into polyamide in small amounts significantly improves its mechanical, thermophysical and insulating properties but reduces its elasticity.

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References

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