X-ray and thermogravimetric studies of montmorillonite modified with cationic urethane oligomers

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Abstract.
In this work, we show that, the possibility of synthesis of urethane oligomer on the surface of montmorillonite nanoparticles. This synthesis is possible due to the chemical adsorption of the cationic urethane oligomer with available, terminal amino groups. In a suspension of functionalized amino groups modified montmorillonite the reactions of addition of aromatic and aliphatic diisocyanates were carried out, as well as sequential addition of aromatic diisocyanate, glycerol, and again diisocyanate. Using the WAXS method, the interlayer distance of all types of the obtained modified montmorillonite was determined. Thermogravimetric analysis data were compared with X-ray data.

Keywords:
montmorillonite modification cationic oligourethane
Mt modified with organic cations is dispersed in a polymer matrix, where it acts as a reinforcing agent improving the properties of polymer material. Sometimes, conventional alkylammonium cations are not suitable for the montmorillonite (Mt) modification. In the case of polar polymers, such as polyurethanes, polyamides, polyepoxides, Mt modified with aliphatic surfactants does not lead to exfoliation in the polymer matrix. This is due to the lack of a sufficiently high-quality interaction between the nanofiller and the polar polymer matrix [1 - 3]. The authors of this work previously synthesized cationic oligourethanes having two sufficiently large fragments of 17 to 21 atoms length and having a polar urethane nature [4]. In this work, oligourethane ammonium chloride (OUAC) was synthesized based on N-methyldiethanol amine (NMDEA), 1,6-hexamethylene diisocyanate (HMDI), and isopropyl alcohol. This cationic oligourethane has two polar fragments with a length of 17 atoms, which provides an increase in interplanar spacing and allows the modified Mt to delaminate in an environment of polar organic solvents. In addition, such a modifier provides high affinity for the polar polymer, forming nanocomposites with fully exfoliated Mt, which increases the strength of the polyurethane material by an average of 40%. This work is a logical continuation of the previously obtained results. However, the new modifier oligourethane amine ammonium chloride (OUAAC) with terminal aminogroups which was synthesized on the basis of NMDEA and HMDI revealed completely new possibilities in the field of organoclays and organo/inorganic nanocomposites creation. Namely, the ability to carry out stepwise synthesis on the surface of modified Mt nanoparticles by the mechanisms of both polyaddition and polycondensation. This work gives a few examples of such synthesis with the use of aliphatic and aromatic diisocyanate, as well as an example of the sequential addition of aromatic diisocyanate, glycerol and repetitively aromatic diisocyanate.

The structure of modified Mt was studied using the wide-angle X-ray scattering technique (WAXS) [5]. X-ray optic scheme of DRON-4-07 diffractometer was arranged according to Debye Sherer method (transmission). CuK λ - radiation was monochromatized with a Ni-filter. A scintillation counter in an automated step-by-step scanning mode was used to detect
scattered X-rays. The measured values of the scattering intensity were adjusted to attenuate the incident X-ray beam of the test specimens and further deviation of the background X-ray scattering intensity by the collimator system. The values of the scattering intensity were normalized to the scattering volume. Fine-dispersed powders of Mt and Mt/M were placed into the cells.

The scattered intensity was recorded under the conditional scanning of the scintillation detector at scattering angles from (2 to 40)°. Bragg's equation was used to determine the distance (d) between particles layers in the Mt [6]:

$$d = n \lambda (2\sin \theta_{\text{max}})^{-1},$$

wherein $n$ - is the serial number of the diffraction peak in the diffraction patterns ($n = 1$), $\lambda$ - wavelength (for CuKα $\lambda = 0.154$ nm), $\theta$ - angle of X-ray scattering.

X-ray studies of all four types of organomodified Mt and initial Na-Mt showed a gradual increase of interplanar spacing with an increase of the organic component (Fig. 1).

![Figure 1](image.png)

**Figure 1**

WAXS of initial Na-Mt and four types of organomodified Mt:
1 - Na-Mt; 2 - OUAA/Mt; 3 - HMDI OUAA/Mt; 4 - DPMDI OUAA/Mt; 5 - DPMDI +Gl+ DPMDI OUAA/Mt
Thermogravimetric study was carried out to determine the content of organic part in modified Mt. For this purpose the derivatograph Q-1000, (MOM) was used. The measurements were conducted in ceramic cone-like crucible, with Al₂O₃ , under the air atmosphere, at temperature of (25–800) °C, at heating rate of 10 deg min⁻¹.

The analysis of the interlayer spacing of organomodified Mt and the comparison of TGA data allow us to draw interesting conclusions. So, the HMDI OUAA/Mt has a greater interplanar distance d₀₀₁ = 1.54 nm than the OUAA/Mt (d₀₀₁ = 1.45 nm), which is quite natural. However, the DPMDI OUAA/Mt sample has d₀₀₁ = 1.47 nm, which is less than that of the HMDI OUAA/Mt and is almost close to the OUAA/Mt index. While the amount of organic component in the DPMDI OUAA/Mt sample is greater than in both other samples. This fact can be explained by a rigid and relatively flat moiety of DPMDI, which makes it possible to form a compact organic layer on the nanoparticles surface. This version is confirmed by a slight increase of d₀₀₁ = 1.84 nm in the sample of DPMDI + Gl + DPMDI OUAA/Mt which has an organic matter amount in 2.4 times higher than in OUAA/Mt. The table 1 summarizes data on the organic matter content and interplanar distance d₀₀₁.

<table>
<thead>
<tr>
<th>№</th>
<th>Sample</th>
<th>2θmax, °</th>
<th>d₀₀₁, nm</th>
<th>W, % wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na-Mt</td>
<td>6,8</td>
<td>1,3</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>OUAA/Mt</td>
<td>6,1</td>
<td>1,45</td>
<td>23</td>
</tr>
<tr>
<td>3</td>
<td>HMDI OUAA/Mt</td>
<td>5,7</td>
<td>1,54</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>DPMDI OUAA/Mt</td>
<td>6</td>
<td>1,47</td>
<td>46</td>
</tr>
<tr>
<td>5</td>
<td>DPMDI + Gl + DPMDI OUAA/Mt</td>
<td>4,8</td>
<td>1,84</td>
<td>56</td>
</tr>
</tbody>
</table>

The table well illustrates that the increase of the organic component is not proportional to the increase of interplanar distance, however, it is associated with the nature of macromolecules in the interlayer spacing, that is connected with different configuration and orientation of aromatic and aliphatic urethane fragments. At the same content of 1.5% wt in DMF medium the DPMDI OUAA/Mt sample significantly differs from the OUAA/Mt sample. The DPMDI OUAA/Mt sample forms a bulk suspension, while the OUAA/Mt is a liquid dispersion, while sample DPMDI + Gl + DPMDI OUAA/Mt forms a thick gel.
The possibility of synthesis of regular structure oligomer on the nanoparticles surface has been shown by the example of stepwise diisocyanates addition; it can be used for matrix synthesis on montmorillonite nanoparticles. Montmorillonite modified with oligourethane amine ammonium chloride offers great opportunities for the design of the organic layer on the nanoparticles surface using both diisocyanates and other functional compounds, such as anhydrides and others. The use of montmorillonite with a reactive surface opens up enormous opportunities in the field of creation of hybrid organo/inorganic nanocomposites based on polar polymers.

References:


