Monmorillonite modified with oligourethane ammonium chloride and based nanostructured polymers

Savelyev Yuri, Gonchar Alexey, Travinskaya Tamara

Institute of macromolecular Chemistry, NAS of Ukraine, Kharkovskoe shosse, 48, 02160 Kiev, Ukraine

Email address:

yusav@i.kiev.ua (S. Yuri), lexgon@ukr.net (G. Alexey), travinskaya-tamara@rambler.ru (T. Tamara)

Abstract: For the purpose of developing of polymer nanocomposites based on polar polymers - polyurethane and related polymers, a method of modifying the montmorillonite (MMT) with a new modifier containing urethane groups in it structure has been first elaborated. Exchange capacity of the MMT surface was determined by adsorption of methylene blue; the structure of the modifier was confirmed by X-ray analysis, the content of the organic component in the modified MMT was measured by thermogravimetric analysis. The molecular weight and molecular weight distribution of the modifier was determined by size exclusion chromatography. The resulting modified MMT has been designed to form nanostructured composites on the basis of polymers having polar groups in their composition, including polyurethanes, with the aim to increase the physical and mechanical properties of based film materials. The new modifier – oligourethane ammonium chloride provides high affinity of MMT with the polymer matrix due to the possibility of hydrogen bonds formation. The intercalation of modifier into MMT interlayer space (increasing the distance between the layers after modification by 0.68 nm), as well as the total exfoliation of MMT in polyurethane urea matrix, characterized by the disappearance of the absorption peak which is responsible for layered structure has been proved by the WAXS method. Physic-mechanical tests demonstrated an increase in film strength of the polymer nanocomposite compared to the polyurethane matrix by 40% at a sufficiently low MMT (0.5%) content.

Keywords: Monmorillonite, Modifier, Nanocomposites, Polyurethane, Exfoliation

1. Introduction

Creation of polymeric materials based on polyurethanes and other related polymers of high performance has always been important problem of polymer science and technology. One of the ways of obtaining such polymeric materials is to introduce into the polymer matrix the nanoparticles of inorganic nature, in particular layered silicates, such as montmorillonite (MMT) [1, 2]. Linear dimension of inorganic layers of MMT is about 200 nm in length, and 1 nm in width [3]. Due to such area-thickness ratio the MMT has a large specific surface and serves as a carrier of nanostructure. In case of complete exfoliation of MMT in a polymer matrix a significant increase in strength can be achieved at a low content of organoclay [4]. The exfoliation of MMT in the polymer matrix is achieved, primarily, when inorganic and organic components are compatible. The lack of compatibility between inorganic and organic components is the main problem which is to be solved at the creation of

such materials. The compatibility of the organic and inorganic constituents can be attained by modification of MMT with organic matter. The layers of MMT form clusters with gaps inside them, which are called "packs" or "galleries". Isomorphous substitution of the cations in the middle of the layers (Mg^{2+} replaces Al^{3+} in the octahedral structures or Al^{3+} replaces Si^{4+} in the tetrahedral structures) generates negative charges that are counterbalanced by alkali or alkaline earth cations presented in the metal layers [1]. Inorganic cations in the middle layer may be replaced by other cations, in particular organic. Chemical adsorption of organic cations by ion-exchange mechanism increases the space between the layers and reduces the surface energy, imparting a surface with hydrophobic properties [3]. Usually the layered silicates are converted into hydrophobic materials by adsorption on the surface layers of clay water-repellent substances by ion exchange of interplanar cations with onium cations of general structure $R_{n+1} E^+ X^-$ (R - organic radical, E - element of V-VII group, X = Hal, OH).

In order to modify MMT by ion exchange the natural MMT must be converted to the sodium (rarely to potassium) form by treatment with alkali metals carbonates [5], since the alkali metal cations are replaced on the organic cations much better then alkaline-earth of natural MMT. In order to create polymer composites based on polar heterochain polymers the following ways of MMT modification have been used:

- modification with cationic surfactants (ammonium and phosphonium cations) [6]
- modification with reactive compounds in the polycondensation reactions (ammonium and phosphonium ions containing amine, hydroxyl, carboxyl groups) [3, 5]
- modification with monomers in polycondensation reactions followed by the chain growth in the interlayer space [1, 3]

A disadvantage of the first modification method is the nonpolar nature of the used surfactants. As a result of varying the nature of the organic modifier and the polymer matrix the particles of the modified MMT form agglomerates that do not contribute to the intercalation and exfoliation of polyurethane into the interplanar space of MMT.

Disadvantages of the second modification method are a small molecular size of reactive modifiers' molecules which does not provide a sufficient organophilicity of the mineral surface that complicates the penetration of the monomer molecules into interplanar space. The same drawbacks are observed in case of the third modification method, namely modification with diamines, one of the amino groups of which is in a salted form and is capable to ion exchange reactions in interplanar space of MMT. The sizes of these monomer molecules are not large enough to provide sufficient organophilicity of MMT to overcome the agglomeration of the particles.

Previously we have developed a method of combined modifying of MMT with two types of modifiers: • cationic surfactant (cetylammonium bromide), which imparts the organophilicity to MMT surface and facilitates the dispersion of the mineral in organic medium; and • a bifunctional amine-containing compounds: dimethylaminoethyl methacrylate, N-methyl diethanolamine, and tris (hydroxymethyl)aminomethane. The developed method of MMT functionalization allows to obtain on its surface an organophilisized mineral containing reactive groups of different nature (acrylate, hydroxy, amine), capable to participate in reactions of photoinitiated polymerization and polycondensation [7], which should increase the physical and mechanical properties of polymers. These, obtained by photoinitiated polymrezation of oligomeric systems nanocomposites, have a tensile strength exceeding that of the polymeric matrix by 85 - 90% [8].

This paper proposes a method of MMT modification using the ammonium ions as surfactants, which includes the urethane groups – oligourethane amonium chloride (OUAC). OUAC molecule is sufficiently sterically large to provide the intercalation and exfoliation of MMT particles in polar organic media [9, 10]. A new approach to MMT modification consists in the use of synthesized in our laboratory surfactants with urethane groups in their structure in contrast to the classical use of surfactants composed of an ionic group and of an aliphatic large fragment ($C_{12} - C_{20}$). MMT modified with such cationic surfactants can form stable hydrogen bonds with the polymer matrix of polyurethanes, polyamides, polyimides, etc. Hydrogen bonding between the modified surface of MMT and polyurethane macromolecules provides a complete exfoliation of the modified MMT particles and strong physical interaction between inorganic and organic components. The high affinity of the modified nanofillers with polymer matrix provides the increased strength of polyurethane film and of other polar polymers based materials.

2. Experimental Section

2.1. Materials

We used a natural montmorillonite from clay-field "Askaniya" (Georgia).

Commercial N-methyldiethanol amine (NMDEA) [Aldrich], and 1,6-hexamethylene diisocyanate (HMDI) [Aldrich] were used as initial components for the synthesis of nanomodifier - oligouretanamonium chloride (OUAH),. Isopropyl alcohol was distilled in the presence of anhydrous calcium chloride and the fraction with bp = 82 °C was isolated. Polyoxytetramethylene glycol with molecular weight of 1000 (POTMG-1000) [Aldrich] and HMDI [Aldrich] were used for synthesis of polyurethane urea. To determine the exchange capacity of MMT the indicator of methylene blue (MB) (ZAT "Khimservice", Russia) was used.

2.2. Methods

2.2.1. Preparation of the Sodium form of MMT

For obtaining of the Na-form of MMT (Na-MMT), the natural MMT suspension in distilled water containing 5% of mineral was prepared followed by 1 h boiling with sodium carbonate in a weight ratio of MMT:sodium carbonate = 100:1. The resulting Na-MMT was separated from sodium carbonate solution by fourfold centrifugation with washing with distilled water. The dry matter content in the Na-MMT suspension was determined gravimetrically. The resulting Na-MMT suspension was used to obtain the modified MMT.

2.2.2. Measurement of the Exchange Capacity of Na^+ MMT

Exchange capacity of the MMT surface has been determined using the method of photocalorimetry by analysis of the adsorption of indicator of methylene blue on the surface of Na-MMT by [11]. Based on obtained data the ratio of modifier to the amount of MMT was calculated. The study of the adsorption of MMT was carried out by adding to

the samples of different amounts of MB indicator's suspension. Adsorption was carried out for 2 days. The aqueous solution was separated from the MMT and the concentration of the indicator MB in solution was measured by photocalorimeter CK-2PM (PO "ZOMZ", Russia).

Adsorption α mmol / g, was calculated according to

$$a = \frac{(C_0 - C_p) \cdot V}{g}$$

where: C_0 - initial concentration of MB;

C_p - equilibrium concentration of MB (per 1 g of MMT) after adsorption;

V - volume of an aqueous sample solution, l;

g - mass of the MMT sample.

Chemical adsorption, which corresponds to the ion exchange capacity of MMT was determined according to the graph of the adsorption isotherm at the exit of the curve on the plateau (Figure 1). The value was equal to 1.5 mmol / g
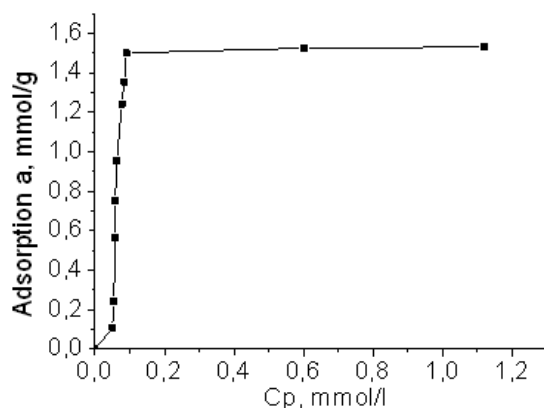

Fig 1. Isotherm of adsorption of the indicator MB

2.2.3. X-Ray Studies

WAXS difractograms were obtained using DRON difractometer under the cupreous anode radiation with nickel filter in initial beam. Optical scheme of difractometer was modified for the "clearance" shooting. The details of WAXS carrying out are presented in [12]. X-ray diffraction study was carried out in CuKα radiation (power 30 kVt/40 mA) monohromazed with Ni-filter at 20 ± 2 °C.

Such roentgen-optical scheme provides studying of peculiarities of the short-distance ordering and average-scale ordering in the interfacial distance range from 0,1 up to 10 nm and facilitates the conducting of necessary normalization techniques, such as scattering regulation on equal scattering volume and X-rays absorption in the sample. In order to insert the mentioned above corrections we used the measured values of reduction of used by sample radiation. The regulation to equal intensity was carried out with allowance of measured value of intensity scattering by reference pattern.

Studied fine-dispersed nano-filler powders (initial MMT and obtained organically modified MMT) were placed into the cells with thickness of about 0,2 mm having [poly(ethylene terephthalate)] windows with thickness of 0,017 mm. Polyurethane-MMT organic-inorganic nanocomposites were studied in the form of films with the thickness of 0,5-0,9 mm. Registration of scattered intensity was carried out under condition of step-type scanning of scintillation detector in the scattering angles range from 2 to 40°. The distance (d) between layers of particles in the MMT was determined from Bragg's equation [13]:

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

where n - the serial number of the diffraction peak in the diffraction patterns (n = 1), λ - wavelength of the characteristic X-rays (for CuKα λ = 0,154 nm), θ - angle of X-ray scattering

2.2.4. Physic-Mechanical Testing

Measurements were performed on a tensile testing machine FU-1000 (VEB MWK "Fritz Heckert", Germany) at a tensile speed of 100 mm / min. and temperature 25 °C.

2.2.5. IR-Spectroscopy

OUAC sample was obtained from an aqueous solution onto irtran. IR spectra were measured using infrared Fourier transform spectrometer «Tensor-37» Bruker / FT-IR-Spectrometer (Germany) in the range of wave numbers of 4500-500 cm-1. The assignment of the bands was performed according to [14].

2.2.6. TGA Measurements

Thermogravimetric analysis (TGA) of modified MMT was carried out using a Q-1000 derivatograph, (MOM, Hungary) under the following conditions: temperature range: 20-1000 °C, average heating rate – 10 °C/min; initial weight of samples: 100 mg; inert substance: Al_2O_3; medium: air (static); sample holder: a ceramic cone-like crucible.

2.2.7. Synthesis of Macrodiisocyanate (MDI)

Synthesis of macrodiisocyanate was carried out in a three-necked reactor, equipped with input-output device of inert gas (argon) in amount corresponding to the ratio of functional groups – NCO:OH = 2:1. The resulting mixture was heated in a dry inert gas under the stirring at 80 - 85 °C. The reaction was stopped by cooling the reactor to 15 °C. The content of isocyanate groups in the MDI should be close to 6.3 ± 0.1 % wt. Scheme of MDI synthesis is performed lower:
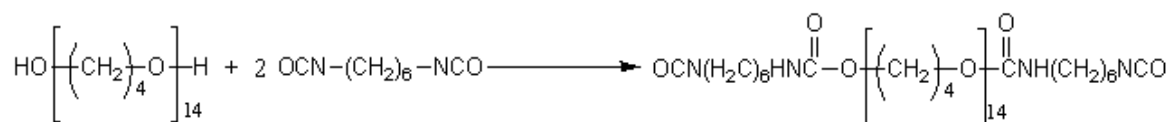
2.2.8. Synthesis of Polyuretane Urea

HMDI based MDI was used in the synthesis of polyurethane urea (PUU). The calculated amount of water in dimethyl formamide (DMF) was added to synthesized MDI at the temperature of 55 °C under continuous stirring; the NCO:H$_2$O ratio = 2:1. The chain extension process is the reaction of isocyanate groups of MDI with water, resulting
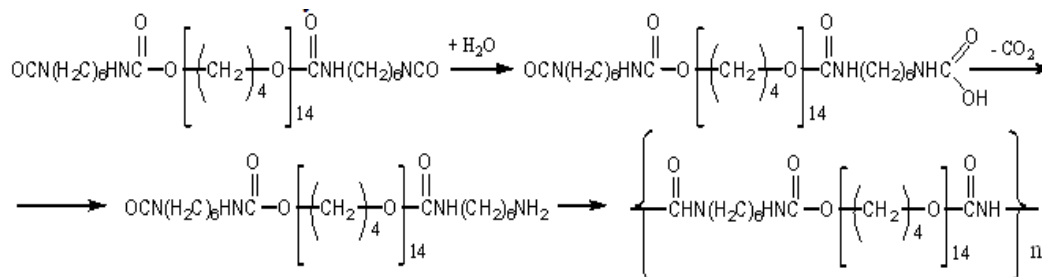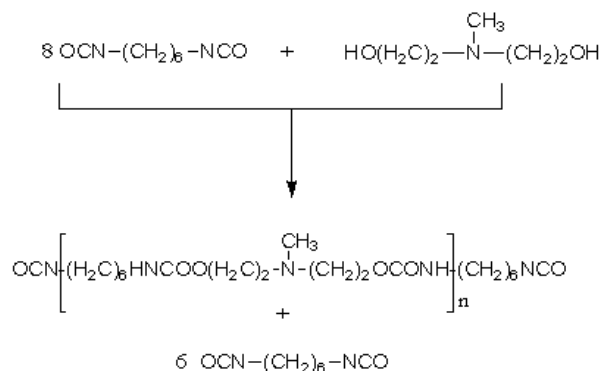
in formation of an unstable carbamine acid which decomposes into CO$_2$ and amine, the resultant amino group reacts with the isocyanate groups of MDI. The chain extension process lasted for two hours, whereupon the resulting polymer solution was poured into a glass container. Scheme for the synthesis of PUU is as follows:

OCN(H$_2$C)$_6$HNC—O$\left[$(CH$_2$)$_4$O$\right]_{14}$CNH(CH$_2$)$_6$NCO + H$_2$O $\longrightarrow$ OCN(H$_2$C)$_6$HNC—O$\left[$(CH$_2$)$_4$O$\right]_{14}$CNH(CH$_2$)$_6$NHC$\begin{smallmatrix}O\\OH\end{smallmatrix}$ − CO$_2$ $\longrightarrow$

$\longrightarrow$ OCN(H$_2$C)$_6$HNC—O$\left[$(CH$_2$)$_4$O$\right]_{14}$CNH(CH$_2$)$_6$NH$_2$ $\longrightarrow$ $\left[$CHN(H$_2$C)$_6$HNC—O$\left[$(CH$_2$)$_4$O$\right]_{14}$CNH$\right]_n$

2.2.9. Determination of the Molecular Weight (MW) and Molecular Weight Distribution (MWD)

MW and MWD of oligomers were determined by size exclusion chromatography using liquid chromatograph IC -8800 DuPont. The solution of polystyrene in DMF was used as the standard. Bimodal columns CN-Zorbax were used for MWD determination.
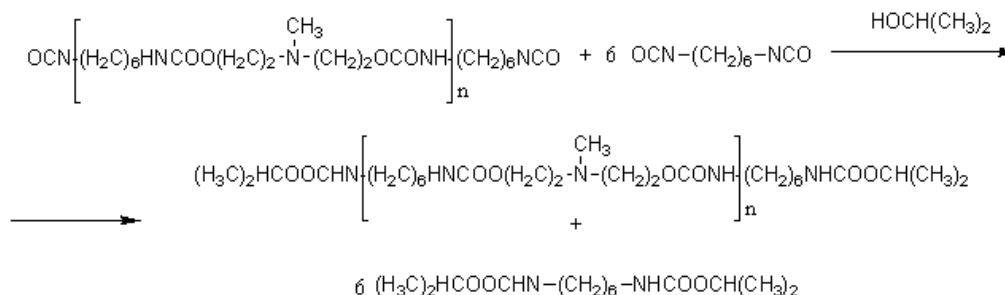
3. Results and Discussion

Based on the fact that the chemical modification of MMT is carried out predominantly with aqueous solutions of cationic surfactants with a concentration below the critical micelle concentration, we have proposed a scheme for the obtaining of cationic surfactant solution - OUAC, with a concentration of 4x10^{-3} mol/l. A fourfold excess of HMDI was used for obtaining the modifier with a minimum molecular weight.

3.1. Synthesis of Oligouretanamonium Chloride (OUAC)

Synthesis of OUAC was carried out in three stages. In the first step the reaction between N-MDEA and HMDI at NCO:OH ratio = 8:1 took place:

8 OCN—(CH$_2$)$_6$—NCO + HO(H$_2$C)$_2$—N(CH$_3$)—(CH$_2$)$_2$OH

$\downarrow$

OCN$\left[$(H$_2$C)$_6$HNCOO(H$_2$C)$_2$-N(CH$_3$)-(CH$_2$)$_2$OCONH$\right]_n$(CH$_2$)$_6$NCO
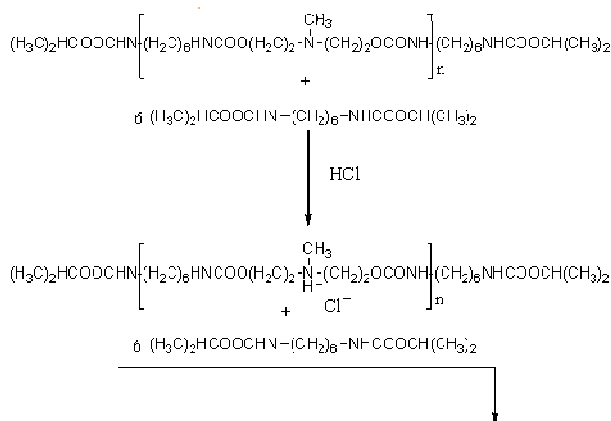
+

6 OCN—(CH$_2$)$_6$—NCO

where n = 1,8.

The second step involves the interaction of the isocyanate groups with the excess of isopropyl alcohol which serves both as reactant and solvent:

OCN$\left[$(H$_2$C)$_6$HNCOO(H$_2$C)$_2$-N(CH$_3$)-(CH$_2$)$_2$OCONH$\right]_n$(CH$_2$)$_6$NCO + 6 OCN—(CH$_2$)$_6$—NCO $\xrightarrow{\text{HOCH(CH}_3)_2}$

$\longrightarrow$ (H$_3$C)$_2$HCOOCHN$\left[$(H$_2$C)$_6$HNCOO(H$_2$C)$_2$-N(CH$_3$)-(CH$_2$)$_2$OCONH$\right]_n$(CH$_2$)$_6$NHCOOCH(CH$_3$)$_2$

+

6 (H$_3$C)$_2$HCOOCHN—(CH$_2$)$_6$—NHCOOCH(CH$_3$)$_2$

In the third step, a solution of OUAC with concentration of 4x10^{-3} mol/l was obtained by adding the reaction mass to the 4.1 mmol/l HCl solution. HCl solution of predetermined concentration was prepared from 0.1N solution of HCl and distilled water. The product of interaction of HMDI with isopropyl alcohol (diurethane) precipitated in water, and the resulting product OUAC after neutralization of

oligouretanamine with HCl dissolved in water.

The processes, taking place in a third stage of OUAC synthesis are presented as follows:

$$(H_3C)_2HCOOCHN-[(H_2C)_6HNCOO(H_2C)_2-\overset{CH_3}{\underset{+}{N}}-(CH_2)_2OCONH-(CH_2)_6NHCOOCH(CH_3)_2]_k$$

$$+\ \delta\ (H_3C)_2HCOOCHN-(CH_2)_6-NHCOOCH(CH_3)_2$$

$$\downarrow HCl$$

$$(H_3C)_2HCOOCHN-[(H_2C)_6HNCOO(H_2C)_2-\overset{CH_3}{\underset{+\quad Cl^-}{N}}-(CH_2)_2OCONH-(CH_2)_6NHCOOCH(CH_3)_2]_n$$

$$+\ \delta\ (H_3C)_2HCOOCHN-(CH_2)_6-NHCOOCH(CH_3)_2$$

The resulting precipitate of the product of reaction of excess of HMDI with isopropanol was filtered through the filter paper to give a clear solution of ammonium salts (OUAC) of a given concentration (4×10^{-3} mol/l).

3.2. IR-Spectrum of OUAC

The study of the OUAC IR spectrum confirmed the chemical structure of the modifier, the presence of urethane and ionic groups.

OUAC spectrum (Fig. 2) displays the clearly visible bands corresponding to NH of the urethane fragment (amide I - 1695 cm-1, amid II - 1540 cm-1), as well as a band corresponding to the trans- associated form of the NH group -(νNH 3300 cm^{-1}). The absorption band corresponding to the C - N (-νC - N - 1260 cm^{-1}) vibrations is clearly visible. The characteristic broad shoulder 2640 cm^{-1} confirms a presence of coordinate covalent bond NH$^+$ in the fragment (CH3)NH$^+$. All other absorption bands correspond to the presence of aliphatic fragments (- $(CH_2)_6$ -, - $(CH_2)_2$ -, - CH_3, and - CH $(CH_3)_2$).
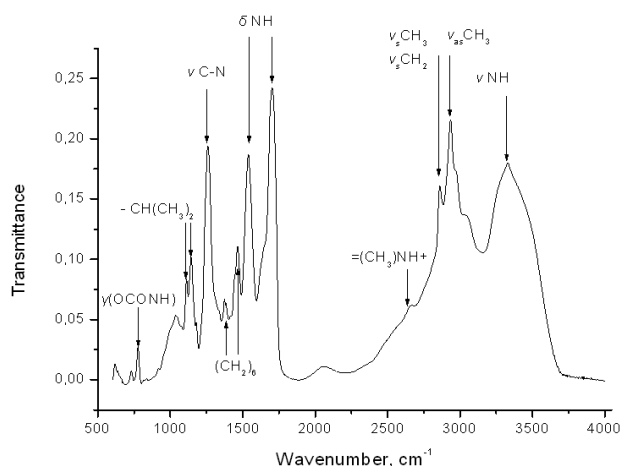

Fig 2. IR spectrum of OUAC

3.3. Size Exclusion Chromatography of OUAC

The weight-average molecular weight and the number-average molecular weight of OUAC along with the MWD were determined by size exclusion chromatography. The weight-average molecular weight was about 820 g /mol and the number-average - 680 g / mol. These data confirmed

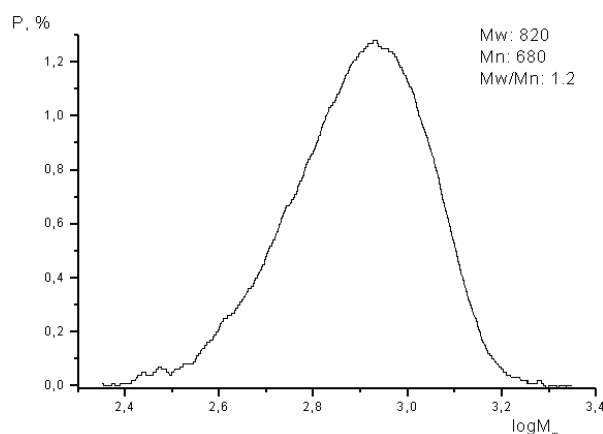the theoretical conception re the structure of OUAH (Fig.3).

Fig 3. MWD curve of OUAC

3.4. Modification of MMT

Modification of MMT was carried out by addition to suspension of Na-MMT the solution of OUAC with 50% excess relative to calculated exchange capacity of Na-MMT. After adding an OUAC solution the resulting mixture was diluted with distilled water to a ratio of 1 g MMT per 500 ml of water. At addition of OUAC solution to the MMT suspension the instantaneous coagulation of MMT particles followed by formation of a white precipitate has been observed. Modification was performed 48 hours, whereupon the precipitate of modified MMT was filtered, dried in an oven at 60 ^{0}C till constant weight and then crushed in an agate mortar in a ball mill.

To assess the content of the organic component in the modified MMT, the TGA study was conducted (Table 1). TGA data showed that the content of organic part was about 40%. This value substantially corresponds to its theoretical content.

Table 1. Content of organic part in modified MMT

Adsorption of modifier, mmpl/g	Theoretical content of modifier, wt %	Content of organic part according to TGA, wt %
1,5	43	40

3.5. Swelling of the Modified MMT in Organic Solvents

Swelling study of modified MMT in organic solutions showed that the modified MMT formed a stable gel in an aprotic organic solvent such as dimethyl formamide and dimethyl sulfoxide. Gel formation indicates a high degree of intercalation of the solvent into the interlayer space of MMT and physical network formation.

3.6. X-Ray Studies

WAXS results (Fig. 4) have shown, that modified with OUAC montmorillonite has a larger interlayer spacing (d_{001} = 1,94 nm) in comparison with the original natural MMT (d_{001} = 1.26 nm).
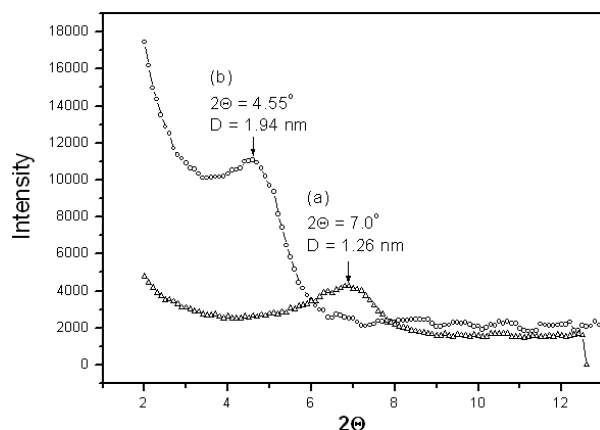
Fig 4. WAXS profiles of natural and modified MMT

The distance between the MMT layers after modification increases up to 0.68 nm. It should be noted that the "unification" of inorganic cations in the middle of the layers in the case of Na-MMT reduces the interlayer distance d_{001} till 1.15 nm. Thus, the effect of increasing of the interlayer distance of MMT as a result of modification with organic compound can be estimated as 0.79 nm.

X-ray studies of modified MMT and nanocomposites based on PUU with modified with OUAC MMT as well as mechanical mixture of modified MMT with the original polymer matrix PUU (Fig. 5) proved a complete and systematic exfoliation of nanofillers in the PUU polymer matrix. The absence of the characteristic absorption peak of the modified MMT in all nanocomposites samples containing 0.5- 5.0 wt % of the latter testifies to the complete exfoliation. The absorption curve of mechanical mixture of polymer with modified MMT has the absorption peak $2\Theta = 4.55$, which is characteristic for the modified MMT. This indicates that the polymer matrix by itself does not affect the character of radiation absorption by modified MMT.
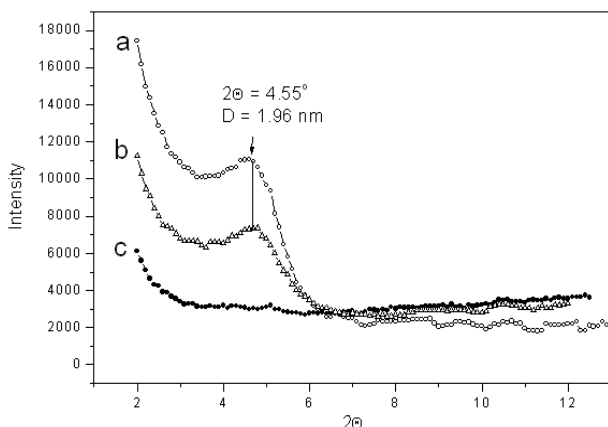

Fig 5. X-ray diffraction profiles of (a) modified MMT, (b) mechanical mixture of the polymeric matrix with modified MMT (c) nanocomposite containing 5 wt% of modified MMT.

3.7. Physic-Mechanical Properties

Physic-mechanical tests of the polymer matrix and based nanocomposites with a concentration of the modified with OUAC montmorillonite of 0.5, 2.5, and 5.0 wt % have shown, that at MMT content of 0.5 wt %   the increase of the tensile strength by 40 % in relation to the initial index of PUU took place. With an increase of MMT content up to 2.5 wt %, a reduction of tensile strength in compare with a sample containing 0.5 wt %, is observed. However, this index exceeds that of the original PUU matrix by 25.0 %. The nanocomposite containing 5.0 wt % of MMT has almost lost its strength (Fig. 6).
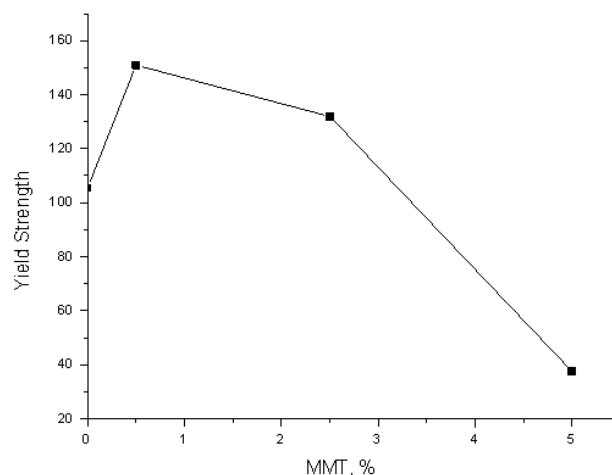

Fig 6. Tensile strength vs modified MMT content

The sharp increase of the strength of the PUU-based material with low content of modified MMT (0.5 wt %) testifies to a high degree of the interaction of nanofiller with the PUU matrix which is conditioned by the hydrogen bonds formation between the urethane groups of modified MMT with urethane groups and polar fragments of urea. Strength losses at the increase of MMT concentration is probably the result of intercalation of all PUU macromolecules into the interlayer space of modified MMT and converting of the polymeric composition to the organoclay, where the physical strength begins to be determined by physical net, formed by nanoparticles of organoclay. Thus, the whole polymer is located in the space between the layered plates of MMT. This effect indicates a high structure-forming ability of modified with OUAC MMT.

4. Conclusions

We have first developed a method of MMT modification with a modifier containing urethane groups - OUAC. Modified with OUAC MMT is assigned for the formation of nanocomposites on the basis of polymers, having polar groups in its structure in order to increase the strength of polymeric materials. In contrast to classical surfactants which are traditionally used as MMT modifiers, a new modifier provides the high affinity between the modified MMT and polymer matrix due to hydrogen bonds formation. X-ray diffraction data showed the complete exfoliation of the modified MMT in the PUU matrix, which indicates a high degree of affinity of the new nanofiller to the polymer matrix. Modified with OUAC MMT improves the strength of the polymer matrix by 40 % at a low concentration (0.5

wt. %), and, respectively, has great practical significance for the production of polar polymer based film materials with high performance characteristics. The starting substances used in the synthesis of a new modifier are the available and cheap monomers for the polyurethane production, which are widely produced by chemical industry. The cost of production of a new MMT modifier does not exceed the cost of standard linear polyurethane. A small amount of modifier required to significant increase of the strength of the polymer material, the low cost of natural MMT, and the simplicity and the low cost of technology provides an economic benefit of using new nanofiller in production of polar polymer based nanocomposites.

Acknowledgements

References

[1] Pavlidoua S., Papaspyridesb C. D. A review on polymer–layered silicate nanocomposites. Progress in Polymer Science 2008, 33, 1119–1198.

[2] Kiliaris P., Papaspyrides C.D. Polymer/layered silicate (clay) nanocomposites: An overview of flame retardancy. Prog. Polym. Sci 2010, 35, 902–958.

[3] Suprakas Sinha Ray, Masami Okamoto. Polymer/layered silicate nanocomposites: a review from preparation to processing. Prog. Polym. Sci. 2003, 28,. 1539–1641.

[4] Gorrasi G, Tortora M, Vittoria V, Galli G, Chiellini E. Transport and mechanical properties of blends of poly(ε-caprolactone) and a modified montmorillonite – poly(ε -caprolactone) nanocomposite. J Polym Sci. Polym Phys 2002, 40, 1118–24.

[5] Alexandre M, Dubois P. Polymer–layered silicate nanocomposites: preparation, properties and uses of a new class of materials. Mater Sci Eng R 2000; 28,1–63.

[6] Decker C., Zahouily K., Keller L. et al. Ultrafast sunthesis of bentonite-acrylate nanocomposite materials by UV-radiation curing. J. Mater. Sci. 2002, 37,. 4831–4838.

[7] Patent Ukraine 7346.. Savelyev Yu. V., Gonchar A.N., Litviakov V.I., Serov V.G. Publ. 25.11.08. Bul. № 22 (in Ukrainian)

[8] Savelyev Yu. V., Gonchar A.N. Nanocomposites based on ionic oligourethane acrylate and montmorillinite. All materials. Encyclopedic guide. 2010, 2, 16-21 (in Russian).

[9] Patent Ukraine 74739. Savelyev Yu. V., Gonchar A.N. Publ. 12.11.2012. Bul. №21 (in Ukrainian).

[10] Patent Ukraine 74740. Savelyev Yu. V., Gonchar A.N. Publ. 12.11.2012. Bul. №21 (in Ukrainian).

[11] Sanchez J., Beltran A., Alonso J., Jimenez C. Development of a new ion-selective field-effect transistor sensor for anionic surfactants: Application to potentiometric titrations. Analytica Chimica Acta. 1999, 382, 157 – 164.

[12] Lipatov Yu.S., Shilov V.V., Gomza Yu. P., Krugliak N.E. X-ray diffraction methods for the study of polymeric systems. Eds: Nauk. Dumka: Kiev.: 1982, 296 P. (in Russian).

[13] Glatter O., Kratky, O. Small-angle X-ray scattering. Eds: Academic Press. London, 1982.

[14] Norman B., Lawrence H., Stephen E. Introduction to Infrared and Raman Spectroscopy. Eds: Academic Press Inc., 1990.