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GONCHAR OLEKSIJ,

Institute of macromolecular Chemistry NAS of Ukraine, 48, Kharkivske shose, Kyiv, 02160, Ukraine,
e-mail: lexgon@ukr.net

ORCID: 0000-0001-8356-9283

SAVELYEV YURI,

Institute of macromolecular Chemistry NAS of Ukraine, 48, Kharkivske shose, Kyiv, 02160, Ukraine,
e-mail: yuri2savelyev@gmail.com

ORCID: 0000-0003-3356-9087

TRAVINSKAYA TAMARA,

Institute of macromolecular Chemistry NAS of Ukraine, 48, Kharkivske shose, Kyiv, 02160, Ukraine,
e-mail: travinskaya-tamara@rambler.ru

ORCID: 0000-0002-6109-1116

**POLYURETHANEACRYLATE/MONTMORILLONITE
NANOCOMPOSITES**

In order to create polymer nanocomposites with high performance on the basis of polyurethaneacrylates (PUA) with montmorillonite (MMT), three methods of chemical modification of the layered silicate surface have been developed. The first modification method is based on using of two different functional modifiers (organophilic and reactive), the second method is based on modification with synthesized by us compound which contains urethane groups, and the third one is based on using synthesized by us modifier containing urethane and other reactive groups. Exchange capacity of the MMT surface was determined by adsorption of indicator "methylene blue". Intercalation of modifier into the interlayer space of MMT was confirmed by X-ray analysis; the content of organic component in the modified MMT (MMT/M) was determined by thermogravimetric analysis. The resulting organoclay is purposed for the formation of nanostructured composites based on cross-linked polyurethane acrylates with improved physical and mechanical properties. The obtained polyurethaneacrylate nanocomposites with different type MMT/M exhibit the increased in 1,6–2,6 times tensile strength as compared to original polymer matrix. WAXS method has proved an intercalation of modifier into MMT interlayer space (increased distance between layers after modification), as well as the total exfoliation of MMT in PUA matrix, characterized by the disappearance of the absorption peak which is responsible for layered structure.

Keywords: montmorillonite, modification, polyurethane acrylate, nanocomposites.

Introduction

Nanocomposites are a new class of composites, for which at least one dimension of the dispersed particles is in the nanometer range [1]. Nanocomposites based on layered silicates are the most investigated probably because the starting claymaterials are easily available and because their intercalation chemistry has been studied for a long time [2]. The

polymer/layered silicate nanocomposites are characterized by increased strength and heat resistance as well as reduction of gas permeability and flammability [1]. Creation of polyurethane acrylate (PUA) - organoclay based nanocomposites with high performance properties is a real chance to improve the basic properties of initial PUA polymer matrix. The increase of the strength and durability of PUA based materials may be achieved by

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incorporation of organoclay nanoparticles into the polymer matrix [3]. In order to modify the natural MMT by ion exchange method, it should be converted to the sodium (rarely to potassium) form by treatment with alkali metals carbonates [4], since the alkali metal cations are easier replaced on the organic cations compared to alkaline-earth cations of natural MMT. There are the following ways of MMT modification used in the field of polymer nanocomposites based on polar heterochain polymers:

- modification with cationic surfactants (ammonium or phosphonium cations) [5]
- modification with reactive compounds in the polycondensation and polymerization reactions [3, 6]
- modification with monomers during the reaction of polycondensation followed by the chain growth in the interlayer space [1, 6].

The first method of modifying MMT has the disadvantages associated with the aliphatic nature of the used surfactants. The different nature of the organic modifier and polymer matrix causes agglomeration of the modified MMT particles. Agglomeration does not contribute to the intercalation and exfoliation of polyurethane into the interplanar space of MMT. The second method has the disadvantages of the small size of reactive modifiers' molecules which does not provide a sufficient organophilicity of the inorganic surface that complicates the penetration of the monomer molecules into the interplanar space. The same disadvantages are observed in the case of the third modification method. In the case of modification by diamines, one of the amino groups of which is in a salt form and able to the chemical adsorption on the surface of MMT particles. Accordingly, that leads to an agglomeration of modified MMT particles due to the sufficiently not large size of the monomer molecules.

In order to create polymer nanocomposites with high performance on the basis of polyurethane acrylates (PUA) with montmorillonite (MMT), three methods of chemical modification of the layered silicate surface have been developed.

The first modification method is based on combined modifying of MMT with two types of modifiers: cationic surfactant (cetylammonium bromide), which imparts organophilicity to MMT surface and facilitates dispersion of the mineral in organic medium; and a functional amine - dimethylaminoethyl methacrylate. The developed

method of MMT functionalization allows to obtain an organophilized minerals containing reactive groups (acrylate) on its surface, capable to participate in reactions of photoinitiated polymerization, which should increase the physical and mechanical properties of polymers.

The second method of MMT modification lies in use of ammonium ions as surfactants, which include the urethane groups – oligourethane ammonium chloride (OUAC). Its molecule is sufficiently sterically large for provide the intercalation and exfoliation of MMT particles in polar organic media. The new approach of MMT modification in contrast to the classical use of surfactants composed of the ionic group and aliphatic fragment ($C_{12} - C_{20}$), consists of the use of synthesized by us surfactants with urethane groups in their structure. Such cationic surfactants provide stable hydrogen bonds between the surface of the modified MMT and the polymer matrix of the polar polymer. Hydrogen bonding between the modified surface of MMT and polyurethane matrix 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 the polymer matrix provides an increase in the physical and mechanical properties of the polyurethane nanocomposite.

The third method is differs from the previous second by the presence in the molecule of a modifier, which is synthesized similarly to OUAH, the reactive methacrylate groups. The new modifier - oligourethane methacrylate ammonium chloride (OUMAAC) is having both urethane and reactive methacrylate groups. Reactive methacrylate groups form chemical bonds with oligourethane acrylate matrix during the *in situ* polymerization. Modified surface of MMT nanoparticles, exfoliated due to the presence of urethane groups, provides not only physical but also chemical affinity with polymer matrix. Physical and chemical bonds of nanofiller with polyurethane acrylate matrix provides a significant increase of polymer nanocomposite service properties as compared to the initial polymer matrix.

Experimental

Materials.

Natural montmorillonite from the Askania (Georgia) clay deposit was used. MMT modifiers:

cetylammmonium bromide (CTAB) [Aldrich] and dimethylammmoniummethacrylate chloride (DMAEMAC) [Aldrich]. N-Methyldiethanolamine (N-MDEA) [Aldrich], 1,6-hexamethylenediisocyanate (HMDI) [Aldrich], hydroxyethyl methacrylate (HEMA) [Aldrich] and isopropyl alcohol were used to synthesize the OUAH and OUMAH modifiers. Polyoxytetramethylene glycol with molecular weight of 1000 (POTMG-1000) [Aldrich], 4, 4'-diphenylmethane diisocyanate (MDI) and HEMA [Aldrich] were used for synthesis of polyurethane acrylate (PUA). 2-propylolphenyl keton (Darokur-1173) was used as a photoinitiator of polymerization. To determine the exchange capacity of MMT the indicator of methylene blue (MB) was used.

Preparation of the sodium form of MMT.

The suspension of original MMT (5%) in distilled water boiled for 1 hour with sodium carbonate in a weight ratio of MMT : sodium carbonate = 100:1 was used for obtaining of Na-form of MMT (Na-MMT). The fourfold centrifugation, followed by washing with distilled water, was used to separate the resulting Na-MMT from the solution of sodium carbonate. The content of dry matter in Na-MMT suspension was defined gravimetrically. Modified MMT/M was then obtained using the resulting Na-MMT suspension.

Exchange capacity of Na-MMT.

Exchange capacity of the MMT surface was determined by adsorption of indicator "methylene blue" onto Na-MMT surface using photocalorimetry analysis and was described in previous publication [7]. Exchange capacity of MMT used amounts to 1.5 mmol/g.

X-ray diffraction.

The polymer structure in the molecular level was studied by the wide-angle X-ray scattering technique (WAXS) using a DRON-4-07 diffractometer; X-ray optic scheme was arranged to operate in the transmission mode of the Debye-Scherrer method. CuK α -radiation used as produced by an anode X-ray generator was monochromatized with a Ni-filter. The details of WAXS are presented in [8]. Scattered X-rays were detected with a scintillation counter in an automated stepwise scanning mode. The measured values of scattering intensity were corrected for attenuation of the incident X-ray beam by tested samples and subsequent deviation of the intensity of background

X-ray scattering by the collimator system. The values of scattered intensity were normalized to the scattering volume. Fine-dispersed powders of MMT and MMT/M were placed into the cells. 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 [9]:

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

where: n – the serial number of the diffraction peak in the diffraction patterns ($n = 1$); λ – wavelength of the characteristic X-rays (for CuK α $\lambda = 0,154$ nm); θ – angle of X-ray scattering.

IR-spectroscopy.

Samples of modifier were obtained on irtran substrate by pouring from an aqueous solution. FTIR 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 [10].

Mechanical testing.

The tensile device FU-1000 (VEB MWK "Fritz Heckert", Germany) was used. The tensile speed was 100 mm min $^{-1}$ and temperature 25 °C. For each measurement we used three samples. Samples were prepared in a form of strips (width – 4 mm, operating length – 20 mm). Measurements were carried out in accordance with Standard 14236-81; allowed error – 3%.

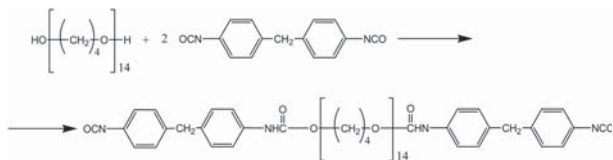
Differential thermogravimetric analysis.

Differential thermogravimetric analysis (DTA) was carried out using a Q-1000 derivatograph, (MOM, Budapest) in the air under the following conditions: average heating rate -10 deg min $^{-1}$; temperature range: 20-1000 °C; the weight of samples: 100 mg; inert substance: Al $_2$ O $_3$; sample holder: a ceramic cone-like crucible.

Prepolymer synthesis.

In order to obtain the prepolymer (PP) the initial components were placed into a three-necked reactor, equipped with input-output device of inert gas (argon) in amount corresponding to the ratio of their functional groups – NCO:OH = 2:1. The resulting mixture was heated under the continuous stirring at 80–85 °C (30 min), followed by cooling the reacting mixture to 15 °C. The estimated content of isocyanate groups in the PP amounted to

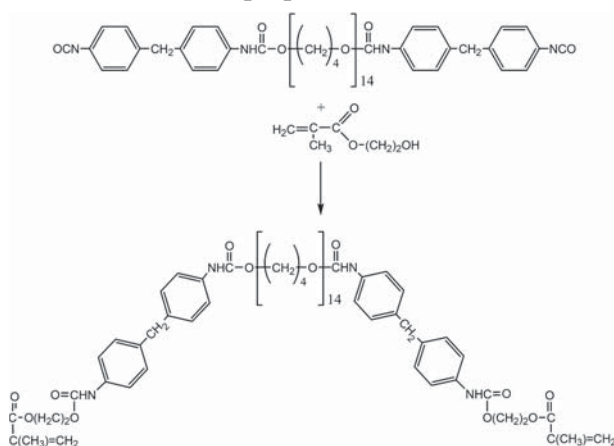
6,3 ± 0,1 % wt. Scheme of PP synthesis is presented below:



Synthesis of oligourethane acrylate (OUA).

OUA was synthesized using MDI based PP. The calculated amount of HEMA in dimethyl formamide (DMF) was added to PP at the temperature of 55 °C under continuous stirring; the NCO:OH ratio = 1:1. The process of OUA formation took no more than 1 h under the continuous stirring at 55 °C.

Scheme of OUA preparation:



Results and discussion

Modification of Na-MMT with different types of modifiers.

The joint adsorption of components was studied using the method of two-phase titration with sodium lauryl sulfate in the presence of indicator MB, which was used for the selective determination of the concentration of the surfactant CTAB [11], which allows to determine the content of CTAB - the only one cationic component, which is a classical surfactant.

In order to study the joint adsorption, the weighted amount of Na-MMT suspension was mixed with solutions of CTAB and DMAEMAC (with different ratio of the latter). The amount of CTAB and DMAEMAC was equivalent to exchange capacity of MMT (1.5 mmol/g). To determine the equilibrium concentration of CTAB, the titration of the solution was carried out after attaining of adsorption equilibrium (in three days).

Two-phase titration of solutions after attaining of adsorption equilibrium showed that CTAB adsorbed on the Na-MMT regardless of DMAEMAC content in solution in an amount which corresponds to the exchange capacity of MMT (1.5 mmol/g). Adsorption isotherms of CTAB mixed with DMAEMAC have the same character as in the absence of the latter (Fig.1).

The adsorption (a , mmol/g) was calculated as the difference between the initial amount of CTAB added to MMT suspension in solution with concentration C_0 and the amount of CTAB remaining after adsorption onto 1 g of montmorillonite according to:

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

where: C_0 - initial concentration of CTAB; C_p - equilibrium concentration of CTAB (per 1 g of MMT) after adsorption; V - a volume of an aqueous sample solution, l; g - a mass of the MMT sample.

Thus it has been found experimentally that CTAB as strong cationic surfactant capable to displace the DMAEMA ions from the montmorillonite surface. Therefore, modification with CTAB was carried out in an amount that corresponds to half of the ion exchange capacity of the mineral, and DMAEMAC addend was carried out with 30% excess per the residual ion exchange capacity, which was 50% of the initial ion exchange capacity of the mineral. To prove the

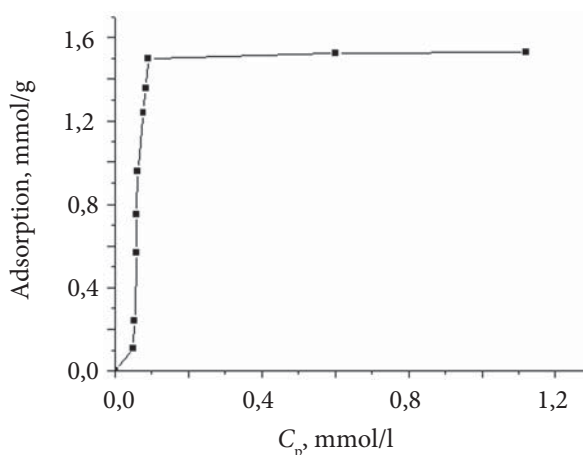


Fig. 1. Adsorption isotherm of the mixture CTAB + DMAEMAC on sodium form of MMT

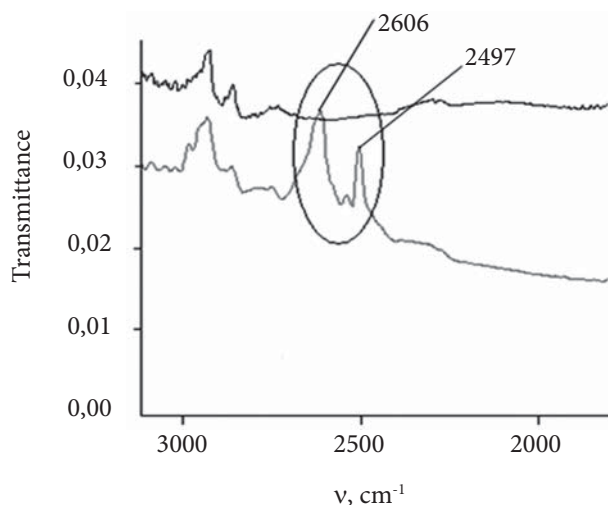


Fig. 2. Fragments of FTIR – spectra of salts before and after attaining of adsorption equilibrium

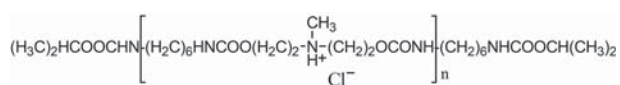
simultaneous co-adsorption of both CTAB and DMAEMAC on the Na-MMT it was necessary to find a way of detection of DMAEMAC ions in aqueous solution. For this purpose we used FTIR spectroscopy. Based on the fact that determination of the low concentrations of DMAEMAC using FTIR spectroscopy is not possible, we decided to analyze the dry residues of salts' aqueous solutions on irtran. FTIR data have shown, that dry residues of DMAEMAC solutions have a visible absorption band with maximum at 2497 cm^{-1} and 2532 cm^{-1} [17], corresponding to NH^+ of alkylammonium. Therefore to prove the joint adsorption the weight amount of Na-MMT suspension was poured with a solution of CTAB and CTAB DMAEMAC in the ratio: CTAB – $0,75\text{ mmol/g MMT}$ and DMAEMAC – $0,75\text{ mmol/g MMT}$, respectively. Preliminary we obtained the FTIR spectrum of dry residue of DMAEMAC solution which was added to MMT. It can be clearly seen the absorption bands with maxima at 2497 cm^{-1} and 2532 cm^{-1} (Fig. 2). After attaining of adsorption equilibrium (in three days) the FTIR spectrum of the dry residue of the solution displayed a complete absence of absorption bands that corresponded DMAEMAC. Thus the adsorption of DMAEMAC was confirmed by comparative analysis of the FTIR spectra of salt solutions “before” and “after” attaining of adsorption equilibrium (Fig. 2).

Absorption band with the maximum at 2606 cm^{-1} in the FTIR spectra (Fig. 2) of dry residues of initial solution of amine salts indicates the presence

of NH^+ of alkyl ammonium cation (bands at 2497 cm^{-1} and 2532 cm^{-1}) whereas in sample after installing the adsorption equilibrium these bands are not found. MMT modification was carried out by adding the modifier solutions (CTAB and DMAEMAC) of preset concentration to aqueous Na-MMT dispersion. After adding CTAB and DMAEMAC solutions the resulting mixture was diluted with distilled water to a ratio of 1 g MMT per 500 ml of water. Modification was carried out for 48 hours, whereupon the precipitate of modified MMT was filtered, dried in an oven at $60\text{ }^\circ\text{C}$ till constant weight and crushed in an agate mortar and in a ball mill. The content of organic component in modified montmorillonite was evaluated using TG data, as the difference between the mass of the sample “before” and “after” thermodestruction with regard to moisture content ($0,5\%$ wt.). The content of organic component in the modified montmorillonite – amounts to $0,75\text{ mmol/g}$ for each of the two components and corresponds to the value of exchange capacity of montmorillonite surface.

Modification of Na-MMT with oligouretane ammonium chloride (OUAC).

Based on the fact that 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 (OUAC) solution, with a concentration of $4 \cdot 10^{-3}\text{ mol/l}$. OUAC synthesis was described in previous publication [12]. The structural formula of OUAC:



$n = 1-3$.

Modification of MMT was carried out by addition to Na-MMT suspension of 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. Addition of OUAC solution to the MMT suspension resulted in instantaneous coagulation of MMT particles followed by formation of a white precipitate. Filtration, drying and grinding of the modified MMT was carried out by analogy with the previous method. To assess the content of

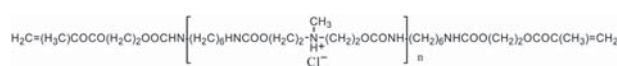
the organic component in the modified MMT, the TGA study was conducted. TGA data showed that the organic part content was about 40 % that substantially corresponds to its theoretical content.

Swelling of modified MMT in organic solvents.

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

Modification of Na-MMT with oligouretane methacrylate ammonium chloride (OUMAAC).

Preparation of cationic surfactant OUMAAC solution with a concentration of $5 \cdot 10^{-3}$ mol/l was carried out similarly to OUAC. OUMAAC Synthesis was described in previous publication [13]. The MMT OUMAAC modification was carried out similarly to the OUAC modification. The structural formula of OUAC:



$n = 1-3$.

X-ray study of natural and modified MMT.

WAXS results (Fig. 3) has shown, that modified MMT has a larger interlayer spacing d_{001} in comparison with the original natural MMT ($d_{001} = 1,26$ nm).

The distance between the MMT layers after modification increases up to 0,68–72,0 nm. It

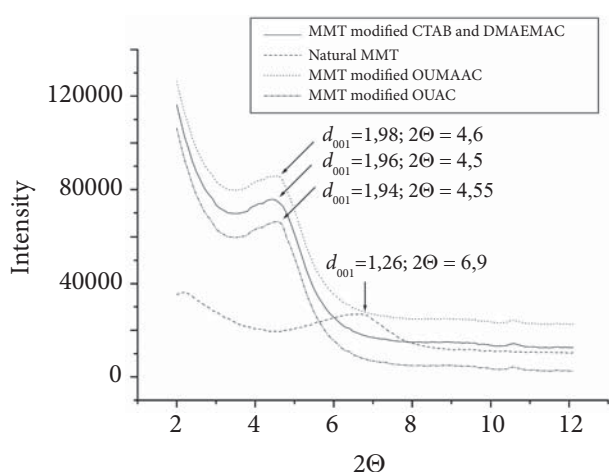


Fig. 3. WAXS profiles of modified (a) and natural (b) MMT

should be noted that the “unification” of inorganic cations in the middle of the layers in 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 0,79–0,83 nm.

The increase in the interlayer distance of MMT (d_{001}) after the modification testifies to intercalation of organic modifier into the interlayer space.

Preparation of nanocomposites based on PUA and modified MMT.

Formation of nanocomposites based on PUA and modified MMT was carried out in a solution of organic solvent. In the case of MMT, modified jointly with CTAB and DMAEMAC we used toluene, in a case of MMT, modified with OUAC and OUMAAC we us dimethylformamide (DMF).

PUA and MMT/M based nanocomposites were prepared in toluene/DMF solution. Solution of toluene/DMF with calculated amount of OUA and modified MTT was sonicated in a glass container, then added to the reactor and stirred at 90 °C for five hours. Then the photoinitiator Darokur-1173 in the amount of 2,5% per OUA weight was added to the reaction mixture which was stirring for one hour. After stirring the resulting mixture in toluene/DMF solution was poured from the reactor into a conical flask with a stopper wherein the resulting mixture was settled.

Settled mixture was cast on glass Petri plates in equal portions to produce the films of uniform thickness. The films were formed by the gradual

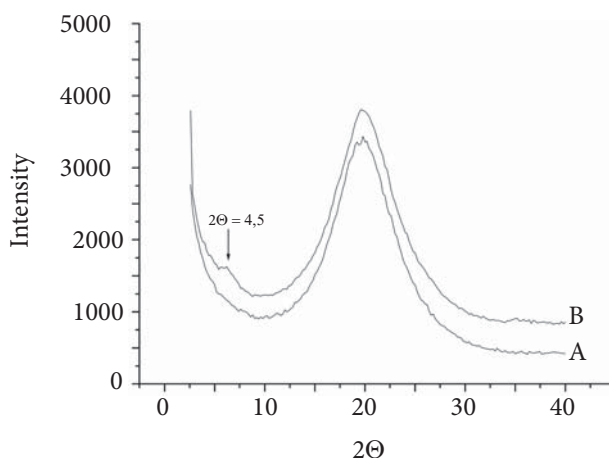


Fig. 4. X-ray diffraction patterns of (A) PUA and (B) nanocomposite PUA/2,5 % MMT (CTAB + DMAEMAC)

evaporation of the solvent under normal conditions. The resulting films were irradiated with a UV-lamp for 30 min at irradiation intensity of 8 W/m². Conversion of methacrylate groups was determined by IR spectra: in 20 min. the band corresponding to methacrylate groups has disappeared.

Thus, by photoinitiated polymerization of OUA the films of polymer matrix PUA and *in situ* nanocomposites PUA/MMT/M with the content of modified mineral of 2,5 wt % have been obtained.

WAXS patterns of PUA/MMT/M nanocomposite.

It was found by WAXS method that exfoliation of nanofiller in MMT modified with CTAB + DMAEMAC based nanocomposite was not observed. Lack of exfoliation is illustrated by the presence of absorption peak characteristic for the modified MMT on the curve corresponding to the nanocomposite (Fig. 4).

Unlike the first type of nanocomposite, the complete exfoliation of the nanofiller was observed for nanocomposites based on MMT modified with OUAC or OUMAAC.

The absence of the characteristic absorption peak of the MMT/(OUAC or OUMAAC) in nanocomposites' WAXS patterns (Fig. 5, c) containing 2,5 wt % of the nanofiller, testifies to the it complete and systematic exfoliation in the PUA matrix. The absorption peak $2\Theta = 4,6$ in the diffraction pattern of mechanical mixture (b) is characteristic for the MMT/M, indicating that polymer matrix by itself

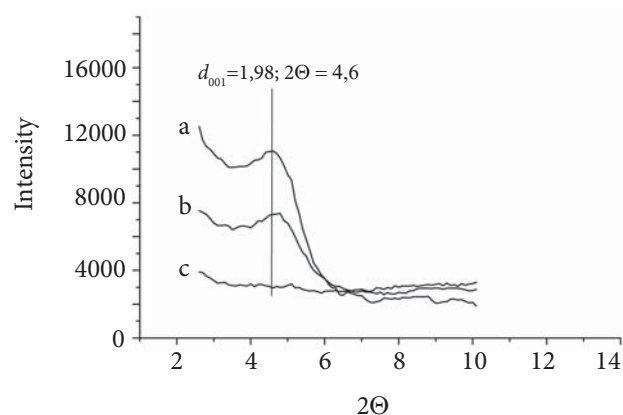


Fig. 5. X-ray diffraction patterns of (a) MMT/(OUAC or OUMAAC), (b) mechanical blend of the PUA with MMT/(OUAC or OUMAAC) (c) nanocomposite PUA/2,5 % MMT/(OUAC or OUMAAC)

does not affect the character of MMT(OUAC or OUMAAC) radiation absorption.

Physic-mechanical properties nanocomposites.

Comparative analysis of the tensile strength of all obtained nanocomposites with the same content of modified MTT (2,5 wt%) has shown a significant increase of tensile strength relative to the original polymer matrix PUA (Fig. 6).

It was found that nanocomposite with MMT (CTAB + DMAEMA) has in 1.9 times higher strength than that of the original PUA matrix. Increase of the strength of nanocomposite with MMT (CTAB + DMAEMAC) may be the result of chemical bonds formation between PUA and DMAEMAC on the MMT surface.

Nanocomposite with MMT (OUAC) and nanocomposite with MMT (OUMAAC) possess the strength in 1,6 and 2,6 times higher than that of the original PUA matrix, correspondingly. Such difference in the results is probably due to the fact that MMT (OUAC) can not form chemical bonds with PUA matrix.

Comparative analysis of the strength indices of that all obtained nanocomposites has clearly illustrated the strengthening effect of reactive modifiers DMAEMAC and OUMAAC.

Nanocomposite with MMT (OUAC), despite the exfoliation of nanofiller and the formation of hydrogen bonds with PUA macromolecules, is inferior to nanocomposite with MMT (CTAB + DMAEMAC) for which the exfoliation of the nanofiller is not typical.

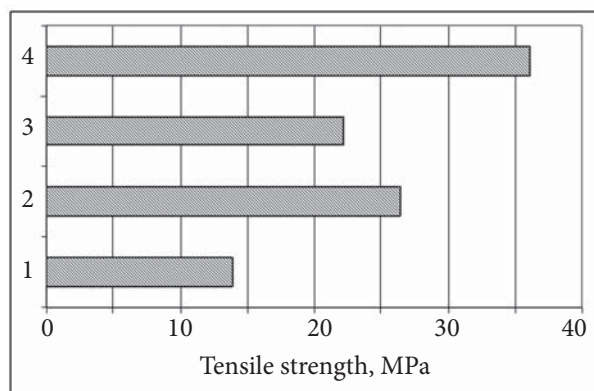


Fig. 6. Tensile strength of the nanocomposites: 1 – PUA; 2 – PUA with MMT(CTAB + DMAEMA); 3 – PUA with MMT(OUAC); 4 – PUA with MMT(OUMAAC)

Conclusions

Three methods of chemical modification of the layered silicate surface have been developed.

New polyurethane acrylate nanocomposites based on newly created modified MMTs with high performance have been synthesized by *in situ* polymerization method.

The first modification method is based on using of two different functional modifiers (organophilic and reactive), the second method is based on modification with synthesized compound which

contains urethane groups, and the third one is based on using of synthesized modifier containing urethane and other reactive groups.

Developed polyurethane acrylate/organoclay nanocomposites have shown a significant increase of strength indices.

The complete exfoliation of the nanofiller in nanocomposite based on MMT modified with OUAC or OUMAAC has been confirmed by WAXS.

Developed methods of montmorillonite modification are universal and can be applied to MMT of various origins (deposits).

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О.М. Гончар,

Інститут хімії високомолекулярних сполук НАН України, 02160, Київ, Харківське шосе, 48, Україна
e-mail: lexgon@ukr.net

Ю.В. Савельєв,

Інститут хімії високомолекулярних сполук НАН України, 02160, Київ, Харківське шосе, 48, Україна
e-mail: yuri2savelyev@gmail.com

Т.В. Травінська,

Інститут хімії високомолекулярних сполук НАН України, 02160, Київ, Харківське шосе, 48, Україна
e-mail: travinskaya-tamara@rambler.ru

НАНОКОМПОЗИТИ ПОЛІУРЕТАНАКРИЛАТ/МОНТМОРИЛОНІТ

Для створення полімерних наноконкомпозитів на основі поліуретанакрилатів (ПУА) з монтморилонітом (ММТ) розроблено три методи хімічної модифікації поверхні шаруватого силікату. Перший метод модифікації заснований на використанні двох різних функціональних модифікаторів (органогільний та реакційноздатний), другий метод заснований на модифікації синтезованим нами олігомером, що містить уретанові групи, а третій – на основі синтезованого нами модифікатора, що містить уретанові і реакційноздатні групи. Обмінну здатність поверхні ММТ визначали адсорбцією показника «метиленовий синій». Інтеркаляція модифікатора в міжшаровий простір ММТ підтверджена рентгенографічним аналізом. Вміст органічного компонента в модифікованому ММТ (ММТ/М) визначали термогравіметричним аналізом. Отримана органоглина призначена для створення наноструктурованих композитів на основі зшитих поліуретанакрилатів з поліпшеними фізико-механічними властивостями. Отримані поліуретанакрилатні наноконкомпозити з різним типом ММТ/М демонструють підвищену в 1,6 – 2,6 рази міцність на розрив порівняно з вихідною полімерною матрицею. Методом WAXS доведено інтеркаляцію модифікатора в прошарок ММТ (збільшена відстань між шарами після модифікації), а також повне відшарування ММТ у матриці ПУА, що характеризується зникненням піка поглинання, який відповідає за шарувату структуру.

Ключові слова: монтморилоніт, модифікація, поліуретанакрилат, наноконкомпозити.