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M. P. Sukhyi[1], V. I. Tomilo[1], K. M. Sukhyi[1], E. A. Belyanovskaya[1], G. Vaivars[2]

[1]State Higher Education Institution "Ukrainian State University of Chemical Technology", ksukhyy@gmail.com

[2]University of Latvia, Jelgavas 1, LV-2004, Riga, Latvia, Guntars.Vaivars@cfi.lu.lv

ORGANO-MONTMORILLONITE MODIFIED BY POLYIONENES FOR POLYMER COMPOSITES

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The technology for producing montmorillonite modified with polyionenes has been developed. It was shown that macromolecular polymer intercalation of the quaternary ammonium salt of montmorillonite intercrystalline space is accompanied by an increase in interlayer distances from 1.08 to 1.67 nm. A method for the synthesis of montmorillonite modified with polyionenes is proposed. The optimal conditions for the sorption of polymeonene molecules by montmorillonite were found: the concentration of the aqueous dispersion of montmorillonite is 1%, the temperature of the reaction medium is 40 ° C, the ratio of montmorillonite-polyionene is 3: 1, the processing time is 24 hours.

Key words: modification, montmorillonite, polyionenes, exfoliation.

Introduction

The global miniaturization trends testify the science and technology objects to be decreased up to nano-size through the depletion of miniaturization possibilities via the traditional technologies [1-3]

Nano-phase materials science differs from the traditioanal materials science by working-out of innovative materials. The functional parameters of mentioned materials being defined not only by microdomain properties but processes as found to be on atomic and molecular level in monolyaers and nanovolumes [4-7]

Respectively, the modeling of processes of materials conversion dealt filled with fine particles is focused on determining of particles-aggregates interaction energy. Consequently, the second main task for obtaining of polymer composites with applying of nanomaterials is concerned with consent of energetic conditions for nanoparticles division keeped by their equal distribution. Mentioned conditions can be derivated due to choice of optimal proportions operating parameters-design working elements of device [8-12].

The purpose of this work is to develop a technology for producing montmorillonite modified with polyions

Materials and methods of research

Montmorillonite obtained from bentonite BR ('Dashukov bentonites Ltd', Cherkassy minefield, ukraine) is studied in present work. Bentonite is grey powder consisted about of 85 % of montmorillonite.

Polyionene based on epoxide diane resine ED-20 is synthesized by known technoques. Solutions in isopropylic alchohol of both 10 % ED-20 and dimetilaminehydrochloride are mixed up in equimolar ratio. The reaction mixture was incubated at 25ºC during two hours when stirred continuously. Then, polyionene is synthesized with chroramine obtained by addition polymerization. The reaction mixture is incubated at 60ºC during six hours.

Montmorillonite surface lamenes modification involves the next steps: elutriation, lamens surface activation polyionene modification. Elutration was carried out to separation of montmorillonite fraction from bentonite. Lamen surface was activated for transformation of Ca^{2+} montmorilinite into Na^{+}-montmorillonite by cation exchange in interlayer surface of montmorillonite because of cationic activity of Na^{+} montmorillonite exceeds by degree of order cationic activity of Ca^{2+} montmorilinite and Mg^{2+} montmorilinite that resulted in exceeding efficiency exchange reaction of Na^{+} and $N^{+}(R_3)$. Montmorillonite modification with polyionene concerns with substitution of exchangeable cation on polyionene cation [13–16].

Modified montmorillonite is synthesized according to the next techniques:

- eluctration of montmorillonite fraction;

– preparing of 1 % bentonite water dispersion;

– desilting of dispersion during 1 hour followed by separation of montmorillonite dispersion;

– separation and drying of precipitate;

– preparing of 1 % montmorillonite suspension, desilting during 1 hou and decantation of high disperse fraction;

– immixture with water at ratio 1 : 100, disilting during 1 hour and decantation of high disperse fraction.

– elutriation repeated 3 – 4 time;

Elatration is carried out to separate high disperse montmorillonite fraction of bentonite.

– activation is carried out by addition 5 % water solution of Na_2CO_3 to 1 % montmorillonite water dispersion followed by incubating at 85 – 85 ^{0}C during 15 min. Then montmorillonite with modified lamens surface is obtained.

– Modification is carried out according to techniques. Water solution of 15 % polyionenes is added into water dispersion of 1 % of activated montmorillonite when stirred intensively. Mixture is incubated at 40ºC when stirred during 24 hours. The solid phase is separated with centrifuge and vacuum-dryed at 60 ºC up to constant mass. Dry residue is comminuted, bolted through № 250 and dryed in air circulated oven at 80ºC.

To determine optimal parameters of montmorillonite modification processes influence of temperature and equivalence ratio on process kinetic of polyionene sedimentation on surface of crystal layers (lamens) is studied.

Found that the optimal conditions sorption montmorillonite polyionens molecules observed when these parameters: the concentration of aqueous dispersion of montmorillonite - 1%, the temperature of the reaction medium is 40 OC, the ratio% - polyionic 3:1, the processing time - 24 hours.

Results and discussion

The data concerning WAXS for montmorillonite provide to evaluate crystallinity velocity of montmorillonite and detect a periodicity of montmorillonite crystalline layers (lamenes) order. It caused the determination of both of distance between montmorillonite layers and their dimension and as a consequence in identification of nanosized modified motnmorillonite. WAXS profiles of researched montmorillonite are shown on Fig. 1.

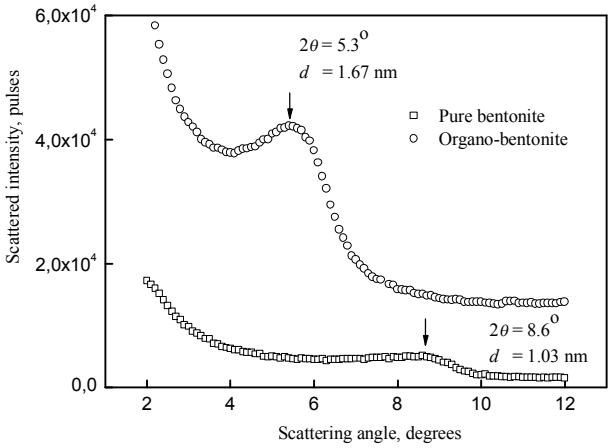

Fig. 1. X-ray diffraction patterns of bentonite and organo-bentonite.

Non-modified montmorillonite demonstrate a little diffusive peak at **2θ = 8.6^0** responded technically to a distance between crystal layers d = 1,03 nm. For the montmorillonite modified with polyionene peak is observed to shift in low-angels diapasone **2θ = 5.8^0**. Replacement of interlayer exchange ions on polymeric cations is accompanied with distance rise between cristaline layers up to 1.67 nm, both position and shape of wide angle maximum (intensivity and half-wildth) being changed whereas direct coupling with crystallinity of macrolattice, ie paracristalline order.

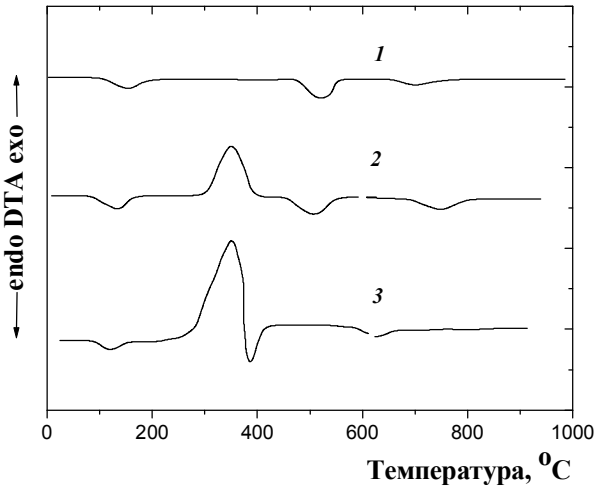

Fig. 2. Thermograms of montmorillonite (1), montmorillonite modified with polyionene (2) and polyionene (3).

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of montmorillonite. Respectively, replacement of interlayer metal cations to polyionenes cations occur to resulted in decay of interlayer bonds.

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Synthesized organic montmorillonite are researched by DTA method. Thermograms of initial montmorillonite, montmorillonite modified with polyionene and polyionene are presented on Fig. 2.

Initial montmorillonite thermograms are characterized with double thermic endoeffect at 130 ^{O}C and 200 ^{0}C corresponded to adsorbed water loss and endoeffect at 540 ^{0}C resulted from mineral dehydroxilation.

On modified montmorillonite curve exo-thermic peak is observed at 250 ^{0}C, it being corresponded to polyionene decomposition. For comparison of both corresponding exotherms and mass loss curves the polyionenes content in montmorillonite is determined to be 12 %.

Conclusions

The montmorillonite modified by polyionens have been obtained. Shown that the macromolecular polymer intercalation of a quaternary ammonium salt of montmorillonite intercrystalline space accompanied with increased interlayer distances 1.08 nm to 1.67 nm. The technique of synthesis of modified montmorillonite by polyionens have been presented. It was found that the optimal conditions sorption montmorillonite polyionens molecules are observed when the next parameters: the concentration of aqueous dispersion of montmorillonite - 1%, the temperature of the reaction medium is 40 ^{O}C, the processing time - 24 hours, the ratio% - polyionic as 3:1.

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М. П. Сухий[1], В. І. Томіло[1], К. М. Сухий[1], О. А. Беляновська[1], Г. Вайварс[2]

[1]Державний вищий навчальний заклад "Український державний хіміко-технологічний університет", ksukhyy@gmail.com

[2]University of Latvia, Jelgavas 1, LV-2004, Riga, Latvia, Guntars.Vaivars@cfi.lu.lv

ОРГАНО-МОНТМОРІЛОНІТ, МОДИФІКОВАНИЙ ПОЛІІОНЕНАМИ, ДЛЯ ПОЛІМЕРНИХ КОМПОЗИТІВ

Розроблено технологію отримання монтморилоніту, модифікованого поліоніонами. Було показано, що макромолекули полімерної четвертинної амонієвої солі інтеркалюють у міжкристалічний простір монтморилоніту, що супроводжується збільшенням міжшарових відстаней з 1,08 до 1,67 нм. Запропоновано метод синтезу монтморилоніту, модифікованого поліоніонами. Виявлено оптимальні умови сорбції молекул полімеону монтморилонітом: концентрація водної дисперсії монтморилоніту – 1%, температура реакційної середовища – 40 ° С, відношення монтморилоніту-поліонієну – 3: 1, обробка час – 24 години.

Ключові слова: модифікація, монтморилоніт, поліоніони, відлущування.