

Studying the structure of the polyamide-based polymer composite materials obtained by the *in situ* polymerization of ϵ -caprolactam and extrusion

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This research paper delves into the investigation of the structure and properties of the polyamide PA-6-based polymer composites obtained by the methods of anionic *in situ* polymerization of ϵ -caprolactam and extrusion with the mechanical mixing of PA-6 and fillers in an extruder. To do the research, the researchers used a nanofiller, i.e. organomodified montmorillonite (oMMT) and also modified (MZ) and unmodified (Z) synthetic aluminosilicate (zeolite). The effect of the fillers on the structure of the polymer matrix was investigated using X-ray structure analysis (XSA) and transmission electron microscopy (TEM). Using these methods, it was established that the anionic *in situ* polymerization of ϵ -caprolactam in the oMMT interlayer space results in the formation of exfoliated composites in a significantly smaller amount. It was established that the modification of the zeolite surface with ammonium polyphosphate prevents the agglomeration of the filler particles, ensuring thus a more uniform distribution of them within the polymer matrix. A comparison of the structure of composites obtained by the methods of the *in situ* polymerization of ϵ -caprolactam and extrusion showed that the structures formed using these methods are similar. A comparative analysis of the properties showed that an increase in the modulus of elasticity for the both types of composites is accompanied by a decrease in the impact resilience due to an increase in the PCM stiffness. A decrease in the amount of the residual monomer in the composites obtained by extrusion is conditioned by the additional thermal effect during the composite production.

Keywords: polymer composites, nanocomposites, structure, properties, ϵ -caprolactam, extrusion, and *in situ* polymerization.

Дослідження структури полімерних композиційних матеріалів на основі поліаміду, одержаних полімеризацією ϵ -капролактаму *in situ* і екструзією.
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У представленій роботі досліджені структура і властивості полімерних композитів на основі поліаміду ПА-6, що одержані методом аніонної полімеризації ϵ -капролактаму *in situ* та екструзійним методом при механічному змішуванні ПА-6 із наповнювачами в екструдері. У дослідженнях використовували нано­наповнювач – органомодифікований монтморилоніт (оММТ) та модифікований (МЦ) і немодифікований (Ц) синтетичний алюмосилікат (цеоліт). Методом рентгеноструктурного аналізу (РСА) і трансмісійної електронної мікроскопії (ТЕМ) досліджений вплив наповнювачів на структуру полімерної матриці. Цими методами встановлено, що аніонна полімеризація ϵ -капролактаму в міжшаровому просторі оММТ в значно меншій кількості призводить до формування ексfolіюваних композитів. Встановлено, що модифікація поверхні цеоліта амонійполіфосфатом призводить до перешкоди агломерації часток наповнювача, що забезпечує більш рівномірний їх розподіл в об'ємі полімерної матриці. Порівняння структури композитів, одержаних полімеризацією

ϵ -капролактаму *in situ* і екструзійним шляхом показало, що сформовані структури за рахунок полімеризації *in situ* і екструзійним шляхом аналогічні. Порівняльний аналіз властивостей показав, що підвищення модуля пружності для композитів обох типів супроводжується зменшенням ударної в'язкості за рахунок збільшення жорсткості ПКМ. Зменшення кількості залишкового мономеру у композитів, одержаних екструзією, пов'язано з додатковим тепловим впливом при одержанні композитів

1. Introduction.

Polymer nanocomposites are the systems that contain reinforcing elements (fibers, plates, etc.) with different length-to-cross section ratios (it creates the reinforcing effect) embedded into a polymer matrix.

The transition from micro-sized to nano-sized fillers in polymer-matrix composites can significantly change a number of operational and technological properties (strength, electrical and thermal conductivity, etc.).

The nanosized nature of filler particles can also enable the production of polymer composite materials (PCMs) with unusual structure and properties, for example, capacity for biodecomposition and reduced gas permeability.

The scientists paid special attention to hybrid (organo-inorganic) nanocomposites obtained by polymerization (polycondensation) using the so-called *in situ* methods.

Polymerization methods include the polymerization used for the production of PCM based on PA-6 polyamide and organomodified montmorillonite [1]. The essence of this method is described in [2].

This method has been studied from two perspectives, in particular kinetics and thermodynamics [3]. It has been established that to successfully obtain exfoliated nanocomposites, the polymerization rate in the intragallery space of the layered nanocomposite should be higher than the polymerization rate in the volume of mixture. On the other hand, the authors point out [3] that the production of a nanocomposite by the *in situ* polymerization of the monomer is also conditioned by the thermodynamic affinity of the polymer and montmorillonite. This promotes the diffusion of the monomer into the intralayer space of organomontmorillonite and further reaction progress, as well as a shift of the thermodynamic equilibrium in such a way that a large amount of monomer penetrates between the silicate layers, and it results in the exfoliation of the layered silicate. The production of nanocomposites from polymer melts has been studied to a much lesser extent [4].

Intercalation of polymer chains into organo-clay galleries can occur directly by heating a

mixture of polymer and dispersed mineral filler above the polymer vitrification or melting temperature. As soon as a sufficient mobility of the polymer chains is attained, these intercalate into the intralayer space of the silicate leading to an increase in the basal space of the layered filler. In this case, the intercalation process is greatly influenced by the degree of interaction of the polymer with the organomodified silicate [5].

The investigations carried out by us [6] have shown that the formation of exfoliated nanocomposites requires an optimal balance between the time of the mixture kept in the extruder and the level of shear forces. In this case, the rheological and thermodynamic patterns of the original components of the mixture are considered to be the determining parameters that influence the degree of exfoliation and the final properties of the resulting nanocomposites.

It should be noted that the known nanocomposites are based on PA-6 polyamide, obtained by the hydrolytic polymerization of ϵ -caprolactam.

This polymerization method has a number of significant drawbacks, in particular the availability of an induction period, rather long process, and a large number of auxiliary operations such as washing, filtering, etc. Therefore, it was of interest to study nanocomposites based on inorganic and organoinorganic fillers and PA-6 polyamide obtained by anionic *in situ* polymerization of ϵ -caprolactam and extrusion (with mechanical mixing of PA-6 with fillers in an extruder) and compare their structures and some properties.

Anionic polymerization allows us to reduce the duration of the process to 3 or 4 minutes (instead of 24 hours of hydrolytic polymerization) and eliminate many drawbacks inherent in hydrolytic polymerization.

2. Experimental.

The research done required the use of such materials as ϵ -caprolactam of a "chemically pure" grade, produced by BASF (Germany); sodium salt of caprolactam, grade "chemically pure", produced by Karangin Co (Iran); hexamethylene diisocyanate, chemically pure, produced by Rhodia (France); synthetic zeolite (synthetic

aluminosilicate) $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 1,8\text{H}_2\text{O}$ of a “chemically pure” grade (TU 130.101.1360); ammonium polyphosphate, chemically pure, produced by Bovelniem (Austria); organomodified montmorillonite Cloisite 30B $\text{m}(\text{Mg}_3[\text{Si}_4\text{O}_{10}][\text{OH}]_2)\cdot \text{p}((\text{Al}_2\text{Fe}_3)_2[\text{Si}_4\text{O}_{10}][\text{OH}]_2)\cdot \text{nH}_2\text{O}$ of a “chemically pure” grade, produced by Southern Clay Products (USA).

For experimental studies, polyvinyl alcohol, grade 17-99 (China) and distilled water (DSTU ISO 3696:2003) were used.

The procedure for the synthesis of PA-6 by anionic polymerization of ϵ -caprolactam is described in detail in [6]. The production of PA-6 by anionic polymerization of ϵ -caprolactam in the presence of the studied fillers was carried out according to the same method, introducing a specified amount of the fillers into the ϵ -caprolactam melt with the stirrer running at a speed of 130 rpm. The mixture was stirred for 5 minutes and then the reactor temperature was raised to $170\pm 5^\circ$ and the process was continued for 3-4 minutes until polymerization was completed and then the resulting polymer was unloaded from the reactor.

The zeolite surface modifying technique consisted in the adsorption of ammonium polyphosphate onto its surface from a 2% solution of polyvinyl alcohol in water. The mixture was stirred at 90 to 95°C until polyvinyl alcohol was completely dissolved during the time period of 0.5 to 1 hour. Zeolite in the amount of 10 mass % and ammonium polyphosphate in the amount of 5 mass % were loaded into the cooled solution. The mixture was stirred at room temperature for 1 to 2 hours, and the filler was separated from the solution by filtration and it was dried at 50°C for 3 to 4 hours. The filler obtained in this way was used for further research.

To produce PCM by extrusive mixing, a ZSK-25 twin-screw laboratory extruder (Coperion, Germany) was used, L:D ratio = 44:1. The mixing speed (120 rpm) was the same for all compositions. Temperature by zones was as follows: 1 – 220°C , 2 – 245°C , 3 – 265°C , the head temperature was 270°C . The extrudate was granulated and used to obtain specimens for further testing.

Test specimens (in the form of the blades) made of PA-6 polyamide with fillers were obtained by pressing at a temperature of 250°C and a pressure of 20 MPa using a Minitest press from Toyoseki (Japan).

X-ray studies were carried out using a Philips X Pert diffractometer (Holland). Filter irradiation lamps with a copper anode (irradiation light wavelength $\lambda = 0.0178897$ nm) were used during these studies. The lamp operating parameters were as follows: $U=40$ kV, $I=30$ mA. The studies were carried out in the range of 2θ angles varying from 1.110° to 9.990° , the duration of the measuring pitch was 0.1° , and the pulse measurement time was 8 s.

The impact resilience of the specimens was determined according to ASTM D 256 using a Zwick/material prufund device. The destructive tensile strength and relative break elongation were determined according to the ASTM D 638 method using a Santam device (Iran) at a tensile speed of 5 mm/s. The elastic modulus was calculated using the generally accepted method.

Electron microscopic studies were carried out using a transmission transparent electron microscope TEM SM 200 Philips (Holland) at an accelerating voltage of 50 kV. Films for research were prepared by deposition onto a fresh cleaved salt single crystal and onto a quartz substrate. The film was separated from the salt substrate by dissolving the latter in warm distilled water.

The content of residual monomer was determined by boiling a polymer specimen in water for an hour, followed by drying the specimens at 80°C for 24 hours. The content of residual monomer X was determined by the formula:

$$X = \{(m_0 - m_1) \cdot 100\} / m_0, \%,$$

where m_0 is the original specimen mass, g;
 m_1 is the specimen mass after the boiling and drying, g.

3. Results and discussion

The X-ray structure analysis (XSA) and transmission electron microscopy (TEM) were used to study the structure of inorganic layered fillers and organic-inorganic composites based on them, obtained by the methods of the *in situ* polymerization of ϵ -caprolactam and extrusion. The combination of these two research methods makes it possible to estimate the value of the interlayer distance in layered silicates by the XSA method, and the TEM method allows for indirect measurement of the spatial distribution of silicate layers. Therefore, TEM is a necessary addition to the X-ray structure analysis, and it allows us to draw correct conclusions on the structure of nanocomposites.

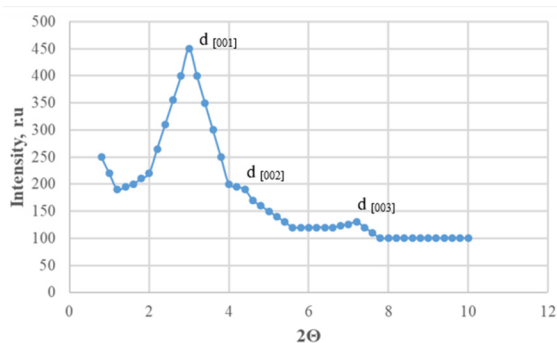


Fig.1 – X-ray diffraction pattern of the original oMMT

To establish the influence of the filler on the structure of the polymer matrix in the domain of short-range orders, we used the small-angle X-ray structure method in the range of diffraction angles $2\theta = 0-10^\circ$.

In their natural state, clay minerals and natural ion exchangers are characterized by high hydrophilicity that excludes the possibility of their dispersion in hydrophobic organic media. Replacing an inorganic exchange ion by an organic one with a sufficiently long hydrophobic tail promotes the formation of mineral particles of a high compatibility with organic media, facilitating thus their use as PCM fillers.

In such systems, the interlayer distance remains constant throughout the entire volume, which makes it possible to calculate it using the Bragg equation:

$$\lambda = 2d\sin\theta, \quad (1)$$

where λ is characteristic x-ray wavelength, d is the distance between the diffraction lattice planes, θ is a half diffraction angle

Intercalation/exfoliation processes were monitored in the layered silicate by the presence or absence of the characteristic peak $d_{[001]}$, which is an indicator of the presence of a nanophase and it also characterizes the space between the filler layers (basal space).

Figure 1 shows a diffraction pattern of the original oMMT (Cloisite 30B), which is characterized by the presence of three diffraction peaks. The diffraction peak $d_{[001]}$ is observed at $2\theta = 2.7^\circ$, which corresponds to the interlayer space of $d = 3.15$ nm. The presence of secondary and tertiary diffraction peaks $d_{[002]}$ and $d_{[003]}$ at $2\theta = 4.6^\circ$ (1.92 nm) and $2\theta = 7.2^\circ$ (1.23 nm), respectively, can be explained by the fact that the intercalation of the organic modifier into the the MMT interlayer space has an uneven passage pattern, and, consequently, there are areas with a lower degree of intercalation, char-

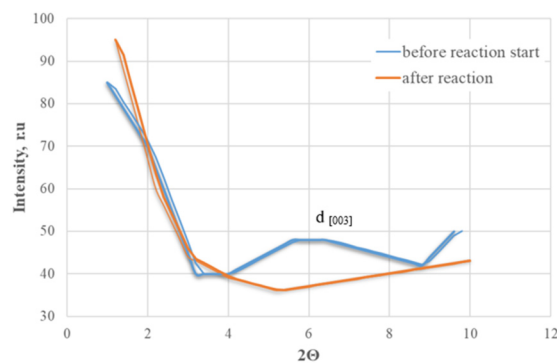


Fig. 2 – X-ray diffraction pattern of the PA-6 + 1% oMMT nanocomposite before the start of the polymerization reaction and after the polymerization reaction

acterized by the $d_{[002]}$ diffraction peak, and the areas in which the organic modifier intercalation has not taken place at all, characterized by the diffraction peak $d_{[003]}$.

Figure 2 shows the diffraction patterns of PA-6/oMMT nanocomposites before the start of the *in situ* polymerization process (curve a) and on completion of the polymerization process (curve b).

The diffraction pattern of the mixture after mixing in the reactor before the start of polymerization shows that $d_{[001]}$ and $d_{[002]}$ diffraction peaks are absent, and the $d_{[003]}$ peak shifts to the domain of smaller angles ($2\theta = 5.7^\circ$), which corresponds to $d = 1.56$ nm. In our opinion, such a change in the diffraction pattern is due to the fact that the intercalation of the monomer into the interlayer space of MMT domains that are not affected by organomodification occurs with greater difficulty than that into organomodified domains.

The absence of any crystalline peaks in the diffraction pattern of the formed PA-6/oMMT nanocomposite indicates that after intercalation of the monomer into the oMMT interlayer space, the interlayer space is increased even more during further reaction, resulting in the formation of a completely exfoliated nanocomposite.

The formation of such a nanocomposite can be explained by a very good compatibility of the filler and ϵ -caprolactam.

It can be assumed that the interaction may occur between the oMMT and PA-6 particles due to the good thermodynamic affinity between them, for example, through hydrogen bonds.

It should be noted that the experimental XSA data for nanocomposite specimens obtained by extrusion are similar to the experi-

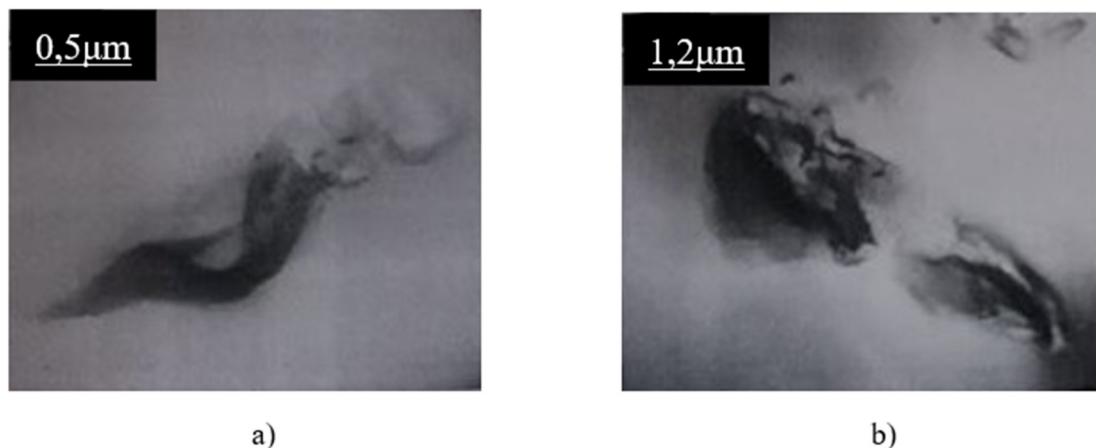


Fig. 3 – TEM microphotographs of PA-6 + 1% oMMT specimens: a) before the start of the *in situ* polymerization reaction; b) at the initial stage of mixing in the extruder

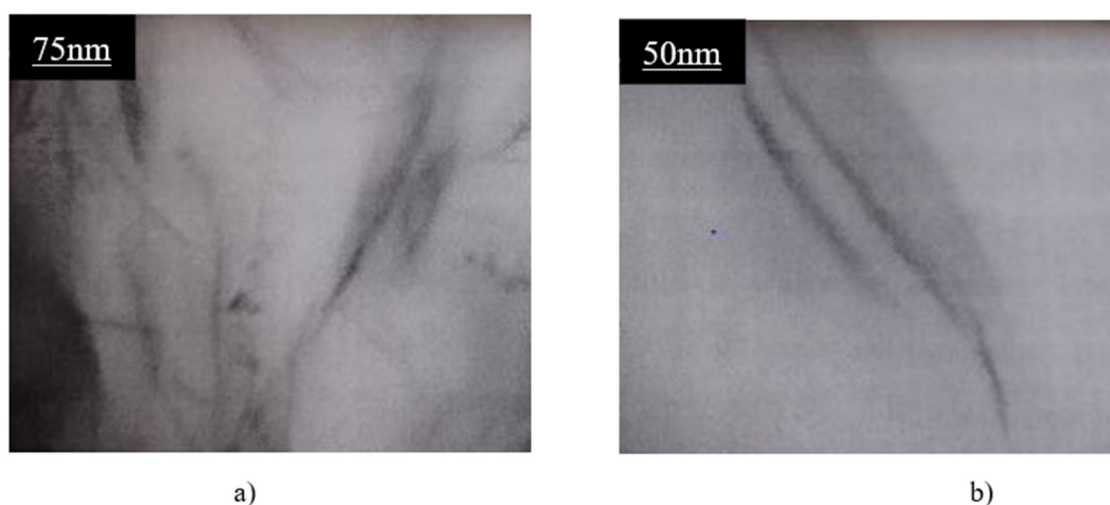


Fig. 4 – TEM microphotographs of PA-6 + 1% oMMT specimens: a) nanocomposite obtained by the *in situ* polymerization of ϵ -caprolactam; b) nanocomposite obtained by extrusion.

mental XSA data for specimens obtained by *in situ* polymerization.

The data available for the structure of nanocomposites obtained both by *in situ* polymerization of ϵ -caprolactam and by the extrusion method are in full compliance with the data obtained by TEM (Fig. 3, 4).

Fig. 3 and Fig. 4 show that before the start of the *in situ* polymerization reaction of ϵ -caprolactam (Fig. 3a) and at the initial stage of mixing in the extruder (Fig. 4b), oMMT particles have the form of “tactoids”, while in the final nanocomposites obtained both by the *in situ* polymerization of ϵ -caprolactam (Fig. 5a) and by extrusion (Fig. 5b), o-montmorillonite particles are completely exfoliated.

The TEM method was also used to evaluate the effectiveness of surface modification of NaA zeolite during the PCM formation.

Figure 5 shows micrographs of composites based on unmodified synthetic NaA zeolite and modified synthetic NaA zeolite by immobilizing ammonium polyphosphate (APP) on its surface.

Fig. 5 shows that the condition of the filler surface affects the formation and quality of the resulting PCMs. The unmodified zeolite is present in the polymer matrix in an agglomerated state (Fig. 5a), while zeolite with APP immobilized on its surface does not form agglomerates (Fig. 5b). More uniform dispersion of the modified zeolite in the polymer matrix, as was shown earlier, results in an improved set of properties of the formed PCM.

Table 1 presents the PCM properties obtained by anionic *in situ* polymerization of ϵ -caprolactam and by the extrusion method by mixing PA-6 and oMMT in an extruder.

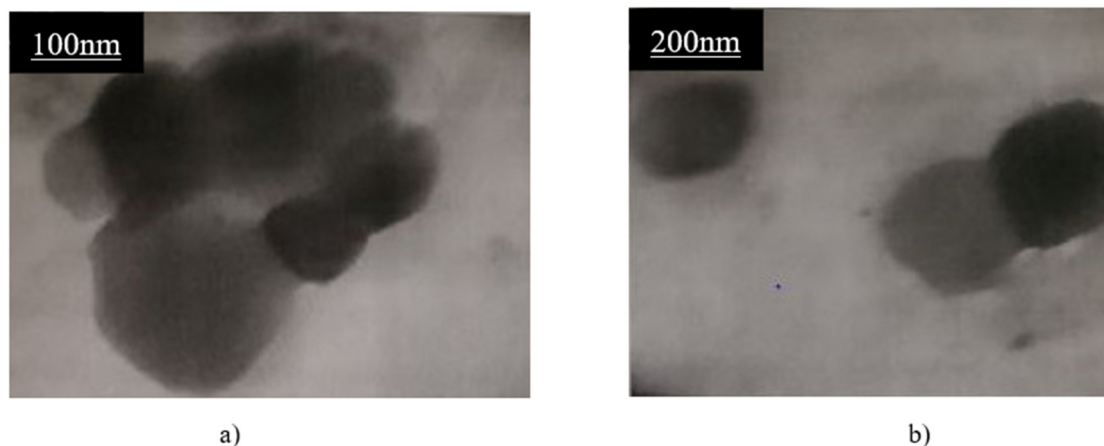


Fig. 5 – TEM microphotographs of zeolite specimens: a) unmodified; b) modified.

Table 1 - Properties of PCM obtained by anionic *in situ* polymerization of ϵ -caprolactam and by extrusion method

Composite composition	Property indicators					
	Polymerization in situ			Extrusion method		
	α , $\kappa\text{J}/\text{M}^2$	E, MPa	Residual monomer, % mass.	α , $\kappa\text{J}/\text{M}^2$	E, MPa	Residual monomer, % mass.
Unfilled samples	11,20	1200	2,5	7,07	1084	0,9
PA-6 + 1 % oMMT	10,60	1330	5,0	9,0	1280	0,5
PA-6 + 5 % Z	8,40	1325	3,0	5,93	1160	0,5
PA-6 + 5 % MZ	8,30	1320	5,5	4,39	1208	0,5

Analysis of the experimental data given in Table 1 shows that the production of PCM by anionic *in situ* polymerization of ϵ -caprolactam in the presence of such fillers as organomodified montmorillonite and synthetic aluminosilicate (zeolite) with an unmodified and modified surfaces provides higher values of the elastic modulus of PCM (an increase in the elastic modulus is 10 to 11% for PCM obtained by the *in situ* polymerization of ϵ -caprolactam, and 11 to 16% for PCM obtained by extrusion). Moreover, in most cases, an increase in the elastic modulus for PCM of both types is accompanied by a decrease in the impact resilience, which indicates that the introduction of fillers during the *in situ* polymerization and the production of PCM by extrusion contribute to a decrease in the impact resilience index by increasing the PCM rigidity.

Moreover, the content of residual monomer in the case of the extrusion method is significantly lower than that in the case of the *in situ* polymerization. This can be explained by the

additional thermal effect on the PCM during the extrusion process. During the *in situ* polymerization of ϵ -caprolactam, oMMT slows down the reaction, and it results in an increased content of the residual monomer.

The experimental data given in the Table are in good agreement with the PCM structure formed both during the *in situ* polymerization of ϵ -caprolactam and during PCM extrusion.

4. Conclusions.

1. The structure of PCM based on polyamide PA-6 obtained by anionic *in situ* polymerization of ϵ -caprolactam and mechanical mixing of PA-6 with fillers in an extruder has been investigated. The organomodified montmorillonite (oMMT) and such ordinary inorganic fillers as synthetic aluminosilicate (zeolite) both unmodified (Z) and modified (MZ) by immobilizing ammonium polyphosphate on its surface from an aqueous solution of polyvinyl alcohol were studied as filling agents.

2. It has been established that anionic *in situ* polymerization of ϵ -caprolactam in the interlayer space of oMMT results in the formation of exfoliated nanocomposites.

The investigations carried out have shown that in order to obtain exfoliated nanocomposites by extrusion, an optimal balance is required between the time of the mixture kept in the extruder and the level of shear forces. In this case, the rheological and thermodynamic patterns of the initial components of the mixture are considered to be the determining parameters that influence the degree of exfoliation and the final properties of nanocomposites.

3. It has been established that improved properties are achieved by introducing the oMMT nanofiller in smaller quantities (1 mass %) compared to regular inorganic fillers (5 mass % for MZ and Z).

4. Analysis of XSA data shows that the formation of a fully exfoliated nanocomposite (PA-6 + oMMT) is possible due to very good compatibility of the filler and ϵ -caprolactam. It can be assumed that the thermodynamic affinity between the filler particles and PA-6 may result in the interaction between them, in particular, through hydrogen bonds.

It has been established that experimental X-ray structure analysis data for specimens of nanocomposites obtained by extrusion are similar to experimental X-ray structure analysis data for specimens of nanocomposites obtained by the *in situ* polymerization of ϵ -caprolactam.

5. The data relating to the structure of nanocomposites obtained both by *in situ* polymerization and by extrusion are in full compliance with the data obtained by TEM.

The TEM method was also used to evaluate the effectiveness of the modification of zeolite surface during the PCM formation. An unmodified zeolite is present in a polymer matrix in an agglomerated state, while zeolite with a modifier immobilized on its surface does not form agglomerates and it results in improved properties of the formed PCM.

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