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РОЗРОБЛЕННЯ МЕТОДУ ОДЕРЖАННЯ МОНТМОРИЛОНІТ-ПОЛІВІНІЛПІРОЛІДОНОВОГО МОДИФІКАТОРА ТЕРМОПЛАСТІВ

Описано новий метод інтеркаляції монтморилоніту за допомогою полівініл-піролідону. Досліджено структуру і теплофізичні властивості розробленого наномодифікатора та визначено раціональне співвідношення компонентів. Встановлено вплив інтеркальованого монтморилоніту на фізико-механічні властивості суміші полікапроаміду з поліпропіленом. Ці композити характеризуються значно більшими значеннями твердості та модуля пружності порівняно з первинним ПП.

Ключові слова: нанокомпозит, фізико-механічні властивості, полікапроамід, поліпропілен, монтморилоніт-полівінілпіролідонова суміш.

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DEVELOPMENT OF THE OBTAINING METHOD OF MONTMORILLONITE-POLYVINYLPYRROLIDONE MODIFIER FOR THE THERMOPLASTICS

A new method of montmorillonite intercalation by polyvinylpyrrolidone is described in this work. The structure and thermophysical properties of the developed nanomodifier and the components rational ratio were investigated. The effect of intercalated montmorillonite on physico-mechanical properties of the mixture of polycaproamide and polypropylene was determined. These composites are characterized by significantly higher values of hardness and modulus of elasticity compared to the original PP.

Key words: nanocomposite, physico-mechanical properties, polycaproamide; polypropylene, montmorillonite-polyvinylpyrrolidone mixture.

Problem statement. Creation of polymeric nanocomposites based on the polymers of structural designation is a relevant task at present. Of great interest in obtaining the polymeric nanocomposites is montmorillonite, as a nanoscale heterophase. Montmorillonite (MMT) – affordable raw material – is the main component (up to 85 %) of bentonite [1]. Montmorillonite has a special matrix structure that provides it with unique properties. In particular, in the aqueous environment the primary crystalline elements of montmorillonite are broken down into layers   nanoscale elements of the structure [2, 3].

The first attempts at creating composites based on polymers and aluminosilicates were made in 50s of the last century [4]. However, the introduction of approximately 40-50 % by weight of clays (bentonite, hector, etc.) did not lead to the improvement of properties of the polymeric material, first of all, because of the unsatisfactory dispersing of silicate filler [5]. Significant progress in the creation of polymeric-silicate nanocomposites with improved physical and mechanical properties in comparison with the starting polymer and traditional dispersely-filled composites was achieved only in the 90s [6, 7].

Today in the field of development of layered silicate polymeric nanocomposites the main attention is focused on the achievement of high level of nanoparticles exfoliation in the polymeric matrix that specifies

high operational characteristics [2]. Thus the choice of effective organic modifiers of layered silicate is an urgent problem because the modifier ensures high adhesion of the filler with polymeric matrix. From this point of view the study of effect of organic clay on the structure and properties of obtained nanocomposites with unknown nature is of great interest. The determination of mentioned regularities will give the possibility to control the structure and predict the properties of the composites based on organic clay [8].

One of the approaches used to improve thermodynamic compatibility of non-polar polymer with layered silicates is the introduction of polymeric polar modifier [2].

Literature review. In order to achieve a substantial improvement in the properties of the polymeric material, a uniform distribution of nanoparticles of silicate must be achieved in the polymeric matrix. The largest changes in the physical-chemical properties can be expected when introducing anisometric nanoscale filler to the polymer matrix [2, 9]. Particles of lamellar aluminosilicates, in particular, of montmorillonite, have a significant anisometry [10].

Recently, researchers have been paying much attention to obtaining nanocomposites based on the thermoplastic polymeric matrices and a mineral high-polar aluminosilicate – montmorillonite [9, 11].

In article [12], the nanocomposites PP/montmorillonite are obtained by the intercalation of melt using a twin-screw extruder. Using a scanning electron microscope, the authors proved that MMT is dispersed evenly at the nanoscale. The test results of mechanical characteristics of such composites showed that strength at bending of the composites with a low content of MMT (2 % by weight) was higher than that of PP.

By using the method of intercalation from melt [13], the nanocomposites PP and layered silicate Na$^+$-montmorillonite (3 and 7 % by weight) were obtained with the polar modifier   a low-ionized PP of two types that differ in molecular weight and the content of polar groups. The modifier with low molecular weight and high content of polar groups (4 % by weight) contributes to the intercalation of PP, but it binds bad with it and worsens its thermal properties in the nanocomposite. A maximum difference between dynamic module of the nanocomposite with 3 % by weight of clay and the PP module is observed at 80 °C and is around 65 %. It is shown that the compatibility of nonpolar and polar polymers controls the crystal structure and thermal properties of the matrix mixture of polymers and can play a dominant role in the thermal-mechanical behavior of nanocomposites based on the partially crystalline polymers.

In paper [14], the surface of montmorillonite before mixing with PP is modified by a dispersing agent (DAG) with a high molecular weight. It is shown that DAG significantly affects the strength of mechanical properties. Results of the scanning electron microscopy reveal that MMT is dispersed in PP in the form of particles.

As we can see, in most cases, mixing PP with MMT leads to lower mechanical strength of the composite. Although one may note the growth of strength and thermal characteristics during introduction of 3 % by weight of MMT to PP, which is modified by the low-ionized PP [13].

At the same time, mixing a polar PA with a polar MMT provides increased rigidity and mechanical strength of the composite [15] and substantially increases temperature of the start of destruction [9].

Authors of article [16] demonstrated that the intercalated nanocomposite is formed during modification of polyamide-6 by nanosilicate.

The aims of the work:
- development of method for compatibility of montmorillonite (MMT) with polar polymer – polyvinylpyrrolidone (PVP) – in order to use the obtained mixture for the modification of termoplastic polymers;
- investigation of structure and thermo-physical properties of montmorillonite-polyvinylpyrrolidone mixture (MPM), as well as efficiency of MMT intercalation;
- determination of modified montmorillonite effect on physico-mechanical properties of the mixture of polycaproamide (PA-6) and polypropylene.

Experimental Section. To obtain montmorillonite-polyvinylpyrrolidone mixture (MPM) we used polyvinylpyrrolidone with molecular weight of 12600±2700 and "Fluka" montmorillonite supplied by

Sigma-Aldrich firm. PVP and MMT solutions were prepared in water with corresponding concentrations to obtain the following PVP: MMT ratios (w/w): 7:1; 5:1; 3:1; 1:1 and 1:2. Before mixing with PVP the colloid solutions of MMT were pretreated by ultrasonic waves with the frequency of 22 kHz for 3 min using apparatus "Volna UZTA-0.4/22-OM". Then PVP and MMT solutions were mixed using a mechanical stirrer and the obtained solution was treated by ultrasound for 15 min. Ultrasonic waves set in motion a limited volume of treated solution and carry out the local effects with ultrasonic frequencies ensuring high rate and efficiency of mixing. Then mixtures were dried under vacuum at 80°C and obtained films were grinded in agate mortar till fine-dispersed powder was obtained.

To determine the structure of the obtained composites based on PVP with MMT the samples were investigated using X-ray, differential-thermal and thermogravimetric analyses.

Nanocomposites based on polypropylene with modified polyamide mixtures and experimental samples were obtained according to the procedure described in [17].

The tensile strength and the relative elongation at break were determined according to the standard method [10]. Standard dumbbell-shaped samples with a total length of 150 mm, a head width of 20 mm, a working section length of 50 mm, width of 10 mm and a thickness of 4 mm were prepared using the injection molding method. Tests were performed on a TiraTest 2200 tensile-testing machine (Germany) with an extension rate of 50 mm/min. Young modulus was measured on 050/RT-601U tensile-testing machine (Kimura Machinery, Japan). The shear modulus and bulk modulus of the samples were determined from the relations [18]:

$$G = \frac{E}{2(1+\upsilon)};$$ (1)

$$K = \frac{E}{3(1-2\upsilon)},$$ (2)

where E – Young modulus, MPa; G – shear modulus or modulus of rigidity, MPa; K – bulk modulus, MPa; υ – the Poisson's ratio, which is 0.30–0.35 at E ≥ 2000 MPa, and increases to the limit value of 0.50 with the decrease of Young modulus [18].

Brinell hardness was determined at the load of 312.5 N on a Brinell tester of KM-0.2 type (Hungary), which allows to fix the ball indentation depth.

Results and Discussion. X-ray photographs of pure MMT (Fig. 1a) demonstrate clear reflexes typical of clay alumosilicates crystal structure. Two wide plateaus typical of polymer amorphous structure are observed at PVP roentgenogram. X-ray photograph of the composite with the ratio MMT: PVP = 2:1 is similar to that of pure MMT. The reason is a great amount of MMT in the composite but intensity of peaks is less and they are wider. It means that PVP chains get into interlayer space of MMT. X-ray photographs of the samples with the ratio MMT: PVP = 1:3 and 1:5 (Figs. 1b) are similar to those of pure PVP. The difference is the appearance of shifted and less intensive (compared with MMT) peaks at the angles 2θ = 26.77° and 2θ = 34.66° for MMT: PVP = 1:5 typical of reflexes for pure MMT (for MMT – 2θ = = 26.57° and 2θ = 35.03°, respectively). At the same time the intensive peak at 2θ = 45.57° (typical of pure MMT) disappears at the roentgenogram of the sample with MMT: PVP = 1:5. Moreover, for these samples the view of amorphous plateau differs from that of PVP. The obtained results reveal the formation of fluctuation net between PVP and MMT macromolecules and new partially crystal structure with increased softening temperature (compared with pure PVP, Table 1). The most complete physical interaction between PVP and MMT occurs at the ratio MMT: PVP = 1:5 because peaks typical of pure MMT are almost absence at X-ray photograph due to the high level of exfoliation.

The results of DTA (Fig. 2) and TG (Fig. 3) analyses also indicate the presence of physical interaction between PVP and MMT macromolecules. For the studies we used MPM samples with the ratio MMT: PVP = 1:5, 1:3 and pure PVP.

Mass losses of the sample 1 (8 %), sample 2 (1.5 %) and sample 4 (4 %) within the temperature range of 20–130°C are accompanied by the appearance of endothermal effect at DTA curves (Fig. 2) and correspond to extraction of physically bounded water from the composites. The further mass loss in the

range of 130-200°C may be explained by extraction of chemically bounded water. In this area exothermal effect is observed at DTA curves for all samples (Fig. 2) caused by predominant effect of redox reactions in PVP chain. It should be noted that the most intensive processes proceed in the sample 1 (PVP) because the highest exothermal effect is observed here. The redox processes with the lowest intensity proceed in the sample 2 (MMT: PVP = 1:5). The reason is the formation of fluctuation net between PVP and macromolecules and MMT layers during their mixing in the solution under ultrasonic treatment. The least exothermal effect is observed at DTA curve of this sample. Higher exoeffect of the sample 3 in this temperature region may be explained by MMT excess in the composite and formation of random structure.
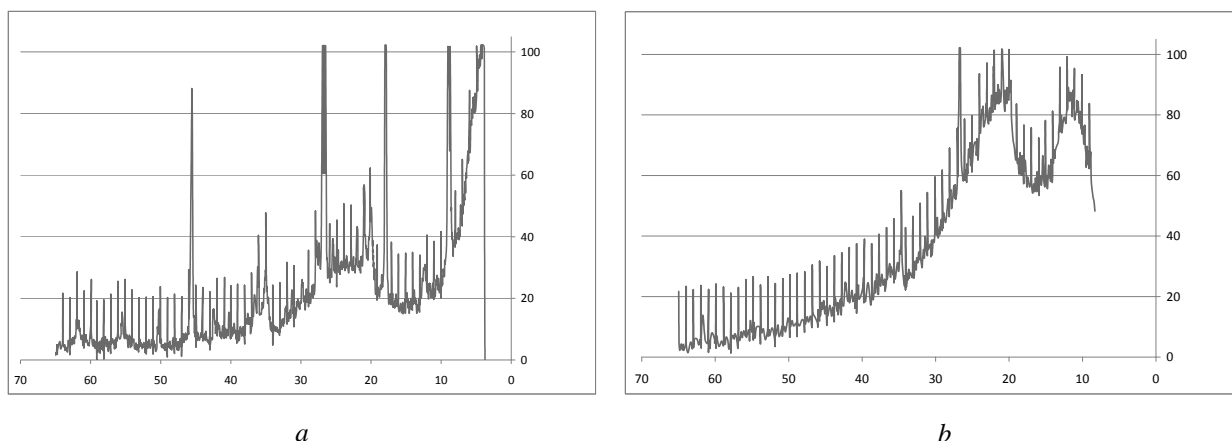

a   *b*

Fig. 1. X-ray photographs of MPM and pure compounds: a) MMT; b) MMT: PVP = 1:5

Table 1

Softening temperature of MPM depending on components ratio

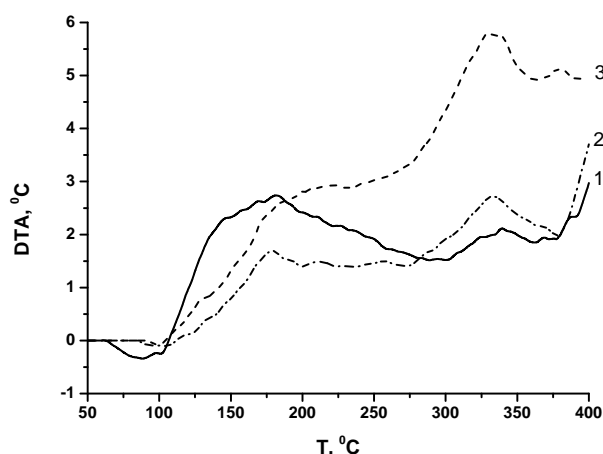| Sample	PVP	MMT: PVP 1:7	MMT: PVP 1:5	MMT: PVP 1:3	MMT: PVP 1:1	MMT: PVP 2:1
T_{soft}, [°C]	176-178	195-197	210-212	205-208	-	-

Fig. 2. Differential thermal analysis of MPM
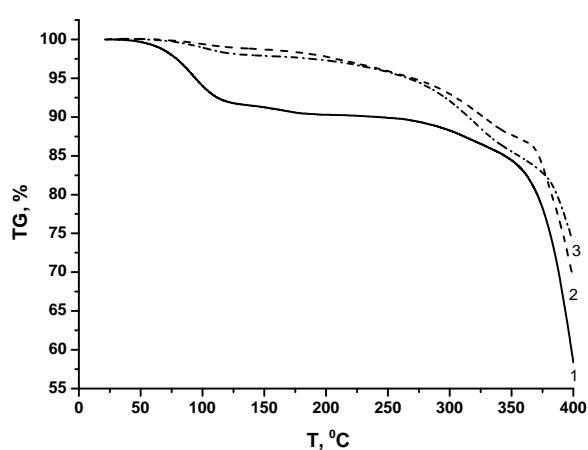*1 – PVP; 2 - MMT: PVP = 1:5; 3 - MMT: PVP = 1:3*

Fig. 3. Thermogravimetric analysis of MPM:
1 – PVP; 2 – MMT: PVP = 1:5; 3 – MMT: PVP = 1:3

Thermal destruction of the sample 3 is shifted toward the area of lower temperatures (220–240 °C) compared with the sample 2. Mass loss here is 1.7 %.

Exothermal effect at DTA curve of the sample 1 with in 320–350 °C is accompanied by mass loss of 1.5 %. It corresponds to thermal-oxidative destruction of PVP chains. The beginning of thermal-oxidative processes in the samples 2 and 3 is shifted toward the area of lower temperatures. The reason is

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acceleration of the mentioned processes under the influence of MMT solid surface. Thermal-oxidative destruction of the sample 2 takes place within 280–360 °C. It is accompanied by clear exothermal effect at DTA curve with the maximum at 335 °C and mass loss of 7.5 %. Thermal-oxidative destruction of the sample 3 takes place within 250–360 °C. Exothermal effects with the maximum at 330°C and intensive mass loss of 12.2 % correspond to this destruction.

So, there is a physical interaction between PVP and MMT macromolecules if their aqueous solutions are mixed in ultrasound field with the frequency of 22 kHz. Higher thermal stability of the obtained composites (compared with pure PVP), the results of X-ray and DTA analyses confirm the above-mentioned fact.

The developed MPM may be used as a modifier for polar and non-polar polymers. From the economic and technological points of view the composite with MMT: PVP = 1:5 is the most profitable one, therefore it is interesting to study its effect on the properties of thermoplastic polymers.

To demonstrate the effect of MPM on the structure and properties of nanocomposite based on it we selected the mixture of polyamide-6 and polypropylene. The development of new layered-silicate nanocomposites based on the mixture of polyamide-6 and polypropylene should extend the areas of their application as the construction materials due to their improved physico-chemical characteristics and fire resistance.

Samples of composites have a significantly lower relative elongation compared with the original PP and PA-6 (Table 2). Moreover, for the composites with a modified polyamide content of more than 30 wt % the relative elongation is double less and forced-elastic strain is 4 times less compared with pure PP. So, such materials are characterized by less defective structure and segmental mobility, due to which they are not capable of "cold flow". This also indicates the formation of a material with high stiffness, which correlates well with the results of the heat resistance measurements for the developed composites (the values are significantly higher than those of pure PP). Forced-elastic strain of the composites with modified PA-6 content of 5 wt % is almost the same as for PP.

The addition of modified PA-6 to PP significantly affects the composites hardness (Table 2). Only at 70 wt % of modified PA-6 the strength and hardness of PP-based composites are significantly reduced. The highest value of Brinell hardness was found for the composites with modified PA-6 content of 15 wt %. The hardness of these composites is 2.5 times higher than of pure PP, which is an additional confirmation of the formation of material with increased rigidity.

Table 2

Physico-mechanical properties of PP based composites with modified PA-6

Composite	Composition, wt %	Breaking stressat tension σ_t, MPa	Relative tensile elongation ε, %	Yield point σ_y, MPa	Brinell hardness, N/mm^2	Forced-elastic strain ε_f, %
PP	100	38.7	50	42	110	22
PA-6-210/310	100	50.0	70	65	100	–
PP:(PA-6/MPM)	30:70	31.9	27	31.6	34	4
	50:50	38.4	30	35.0	150	5
	70:30	39.1	28	36.7	209	4
	85:15	40.0	36	35.2	249	14
	95:5	41.0	38	35.0	221	20

To describe the behavior of a linear elastic body, we used the ratio of the stress increase to the corresponding strain, i. e., the modulus of elasticity. There are three main modulus of elasticity: Young's modulus (E), the shear or the hardness modulus (G), the volume elastic modulus (K). Young's modulus describes the material resistance to tension/compressing during elastic deformation. The shear modulus characterizes the material ability to resist the shape changing with preservation of the volume. The volume

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elastic modulus characterizes the ability of the object to change its volume under the influence of a general normal stress, the same in all directions [18].

The elastic modulus of the composites with small content of PA-6 is 2–2.5 times higher than that of pure PP (fig. 4). Young's modulus is also higher by 200–900 MPa than in the case of pure PA-6. Moreover, with the increase in the content of modified PA-6 above 30 wt % the composites modulus of elasticity decreases, but remains higher than those of pure PP and PA-6. The highest value of the elastic modulus was found for the composites with 15 wt % of modified PA-6.
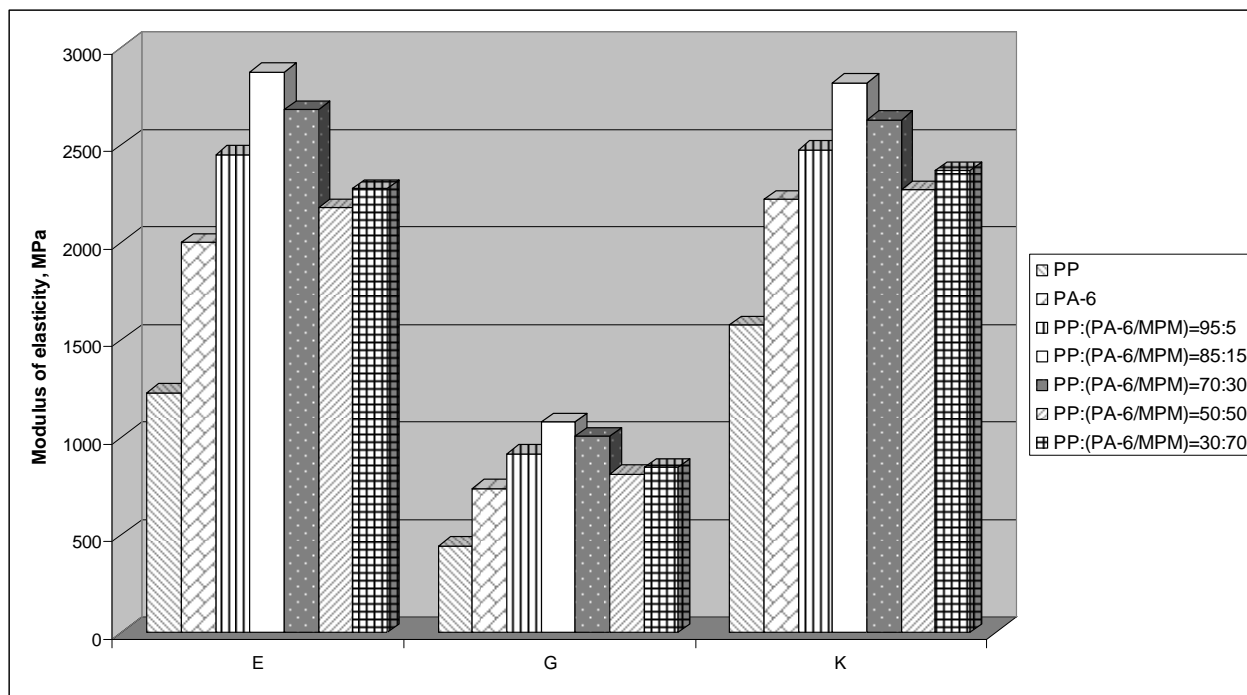

Fig. 4. Elastic-deformation properties of PP based composites with modified PA-6:
E – Young's modulus; G – shear modulus; K – volume elastic modulus

Conclusions. The methods of DTA, DTG, TG, and X-ray analyzes show that, under the conditions of mixing of aqueous solutions of PVP and MMT in the ultrasound field, there is a physical interaction between them. As a result, a composite with an increased thermal stability compared to pure PVP is formed. The most advantageous for use as a nanomodifier is the composition of the MMT: PVP = 1:5, in which the intercalation of MMT occurs most fully.

It was established that in-melt mixing of polypropylene and polyamide, which was modified by PVP-intercalated montmorillonite, forms a nanocomposite with properties that differ significantly from the properties of the original polymers. These composites are characterized by significantly higher values of hardness and modulus of elasticity compared to the original PP. At the same time, it was found that relative elongation and forced elastic deformation of the nanocomposites are reduced by 2 and 4 times, respectively, comparing to pure PP. Such results can be explained by the formation in the structure of the synthesized composites of interpolymeric complexes with physical linkages with the participation of MPM intercalated by low molecular PVP. From the technological and economical standpoints, and based on the material operational properties, the optimum amount of modified polyamide in the mixture is 15–30 wt %.

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