Nanocomposites Based on Polyamide and Montmorillonite Obtained from a Solution

Krasinskyi Volodymyr[1*], Suberlyak Oleh[1], Kochubei Viktoria[1],
Jachowicz Tomasz[2], Dulebova Ludmila[3], Zemke Viktoria[1]

[1] Lviv Polytechnic National University, Department of Chemical Technology and Plastics Processing, Bandera 12 St., 79013 Lviv, Ukraine

[2] Lublin University of Technology, Faculty of Mechanical Engineering, Department of Polymer Processing, ul. Nadbystrzycka 36, 20-618 Lublin, Poland

[3] Technical University of Košice, Faculty of Mechanical Engineering, Department of Mechanical Engineering Technologies and Materials, Masiarska 74 St., 04001 Košice, Slovakia

* Corresponding author's e-mail: vkrasinsky82@gmail.com, t.jachowicz@pollub.pl

ABSTRACT

This work deals with the development of a method for obtaining polyamide and montmorillonite based nanocomposite, which was modified with polyvinylpyrrolidone by mixing in a formic acid solution. The structure and thermophysical properties of the obtained nanocomposites were investigated by means of the X-ray, differential-thermal, thermogravimetric and IR spectroscopic analyses. It was found that nanomodified polycaproamide has a higher crystallinity and higher thermal stability than the original PA-6, and is characterized by considerably higher melt fluidity. The presence of polyvinylpyrrolidone and exfoliated montmorillonite in the nanocomposite structure was confirmed experimentally.

Keywords: polyamide, montmorillonite, polyvinylpyrrolidone, nanocomposite, modification in solution, structure.

INTRODUCTION

Nanocomposites, in contrast to polymers filled with dispersible powders, are a new class of alternative materials, in which nanoscale fillers are dispersed in a polymeric matrix. This contributes in many cases to the improvement of the material properties such as modulus of elasticity, strength, thermal stability, fire resistance and barrier characteristics [4, 16]. Therefore, nanocomposites are an attractive alternative for use in the packaging, medical, automotive, engineering, and other engineering fields [5, 15].

Currently, the most common use of nanofillers are layered silicates, in particular montmorillonite (MMT), hectorite and saponite [2]. Polymer molecules can be intercalated in the gallery of layered silicates, moving their layers apart and forming a homogeneous nanocomposite [3, 6, 12]. The most common methods for producing

the aluminosilicate nanocomposites are polymer modification during polymerization, blending with the viscous-fluid polymer at high shear stresses or mixing in suspension and in solution [1, 17].

In [7], a method for obtaining a modifier for thermoplastic polymers based on MMT - montmorillonite-polyvinylpyrrolidone mixture (MPM) was described. The structure and thermophysical properties of the obtained modifier were investigated by means of the X-ray and differential thermal analysis. The MMT to PVP ratio of 1:5 ppm was found to be the optimum one. Nanomodifier and the PA-6 composites were obtained in the melt [7]. The addition of small quantities of MPM to PA-6 increases the mechanical, thermal and electrical insulation properties of the composites, but reduces their deformability.

In [8, 9], the studies of the composites based on polypropylene (PP)/polycaproamide (PA-6)/MPM mixtures were described. It was shown that

those mixtures were characterized by homogeneity and high thermal stability.

In [10], the interrelation of the physicomechanical and technological characteristics of nanocomposites on the basis of PP/PA-6 mixture with PVP-modified montmorillonite was investigated. A substantial influence of the polyamide-modified polyamide on the properties of composites was shown. It was established that the melt flow index (MFI) of the obtained composites increases by more than twice, compared to the pure PP. It was also shown that – due to the mixing of PP with PA-6/MPM – the hardness, elastic modulus and thermal stability of composites are significantly increased compared to pure PP. This reduces the elongation by half and the elastic deformation of the composites by 4 times.

The previous studies and established regularities have substantiated the feasibility of obtaining PA-6 based nanocomposites modified with PVP montmorillonite, since it forms a technological mixture with polypropylene. However, obtaining a uniform distribution of MMT in the PA-6 during modification in the melt causes considerable difficulties due to the high viscosity [11]. Therefore, it became necessary to find a method for obtaining a homogeneous nanocomposite based on PA-6 and modified MMT. According to our assumptions, mixing PA-6 with a montmorillonite-polyvinyl-pyrrolidone mixture in a formic acid solution is promising. Both PA-6 and MPM are dissolved in formic acid, thus the homogeneous molecular mixing is expected.

The aim of the study was to investigate the method for obtaining a nanocomposite based on PA-6 with MPM by mixing in a formic acid solution and to establish its structure, technological and thermophysical properties.

METHODS

PA6-210/310 polyamide (Belarus) with $MFI_{230/2.16}$ = 19 g/10 min, with melting temperature of 215°C and density ρ_{20} = 1.12 g/cm³, was dried in vacuo at 90°C for 2h before use. As a modifier for polyamide, a montmorillonite-polyvinylpyrrolidone mixture (MPM) obtained from an aqueous solution in an ultrasonic field [7, 17] with a ratio of MMT:PVP = 1:5 ppm was used. Polyvinylpyrrolidone (PVP) with a molecular weight of 12600 ± 2700 produced by Biochem and montmorillonite (Fluka, SIGMA-ALDRICH)

with surface area of 250 m²/g and pH of 4-5 were used to obtain the mixture.

The PA and MPM based nanocomposite was prepared as follows. PA-6 was dissolved in a concentrated formic acid using an electromagnetic stirrer for 2-3 hours without heating. After complete dissolution of PA-6 the MPM (10% wt.% relative to PA-6) was added to the solution. The mixture was stirred thoroughly to form a colloidal solution. The polymer complex was precipitated with an aqueous solution of acetone. The precipitate was filtered off, washed with water and dried in vacuo. The nanocomposite obtained was a fine white powder. For comparative studies, pure PA-6 was similarly precipitated from a formic acid solution.

The objects of research were: sample 1 – PA-6; sample 2 – composite PA-6:MPM = 90:10 ppm; samples 3 and 4 – samples 1 and 2, respectively, which were heat-treated at 250°C for 5 minutes. The thermal analysis of the composites was performed using a Q-1500D derivatograph connected to an IBM compatible personal computer. This device allows determining the mass loss (thermogravimetry – TG), mass loss rate (differential thermogravimetry – DTG) and thermal effects (differential thermal analysis – DTA) simultaneously for the same sample. The studies were carried out under dynamic mode in an atmosphere of air with a heating rate of 3°C/min. The average weight of the sample was 200 mg. The reference substance was aluminum oxide. The derivatographic studies of the samples were carried out in the temperature range of 20-600°C.

The melt flow index (MFI) of the original polymers and their mixtures was determined using an IIRT capillary viscometer [7]. The IR spectra of the powder samples were recorded on an SPECORD M-80 IR spectrophotometer (Carl Zeiss Jena, Germany). The spectra of the obtained powders with petrolatum oil were recorded in the range of 4000 - 400 cm⁻¹ with an integration time of 10 s. The radiographic studies were performed on a DRON-4-07 diffractometer (anode lamps with copper anode and Ni-filter). The studies were performed in the region of 2θ angles from 4 to 45θ, the pulse measurement time was 8 s. The mineral composition of the pyrolysis residue of the PA-6/MPM nanocomposite annealed at 550 °C was determined by X-ray diffractometry using an ADP-2.0 diffractometer (Fe-anticathode, Mn-filter, 30 kV, 10 mA) [14].
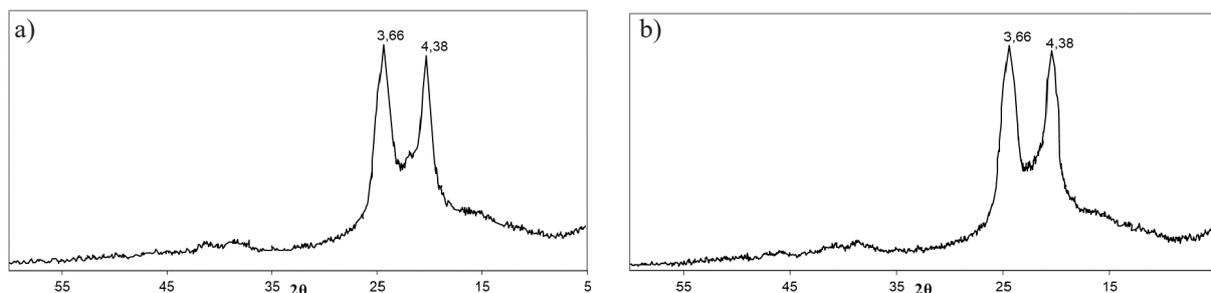
Fig. 1. Diffraction patterns of PA-6 (a) and composite PA-6:MPM = 90:10 ppm (b)

RESULTS AND DISCUSSION

The diffraction patterns of the obtained PA-6/MPM nanocomposite and pure PA-6 (samples 2 and 1, respectively) are the same (Fig. 1). This may indicate that so small quantities of MPM actually do not affect the structure of the original PA-6 polymer matrix. MPM, as described previously [7], is characterized by an amorphous structure.

At the same time, the results of the differential-thermal and thermogravimetric analyses show significant differences in the thermophysical properties of pure PA-6 and PA-6/MPM nanocomposite.

The thermograms of samples 1 and 2 are presented in Figure 2. Table 1 contains the results of thermogravimetric analysis of the samples.

The samples 1 and 2 were heated over six stages, showing different thermal effects at every stage (Fig. 2, curves 1, 2). At the first stage, volatiles (water and solvent) are released in the temperature range of 20-141ºC. This process is accompanied by a small mass loss and appearance of an endothermic effect on the DTA curves. Polyamide transfers from the vitreous physical state to highly elastic state at 80ºC. This process is accompanied by the appearance of minor endo-effects on the DTA curves of the samples.

Table 1. Results of thermogravimetric analysis of the PA-6 based composites

Sample	Thermolysis stage	Temperature range [ºC]	Mass loss [%]
1 (PA-6)	I	20 – 141	1.71
	II	141 – 223	-
	III	223 – 248	-
	IV	248 – 341	5.14
	V	341 – 466	78.03
	VI	466 – 600	10.83
2 (PA-6/MPM)	I	20 – 141	1.84
	II	141 – 220	-
	III	220 – 264	0.7
	IV	264 – 351	6.21
	V	351 – 465	80.33
	VI	465 – 600	8.87
3 (PA-6 heat-treated)	I	190 – 255	-
	II	255 – 346	5.27
	III	346 – 465	79.85
	IV	465 – 600	11.43
4 (PA-6/MPM heat-treated)	I	190 – 237	-
	II	237 – 270	0.24
	III	270 – 352	5.55
	IV	352 – 468	83.99
	V	468 – 600	7.92

a)

b)
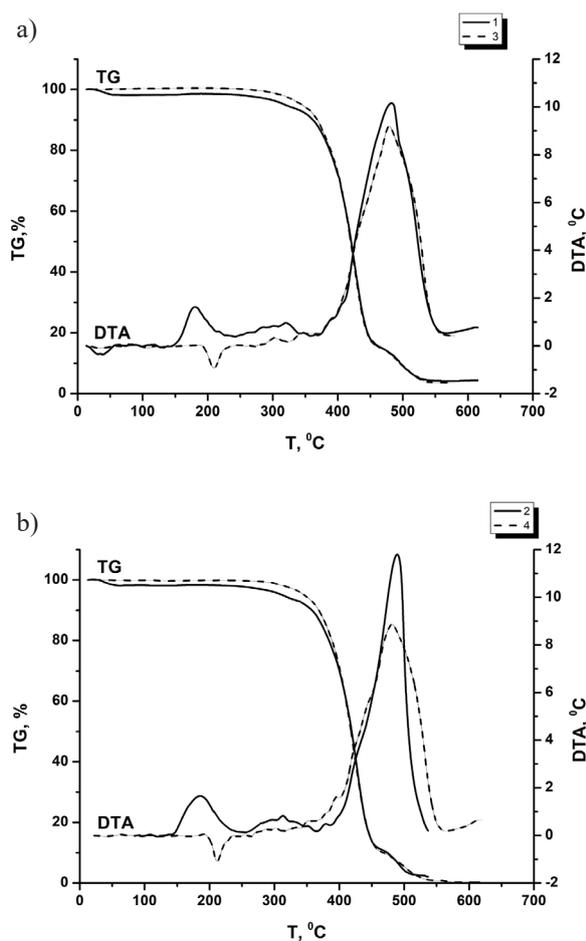
Fig. 2. Thermograms of composites: a) – PA-6 (curve 1) and PA-6 heat-treated at 250ºC for 5 minutes (curve 3); b) – PA-6:MPM = 90:10 ppm (curve 2) and heat treated nanocomposite at 250ºC for 5 minutes (curve 4)

In the temperature range of 141-223ºC the PA-6 crystallization occurs, which is accompanied by the appearance of clear exothermic effects on the DTA curves. This process takes place without mass loss. Samples 1 and 2 were obtained by precipitation from a cold solution, so PA-6 was obtained with a less ordered crystalline phase, resulting in recrystallization when heating. In the modified PA-6, the crystallization processes are more intense, as evidenced by the larger exothermic effect on the DTA curve of sample 2. On the basis of the DTA data, it can be asserted that the MPM modified polycaproamide has a higher degree of crystallinity compared with that of the original PA-6 (greater area of exothermic effect on the DTA curve of sample 2). This is explained by the effect of PVP on the crystallization processes of PA-6.

At the third stage of thermolysis, in the temperature range of 220-264ºC, the melting processes of the formed crystallites occur, supplemented for sample 2 by the destruction of the physical interpolymer structure with a mass loss of 0.7%. Only insignificant endothermic effects are observed on the DTA curves.

In the temperature range of 248-351ºC, at the fourth stage of thermolysis, the thermo-oxidative destructive processes accompanied by a slight mass loss, clear extrema on the DTG curves and the appearance of exothermic effects on the DTA curves were observed. It should be noted that the modified PA-6 has a higher thermal resistance compared with pure PA-6. This is evidenced by the more pronounced exothermic effect of sample 1 and the shift of the thermal oxidation destruction temperature interval for sample 2 to the area of higher temperatures (264-351ºC) compared to sample 1 (248-341ºC). It should be noted that the onset temperature mass loss of sample 2 is also shifted to higher temperatures compared to sample 1 (264°C versus 248°C). The higher by 1% value of mass loss for sample 2 at this stage of thermolysis can be explained by the presence of PVP macromolecules in the composite.

At the fifth stage of thermolysis, in the temperature range of 341-466ºC, a deep thermo-oxidative destruction of the samples occurs, which finishes with the combustion of the destruction residues. These processes are matched by intense mass loss, rapid exothermic effects on the DTA curves and deep extrema on the DTG curves. The onset combustion temperature of the modified PA-6 was also shifted to higher values in comparison with that of original PA-6 (351°C versus 341 °C), although the mass loss was slightly larger for sample 2 due to the presence of PVP.

In the temperature range of 465-600ºC, at the sixth stage of thermolysis, a complete combustion of the carbonized residue of the destruction products occurs. For further studies, samples 1 and 2 were kept in an oven at 250°C for 5 min and cooled at room temperature (Fig. 2, curves 3 and 4, respectively). It was assumed that such treatment would allow the formation of a crystalline structure typical of polycaproamide, which was not completely formed when the compositions were obtained from the cold solution.

On the DTA curves of samples 3 and 4, which were heat-treated, no exothermic effects corresponding to the crystallization processes were observed. Instead, endothermic effects of crystallite
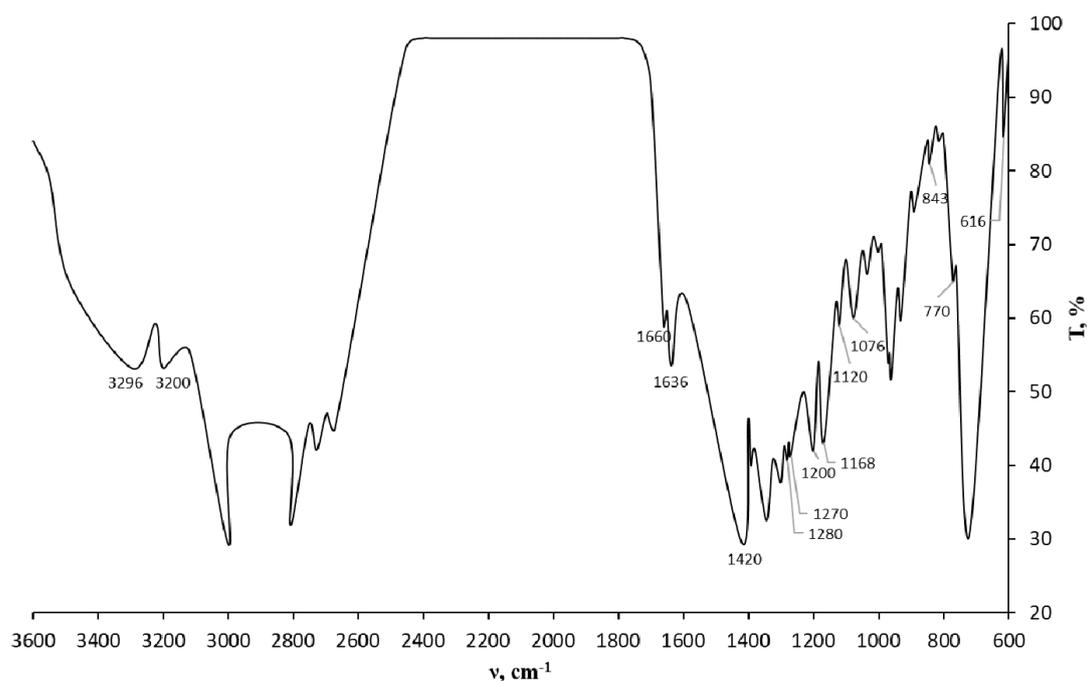
Fig. 3. Infrared spectrum of nanocomposite PA-6:MPM = 90:10 ppm

melting processes formed during the heat treatment, are present on the DTA curves in the temperature range of 190-241ºC. For sample 3, in the temperature range of 237-270ºC there is a slight endothermic effect of the physical interpolymer structure destruction and PVP destruction.

The heat treated samples 3 and 4 are characterized by higher thermal stability in comparison with the original samples 1 and 2. This is evidenced by the shift of thermal oxidative destruction intervals for samples 3 and 4 to the region of higher temperatures. The thermal destruction of heat treated sample 3 begins at 255°C, while the destruction of the heat-treated sample 1 is observed at the temperature of 248°C. The destructive processes for heat-treated sample 4 begin at 270°C. In turn, for sample 2, these processes begin at 264°C.

The increase in the thermal stability for samples 3 and 4 indicates the formation of a denser structure during heating with a degree of crystallinity characteristic of polycaproamide. The obtained PA-6/MPM nanocomposite is characterized by a higher MFI value as compared with pure PA-6. The MFI values for the composite and pure reprecipitated PA-6 are 88 g/10 min, and 78 g/10 min, respectively. It should be noted that MFI of the original PA-6 is 19 g/10 min.

Therefore, all studies, except for the radiographic studies, show significant differences between the structure and properties of PA-6 and PA-6/MPM composites. In order to confirm the formation of PA-6/MPM nanocomposite with unique properties, the IR spectroscopic analysis was performed (Fig. 3). In the IR spectrum of the nanocomposite, the authors observed the absorption band at 1660 cm^{-1}, characteristic of the stretching vibrations of the cyclic amide group in the structure of lactam PVP heterocycle, as well as the band at 1280 cm^{-1}, typical of the plane deformation vibrations of the C–H bond in the PVP structure [13]. Such bands are absent in the PA-6 spectrum, where the absorption bands characteristic of polycaproamide are observed. IR spectroscopy confirms the PVP presence in the PA-6/MPM nanocomposite structure. This indicates that PVP is physically bound with PA and MMT and is therefore not washed out with an aqueous solution of acetone during precipitation. Thus, it may be asserted that in the synthesized nanocomposite, MMT is distributed and physically bound with polarized groups of the PVP cycle.

The presence of MMT in the composite is also confirmed by a diffractometric analysis of the pyrolysis residue after holding the samples PA-6 and PA-6/MPM at 550ºC. The mineral composition of the pyrolysis residue is shown in Figure 4. The presence of layered MMT in the synthesized nanocomposite is confirmed by the behavior of the reflex (001), the interplanar distance of which is 1.51 nm for the original MMT [14], and 0.99 nm (Fig. 4) for the heat-treated sample.
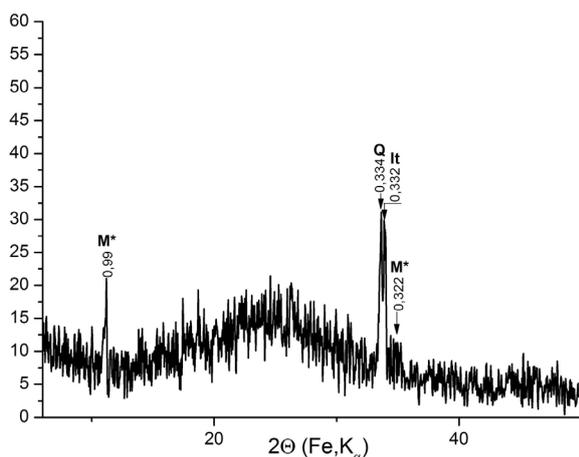
Fig. 4. Diffraction pattern of the pyrolysis residue of PA-6/MPM nanocomposite annealed at 550ºC: M * is dehydrated MMT; Q is quartz; It is a hydromica

CONCLUSIONS

A new method for obtaining a nanocomposite based on PA-6 polyamide with montmorillonite pre-intercalated with polyvinylpyrrolidone, was developed. The method consists of mixing components in a formic acid solution.

The X-ray studies showed the identity of the supramolecular structure of the synthesized nanocomposite and PA-6, precipitated from formic acid solution. At the same time, the results of thermogravimetric and other analyses show significant differences in the structure and properties of PA-6/MPM nanocomposite and pure PA-6. In particular, the comparison of MPM modified polycaproamide and original PA-6 shows a higher degree of crystallinity and thermal resistance higher by 16°C for the synthesized nanocomposite. The resulting PA-6/MPM is characterized by the MFI value which is higher by 10 units than that of pure PA-6; this indicates the formation of a inversion mixture with lower viscosity.

The presence of PVP in the structure of the obtained nanocomposite was confirmed by IR spectroscopy, and the presence of exfoliated MMT was confirmed by the X-ray diffractometric analysis of the nanocomposite pyrolysis residue.

Acknowledgements

REFERENCES

1. Alexander M, Dubois P. Polymer nanocomposites: Synthesis, characterization, and modeling. Materials Science and Engineering, 2000, 28, 1–63.

2. Aranda P, Mosqueda Y, Pérez-Cappe E et al. Electrical characterization of poly(ethylene oxide)-clay nanocomposites prepared by microwave irradiation. Journal of Polymer Science Part B: Polymer Physics, 2003, 41(24), 3249–3263.

3. Elbokl T and Detellier C. Aluminosilicate nanohybrid materials. Intercalation of polystyrene in kaolinite. Journal of Physics and Chemistry of Solids, 2006, 67(5-6), 950–955.

4. Gaaz T, Sulong A, Akhtar M at al. Properties and Applications of Polyvinyl Alcohol, Halloysite Nanotubes and Their Nanocomposites. Molecules, 2015, 20(12), 22833–22847.

5. Krasinskyi V., Gajdos I., Suberlyak O., Antoniuk V., Jachowicz T. Study of the structure and thermal characteristics of nanocomposites based on polyvinyl alcohol and intercalated montmorillonite. Journal of Thermoplastic Composite Materials. – First Published October 8, 2019.

6. Krasinskyi V., Suberlyak O., Antoniuk V., Jachowicz T. Rheological Properties of Compositions Based on Modified Polyvinyl Alcohol. Advances in Science and Technology Research Journal, 2017, 11(3), 304–309.

7. Krasinskyi V., Suberlyak O., Dulebová L., Antoniuk V. Nanocomposites on the basis of thermoplastics and montmorillonite modified by polyvinylpyrrolidone. Key Engineering Materials, 2017, 756, 3–10.

8. Krasinskyi V., Kochubei V., Klym Y., Suberlyak O. Thermogravimetric research into composites based on the mixtures of polypropylene and modified polyamide. Eastern European Journal of Enterprise Technologies, 2017, 4 (12), 44–50.

9. Krasinskyi V, Suberlyak O, Kochubei V et al. Effect of small additives of polyamide modified by polyvinylpyrrolidone and montmorillonite on polypropylene technological properties and heat resistance. Advances in Science and Technology Research Journal, 2018, 12(2), 83–88.

10. Krasinskyi V, Suberlyak O, Zemke V et al. The Role of Polyvinylpyrrolidone in the Formation of Nanocomposites Based on acompatible Polycaproamide and Polypropylene. Chemistry & Chemical Technology, 2019, 13(1), 59–63.

11. Krasinskyi V., Suberlyak O., Chekailo M., Dulebova L. Investigation of structure of nanocomposites on the basis of mixture of polypropylene and modified polyamide with using scanning electronic microscopy. Chemistry, Technology and Application of Substances, 2019, 2(1), 138-144.

12. Kryszewski M. Nanointercalates – novel class of materials with promising properties. Synthetic Metals, 2000, 109, 47–54.

13. Mel'nikova O.A., Samkova I.A., Mel'nikov M.YU., Petrov A.YU., Yel'tsov O.S. IK-spektroskopicheskoye izucheniye khimicheskoy struktury polimernykh kompleksov lekarstvennykh veshchestv na osnove polivinilpirrolidona. Uspekhi sovremennogo yestestvoznaniya, 2016, 8, 42-49.

14. Moore D. M., Reynolds Jr. R. C. X-ray Diffraction and the Identification and Analysis of Clay Minerals. Oxford New York: Oxford University Press, 1997, 376.

15. Pinnavaia T and Beall G. Polymer-Clay-Nanocomposites. 1th ed. New York: Wiley, 2000, 370.

16. Shokrieh M, Esmkhani M and Taheri-Behrooz F. A novel model to predict the fatigue life of thermoplastic nanocomposites. Journal of Thermoplastic Composite Materials 2015, 28(11), 1496–1506.

17. Suberlyak O, Krasins'kyi V, Shapoval I et al. Influence of the mechanism and parameters of hardening of modified novolac phenol-formaldehyde resins on the physicomechanical properties of the composite. Materials Science, 2011, 46(5), 669–678.