ANALYSIS OF THE INFLUENCE OF INTERCALATED MONTMORILLONITE ON HOMOGENIZATION OF PP/PA-6 NANOCOMPOSITE IN MELT

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The relationship between the structure, physical-mechanical, and elastic-deformation characteristics of newly formed nanocomposites based on a mixture of PP/PA-6 (Polypropylene/polyamide-6) with montmorillonite (MMT), which was modified with polyvinylpyrrolidone (PVP), is investigated in this work. The influence of the content of modified PA-6 on the nature of its distribution in the polymer matrix of PP was investigated using microscopic analysis. It is shown that the content of the modified PA-6 significantly affects the nature of the distribution and structure of the composites obtained in the melt. It was found that the most homogeneous structure is characterized by composites with the content of modified PA-6 from 15 to 30 wt%. It is shown that due to the mixing of PP with modified polyamide, the hardness and modulus of elasticity of composites significantly increase compared to pure PP. This reduces the relative elongation of the composites by 2 times.

KEYWORDS

Polypropylene, polyamide, montmorillonite, polyvinylpyrrolidone, nanocomposite, structure, scanning electron microscopy.

1 INTRODUCTION

"New" nanotechnology must meet such conditions [Olejnik 2008]:

- the structures under study must have at least one dimension below 100 nm,
- chemical and physical properties must be controlled in the production process.

It is obvious, that polymer nanocomposites are part of nanotechnology because usually the size of at least one of their components is measured in nanometers – in the range from 1 nm to several hundred nm. Major research into such systems began in the early decade of the 20th century and has made continuous progress over 10 years, and as early as 2002, half of all research on nanocomposites concerned those with a polymer matrix [Kacperski 2003].

Polymer nanocomposites – are a rapidly growing field of nanostructured materials with additional functionality due to nanosized filler particles, which give materials a number of specific properties compared to macroscopically filled polymer composites [Dulebova 2017]. A significant amount of research is needed to fully elucidate the behavior of nanointerfaces in the polymer matrix, and it should be said that these studies are still in their infancy [Kacperski 2003].

The most frequently used nano-additives in the processing of polymeric materials are aluminosilicate nanofillers: montmorillonite (MMT) (fig. 1) and galluazite [Ahmad 2009, Kiliaris 2010, Kovalevski 1994]. Recently, much attention is paid to kaolin materials, because they are very common in nature, being the main element of the earth's crust. Such materials can be successfully used for the manufacture of organic-inorganic hybrid materials used in various industries and environmental protection [Wierzbicka 2016, Liu 2007, Vahedi 2014]. Nanofillers can have different shapes, such as plates, grains, needles, fibers, or nanotubes [Żymankowska-Kumon 2012].

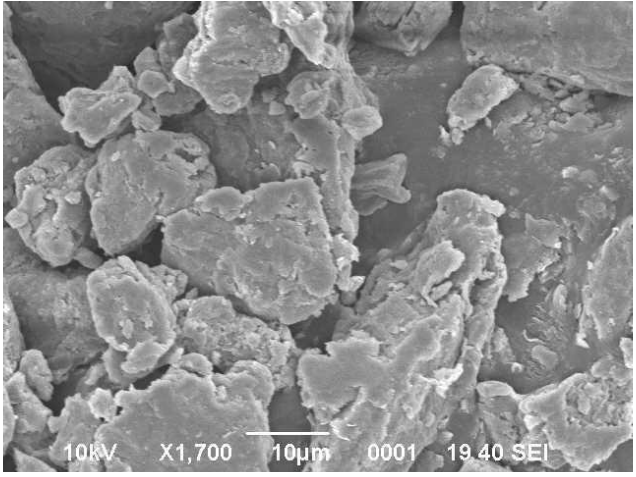

Figure 1. SEM picture of montmorillonite

The structure of MMT is three-layer (2:1): two layers of silicon-oxygen tetrahedra, turned vertices to each other, covers the layer of aluminohydroxyl octahedra on both sides. Due to this, the connection between the packets is weak, the interpacket distance is large and ions, water molecules, and other polar substances can penetrate into it. Due to this, the mineral swells strongly when wet [Zaini 2014]. The presence of isomorphic substitutions, a huge specific surface area (up to 600-800 m^2/g), and the ease of penetration of ions into the interpackage space causes a significant capacity of cation exchange (80-150 mol-eq/100g) [Tyagi 2006]. Montmorillonite is an elongated plate with a length of 100 to 200 nm. The chemical composition of MMT is variable: the content of SiO_2 – 45-55%, Al_2O_3 – 18-20%, MgO and Fe_2O_3 – very little, Na_2O and CaO – up to 1.5%, H_2O – up to 24-26% [Sakizci 2010].

Unlike talc and mica, montmorillonite can be layered and dispersed into individual layers 1 nm thick and about 70 to 150 nm wide. This stratification also causes the specified essential increase in the ratio of the surface area to volume. Aluminosilicate composites can be divided into three types: conventional composites, nanocomposites with inclusions, and layered nanocomposites. If the particles of montmorillonite (tactoids) are partially distributed in the polymer, they are called nanocomposites with inclusions, and when completely distributed on individual plates - stratified nanocomposites [Youssef 2017]. To improve the dispersion and mixing with the polymer matrix, the clay must be pre-modified, the appropriate surface treatment [Omurlu 2016].

The properties of polymer composites as structural materials, in addition to the physical and mechanical properties of the components, are also strongly influenced by the size of the distribution surface of the dispersed phase and the nature of the interactions between the monolithic and dispersed phases [Dulebova 2015]. As many studies and experiments have shown, the mechanical properties of the composites increase when the ratio of the sides of the filler increases, and its transverse size decreases [Wierzbicka 2016, Beatrice 2012, Tesarikova 2016]. The specific surface area of the filler increases, as a result of which the forces of interaction between the polymer matrix and the filler particles increase. That is why nanocomposites have high mechanical properties even at low filler content (from 3 to 5 wt%). Therefore, the properties largely depend on the dispersion of the filler in the polymer matrix [Li 2009, Jachowicz 2014].

Mixtures based on polypropylene (PP) and polyamide (PA) attract great attention as structural materials, the mixing of which allows reducing the negative characteristics of the initial polymers [Krasinskyi 2017a, Suberlyak 2014, Meng 2010, Kusmono 2008]. Thus, non-polar PP during mixing with polar highly hydrophilic PA significantly reduces the water absorption of the material. As a result, the effect of moisture on the mechanical and thermal properties of composites is reduced. On the other hand, mixing PP with PA allows expanding the temperature range of operation of the material at negative temperatures (decreases the brittleness temperature of PP) [Guowang 2008].

However, to obtain a homogeneous mixture of PP with PA, it is necessary to use compatibilizers, usually of complex chemical structures, in particular maleinized PP [Guowang 2008]. But in this case, the probability of chemical crosslinking of macromolecules increases due to the interaction of anhydride groups with peptide groups of PA.

Polyvinylpyrrolidone (PVP) has an initiating effect in the polymerization of hydroxyalkylene methacrylates as an active complexing agent [Grytsenko 2019a, Bashtyk 2019, Grytsenko 2019b]. It also actively responds in the formation of new polymer matrices of the liquid-structured type [Suberlyak 2012, Suberlyak 2011]. PVP also promotes the formation of homogeneous polymer mixtures based on amphipolar polymers [Gnatowski 2006, Krasinskyi 2017b]. At the same time, PVP intercalates montmorillonite (MMT) [Krasinskyi 2017a, Suberlyak 2014, Krasinskyi 2017c], which is the basis for the creation of thermoplastic nanocomposites, in particular on the basis of mixtures of polyamide and polypropylene.

In previous works [Krasinskyi 2017b, Krasinskyi 2018] the authors proposed a method of obtaining a nanocomposite based on a mixture of PP/PA-6 with high heat resistance. Initially, a nanocomposite based on PA-6 with MMT was obtained, which was intercalated with low molecular weight PVP. Then, by mixing in the melt, a mixture based on PP and the synthesized nanocomposite was obtained. The use of MMT, intercalated PVP, increased the heat resistance of PA-6, and PVP associated with PA-6, increased the compatibility of polypropylene with polyamide, which precluded the use of reactive compatibilizers of complex chemical structure. Based on thermogravimetric and differential thermal studies, it is shown that the addition to PP from 15 to 30 wt% PA-6, which is modified by intercalated MMT, significantly increases the heat resistance of the material [Krasinskyi 2018].

The aim of this study was to perform microscopic analysis of the distribution of nanocomposite based on PA-6 with MMT, which is intercalated PVP, in a polypropylene matrix, and to investigate the effect of nanocomposite content on the nature of distribution and physical and mechanical properties of the mixture.

2 MATERIALS AND METHODS OF RESEARCH

The following reagents were used for the experiments.

Polypropylene (PP) of Moplen HF501N brand (Lyondell Basell Industries) with melt flow index $MFI_{230/2.16}$ = 9.50 g/10 min, Vicat softening point 155 ºC, density ρ_{20} = 900 kg/m^3 and bulk density ρ_b = 530 kg/m^3.

Polyamide of PA6-210/310 brand (JSC "Grodno Azot", Belarus) with $MFI_{230/2.16}$ = 19 g/10 min, melting temperature 215 ºC, density ρ_{20} = 1120 kg/m^3, relative viscosity 2.68. Before use, PA-6 was dried under vacuum at 90 ºC for 2 h.

Montmorillonite-polyvinylpyrrolidone mixture (MPM) with MMT:PVP ratio of 1:5 obtained from the solution in the ultrasonic field [Krasinskyi 2017a, Krasinskyi 2017b, Krasinskyi 2017c] was used as a modifier for polyamide. The content of MPM in PA-6 was 10 wt%.

Polyvinylpyrrolidone (PVP) (LLC "AK Sintvita", Russia) with a molecular weight 12600±2700 g/mol, softening temperature 140–160 ºC, ρ_{20} = 1190 kg/m^3 was dried before mixing under vacuum at 60–70 ºC for 2–3 h.

Montmorillonite 69911 (Sigma-Aldrich), untreated, with a surface area of 250 m^2/g and pH = 4–5.

Nanocomposites based on polypropylene with modified polyamide mixtures and experimental samples were obtained according to the procedure described in [Krasinskyi 2017b].

The microstructure of the obtained samples was examined on a scanning electron microscope brand REM-106 of the Ukrainian company "Selmi". This is a high-resolution microscope operating in high and low vacuum mode. Used to study the structure and chemical composition of materials. The microscope can operate in the mode of secondary and reflected electrons.

For studies were used fractures of samples of composites based on PP with the content of modified PA-6 from 5 to 70 wt%. Fractures of the surface of the samples were cut off by guillotine and glued to slides compatible with the microscope slide. Before placing the samples in the vacuum chamber of the microscope, their surface was sprayed with a thin layer of gold to obtain an electrically conductive film, which facilitated observation under a microscope. Then the samples were placed on a microscope slide, which can move in three mutually perpendicular directions, allowing the inclination of the sample to the electron-optical axis and rotation around the axis. The study was performed under a low vacuum (60 Pa).

The tensile strength of the samples, the elongation at break was determined by standard methods according to GOST 11262-2017 (ISO 527-2:2012). Samples in the form of standard blades with a total length of 150 mm, a head width of 20 mm, a working part length of 50 mm, a working part width of 10 mm, and a thickness of 4 mm were made for injection moulding. The tests were performed on a bursting machine brand TiraTest 2200 (Germany) at a tensile speed of 50 mm/min. Determination of Young's modulus of tensile samples was carried out on a rupture machine brand 050/RT-601U of the Japanese company "KIMURA MACHINERY", Hiroshima [Suberlyak 2011]. The shear modulus and the bulk elastic modulus of the samples were determined from the relations:

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

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

where:

E – Young`s modulus, MPa;

G – shear or stiffness modulus, MPa;

K – modulus of volumetric elasticity, MPa;

υ – Poisson's ratio, which for thermoplastic polymers with a modulus of elasticity E ≥ 2000 MPa is from 0.30 to 0.35, and increases to the limit value of 0.50 with the decrease of Young`s modulus.

The Brinell hardness of the samples was determined by a load of 312.5 N on standard blades on a Brinell hardness tester of the IGV KV-02 brand of Hungarian production, which makes it possible to record the depth of indentation of the ball with a diameter of 5 mm in the sample.

3 RESULTS AND DISCUSSION

Figures 2-7 show the results of microscopic observations (SEM) of polymer composites based on PP with different content of modified PA-6. Figure 2 shows the fracture of the surface of pure polypropylene without additives. The surface is homogeneous without visible inclusions, even at high magnifications.

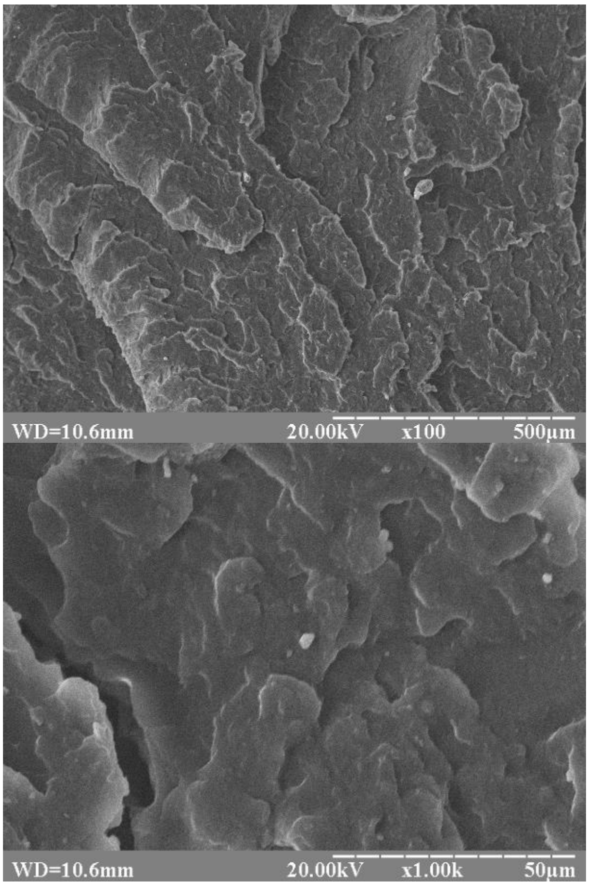

Figure 2. SEM images of the original polypropylene

Figure 3 shows the fracture of the composite surface containing 5 wt% PA-6 modified with MPM. On the surface of the polymer, you can see agglomerates of modified PA-6 of different sizes (from several to ten microns). From figure 3 it is also possible to understand the nature of the embedding of agglomerates in the matrix – the polymer does not adhere firmly to their surface, which may indicate poor adhesion of agglomerates to the polymer. With increasing content of modified PA-6 in the composite to 15-30% by weight. (fig. 4-5) the size of the agglomerates is significantly reduced, and their distribution becomes more uniform. We can also talk about the best adhesion of agglomerates of modified PA-6 to the matrix of polypropylene in such samples.

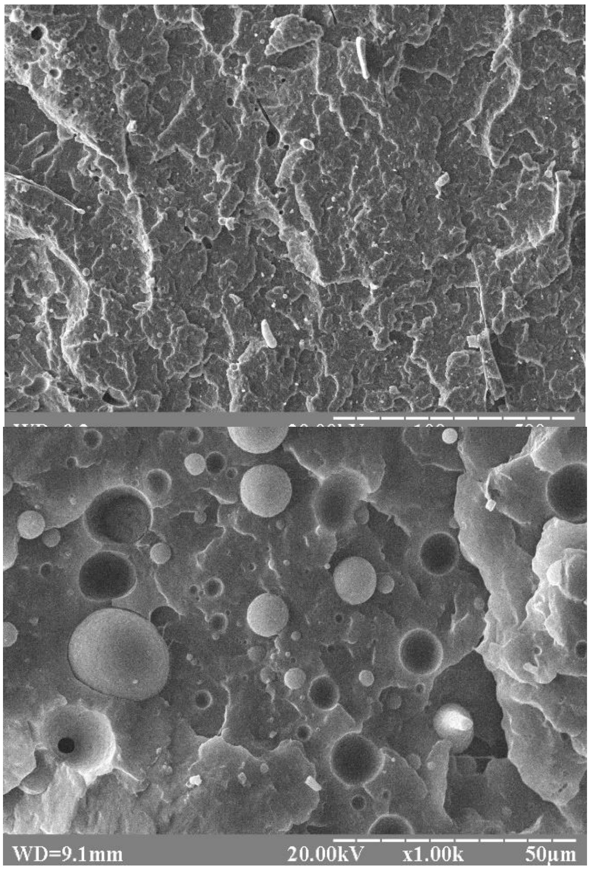

Figure 3. SEM images of the polypropylene which contains 5 wt% PA-6 modified with MPM

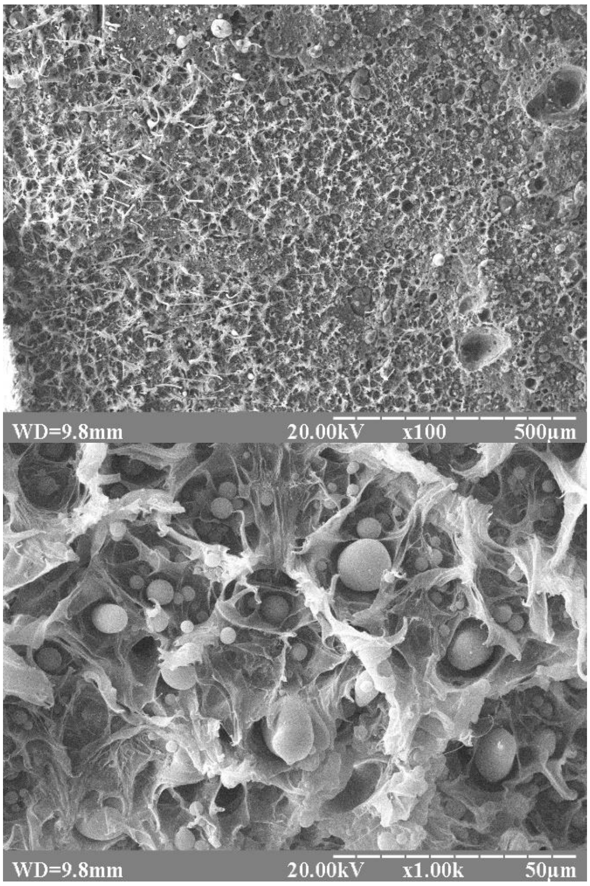

Figure 4. SEM images of the polypropylene which contains 15 wt% PA-6 modified with MPM

As you can see, the most homogeneous structure is characterized by composites with the content of modified PA-6 from 15 to 30 % by weight. (fig. 4-5). The photomicrographs of their fractures show a lamellar structure and a small number of inclusions of agglomerates of modified PA-6 of small size, which may indicate complete stratification of MMT. Such results correlate well with the results of studies of the heat resistance of composites [Krasinskyi 2017b, Krasinskyi 2017c] and physical and mechanical properties (Table 1). The Young's modulus (2680-2874 MPa) and hardness (209-249 N/mm^2) of these composites are 2-2.5 times higher, and the temperature of the beginning of thermooxidative destruction (322 ºC) is 120 ºC higher than pure PP.

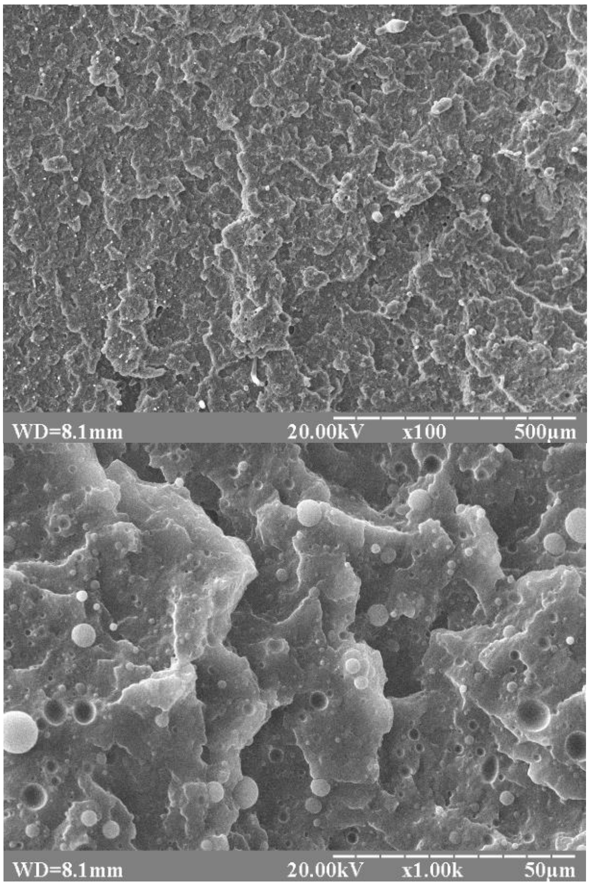

Figure 5. SEM images of the polypropylene which contains 30 wt% PA-6 modified with MPM

With increasing content of modified PA-6 in the composite above 50 wt%, the structure of the material becomes more and more heterogeneous, a significant number of residues of PA-6 agglomerates appear (fig. 6-7). The content of PA-6 70 wt% large cavities is formed in the structure of the material and a significant amount of undistributed PA-6 is observed, which is the cause of reduced values of tensile stress, relative tensile elongation, Brinell hardness (Table 1) and heat resistance [Krasinskyi 2017b].

To verify the results of SEM, the images were compared with micrographs obtained by other authors who studied the dispersion of nanofillers using SEM. In the work [Chen 2016], are presented microphotographs of the distribution of galluazite nanotubes in a polylactide matrix. Despite the presence of agglomerates with a size of 20-30 µm, the authors of these works, define the degree of dispersion, as a good one.

In works [Liu 2014] and [Deng 2009] are described SEM images showing the distribution of nanotubes in epoxy composites using two different methods of homogenization. The authors substantiated the advantage of the ball mill over mechanical mixing. Using this method of homogenization, SEM images showed agglomerates of nanotubes of significant size.

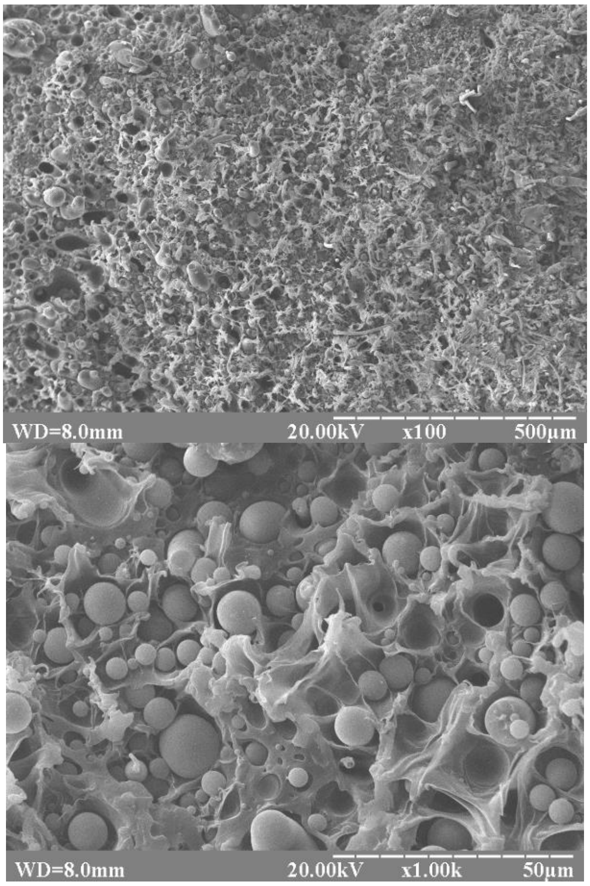

Figure 6. SEM images of the polypropylene which contains 50 wt% PA-6 modified with MPM

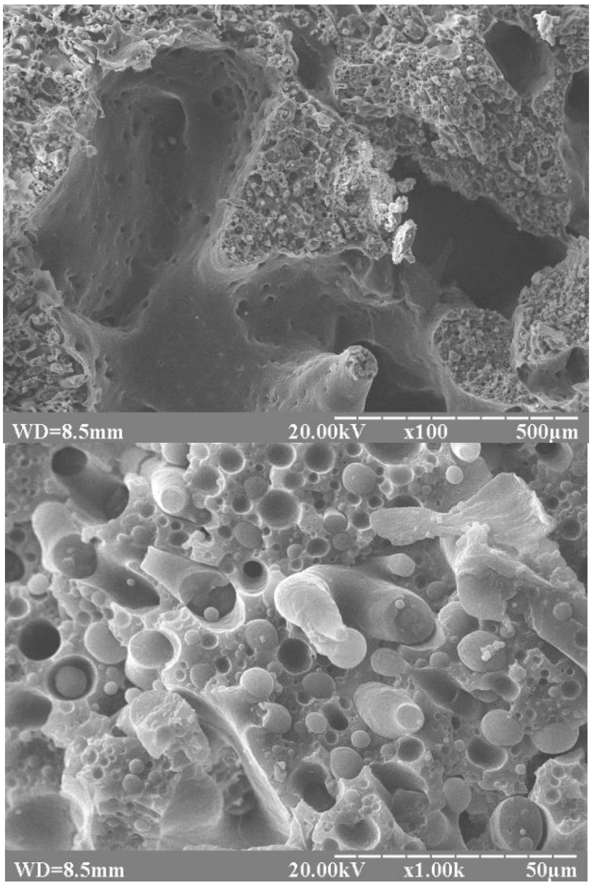

Figure 7. SEM images of the polypropylene which contains 70 wt% PA-6 modified with MPM

However, our studies indicate the necessity to improve the method of mixing the components to achieve full stratification of the nanocomposite based on PA-6 in polypropylene.

Polymers are characterized by a wide range of mechanical characteristics, which strongly depends on their structure. In addition to the structural parameters, the mechanical properties of polymers are significantly influenced by external factors: temperature, time and loading frequency/speed, pressure, type of the stressed state, preliminary heat treatment, the state of the environment, etc.

In order to establish the influence of the content and distribution of the modified PA-6 in the matrix of PP on the physical and mechanical properties of the obtained composites, they were investigated under uniaxial tension. The results obtained are presented in table 1.

Composition	Content, wt%	Tensile stress σв, MPa	Relative tensile elongation ε, %	Brinell hardness, N/mm^2	E, MPa	G, MPa	K, MPa
PP	100	39±2	50±2	110±6	1230±8	446±8	1577±8
PA-6	100	67±2	60±2	100±6	2000±9	741±9	2222±9
PP:(PA-6/MPM)	30:70	32±2	27±2	34±3	2274±9	849±9	2369±9
	50:50	38±2	30±2	150±6	2178±9	813±9	2269±9
	70:30	39±2	28±2	209±7	2680±10	1008±10	2627±10
	85:15	40±2	36±2	249±8	2874±10	1080±10	2818±10
	95:5	41±2	38±2	221±7	2450±10	918±10	2475±10

Table 1. Physical-mechanical and elastic-deformation properties of the PP with modified PA-6

Samples of composites have a much smaller relative tensile elongation compared to the original PP and PA-6 (Table 1). Moreover, the relative elongation of composites containing modified polyamide more than 30 wt% is almost 2 times smaller than pure PP. These composites are also characterized by very low values of forced-elastic deformation, which is 4 times less than pure PP [Krasinskyi 2019]. Thus, such materials are characterized by less structural defects and low segmental mobility, as a result of which they are not capable of "cold fluidity". This also indicates the formation of a material with high rigidity.

The addition of modified PA-6 to the PP significantly affects the hardness of the composites (Table 1). Only the content of the modified PA-6 70 wt% the strength and hardness of composites based on PP is significantly reduced. The highest Brinell hardness is characterized by composites based on PP with the content of modified PA-6 15 wt%. The hardness of these composites is 2.5 times higher than pure PP, which is an additional confirmation of the formation of a material with high rigidity.

To describe the behavior of a linear elastic body, the ratio of the stress increase to the corresponding deformation, ie the modulus of elasticity, is used. There are three main moduli of elasticity: Young's modulus (E), shear modulus or stiffness modulus (G), bulk elasticity modulus (K). The Young's modulus characterizes the resistance of a material to tension/compression during elastic deformation. The shear modulus characterizes the ability of a material to resist shape change while maintaining volume. The modulus of bulk elasticity characterizes the ability of an object to change its volume under the action of comprehensive normal stress, the same in all directions.

Elastic-deformation properties of PP and its composites with modified PA-6 are summarized in table 1. As you can see, the modulus of elasticity of composites based on PP with modified PA-6 is 2 times higher than pure PP, with content of modified PA-6 up to 30 wt%. The Young's modulus is also higher by 200-900 MPa than in the case of pure PA-6. Moreover, with increasing content of modified PA-6 in composites more than 30 wt%, their modulus of elasticity decreases but remains higher than pure PP and PA-6. The highest values of the modulus of elasticity are characterized by composites with the content of modified PA-6 15 wt%.

4 CONCLUSIONS

It can be assumed that the presence of agglomerates in the production of polymer nanocomposites is not uncommon. Many studies describe the presence of such clusters of nanofillers, which reach even a few tens of micron and consider the degree of dispersion as good.

Based on microscopic studies, it was found that the distribution of nanocomposite based on PA-6 with MMT, which is intercalated PVP, in the matrix of polypropylene is the most homogeneous in the content of modified PA-6 from 15 to 30 wt%. Such composites are characterized by a lamellar structure and a small number of inclusions of agglomerates of modified PA-6 with the smallest size (from particles of microns to 5 microns), which may indicate complete stratification of MMT. With a lower content of modified PA-6 in the structure of the composite is dominated by agglomerates of larger sizes (from 5 to 20 µm), they are distributed unevenly, and their adhesion to PP is low. The increase in the content of the modified PA-6 in the composite above 30 wt%, leads to the formation of an inhomogeneous structure with a large number of agglomerates of different sizes (from 1 to 15 µm), which will negatively affect the physical and mechanical properties of the material and heat resistance.

It was found that mixing in the melt of polypropylene with polyamide, which is modified by intercalated with PVP montmorillonite, leads to the formation of a nanocomposite with properties that differ significantly from the properties of the original polymers. Composites are characterized by significantly higher values of hardness, modulus of elasticity, and heat resistance compared to the original PP. At the same time, it was found that due to the mixing of PP with modified polyamide, the relative elongation is reduced by almost 2 times. Such results can be explained by the formation in the structure of the developed composites of inter-polymer complexes with physical bonds with the participation of MMT, which is intercalated by low molecular weight PVP. From a technological and economic point of view, as well, based on the performance characteristics of the material, the most optimal amount of modified polyamide in the mixture is from 15 to 30 wt%.

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