

THE ROLE OF POLYVINYLPIRROLIDONE IN THE FORMATION
OF NANOCOMPOSITES BASED ON ACOMPATIBLE
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Abstract. The interrelation of physico-mechanical and technological characteristics of newly created nanocomposites on the basis of polypropylene (PP)/polyamide (PA-6) mixture with PVP-modified montmorillonite has been investigated. The significant impact of modified polyamide on technological, physical and mechanical properties and heat resistance of polypropylene has been determined. It has been established that the melt flow index of the resulting composites increases by more than 2 times, compared with pure PP. The hardness, modulus of elasticity and heat resistance of composites were found to be considerably increased in comparison with pure PP due to polypropylene mixing with modified polyamide. At the same time, the percent elongation and the forced-elastic strain of composites are reduced by 2 times.

Keywords: polypropylene, polyamide, montmorillonite, polyvinylpyrrolidone, mixture, nanocomposite, modification.

1. Introduction

Recently, scientists have paid great attention to the mixtures based on polypropylene (PP) and polyamide (PA), the mixing of which allows to reduce the negative characteristics of the original polymers [1, 2]. For example, non-polar polypropylene during mixing with polar high-hydrophilic polyamide significantly reduces water absorption of the material. As a result, the effect of moisture on the mechanical and thermal properties of composites decreases. On the other hand, PP and PA mixing can extend the temperature range of material exploitation at the subzero temperatures (the brittle temperature of PP decreases) [1].

Polyvinylpyrrolidone (PVP) initiates the polymerization of hydroxyalkylene methacrylates as an active complexing agent [3-5], forms new polymeric random cross-linked matrices [6-9] and contributes to the formation of homogeneous polymer mixtures based on amphipolar polymers [10, 11]. At the same time PVP intercalates montmorillonite (MMT) [12-14], which is the basis for the formation of thermoplastic nanocomposites, in particular of those based on polyamide and polypropylene mixtures.

To obtain PP/PA homogeneous mixture, the compatibilizers of complex chemical structure, namely maleinized PP [2], are traditionally used. But in this case the probability of chemical cross-linking between PP and PA increases as a result of the anhydride and peptide groups reaction.

A method for obtaining a nanocomposite based on PP/PA-6 mixture with increased physico-mechanical characteristics, using the positive effect of PVP for obtaining a homogeneous mixture [10] and MMT for increasing the strength characteristics of the composite is proposed [15, 16]. At first nanocomposite based on PA-6 with MMT, which is intercalated with polyvinylpyrrolidone is synthesized. Then a mixture on the basis of PP and synthesized nanocomposite is obtained. It is assumed that PVP-intercalated montmorillonite will increase the strength and heat resistance of PA-6. At the same time PVP associated with PA-6 will contribute to the compatibility of polypropylene with polyamide, which eliminates the use of reactive composites of a complex chemical structure.

The aim of this work is to investigate the relation between physico-mechanical and technological characteristics of newly created nanocomposites based on PP/PA-6 mixture with PVP-modified montmorillonite and to determine the optimal composition of nanocomposite with increased physico-mechanical characteristics and heat resistance.

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2. Experimental

The following reagents were used for the experiments.

Polypropylene (PP) of Moplen HF501N brand (Lyondell Basell Industries) with the melt flow index $MFI_{230/2.16} = 9.50$ g/10 min, Vicat softening point 428 K, density $\rho^{20} = 0.900$ g/cm³ and bulk density $\rho_b = 0.53$ g/cm³.

Polyamide of PA6-210/310 brand (JSC “Grodno Azot”, Belarus) with $MFI_{230/2.16} = 19$ g/10 min, melting temperature 488 K, density $\rho^{20} = 1.12$ g/cm³, relative viscosity 2.68. Before use, PA-6 was dried under vacuum at 363 K for 2 h.

Montmorillonite-polyvinylpyrrolidone mixture (MPM) with MMT:PVP ratio of 1:5 obtained from the solution in the ultrasonic field [11, 12, 14] was used as a modifier for polyamide.

Polyvinylpyrrolidone (PVP) (LLC “AK Sintvita”, Russia) with a molecular weight of 12600±2700, softening temperature 413–433 K, $\rho^{20} = 1.19$ g/cm³ was dried before mixing under vacuum at 333–343 K for 2–3 h.

Montmorillonite 69911 (Sigma-Aldrich), untreated, with a surface area of 250 m²/g and pH = 4–5.

Nanocomposites based on polypropylene with modified polyamide mixtures and experimental samples were obtained according to the procedure described in [11].

The melt flow indices of the starting polymers and their mixtures were determined using a capillary plasticator IIRT.

The tensile strength and the relative elongation at break were determined according to the standard method [9]. 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 [17]:

$$G = \frac{E}{2(1+\nu)} \quad (1)$$

$$K = \frac{E}{3(1-2\nu)} \quad (2)$$

where E is Young modulus, MPa; G is shear modulus or modulus of rigidity, MPa; K is bulk modulus, MPa; ν is the Poisson's ratio (0.30–0.35 at $E \geq 2000$ MPa, and increases to the limit value of 0.50 with the decrease of Young modulus) [17].

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.

Heat resistance was determined according to Vicat method. The samples in the form of tablets of 11.28 mm in diameter and thickness of 3–5 mm were cut out from the blades obtained by injection molding. The tests were performed on a Hepler consistometer at the load of 50 N.

3. Results and Discussion

To determine the ability of polymeric materials to be processed and the process technological parameters it is necessary to know polymers operational characteristics. The main property is the melt flow index (MFI). The PTRs of the polypropylene based composites were determined, depending on the components ratio. The results are summarized in Table 1.

The addition of MPM-modified polyamide-6 to polypropylene increases the MFI values. With a modified polyamide content of 15 wt % and more the MFI values of the composites are higher than those of the original PP and PA-6. The addition of even 5 wt % of the modified polyamide increases MFI values by almost 2 times compared with PP, which indicates the formation of an inverse mixture in a mold with a lower viscosity. In this regard, these changes have been taken into account for the processing of composites by the injection molding. The samples obtained *via* mentioned method were used to study the physico-mechanical properties and heat resistance.

Table 1

Dependence of composites MFI on their composition

Composite	Composition, wt %	$MFI_{230/2.16}$, g/10 min
PP (pure)	100	9.50
PA-6 (pure)	100	19.0
PP:(PA-6/MPM*)	95:5	17.85
	85:15	22.92
	70:30	23.1
	50:50	25.9
	30:70	29.5

Note: * PA-6/MPM = 90/10

Polymers are characterized by a wide range of mechanical characteristics, which strongly depend on their structure, as well as the external factors: temperature, time and loading frequency/speed, pressure, type of the stressed state, preliminary heat treatment, the state of the environment, *etc.*

The peculiarity of the polymers mechanical properties is their satisfactory strength, but low hardness compared with the metal materials. Polymers are characterized by anisotropy of properties, reduced strength and development creep with a prolonged loading. However, polymers have a high fatigue resistance; their mechanical properties are more dependent on temperature than those of metals.

Polymer materials are divided into solids with a modulus of elasticity $E = 1-10$ GPa (plastics, fibers, films) and soft, high-elastic materials with a modulus of elasticity $E = 1-10$ MPa (rubber). The mechanism and patterns of destruction of both are significantly different.

To establish the destruction mechanism of the investigated samples, they were examined under conditions of uniaxial tension. Stress-strain diagram is presented in Fig. 1.

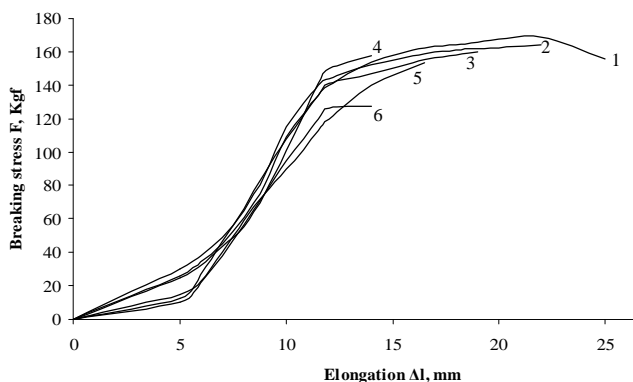


Fig. 1. Stress-strain curves of the composites depending on the composition: PP (1); PP:(PA-6/MPM) = 95:5 (2); PP:(PA-6/MPM) = 85:15 (3); PP:(PA-6/MPM) = 70:30 (4); PP:(PA-6/MPM) = 50:50 (5); PP:(PA-6/MPM) = 30:70 (6)

For PP we observe a curve (*curve 1*), typical of crystalline polymers, *i.e.*, it is possible to conventionally distinguish three sections (stages) on the curve. At the first stage the elastic strain develops which is characterized by relatively high values of the elastic modulus, small values of relative elongation and described by Hooke's law. At the moment when the stress reaches such a magnitude that strain can not develop completely inversely, in the working part of the test sample we observe the so-called "neck" – the local narrowing of the sample cross-section. In the stress-strain diagram, this is shown by a slight decrease in stress. The maximum on *curve 1* is denoted as

the yield point (42 MPa). Strain in this section of the curve is called "cold flow". Under further deformation in the working part of the sample there is a process of regrouping and orientation of the chains in amorphous and crystalline fractions in the direction of tension. As soon as the orientation of the whole working part of the sample is over, the stress begins to increase again until the destruction of the oriented area. Thus, for the stages I and III, a low cooling strain is characteristic. Strain at the stage II is retained after removal of the load, but it is not true plastic. If the sample with the "neck" is heated (*i.e.*, relaxation is accelerated), then the "neck" disappears and the sample takes the original form. This indicates that the strain at the second stage is reversed. But since a thermal motion energy is not enough to achieve such strains, and significant stresses are additionally required, they are called forced-elastic strains.

The stress-strain curves of the composites (*curves 2-6*, Fig. 1) differ from pure PP by character – the stress is constantly increasing in direct proportion to the strain and the samples destruction occurs at the stage of the neck formation at small values of relative elongation at break, which are within up to 38 % (22 mm), although the breaking stress is higher than for pure PP. This means that the strength of these composites is within the limits of recrystallization stress. The values of the yield point of the composites are significantly lower than those of pure PP (Table 2).

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, see Table 4). 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 that of pure PP, which is an additional confirmation of the formation of material with an increased rigidity.

Table 2

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

Composite	Composition, wt %	Breaking stress at tension S_t , MPa	Relative tensile elongation e , %	Yield point S_v , MPa	Brinell hardness, N/mm ²	Forced-elastic strain e_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

Table 3

Elastic-deformation properties of PP based composites with modified PA-6

Composite	Composition, wt %	E , MPa	G , MPa	K , MPa
PP	100	1230	446	1577
PA-6-210/310	100	2000	741	2222
PP:(PA-6/MPM)	30:70	2274	849	2369
	50:50	2178	813	2269
	70:30	2680	1008	2627
	85:15	2874	1080	2818
	95:5	2450	918	2475

Table 4

Vicat softening points of PP based composites with modified PA-6

Composite	Composition, wt %	T_v , K
PP	100	387
PA-6-210/310	100	478
PP:(PA-6/MPM)	95:5	405
	85:15	421
	70:30	424
	50:50	431
	30:70	434

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 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 [17].

The elastic-deformation properties of PP and its composites with modified PA-6 are summarized in Table 3. The elastic modulus of the composites with small content of PA-6 is 2–2.5 times higher than that of pure PP. 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.

The addition of MPM-modified PA-6 to the composite significantly increases the heat resistance of the composite for Vicat softening point (Table 4). At low content of modified PA-6 (5 wt %) the Vicat softening point increases by 18 K. It should be noted that the increase in the modified PA-6 content increases the Vicat softening point too.

4. Conclusions

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. The melt flow rate of the resulting nanocomposites is much higher than that of pure

PP and PA-6. These composites are also 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 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 a 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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РОЛЬ ПОЛІВІНІЛПІРОЛІДОНУ В УТВОРЕННІ НАНОКОМПЗИТУ НА ОСНОВІ АКОМПАТИБІЛЬНИХ ПОЛІКАПРОАМІДУ І ПОЛІПРОПІЛЕНУ

Анотація. Досліджено взаємозв'язок фізико-механічних та технологічних характеристик новостворених нанокмпозитів на основі суміші ПП/ПА-6 з модифікованим за допомогою ПВП монтморилонітом. Показано суттєвий вплив поліаміду, який модифікований інтеркальованим за допомогою ПВП монтморилонітом, на технологічні, фізико-механічні властивості та теплостійкість поліпропілену. Встановлено, що показник текучості розплаву одержаних композитів збільшується більше, ніж у 2 рази, у порівнянні з чистим ПП. Показано, що внаслідок змішування ПП з модифікованим поліамідом значно збільшується твердість, модуль пружності та теплостійкість композитів у порівнянні з чистим ПП. При цьому зменшуються у 2 рази відносно видовження та у 4 рази вимушено-еластична деформація композитів.

Ключові слова: поліпропілен, поліамід, монтморилоніт, полівінілпіролідон, суміш, нанокмпозит, модифікація.