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INFLUENCE OF THE SILICATE MODIFIER NATURE ON THE STRUCTURE AND PROPERTIES OF POLYCAPROAMIDE

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Abstract. The influence of the nature and amount of the nanosized polyvinylpyrrolidone silicate modifier obtained as a result of the combined sol-gel transition on the supramolecular structure, as well as physical, mechanical and thermo-physical properties of polycaproamide has been determined. The modifier has proved to significantly increase the degree of crystallinity of polymer, and thus tensile strength at break, surface hardness and thermal resistance of a composite.

Keywords: composite, nanotechnology, polycaproamide, nanostructured system, polymer matrix, sol-gel process.

1. Introduction

Nowadays creation of new composites based on polymer inorganic systems remains a challenging area of polymeric materials technologies. The underlying key to address this issue lies not in the necessity to develop new manufacturing processes but rather to physically modify available polymers using fine-dispersed additives of various nature [1, 2]. In this respect, due to the correct combination of components, the direct impact on the supramolecular structure, the use of modern technological solutions, the required complex of technological and performance characteristics of composite materials is achieved without extra energy and material losses.

Polyamides and polyamide-based composite materials are widely used in different branches of industry. Despite their exceptional operating properties, there are certain drawbacks inherent in polyamides, such as high flammability, insufficient tearing toughness as well as high-water absorption.

That is why more attention is given to make thermoplastic polymer based composites, in particular polyamides and silicate fine-dispersed fillers. Even a small amount of such a filler added to thermoplastic

elevates its physical and mechanical properties, heat resistance, flame retardancy, *etc.*

It is a well known fact that the supramolecular structure is formed due to microreological processes occurred at the stage of their reprocessing, depending considerably on the nature of components, technological parameters of mixing, interactions at the phase interface, propensity of components to crystallize, and the presence of other substances, *etc.* [2, 3]. Therefore, determination of morphological peculiarities of the examined composites may identify factors that influence the technological compatibility of these constituents in the materials specified, as well as predict their technological and performance characteristics.

2. Experimental

This article presents a PA-6 polymer-silicate modifier as a fine-dispersed polyvinylpyrrolidone silicate composite, obtained as a result of the sol-gel transition of a sodium liquid glass (Na-LG) solution, which has been previously modified by polyvinylpyrrolidone (PVP) under the influence of hydrochloric acid (the size of primary particles is 10 ± 2 nm, their agglomerates are of 170–350 nm and the PVP content in the modifier equals to 4.8–10 wt %) [4–6]. In addition, to determine the method of obtaining the modifier and the influence of its nature on properties and structure of PA-6, precipitated Na-LG, solid-state PVP along with precipitated Na-LG have been added separately to polymer samples.

Modified thermoplastic composites have been obtained in the following way. Bulk components in the appropriate ratio were previously mixed in the drum mixer (granulated thermoplastic PVP was powdered with silicate composite) during 15–20 min. Being obtained in such a way, the mechanical mixture underwent drying for

8–10 h in the air vacuum dryer of 2B-131 type at 363 K (residual pressure for PA-6 composites – 2.5 kPa).

In order to conduct researches, modified thermoplastics have been prepared by direct mixing of components in the laboratory extruder Cellier, equipped with a screw conveyor of 700 mm length and 25 mm diameter, with subsequent extrusion, grinding and cooling of the rod-like material. Screw conveyor speed of the extruder is 15–150 rpm. The temperature inherent in extruder zones for PA-6 based composites (PA 6-120/321, Ukrainian standards 6-06-C9-93) is in the range of 453–463 K, 473–483 K and 493–508 K; the plastication time corresponds to 30–35 sec. The obtained extrudate has been grinded with the toothed roll crusher.

X-ray diffraction analyses have been carried out using a DRON-4-07 diffractometer equipped with a lamp, including a copper anode and a nickel filter, to determine the method of obtaining the modifier, as well as the influence of its nature on the supramolecular structure of PA-6.

The Q-1500 D derivatograph of the Pauli-Paulik-Erdey system was utilized for thermal analysis of samples under ambient atmospheric conditions in the dynamic mode at heating rate of 10 °/min within the temperature range of 293–773 K. The mass of samples was 400 mg, sensitivity ranked along the thermogravimetric analysis (TGA) scale constituted 50 mg, and along the differential-thermal analysis (DTA) scale – 250 μ V. Al_2O_3 was used as a reference substance.

3. Results and Discussion

The results obtained by applying X-ray diffraction analyses are presented in Fig. 1. As one can see, diffraction reflexes are reflected from the crystalline phases of PA-6 with its composites observed in the range of $2\theta = 18\text{--}28^\circ$ diffraction angle. Moreover, it should be noted that diffraction patterns of PA-6 and PA-6 based composites are similar in general view. Reflexes reflected from the crystalline phases of unmodified PA-6 are attributed to diffraction angles, such as $2\theta = 20.1; 21.4$ and 23.50 , and the maximum of the amorphous phase corresponds to $2\theta = 20.7^\circ$.

The character of experimental curves of modified PA-6 significantly depends on the modifier nature. The intensity of reflexes of $(002)\alpha$ and $(200)\alpha$ planes reflected from the crystalline phases of modified samples unlike reflexes of these planes for unmodified PA-6 is subjected to changes: reflexes of both $(200)\alpha$ and $(002)\alpha$ planes tend to increase, while the reflex of the $(002)\alpha$ plane is stronger than that of $(200)\alpha$. This apparently results from the redistribution of PA-6 intermolecular interactions affected by particles of the modifier that leads to changes in the

arrangements of polymer chains during crystallization.

The presence of polar silicate particles and PVP macromolecules enables the antiparallel packing of PA-6 chains. Due to a large volume of PVP macromolecules with a helical (spiral-shaped) conformation, the size of crystallites changes considerably – γ -phase crystalline formations in particular. Diffraction angles of reflected beams are observed to shift, whereas reflex intensity of hexagonal packing of polycapramide chains remains almost constant [7, 8].

To prove these considerations, the following X-ray diffraction parameters of modified materials were detected using WAXSFIT [9] software package: degree of crystallinity (S_c), average size of crystallites (L_{hkl}) and interplanar spacings (d_{hkl}). Depending on the nature of the PVP silicate modifier, the results obtained here are listed in Table 1.

Addition of the PVP silicate modifier to PA-6 causes a significant increase in its crystallinity degree. We assume that an increase in the crystallinity degree of modified materials in comparison to unmodified PA-6 can be explained by the fact that interactions between particles of a fine-dispersed modifier and certain groups as well as PA-6 macromolecules during a viscous flow, followed by further cooling of the melt, influence supramolecular formations to such an extent so that those particles themselves become additional crystallization germs. Crystallites also undergo changes in size. In particular, an average crystallite size is observed to reduce when precipitated Na-LG, especially co-precipitated Na-LG and PVP are added to PA-6. At the same time the influence of the modifier based on the physical mixture of Na-LG and PVP induces crystallites with increased sizes. The interplanar spacings almost do not change.

During formation of the supramolecular structure of the composite, it is worth mentioning that the macrochain geometry, various types of packing of neighbouring chains [6, 8], and in some cases the occurrence of helical PVP macromolecules affects the creation of hydrogen bonds.

PA-6 may exhibit polymorphic transition from a triclinic to hexagonal shape during the crystallization process. This in turn can induce a higher rotational freedom of a macrochain and increase the value of entropy for crystalline structures. Compared with PA-6 macromolecules, the existence of PVP macromolecules having a larger volume leads to an increased rotational freedom of the chain and thus enables the hexagonal packing of polycapramide macromolecules. These factors change the size of γ -phase hexagonal crystalline structures of the composites under examination.

Changes in supramolecular structures of modified materials appear to influence thermo-physical properties thereof.

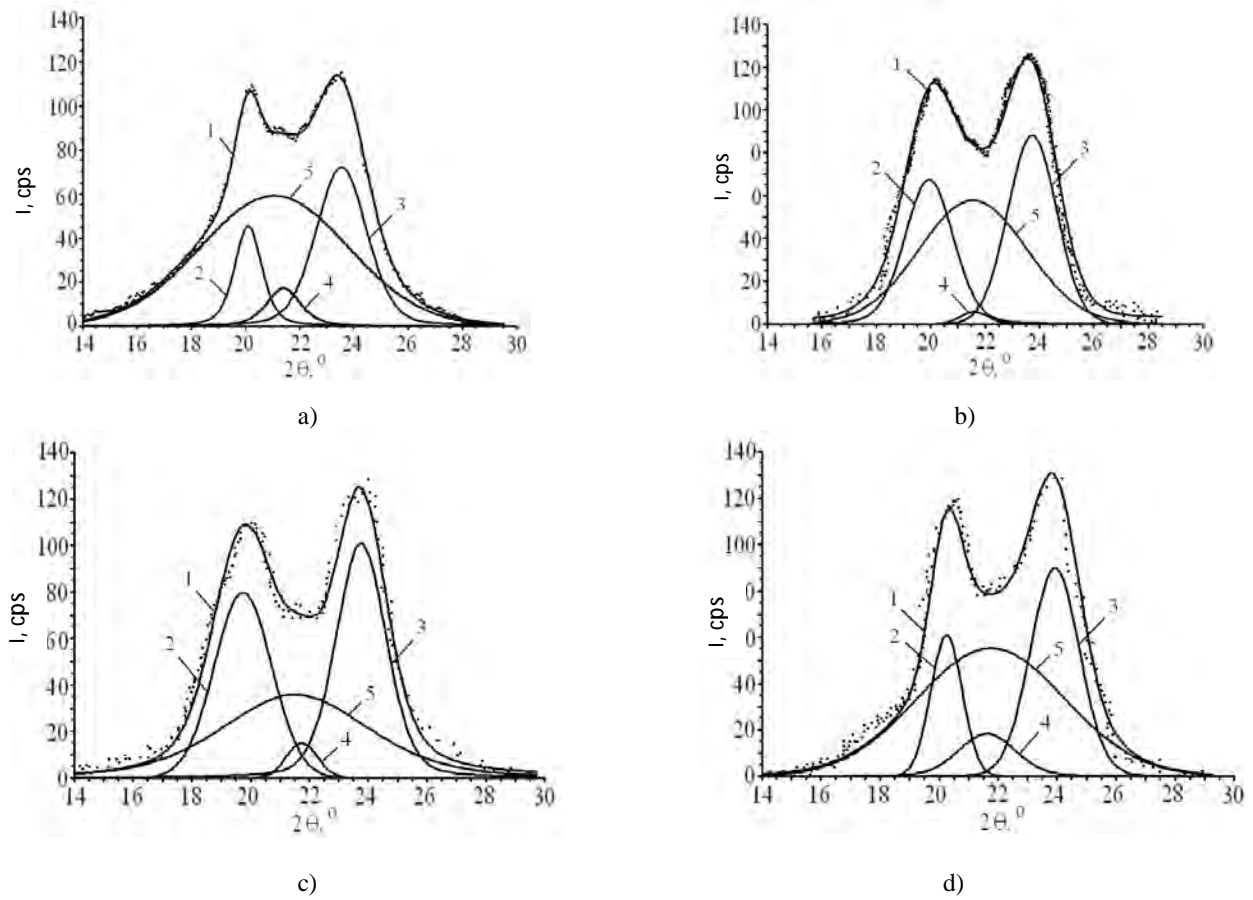


Fig. 1. Diagram of X-ray scattering intensity of modified polycapraamide: approximating diffraction curve (1); optimized curves of reflex intensity of $(200)\alpha$ - (2), $(002)\alpha$ - (3), γ - planes (4) and amorphous phase (5). Modifier: without a modifier (a); precipitated Na-LG (b); co-precipitated Na-LG and PVP (c) and physical mixture of precipitated Na-LG and PVP (d). Modifier content is 5 wt %

Table 1

Research results of X-ray diffraction analysis for modified PA-6

| Modifier | $S_c, \%$ | Plane | $2\theta, ^\circ$ | $L_{hkl}, \text{\AA}$ | $d_{hkl}, \text{\AA}$ |
|--|-----------|----------------|-------------------|-----------------------|-----------------------|
| Without a modifier | 41.1 | $(200) \alpha$ | 20.1 | 68.2 | 4.4 |
| | | $(200) \gamma$ | 21.4 | 53.7 | 4.2 |
| | | $(002) \alpha$ | 23.5 | 38.3 | 3.8 |
| Precipitated Na-LG | 55.9 | $(200) \alpha$ | 19.9 | 40.7 | 4.5 |
| | | $(200) \gamma$ | 21.6 | 72.7 | 4.1 |
| | | $(002) \alpha$ | 23.7 | 41.6 | 3.7 |
| Coprecipitated Na-LG and PVP | 64.9 | $(200) \alpha$ | 19.7 | 37.9 | 4.5 |
| | | $(200) \gamma$ | 21.7 | 70.9 | 4.1 |
| | | $(002) \alpha$ | 23.8 | 42.1 | 3.7 |
| Physical mixture of PVP and precipitated Na-LG | 48.2 | $(200) \alpha$ | 20.3 | 69.4 | 4.4 |
| | | $(200) \gamma$ | 21.6 | 37.5 | 4.1 |
| | | $(002) \alpha$ | 23.9 | 44.5 | 3.7 |

In an attempt to prove this fact, the derivatographic analysis was carried out. The obtained results are shown in Fig. 2.

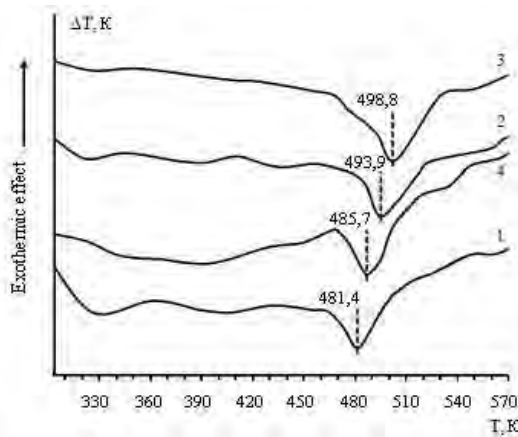


Fig. 2. DTA results for modified PA-6 composites. Modifier: without a modifier (1); precipitated Na-LG (2); co-precipitated Na-LG and PVP (3) and physical mixture of precipitated Na-LG and PVP (4). Modifier content is 5 wt %

Based on the DTA data obtained here, it may be concluded that samples of unmodified PA-6 show a lower thermal resistance as compared to the modified samples. It was determined that maximums of endothermic effects which correspond to the melting process of the modified samples tend to shift into the range of higher temperatures (481–499 K). PA-6, which is modified by the co-precipitated Na-LG and PVP, shows the highest values of heat and thermal resistance (melting and destruction temperature – 498.8 and 565.3 K, respectively), whereas PA-6 without a modifier falls to the lowest values – 481.4 and 550.1 K, respectively.

Depending on the nature of a modifying additive, PA-6 based materials exhibit the shift of endothermic peaks to the range of higher temperatures by the following procedure: without a modifier < physical mixture of PVP and Na-LG < precipitated Na-LG < co-precipitated PVP and Na-LG. This may account for the formation mechanism of orderly structures in the presence of the modifier.

DTA results for samples of modified PA-6 composites are in good agreement with data on heat resistance suggested by Wick (T_v) (Table 2).

The addition of the modifier to the PA-6 structure is seen to induce an increase in heat resistance proposed by Wick. The maximum value corresponds to composites containing a modifier on the basis of the co-precipitated Na-LG and PVP, the minimum to – PA-6. This is probably due to the fact that the PVP silicate modifier based on the co-precipitated Na-LG and PVP has a considerable impact on PA-6 supramolecular structures as

a result of mutual interlocking of Na-LG and PVP polar groups. On the other hand, the modifier incorporating solid-state precipitated Na-LG and PVP slightly increases the T_v in comparison with pure PA-6. X-ray graphic results prove this fact.

Table 2

Properties of modified PA-6 depending on the modifier origin

| Modifier | σ_b , MPa | ε_s , % | F , MPa | F_T , MPa | T_v , K |
|--|------------------|---------------------|-----------|-------------|-----------|
| Without a modifier | 53.4 | 40 | 290.2 | 296.9 | 475 |
| Precipitated Na-LG | 63.9 | 17 | 313.5 | 317.7 | 483 |
| Coprecipitated Na-LG and PVP | 75.3 | 23 | 330.4 | 339.8 | 491 |
| Physical mixture of precipitated Na-LG and PVP | 59.1 | 15 | 291.2 | 299.0 | 477 |

It is expected that changes in the PA-6 supramolecular structures coupled with modifiers will also affect their physical and mechanical properties. That is why physical and mechanical properties of modified PA-6, such as tensile strength at break (σ_b), relative elongation at stretching (ε_s), surface hardness before (F) and after (F_T) thermal treatment have been examined (Table 2).

The value of tensile strength at break is seen to increase significantly when any of the specified PA-6 modifiers is added. The maximum value of σ_b is observed with the use of co-precipitated Na-LG and PVP as a modifier. In our opinion, this may account for the creation of favourable conditions for PCM crystallization in the presence of modifiers which obviously might function as additional crystallization germs to which attention was previously drawn. Moreover, changes in arrangements of thermoplastics coupled with modifiers also influence the value of surface hardness of composites. This value increases with the increased degree of cohesion of PVP and silicate skeleton as well as after the material has been exposed to heat treatment. Generally, the Na-LG-based precipitated modifier exerts a more significant influence on σ_b and ε_s , than a physical mixture of precipitated Na-LG and PVP does. At the same time, the higher degree of cohesion between PVP and the modifier, the more increased values of these indexes are.

4. Conclusions

Based on the experiments conducted here, the technological compatibility of PA-6 with the PVP silicate modifier in the viscous-liquid state resulting from the even distribution of PVP macromolecules within the silicate carcass and intermolecular interactions between

functionally active groups of PVP and thermoplastic is found to exist. It was observed that the PVP silicate modifier in the amount of 4–6 wt % increases the degree of crystallinity by the factor of 1.3–1.6, tensile strength at break – by 40–70 %, whereas surface hardness and heat resistance according to Wick – by 10–20 %.

It was detected that a PCM supramolecular structure is significantly influenced by the nature of the modifier. Changes in reflexes of crystallite phases for PA-6 are observed with the addition of the modifier. An increase in a degree of crystallinity is demonstrated by the fact that fine-dispersed particles of the PVP silicate modifier act as additional centers of the crystallization process. The maximum values of S_c appear to occur when the co-precipitated Na-LG and PVP-based modifier is used, followed by almost no changes in the size of crystallites. Maximums of melting endothermic effects of modified materials are shifted to the range of higher temperatures.

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ВПЛИВ ПРИРОДИ СИЛКАТНОГО МОДИФІКАТОРА НА СТРУКТУРУ І ВЛАСТИВОСТІ ПОЛІКАПРОАМІДУ

Анотація. Встановлено вплив природи і кількості нанорозмірного полівінілпіролідон-силкатного модифікатора, одержаного внаслідок сумісного золь-гель переходу, на характер надмолекулярних структур, фізико-механічні і теплофізичні властивості полікапроаміду. Показано, що модифікатор значно підвищує ступінь кристалічності полімеру і, як наслідок, міцність під час розривання, поверхневу твердість і теплостійкість композиту.

Ключові слова: композит, нанотехнології, полікапроамід, наноструктуровані системи, полімерні матриці, золь-гель процес.