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# INFLUENCE OF METAL-CONTAINING POLYMER-SILICATE FILLER ON THE TECHNOLOGICAL PROPERTIES OF POLYPROPYLENE

**The influence of Ni-containing polymer-silicate filler on the technological properties of polypropylene is presented. It was found that the introduction of silicate fillers modified by polyvinyl alcohol change the flow patterns of polypropylene melts, in particular viscosity increases and anomalous viscosity shifts. The change of thermomechanical curves of polypropylene under the action of modified silicate fillers is shown. It is noted that composite materials based on polypropylene and modified silicate filler are characterized by reduced melt flow index, reduced values of technological shrinkage and slightly increased water absorption.**

**Key words: modifier, polyvinyl alcohol, polypropylene, composite.**

## Introduction

The ability of polymers and polymer composite materials (PCM) to process, the choice of the optimal method of their processing and the calculation of process parameters are determined, above all, by their technological properties [1]. The choice of processing method and optimization of technological parameters of the process is carried out taking into account such characteristics of raw materials as the viscosity and melt flow index, particle size, moisture and volatile content, flowability, bulk density, technological shrinkage, etc. Accurate information on the technological performance of the material also allows you to adjust the modes of its processing, calculate the size of the forms, provide high productivity and reduce the amount of waste of raw materials.

One of the most important properties of polymeric materials, which largely determine their processing capacity, is the rheological characteristics. They make it possible to predict the morphological features of structural structures in polymer composites both in the melt and in the solid state, which, in turn, will affect the performance properties of products based on them. Understanding the essence of the rheological properties of composite materials is very important for establishing the optimal conditions for processing and selection of equipment, control of mechanical and physical properties of products.

Polymeric composite materials largely satisfy the high demands of consumers and successfully compete with various materials of structural and thermotechnical applications. At present, thermoplastic polymers with fillers of various nature, in particular silicates are widely used for their production, since on their basis it is possible to create materials with a complex of new and necessary properties at a low cost [2, 3].

It was established [4, 5, 6] that the physical-mechanical, thermophysical and rheological properties of composite materials containing silicate filler are largely determined by both the nature of the filler itself and its technological compatibility with the polymeric matrix. To increase the technological compatibility with the polymer matrix and directional control of the technological and operational properties of the polymer composite materials, silicate fillers are pre-modified with functionally active high molecular weight compounds [7]. Effective is the developed physicochemical method [8], based on the coprecipitation of sodium liquid glass and functional surface-active polymer modifiers, in particular polyvinyl alcohol (PVA) under the action of metal salts solutions.

However, the mechanism of the specific effect of such fillers and their modifiers on the technological properties of polymers has not been fully investigated, which impedes the widespread adoption of such materials in various industries. At the same time, polypropylene-based composites have become widely used. These materials are characterized by excellent physico-mechanical properties, which makes them indispensable structural materials in many industries [1, 3].

## Materials and methods of research

For the preparation of thermoplastic composites based on polypropylene, Ni-containing modified by polyvinyl alcohol polymer-silicate filler (Ni-SF) was used, which was obtained by co-precipitation of polyvinyl alcohol and sodium liquid glass from aqueous solutions ounder the action of nickel chloride and polypropylene Moplen HF501N (Netherlands).

The components were pre-mixed in the desired ratio in a drum type mixer (powdering a granular thermoplastic with a nucleation agent) for 15–20 minutes. After obtaining the mechanical blend, it was dried for 8–10 h in an air vacuum dryer of 2B-131 type at 363 K. Further the homogenization of the blend were conducted via mixing in a viscous state of components on a Cellier extruder, which is equipped with a screw have length 700 mm and diameter 25 mm. The rotation velocity of the extruder screw is 10–15 rpm. The temperature of the extruder's zones – 443–453, 463–473, 483–493 K. The obtained extrudate was crushed on a crusher gear type. The production of standard samples of granular material for research was conducted by injection molding on a Krauss Maffei KM 110 – 520 C2 molding machine. The filler content was 10 % wt.

The formation of the flow curves of melting of polymer composites was carried out on a MFI apparatus "IIRT-M" using capillaries in length 8 and 25 mm and a diameter of 2,095 ± 0,005 mm.

Technological shrinkage was determined by comparing the size of the molded sample-blade with the size of the form according to ISO 294-4 for 293 K. Samples were tested no earlier than 16 hours. from the moment of their production. Tests were carried out on at least five specimens obtained sequentially in one well. The dimensions of the specimens were measured with a caliper up to 0.01 mm. Water absorption in cold water was performed according to ISO 62:2008.

## Research results and their discussion

In general, the rheological properties of polymer composites depend substantially on the structure of the filler particles (the so-called active filler) in the polymeric environment and their interaction with each other through thermoplastic macromolecules adsorbed on the surface of the particles [9]. The particles of the filler are the centers of formation of a continuous spatial grid, which is formed under the influence of their force fields. The fixation of thermoplastic macromolecules on the surface of the filler particles leads to the formation of an adsorption shell around such particles with high physico-mechanical properties. In this case, modification of the filler leads to the formation of a stronger spatial structural grid, due to the increased technological compatibility of the components.

The dependence of the shear stress and the effective viscosity on the shear rate of the composites based on PP depending on the nature of the filler and the temperature is shown in Fig. 1 and Fig. 2.
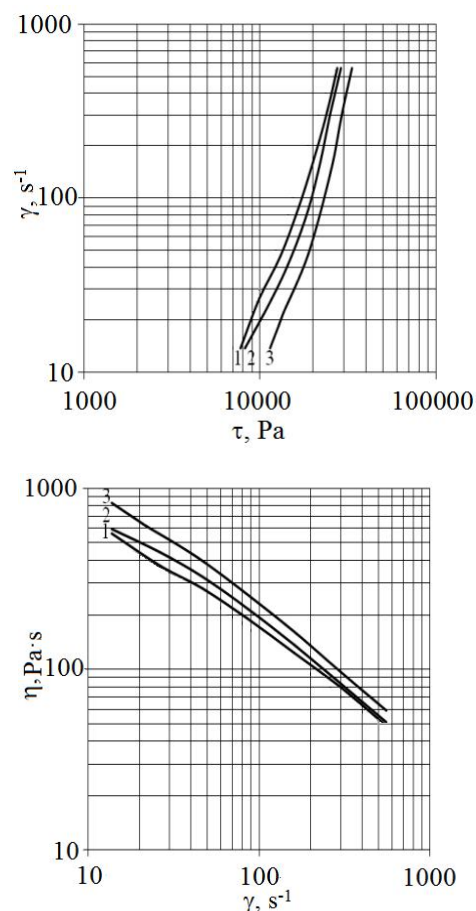


*Fig. 1. The flow curves of composite materials based on PP at 473 K. Filler: 1 – without filler; 2 – unmodified Ni-SF; 3 – modified Ni-SF by PVA*

The rheological properties of the filled materials substantially depend on the nature of the filler. At the same time, under the influence of the filler in the melt of the thermoplastic, a specific supramolecular structure formed by the macromolecules of the polymer and the particles of the filler is formed. Therefore, the nature of all curves in the Newtonian region of the flow is similar to each other. This, in our opinion, suggests that the

process of flow occurs with the particles of the filler, which are covered with adsorption layer of the polymer, resulting in an effective increase in the volume of the dispersed phase. During the flow, such an adsorption layer is capable of being moved as a unit together with the particles of the filler.

At the same time, the introduction of a finely dispersed filler into the polymer results in an increase in the effective viscosity values compared to the incomplete thermoplastic (curves 2, 3 – Fig. 1 and 2 – Fig. 2) and obviously does not significantly affect the temperature coefficient in the viscosity in the Newtonian region of the flow. The mechanism of the flow of such materials is similar between them, and therefore, in our opinion, the gap of bonds between the particles of the filler and the polymer matrix is not observed.

In the case of polypropylene composites (Fig. 1), the introduction of modified Ni-SF by PVA, compared with pure PP, contributes to the displacement of anomalous viscosity in the region of lower shear rate.
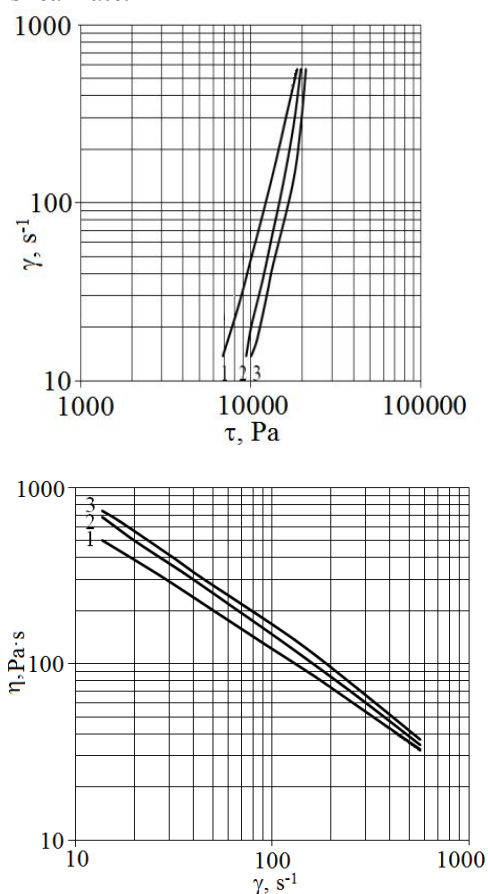
The difference in the appearance of curves in the non-Newtonian region, depending on the nature of the filler, can also be explained by the fact that with the growth of the shear rate, the hydrogen bonds between the functional groups are destroyed, in the first place, the density of the fluctuation grid decreases, which obviously leads to a decrease effective viscosity of PCM. In addition, due to the structure of PVA-silicate particles, the strength of hydrogen bonds formed during the introduction of modified Ni-SF by PVA into thermoplastics will be greater compared to thermoplastics filled with unmodified Ni-SF.

An important characteristic of PCMs is the change in their properties under the action of temperature. Accurate information about the temperature transitions of polymeric materials, in particular the glass transition temperature and the heating temperature, allows you to set the required temperature interval at which the material has sufficient mechanical strength and can be used for practical purposes. To study molecular mobility and relaxation processes in polymers, the thermomechanical method is most often used. The thermomechanical properties of polymers and composite materials based on them are closely related to the operational and technological properties and make it possible to estimate both the temperature limits of the material operation and the temperature intervals of the physical states of the polymers necessary for the choice of rational parameters for their processing and operation. They can be conveniently described using a thermomechanical curve characterizing the deformation that develops over time at different temperatures under specified static stress. The results of thermomechanical analysis of the developed polymer composites are shown in Fig. 3.
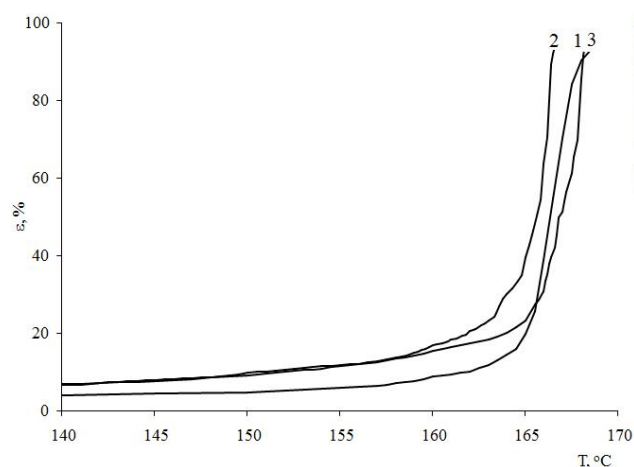




*Fig. 2. The flow curves of composite materials based on PP at 503 K. Filler: 1 – without filler; 2 – unmodified Ni-SF; 3 – modified Ni-SF by PVA*



*Fig. 3. Thermomechanical curves of composites based on PP. Filler: 1 – without filler; 2 – unmodified Ni-SF; 3 – modified Ni-SF by PVA*

The thermomechanical curves of the composites, regardless of the introduction of Ni-containing polymer-silicate filler, are characteristic of crystalline polymers. However, the impact of the filler should be noted. The addition of unmodified Ni-SF changes the slope of the curve when moving to a viscous state. At the same time, the use of modified filler contributes to the reduction of this angle and the shift of the heating temperature to a region of higher temperatures, which is obviously due to the presence of PVA, which is actively involved in the redistribution of intermolecular interactions between the components of the system. It should be noted that the melting point of PP is the highest for composites with modified filler.

Studies were carried out on the establishment of MFI PP depending on filler nature. It was found that the MFI of the obtained materials is somewhat reduced by the introduction of the filler. The smallest reduction is characteristic of composites with unmodified filler.
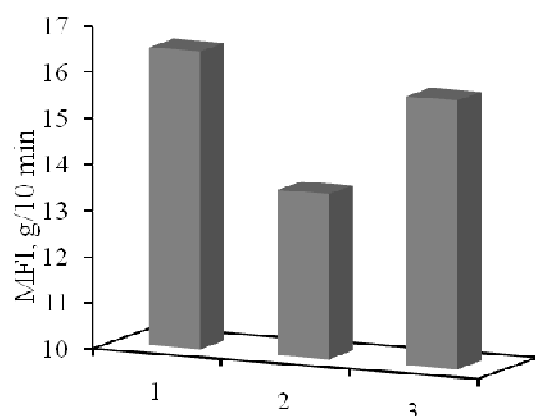


*Fig. 4. The melt flow index of composites based on PP. Filler: 1 – without filler; 2 – unmodified Ni-SF; 3 – modified Ni-SF by PVA*

Apparently, the filler particles interfere with the flow of the polypropylene melt, including by linking the functional groups of the silicate particles (silanol, silandiol and siloxane) with the polypropylene macromolecules.

From the point of view of polymer processing, it is necessary to establish such technological properties of filled composites as technological shrinkage and shrinkage anisotropy, as they are important indicators that determine the accuracy of PCM products and are used to design molding elements of equipment during molding of polymeric materials.

In addition, the technological shrinkage will depend on the structural state of the melt and the nature of the formation of supramolecular structure in the transition from viscous to vitreous state. The values of the technological shrinkage along the flow before $Sh_{\parallel}$ and after thermal treatment $Sh_{\parallel}^{T}$ and perpendicular to the direction of flow respectively $Sh_{\perp}$ and $Sh_{\perp}^{T}$, as well as the anisotropy of shrinkage (a) for PP-based composites are given in Table 1.

As we can see, the introduction of unmodified filler in polypropylene generally reduces the shrinkage value. The established patterns are related to the specificity of intermolecular interactions between the polypropylene macromolecules and the filler and modifier particles, which are additionally influenced by the shear flow. In this case, additional heat treatment contributes to the increasing value of shrinkage of the developed composites, with its greatest impact manifested for unfilled materials.

*Table 1*

**The value of technological shrinkage of composites based on PP Moplen**

| Filler | $Sh_{\parallel}$, % | $Sh_{\perp}$, % | a | $Sh_{\parallel}^{T}$, % | $Sh_{\perp}^{T}$, % | $a^{T}$ |
|---|---|---|---|---|---|---|
| Without filler | 2.56 | 1.76 | 1.45 | 2.73 | 2.03 | 1.34 |
| Unmodified Ni-SF | 2.20 | 1.95 | 1.13 | 2.45 | 2.42 | 1.01 |
| Modified Ni-SF by PVA | 2.48 | 1.93 | 1.28 | 2.83 | 1.60 | 1.77 |

*$Sh_{\parallel}$ – technological shrinkage along the flow before thermal treatment; $Sh_{\parallel}^{T}$ – technological shrinkage along the flow after thermal treatment; $Sh_{\perp}$ – technological shrinkageperpendicular to the direction of flow before thermal treatment; $Sh_{\perp}^{T}$ – technological shrinkageperpendicular to the direction of flow after thermal treatment; a – the anisotropy of shrinkage.*

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Among the technological properties, an important characteristic of PCM is water absorption. During transport and storage, they are capable of absorbing a significant amount of moisture, which, when processed in a viscous state, can lead to partial degradation due to hydrolysis and degradation of performance properties.

Studies have been conducted to establish the water absorption of the developed composites. The results of the studies are shown in Fig. 5.
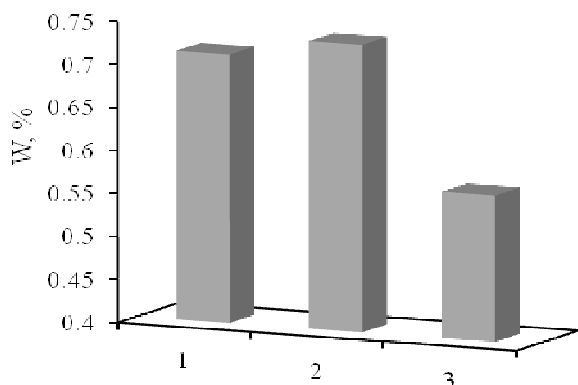


*Fig. 5. Value of equilibrium water absorption of W composites based on PP:*
*Filler: 1 – without filler; 2 – unmodified Ni-SF;*
*3 – modified Ni-SF by PVA*

## Conclusions

Melts of polypropylene materials with unmodified filler have been found to exhibit a higher sensitivity to shear stresses during the flow, as evidenced by the greater influence of shear stress values on effective viscosity. Fillers that aremodified by PVA increase the viscosity of the PP, but the nature of the viscosity of the shear stress compared to unfilled PP does not change. It is established that the introduction of the modified filler helps to shift the anomalous viscosity of the melt of the composite into the region of lower shear stresses.

It was found that the MFI of the PP decreases with the introduction of Ni-containing silicate filler, with the lowest value observed with the introduction of unmodified filler.

It is established that the introduction of unmodified filler in PP reduces the value of technological shrinkage by 9–14 % and slightly increases the water absorption. At the same time, additional heat treatment leads to an increase in the shrinkage value of the developed composites, with its greatest impact being shown for the unfilled materials.

## Reference

1. Bykov E. A., Dehtyarev V. V. (2006). Modern fillers Questions of chemistry and chemical engineering an important factor in improving the competitiveness of composites. *Plastic masses, 1,* 32–36.

2. Moumita Kotal, Anil K. Bhowmick (2015). Polymer nanocomposites from modified clays: Recent advances and challenges. *Progress in Polymer Science. 51* (13), 1127–1187. https://doi.org/10.1016/j.progpolymsci.2015.10.001

3. García M. (2004). *Polymer – inorganic nanocomposites, influence of colloidal silica.* Thesis university of Twente.

4. Yiu-Wing Mai, Zhong-Zhen Yu, (2006). *Polymer Nanocomposites,* Cambridge: Woodhead Publishing Limited.

5. Rakesh K. Gupta, Elliot Kennel, Kwang-Jea Kim (2009) *Polymer Nanocomposites Handbook.* Cambridge: CRC Press.

6. Mittal V. (2009) *Polymer Nanocomposites: Advances in Filler Surface Modification Technique.* New York: Nova Science Publ.

7. Dibyendu Mondal, Md. Masud R. Mollick, Biplab Bhowmick, Dipanwita Maity, Mrinal K. Bain, Dipak Rana, Asis Mukhopadhyay, Kausik Dana, Dipankar Chattopadhyay (2013) Effect of poly(vinylpyrrolidone) on the morphology and physical properties of poly(vinyl alcohol)/sodium montmorillonite nanocomposite films, *Progress in Natural Science: Materials International*, 23 (6), 579–587.

8. Kerber M. L., Vinogradov V. M., Golovkin G. S., Berlina A.A. (Eds.) (2008) *Polimernyye kompozitsionnyye materialy* // SP.: Professiya.

9.Voronin E. F., Nosach L. V., Pahlov E. M. (2007). Peculiarities of adsorption interactions on the surface of the aggregate nanosilica. *Physical chemistry of nanomaterials and supramolecular structures*, 1, 264-285.

10. Masyuk A. S., Levytskyi V. Ye. (2014). Regularities of obtaining of polymer-silicate composites from water-soluble silicates and polymers. *Eastern-European Journal of Enterprise Technologies*, 6/6(72), 29–33.

11. Levytskyi, V. Ye., Masyuk, A. S., Suberlyak, O. V. (2017) Preparation and properties of polymer-silicate composites based on hydrophilic polymers // *Voprosy Khimii i Khimicheskoi Tekhnologii*. 6, 68–74.

12. Bishop E. (1976). *Indicators*. Moskow "Myr".

13. Levytskyi V., Masyuk A., Katruk D. and Bratychak M. (2016) Regularities of obtaining, morphology and properties of metal-containing polymer-silicate materials and polyester composites on their basis *Chemistry & Chemical technology*. 1, 35–40.

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## ВПЛИВ НІКЕЛЬ-ВМІСНОГО ПОЛІМЕР-СИЛІКАТНОГО НАПОВНЮВАЧА НА ТЕХНОЛОГІЧНІ ВЛАСТИВОСТІ ПОЛІПРОПІЛЕНУ

Виявлено вплив Ni-вмісного полімер-силікатного наповнювача на технологічні властивості поліпропілену. Встановлено, що введення силікатних наповнювачів, які модифіковані полівініловим спиртом, змінює характер кривих течії розплавів поліпропілену, зокрема спостерігається підвищення в'язкості та зміщення області аномальної в'язкості. Виявлено зміну термомеханічних кривих поліпропілену під дією модифікованих силікатних наповнювачів. Зазначено, що композиційні матеріали на основі поліпропілену і модифікованого силікатного наповнювача характеризуються зменшеним показником текучості розплаву, зменшеними значеннями технологічної усадки та дещо збільшеним водопоглинанням.

Ключові слова: модифікатор, полівініловий спирт, поліпропілен, композит.