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RHEOLOGICAL PROPERTIES OF MOLTEN MIXTURES OF POLYPROPYLENE/COPOLYAMIDE/CARBON NANOTUBES

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Effect of carbon nanotubes additives on the rheological properties of polypropylene/copolyamide mixture melts has been investigated. The increase in viscosity and elasticity as well as decrease in the capability of the three-component mixture melts of being longitudinally deformed have been determined. These effects are explained by filling under influence of nanosized additives. It has been shown that the systems with nanosized filler are processed on standard equipments with the use of technological parameters applied to initial mixture.

INTRODUCTION

One of the most promising directions of development of modern science and technology is that of nanotechnologies related to obtaining and use of objects with dimensions measured in nanometers. Today the focus is on carbon nanotubes (CNT) which have very wide using and in the near future may become one of the most important industrial products. Carbon nanotubes are diverse in structure and their properties and form a very wide class of nanomaterials. For example, single-wall and multi-wall CNT with a cylindrical arrangement of carbon layers, each layer being formed by coagulation seamless graphene plane with carbon atoms in the corners connecting hexagons. In cross section, they can be not only round but also oval, flattened, or polyhedral [1]. CNTs are characterized by extreme values of mechanical and transport properties, and their bulk density is less than 2 g/dm^3. This causes widespread use of single- and double-wall carbon nanotubes as fillers for polymers and for design of nanocomposites. The introduction of CNT enhances the electrical conductivity, thermal conductivity, heat resistance, temperature of ignition, and improvement of mechanical characteristics, changes in the structure of the polymer, increasing in the degree of crystallinity, and increase the glass transition temperature. Nanocomposites also acquire new functional properties - the cap ability to remove static charges dissipate and absorb microwave and laser radiation, enhance electroluminescence etc. [1, 2]. A significant effect is achieved also for synthetic fibers filled with nanotubes. Depending on the geometrical configuration of CNT the modified fibers obtained have a set of useful unforeseen properties [3]. Using semiconductor properties of CNT, it is possible to create an antistatic monofilament [4].

When the polymer mixture melt flows from a wide reservoir in to a narrow one, the dispersed face polymer forms a great number of streams oriented in the direction of flowing. This opens a new way of obtaining ultrathin synthetic fibers (microfibers). The fibers can be obtained from the composite extrudate by extraction of the matrix polymer with suitable solvent [5]. Introduction of nanosized silica into the polymer mixture melts got to obtaining of polypropylene microfiber with 3–4 times increased specific surface and of filter materials which combine high cleaning efficiency and productivity [6].

The aim of this research is examination of the effect of additives of CNT on the rheological properties of polypropylene/copolyamide mixture melts.

EXPERIMENTAL

Objects of research – polypropylene/copolyamide mixture melts (PP/CPA) of the 30/70 wt. % with an addition of CNT. Initial polymers are industrial products - polypropylene

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grade 21060 (TU 05-1756-78) produced by Lysychansk Chemical Plant (Ukraine); copolyamide – copolymer ε-caprolactam and AG salt (salt of hexamethylenediamine and adipic acid) in 50:50 ratio, grade PA-6/66 (OST 6-05-438-78) produced by Sverdlovsk Chemical Plant (Russia). The characteristics of the initial PP and CPA (viscosity (η), magnitude of swelling (B), regime of flow (n)) are listed in Table 1.

Table 1. Characteristics of the initial polymers

Polymer	T_m, ºC	η^*, Pa·s	n^*	B^*
PP	169	300	1.8	2.1
CPA	170	1230	1.2	1.4

$^* T = 190$ ºC; $\tau = 5.7 \cdot 10^4$ Pa

To modify the properties of polypropylene microfibers multiwall CNTs were chosen. Their characteristics are as follows: external diameter of the nanotubes 10–20 nm, temperature of 5 % weight loss after elimination of mineral impurities – 575 ºC, specific surface area – 340 m²/g [7]. The concentration of CNT was 0.05, 0.1, 0.5, 1.0, and 5.0 wt. % by weight of polypropylene.

It is known that the excess surface energy leads to the agglomeration of nanoparticles and their aggregation, and therefore an important task in creating nanocomposites is necessary to ensure uniform distribution of the filler in the polymer matrix [2]. Therefore, mixing and blending of polymers were carried out using a LGP-25 combined screw-disk extruder having significant tensile stresses where between mobile and immobile disks which improve the uniformity of mixing of polymer with additives. To maximize the content of CNT in the fiber-forming component (PP) and to distribute homogeneously nanotubes in the mixture, they are previously introduced into the melt of PP, and then obtained pellets of PP/CNT are mixed with CPA. The viscosity (η) of melts of PP, CPA, and their mixtures were measured by capillary viscosimetry a using MV-2 microviscometer in the range of shear stress $\tau = (0.1 - 5.7) \cdot 10^4$ Pa, at the temperatures (T) of 190, 210, and 220 ºC. Elastic properties were estimated for the magnitude of swelling (B). The extrudates were annealed as described in [8]. Guarantee experimental error in the determination of η and B was ± (2÷5) %. Regime of flow n was determined using tangent of an angle slope of the tangent to the abscissa axis in a given point of the flow curve. The can ability of the melt to the longitudinal deformation was estimated by the maximum possible

maximum possible spinneret stretching (F_{max}). Guarantee of error is ± 7 %.

RESULTS AND DISCUSSION

Filled polymers are often viewed as a concentrated suspension. For such systems, the possibility of interaction as the particles among themselves and with polymers of mixture should be taken into account. These will influence on the nature of the flow. Thus, the study of dynamic viscosity of polyethylene filled with powder of barium sulfate and calcium carbonate with different size particles showed that with increasing content of additive dynamic viscosity increases, and for suspensions which contain finely dispersed filler it increases abruptly, while for compositions with particles of relatively large size of this critical concentration is not achieved even with the large amount of modifier [9].

Table 2. Effect nanosized fillers on the rheological properties of PP melt

Concentration of CNT, wt. %	η^*, Pa·s		n^*	B^*	F_{max}^*, %
	η_{exp}	η_E			
0	300	–	1.8	2.1	18000
0.05	305	300	1.8	1.6	22000
0.1	315	301	1.8	1.6	27000
0.5	350	302	1.9	1.6	29000
1.0	450	305	1.9	1.5	21000
5.0	480	323	1.9	1.4	15000

$^* \tau = 5.7 \cdot 10^4$ Pa, $T = 190$ ºC

Investigation of the rheological properties of molten polypropylene filled with carbon nanotubes shows of an increased viscosity of the suspension, subject to increase the content of the additive from 0.05 to 5.0 wt. % (Table 2).

This is consistent with the conclusion that nanosized fillers determine thixotropic effect which leads to an increase in the viscosity of polymer melts [2]. For compositions with low concentrations of CNT (0.05÷0.1 wt. %), η increases insignificantly and within the error range coincides with the effective viscosity (η_E) calculated for the Einstein formula for dilute suspensions:

$$\eta_E = \eta_0(1 + 2.5F),$$

where η_0 –viscosity of the medium, F –volumetric concentration of suspended particles.

The nature of the flow of initial and the modified polypropylene melts is almost

unchanged from the content of CNT at all the investigated temperatures and obeys to a power law. As was to be expected, the elasticity of the compositions of melts decreases with increasing concentration of filler, as evidenced by the decrease in the swelling extrudates (Table 3). It is natural for filled polymers and is associated with a reduction in the flexibility of chains of macromolecules. Important practical result is the improvement of capability of the modified PP melt to longitudinal deformation: the maximum possible spinneret stretching increases with the introduction of additives to 1.0 wt. % due to increasing of viscosity and strengthening of the melt stream (Table 2). Fall of F_{max} value with increasing of CNT concentrations to 5 wt. % is caused by the deterioration of the elastic properties of the melt mixture.

Table 3. Effect of additives on the rheological properties of molten mixture of PP/CPA/ CNT

Ingredients PP/CPA/CNT, wt. %	η^*, Pa·s		n^*	B^*	F_{max}^*, %
	η_{exp}	η_{ad}			
100/0/0	300	–	1.8	2.1	18000
0/100/0	1230	–	1.2	1.4	95600
30/70/0	150	951	1.8	5.7	10500
30/70/0.05	160	954	1.7	6.8	7800
30/70/0.1	170	961	1.7	7.2	7600
30/70/0.5	190	966	1.7	7.0	7300
30/70/1.0	210	996	1.6	6.7	6900

* $\tau = 5.7 \cdot 10^4$ Pa, $T = 190\ ^\circ C$

Table 3 and Fig. 1 present data on the effect of CNT on the rheological properties of molten mixtures of PP/CPA mixture melts. Analysis of the results shows that the introduction of CNT to 0,1 wt. % does not change the viscosity of ternary mixtures in comparison with η of melts of the initial binary mixture.

With further increase in additive concentration, η of ternary mixture increases, but remains significantly lower for the additive value. This can be explained by the fact that the melt viscosity of the mixture is a result of several opposing factors. Solid additives of CNT structure the melt and increase its viscosity and, on the other hand, formation of the liquid streams of the dispersed face polymer in matrix CPA leads to decreasing of viscosity. Thus, we can conclude that the fiber forming is responsible for a sharp fall of viscosity of nanofilled mixture melts in comparison with the η of initial PP and CPA. Both modified PP/CPA mixture melts and the

PP/CPA mixture melts and the initial one are non-Newtonian liquids. The degree of deviation from the Newtonian regime estimated by the size "n" is practically independent on the amount of additives (Table 3).
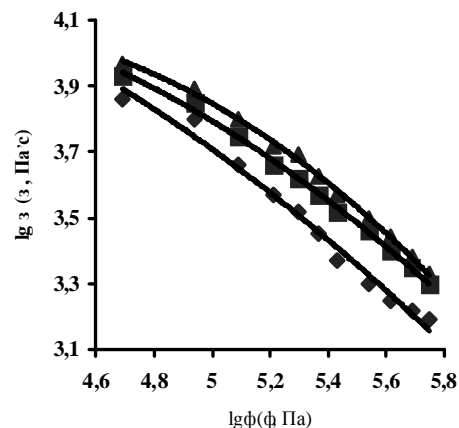

Fig. 1. Curves of flowing of PP/CPA/CNT mixtures melts at temperature 190 °C and ratio of the components, wt. %: 30/70 (♦); 30/70/0,5 (■); 30/70/1,0 (▲)

Effect of filler on the elastic properties of melts of the compositions PP/CPA/CNT can be seen from changing the values of swelling extrudate B, which is an indirect characteristic of elasticity. We see that for extrudates of the ternary mixtures value B is 1.2–1.3 times greater for all studied concentrations of CNT (Table 3). The reason for increasing swelling is that both components of the mixture are characterized by high elasticity and store elastic energy during the flow. In the transition from a wide reservoir into a narrow one, component of dispersed phase droplets are deformed, elongated and form liquid streams. These anisotropic structures are new relaxing elements and cause the growth of elasticity. Since the magnitude of swelling extrudate correlates with the specific fiber formation [5], increasing the B indirectly indicates a change on improving of fiber formation of dispersed polymer phase (PP) in the matrix CPA. Important technological characteristic of polymer melts and their mixtures is the capability to processing in fiber and film, which is determined by the maximum possible spinneret stretching (F_{max}). As it can be seen from Table 3, melts of bi- and three-component mixtures have lesser capability to longitudinal deformation in comparison with the melts of initial components. Fall of mixture spin abilities is a result of several factors – incompatibility between the components

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tors – incompatibility between the components and the weak interaction between the PP and CPA at the interface, a sharp drop shear viscosity and increasing heterogeneity of ternary mixtures. At the same time, it must be emphasized that the values of the maximum possible spinneret stretching allow to process compositions PP/CPA/CNT in fibers and films.

To determine the mechanism of the influence of CNT on flow of melts of PP/CPA mixture, the temperature dependence of viscosity was studied and activation energy of viscous flow (*E*) was calculated at different shear stresses by the Frenkel-Eyring formula:

$$\eta = A_0 e^{E/RT},$$

where A_0 – a factor depending on the molecular nature of the liquid; R – gas constant, which equals 8.3 J/mol·K; T – absolute temperature, K.

It has been found that the temperature dependence of viscosity in coordinates lg $\eta = f(1/T)$ at different shear stresses is expressed by straight lines whose slope remains almost unchanged for the melts of mixtures with different content of filler. It is seen from the data in Table 4, that the values of activation energy of viscous flow *E* insignificantly crease for composites in the presence of CNT what indicates on change of the kinetic flow element under the influence of additives.

Table 4. Effect of CNT addition on the activation Energy of viscous flow of PP/CPA mixture melts

Concentration of CNT, wt. %	E, kJ/mol at $\tau \cdot 10^{-4}$ Pa		
	$\tau = 5.69$	$\tau = 3.47$	$\tau = 1.61$
0	48.3	52.1	52.4
0.05	50.4	53.0	55.0
0.1	50.4	53.0	56.0
0.5	50.0	52.0	53.1
1.0	50.0	52.0	53.1

The activation energy of viscous flow naturally increases with decreasing shear stress (Table 4). Thus, studies have shown that the presence of CNT in PP/CPA mixture melts significantly effect on the regularities of their flowing.

CONCLUSIONS

The effect of carbon nanotubes on the regularities of flowing of polypropylene/copolyamide mixture melts has been studied. It has been shown that addition ied. It has been shown that addition of carbon nanotubes in the concentration range of 0.05–1.0 wt. % influences on the rheological properties of PP/CPA mixture melts. The nature of the flow of modified mixtures does not change and obeys to a power law. Activation energy of viscous flow of PP/CPA/CNT mixture melts insignificantly increases what indicates on change of the kinetic flow element under the influence of nanoadditives. The introduction of CNT in the PP/CPA mixture melts does not impede their processing in the technological parameters that are used for the initial mixture.

Thus, increasing of viscosity and elasticity and reducing values of the longitudinal deformation of melts of ternary compositions is caused by the change processes of structure formation under the influence of nanosized additives. To maximize the content of CNT in the fiber-forming component (PP) and for a homogeneous distribution in the mixture, it is necessary firstly to introduce nanotubes in molten PP and then to mix the obtained pellets of PP/CNT with CPA using a combined screw-disk extruder.

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Реологічні властивості розплавлених сумішей поліпропілен/сополіамід/вуглецеві нанотрубки

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Досліджено вплив домішок вуглецевих нанотрубок на реологічні властивості розплавів поліпропілен/сополіамід. Встановлено підвищення в'язкості та еластичності, зменшення величини повздовжньої деформації розплавів трьохкомпонентних композицій. Ці ефекти пояснюються зміною процесів структуроутворення під впливом нанорозмірної домішки. Показано, що системи з нанорозмірним наповнювачем можуть перероблятися з використанням технологічних параметрів та обладнання, які застосовуються для вихідної суміші.

Реологические свойства расплавленных смесей полипропилен/сополиамид/углеродные нанотрубки

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Исследовано влияние добавок углеродных нанотрубок на реологические свойства расплавов полипропилен/сополиамид. Установлено повышение вязкости и эластичности, уменьшение величин продольной деформации расплавов трехкомпонентных композиций. Эти эффекты объясняются изменением процессов структурообразования под влиянием наноразмерной добавки. Показано, что системы с наноразмерным наполнителем могут перерабатываться с использованием технологических параметров и оборудования, которые применяются для исходной смеси.