

RHEOLOGY OF MELTS OF MIXTURES “POLYPROPYLENE /CO-POLYAMIDE/CNT”

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Introduction

Carbon nanotubes (CNT) have quite wide fields of application and in the nearest future may become one of the most important industrial products. CNT are characterized by record values of the mechanical and transport properties at their low bulk and true densities. This causes widespread use of single-walled and multi-walled nanotubes as fillers for polymers at the creation of composite materials. The introduction of CNT enhances the electrical conductivity, thermal conductivity, heat resistance and temperature of ignition, and improvement of mechanical characteristics, changes in the structure of the polymer, increasing the degree of crystallinity, and increase the glass transition temperature. Composites also acquire new functional properties - the ability to remove static charges dissipate and absorb radio- and laser radiation, enhance electroluminescence etc. A significant effect is achieved also for synthetic fibers filled with nanotubes. Depending on the geometrical configuration of CNT the modified fibers can also have unforeseen properties [1, 2].

During the flow of the melt-phase mixture of polymers from a wide tank in the die holes a component dispersed in other viscoelastic medium is deformed in the jet. This opens a new way of obtaining ultrathin synthetic fibers (microfibers). These fibers can be separated from the composite extrudate by extraction of the matrix polymer in suitable solvent [3]. An objective of this paper was to study the effect of additives of CNT on the rheological properties of melts of mixtures “polypropylene/co-polyamide”.

Experimental

Objects of research are melts of mixtures of polypropylene (PP) and co-polyamide (CPA) in a ratio 30/70 wt% with the addition of CNT. The initial polymers are commercial: PP, grade 21060 (TU 05-1756-78), produced by Lysychansk Chemical Plant, Ukraine; CPA – co-polymer of ε-caprolactam and AG (hexamethylene-diamine and adipinic acid) salt of 50/50, grade PA-6/66 (BST 6-05-438-78), produced by Sverdlovsk Chemical Plant, Russia. Characteristics of the initial PP and CPA are given in Table 1.

Table 1. Characteristics of the initial polymers.

Polymer	Melting temperature, (T _m), °C	Viscosity*, (η), Pa·s	Flow mode*, (n)	Swelling magnitude*, (B)
PP	169	300	1.8	2.1
CPA	170	1230	1.2	1.4

* Temperature (T) 190 °C, shear stress (τ) 5.7·10⁴ Pa

To modify the properties of PP microfibers the multi-walled CNT were selected. Last were produced on a pilot plant designed by Chuiko Institute of Surface Chemistry, NASU and Company “TMSpetsmash-Ltd” by catalytic pyrolysis of unsaturated hydrocarbons [4]. The characteristics of CNT (TU U 26.30969031-014-2007) were as follows: external diameter of the nanotubes 10-20 nm; specific surface area 340 m²/g; specific electric resistance 0.09 Ohm·cm; temperature of 5% weight loss after purification of mineral impurities 575 °C. The used concentrations of CNT were 0.05, 0.1, 0.5, 1.0 and 5.0 wt% by weight of PP.

Mixing of polymers and blending were carried out using a combined worm-disk extruder LGP 25. To maximize the content of CNT in the fiber-forming component (PP) and homogeneous distribution in the mixture of nanotubes were previously introduced into the melt of PP, and then received PP/CNT pellets mixed with CPA. Viscosity (η) of melts of initial PP, CPA and their mixtures is measured by capillary viscometry using microviscometer CF-2 in the range of shearing stress (τ) (0.1-5.7)·10⁴ Pa, at temperatures (T) 190, 210, and 220 °C. Elastic properties of extrudates were estimated by swelling magnitude (B) after annealing as described in [5, 6]. Warranty experimental error in the determination of η and B was ±2÷5%. Flow mode n was determined by the value of the slope of the tangent to the abscissa at a given point of the flow curve. The ability of the melt to the longitudinal deformation was estimated by the maximum plated hood (F_{max}) to guarantee an accuracy of ±7%.

Results and Discussion

Made investigations of the rheological properties of molten PP filled with CNT evidence an increased viscosity of the suspension at increasing the content of the additive from 0.05 to 5.0 wt% (Table 2).

Table 2. Effect of CNT as nanoadditives on the rheological properties of PP melts.

CNT content, wt%	η*, Pa·s		n*	B*	Fmax*, %
	η _{ex}	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

These data confirm the conclusion that nanoadditives determine thixotropy effect, which leads to an increase in the viscosity of melts of polymers [2]. For the composites with low concentrations of CNT (0.05-0.1 wt%) η increases insignificant and within the error coincides with the effective viscosity (η_E), calculated by Einstein' formula for dilute suspensions: η_E = η₀(1+2.5F), where η₀ - viscosity of the medium, F - volumetric concentration of suspended particles.

The nature of the flow of initial and modified PP melts almost unchanged from the content of CNT at all

investigated temperatures and obeys a power law. As it 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 magnitudes of extrudates (Table 2). It is natural for filled polymers and is associated with a reduction in the flexibility of chains of macromolecules. An important scientific and practical results are to improve the ability of the melt of the modified PP to longitudinal deformation: the maximum possible plated hood increases with the introduction of additives to 1.0 wt%, that is caused by strengthening of the jet of melt due to increase in viscosity (Table 2). Decrease of F_{max} with increasing concentrations of CNT to 5 wt% is connected with deterioration of elastic properties of the melt of mixture.

Table 3 presents data on the effect of CNT on rheological properties of molten mixtures of PP/CPA. Analysis of the results shows that the introduction of CNT does not change the general pattern of a sharp drop in the viscosity of binary mixtures in comparison with η of melts of the initial components.

Table 3. Effect of addition of CNT on rheological properties of molten PP/CPA mixtures

Composition PP/CPA/CNT, wt%	η^* , Pa·s		n^*	B^*	F_{max}^* , %
	η_{ex}	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

The experimental values of effective viscosity for melts of binary and ternary compositions in 5-6 times lower than additive quantities. But an important technological characteristic of polymer melts and their mixtures is the ability to processing in fiber and film, which is determined by the maximum plated hood (F_{max}). As it can be seen from Table 3, melts of bi- and three-component mixtures have less ability to longitudinal deformation in comparison with the original components. At the same time it must be emphasized that the values of maximum plated exhaust are in the range, which allows processing composition PP/CPA/CNT in fibers and films.

To determine the mechanism of the influence of CNTs on the patterns of flow of melts of PP/CPA it was investigated the temperature dependence of viscosity at different shear stresses and calculated activation energy of viscous flow (E) using Frenkel - Eiring formula: $\eta = A_0 \cdot e^{E/RT}$, where: A_0 - coefficient, which depends on molecular nature of liquid; R - gas constant; T - absolute temperature. It was established that the temperature dependence of viscosity in coordinates $\lg \eta = f(1/T)$ at different shear stresses is expressed by straight lines, which slope remains almost unchanged for the melts of mixtures with different content of filler. From the data in Table 4 is seen the values of activation energy of viscous flow

increase for composites in the presence of CNT, and this indicates a change in the kinetic part of the flow under the influence of additives. The activation energy of viscous flow naturally increases with decreasing shear stress (Table 4).

Table 4. Effect of addition of CNT on activation energy of viscous flow of PP/CPA melts

CNT content, wt%	E , kJ/mol, at $\tau \times 10^4$ 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

Thus, studies have shown that the presence of CNT in molten PP and initial PP/CPA mixtures significantly affects the regularity of their melts flow.

Conclusions

Effect of CNT on the flow patterns of molten PP/CPA mixtures is studied. It is shown that addition of them in the concentration range of 0.05-1.0 wt% impact on the rheology of melts. The character of the flow of modified mixtures does not change and obeys a power law. Activation energy of viscous flow of composites PP/CPA/CNT increases, which indicates a change in the kinetic part of flowing under influence of nanoadditives. The introduction of CNT in the melts of PP/CPA mixtures does not impede their processing at technological parameters used for the original mixtures.

Thus, it is determined an increase of viscosity, elasticity and reducing values of the longitudinal deformation of melts for ternary compositions due to the change processes of structure formation under influence of nanoadditives. To maximize the content of CNT in the fibre-forming components (PP) and to obtain a homogeneous distribution of additives in the mixture, it is necessary firstly to introduce CNT in molten PP and then obtained pellets to mix with CPA using a combined worm-disk extruder.

References

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