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INFLUENCE OF FULLERENE ON THE RHEOLOGICAL CHARACTERISTICS OF MELTS OF THE POLYAMIDE COMPOSITE FORMING THE STRUCTURE OF A SEMI-INTERPENETRATIVE POLYMER MESH

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The time change in the melt viscosity of the polyamide composite forming at the final stage a polymer with the structure of a semi-interpenetrative polymer mesh has been investigated. To impregnate with the composite melt the carbon fiber for forming carbon-filled plastics, it is necessary to preserve the low viscosity of the melt for a long time. This is achieved by preliminary heat treatment of the composite and introduction of fullerene into it.

The development of composite materials based on polyamide binders having not only high indices of heat resistance and strain-strength characteristics but also a high viscosity of interlaminar fracture calls for new approaches to the obtaining of the polymer matrix.

Workers at the Institute of High-Molecular Compounds (HMC) of the Russian Academy of Sciences have developed a binder forming a polymer mesh named the imide polymerizable oligomer (IPO). It is based on a mixture of acidic ethers of aromatic tetracarboxylic acids and 5-norbornene-2,3-dicarboxylic acid with two diamines [1]. This system is easy to process for obtaining carbon-filled plastic due to its fluidity at low temperatures, but the viscosity of the composite interlaminar fracture is low because of the cross-linked structure [2].

The application of fusible linear aromatic poliamides (PI) in obtaining carbon-filled plastics permits attaining a high crack resistance of the composite but causes a decrease in its heat resistance. Replacing fusible PIs with nonfusible ones leads to a very high complexity of the process of carbon-filled plastic formation [3].

To solve this problem, a polymer composite consisting of 80 mass % of IPO and 20 mass % of polyamide acid (PAA) was obtained. As a result of the heat treatment, the matrix from two polymers having polyimide fragments of the same chemical composition acquires the structure of a semi-interpenetrative polymer mesh [4]. Modification of the binder with the aim of improving the tribological characteristics of the final carbon composite was carried out by introducing into the solution of the mixture of polymers 1.3% of fullerene C_{60} [5].

To obtain carbon-filled plastic, the carbon tape is impregnated with a solution of the polymer mixture (IPO + PAA), dried under certain temperature conditions, and packed into a stack. The thus-obtained stack of prepregs is moulded in a hot press for 1–2 h at a temperature of 300–330°C and a pressure of 0.1–0.3 MPa. In the process of carbon-filled plastic formation, a flow of the binder is needed to impregnate the carbon cloth fibers and, therefore, its viscosity should be low for some time. The binder viscosity depends on the preliminary heat treatment in preparing the prepreg.

The aim of the present paper is to determine the binder melt viscosity under different conditions of heat treatment and estimate the influence of fullerene on the rheological characteristics of the polymer mixture.

Experimental. The IPO was obtained as follows. In a mixture consisting of 90 mass % of ethyl alcohol and 10 mass % of water, at its boiling temperature, dianhydride of 3,3′,4,4′-diphenyloxide tetracarboxylic acid (DA DPO) and anhydride of 5-norbornene-2,3-dicarboxylic acid in a 1:2 molar ratio were dissolved to obtain acidic ethers. The solution was cooled down to room temperature, after which two diamines, 4,4′-diaminediphenyl ether (DADPE) and *m*-diphenylamine (mPDA), in a 1:1 molar ratio were added to it under stirring. Then the prepolymer named the H-complex [6] was heated for 2 h at 100°C and 1.5 h at 150°C to remove ethanol and water and for partial imidization.

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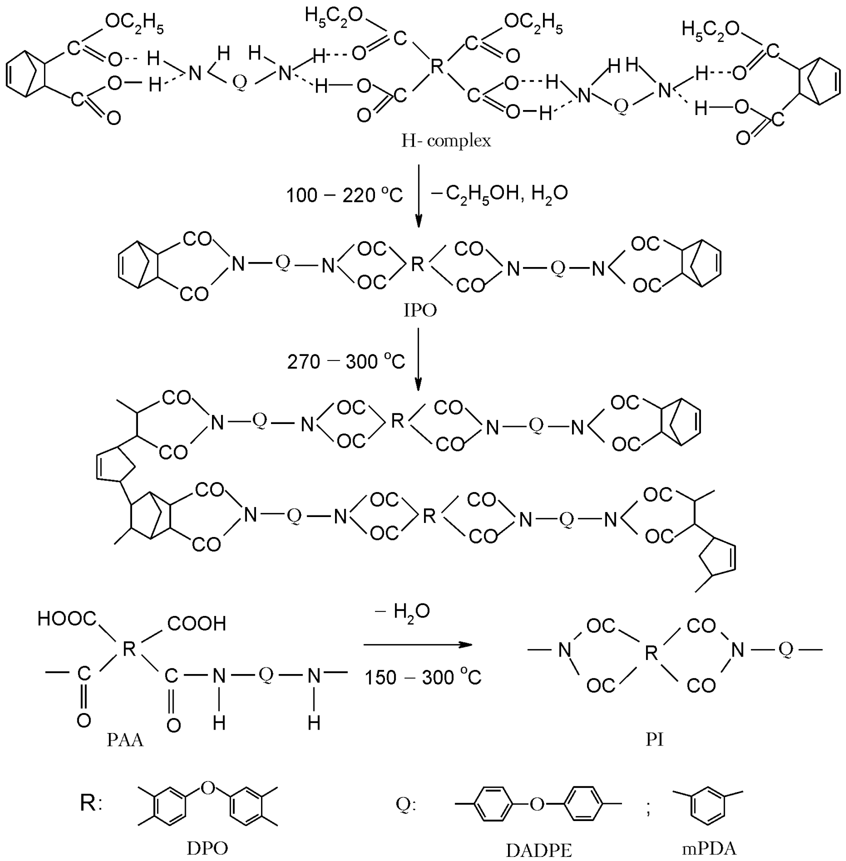

Fig. 1. Scheme of formation of cross-linked and linear polyamides.

PAA was synthesized in a solution of dimethylacetamide (DMA) from DA DPO and a DADPE and mPDA mixture in a 2:1:1 molar ratio by the standard technique [7].

Figure 1 shows the scheme of formation of cross-linked (H-complex → IPO → polymer mesh) and linear (PAA → PI) polymers, from whose mixture, upon heat treatment, a polymer having the structure of a semi-interpenetrative polymer mesh is formed.

The thermally treated IPO prepolymer was dissolved in methylpyrrolidone (MP) and mixed with a PAA solution in an 80:20 ratio. C_{60} fullerene (1.3 mass %) was introduced at the stage of obtaining a polymer composite solution in MP.

To remove the solvent, the binder was vacuum dried at $T = 35^{o}C$ to a constant mass and then heated in three regimes corresponding to the process of obtaining the carbon composite: (1) at $80^{o}C$ for 15 h, (2) at $180^{o}C$ for 1 h, and (3) at $220^{o}C$ for 1 h. To determine the binder melt viscosity, we used the initial composite and samples heated in the above three regimes.

The melt viscosities of the samples were measured on a PIRSP rheogoniometer [8] with a cone-plane working unit, a cone vortex angle of 1^{o}, a diameter of 40 mm, and a rate of shear of 0.013 sec^{-1}.

Results and Discussion. At two temperatures (270 and $300^{o}C$), the time dependences of the melt viscosities of the (IPO + PAA) polymer mixture differing in their regimes of heat treatment have been determined. Table 1 shows the initial melt viscosity (η_0), the rates of increase in the viscosity (change in the viscosity per unit time, $v = \Delta \log \eta/\Delta\tau$), and the lifetimes ($\tau$) of the melts (the lifetime of the melt is the interval from the beginning of the experiment to the practically complete loss of the melt fluidity) depending on the heat treatment ($T_{\text{H.T}}$) of the polymer mixture, i.e., the degree of imidization (α) [6].

The choice of temperatures for analysis is due to the fact that the opening of the norbornene double bonds leading to the mesh formation begins after $270^{o}C$ (according to the data of the dielectric analysis), i.e., at $270^{o}C$ the

TABLE 1. Initial Viscosities, Rates of Increase in Viscosity, and Lifetimes of the (IPO + PAA) Composition Melts Depending on the Heat Treatment (degree of imidization [6])

$T_{\text{H.T}}$, °C	α, %	$\eta_0\cdot10^{-3}$, Pa·sec		$v\cdot10^{-2}$, Pa·sec/min		τ, min	
		270 °C	300 °C	270 °C	300 °C	270 °C	300 °C
—	60	16	25	2.1	3.4	70	37
80	70	32	56	2.2	5.4	70	25
180	85	10	6.3	4.3	10	70	30
220	95	3.2	3.2	5.6	15	83	27

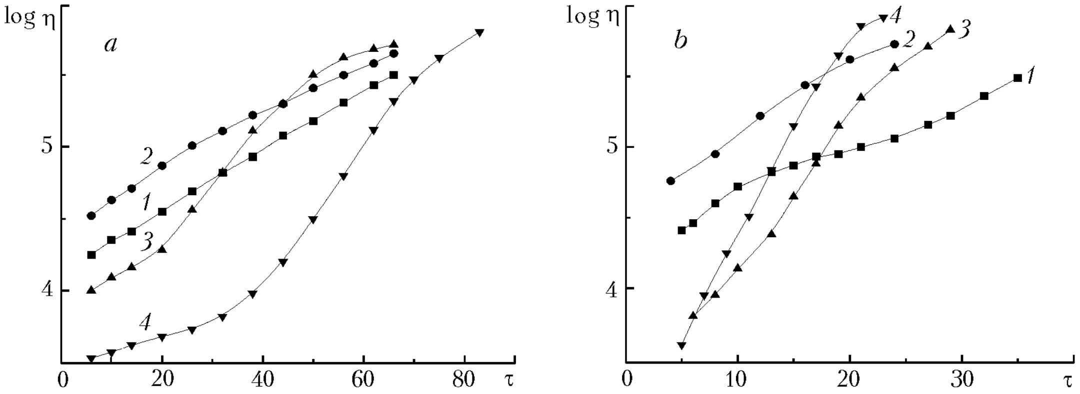

Fig. 2. Time dependences of the IPO + PAA melt viscosity at 270 (a) and 300°C (b). $\dot{\gamma} = 0.013$ sec^{-1}. Heat treatment: 1) without soaking; 2) 80°C and 15 h; 3) 180°C and 1 h; 4) 220°C and 1 h. τ, min; log η, Pa·sec.

increase in viscosity is only due to the composite imidization, whereas the change in the melt viscosity at 300°C is influenced by both the imidization and the mesh formation.

The composites without thermal pretreatment (Fig. 2, curves 1) and those heated for 15 h at 80°C (Fig. 2, curves 2) had very high initial melt viscosities, and the viscosity thereby increased rapidly with time. The initial melt viscosities for the composites without heat treatment are twice as low as for the heated composite because of the partial PAA imidization preventing melting.

While at 270°C the rates of increase in the melt viscosities are close, at 300°C the rate of increase in the viscosity of the sample heated at 80°C is higher than for the sample without thermal treatment.

It should be noted that the measured initial melt viscosities of the initial polymer composite and the composite treated at 80°C for 270°C are lower than for 300°C. This seems to contradict the law of change in the melt fluidity of polymers at different temperatures. However, in these samples this is explained by the fast formation of nonfusible polyamide from PAA at a high temperature. At 300°C, in a very short time, in which measurements are impossible, the composite viscosity increases so that the initial measured viscosities of melts at 270°C turn out to be lower than at 300°C.

In considering the dependences of the melt viscosities of composites heated for 1 h at 180°C (Fig. 2, curves 3) or 220°C (Fig. 2, curves 4), surprising is the fact that for samples having a higher degree of imidization the value of the initial melt viscosity decreases at a temperature of 270°C and especially at 300°C (by more than an order of magnitude compared to the sample heated at 80°C). The rates of increase in the melt viscosity increase naturally with increasing temperature of heat treatment. At 270°C, the increase in the melt viscosity is due to the imidization of the polymer composite. Consequently, in composites with a high initial degree of imidization its completion turns out to be facilitated, which can be explained by the improved compatibility of the system components [4].

Heat treatment for 1 h at 220°C causes practically 100% imidization of the IPO and a high degree of PAA conversion to polyamide. Nevertheless, the initial melt viscosity decreases substantially (the polyamide entering into the composite at 270 and 300°C does not form a melt by itself and the IPO has a high initial melt viscosity), and, what

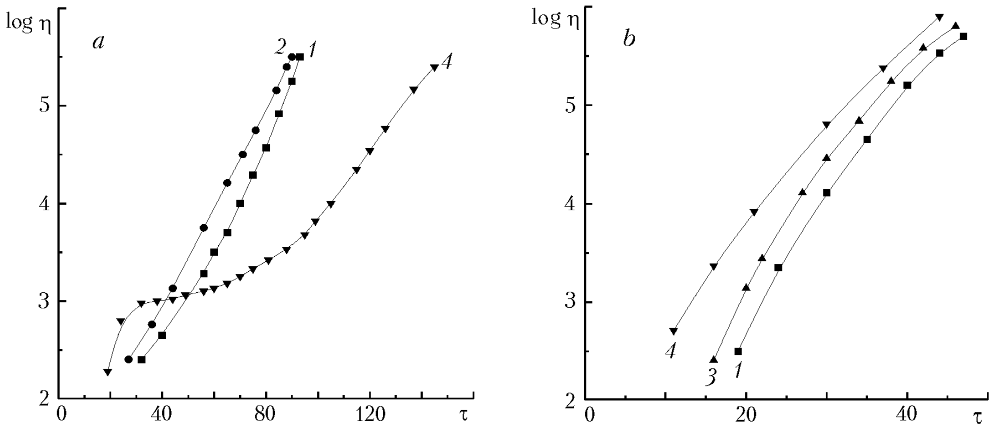

Fig. 3. Time dependences of the IPO + PAA + C_{60} melt viscosity. The experimental conditions and notation are the same as in Fig. 2.

TABLE 2. Time of the Beginning of Viscosity Measurements of the IPO + PAA + C_{60} Melt and Comparison of the Rate of Increase in Viscosity and the Lifetime of the Composites with Fullerene and without Fullerene Depending on the Heat Treatment

τ_0, min		$T_{\text{H.T}}$, °C	$v\cdot10^{-2}$, Pa·sec/min				τ, min			
270 °C	300 °C		270 °C		300 °C		270 °C		300 °C	
$+C_{60}$			$-C_{60}$	$+C_{60}$	$-C_{60}$	$+C_{60}$	$-C_{60}$	$+C_{60}$	$-C_{60}$	$+C_{60}$
32	19	—	2.1	6.1	3.4	12.5	70	93	37	47
27	—	80	2.2	5.0	5.4	—	70	87	25	—
—	16	180	4.3	—	10	13.7	70	—	30	46
19	11	220	5.6	3.7	15	10	83	155	27	44

is more, at 270°C the viscosity remains practically stable for 40 min, and then its rapid growth occurs. The imide fragments of the polymers entering into the composite have the same chemical structure (see Fig. 1), as a result of which a compatible composite is formed to cause a decrease in the initial viscosity. The melt viscosity stabilization at 270°C is likely to be due to the fact that a certain time is needed for the imidization reaction to proceed with the participation of the ends of macromolecules of long chains of PIs formed from PAA. Therefore, in obtaining a carbon-filled composite, preliminary heat treatment of prepregs for 1 h at 220°C is essential. This causes a decrease in the binder melt viscosity and its long-term stability.

To improve the tribological characteristics of the carbon-filled composite [5], 1.3 mass % of C_{60} fullerene was introduced into the initial (IPO + PAA) polymer composite at the stage of its preparation. The influence of fullerene on the melt fluidity under different conditions of composite heat treatment was estimated by the change in the melt viscosity at the same experimental temperatures (Fig. 3).

The greatest change in the behavior of the composite melt is associated with the sharp decrease in the initial melt viscosity under any conditions of heat treatment, whose values are so small ($\eta < 180$ Pa·sec) that the first measurements under the experimental conditions are only possible after 10–30 min from the beginning of the experiment (τ_0). This leads to a marked increase in the lifetime (τ) of the melt of the composite with fullerene as compared to the composite without fullerene (Table 2).

The rates of increase in the melt viscosity of the (IPO + PAA + C_{60}) composite decrease with increasing heating temperature, which is most obvious at 270°C. The composites without fullerene are characterized by an inverse relationship at both temperatures of analysis (Fig. 4). This is due to the fact that the addition of an insignificant quantity of fullerene (1.3 mass %) leads, according to the data of dielectric measurements of the polymer mixture, to a completion of imidization at lower temperature.

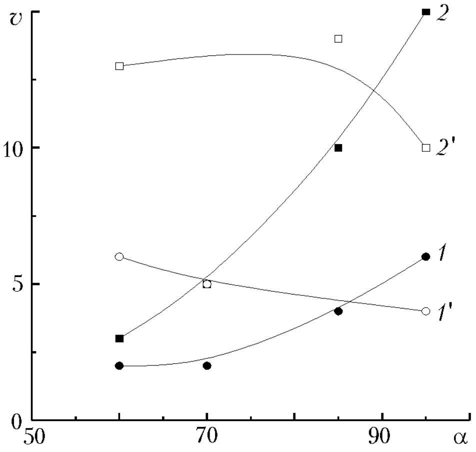

Fig. 4. Rate of increase in the melt viscosity of the IPO + PAA (1, 2) and IPO + PAA + C_{60} (1′, 2′) mixtures depending on the degree of imidization at 270°C (1′, 2) and 300°C (1, 2′). $\dot{\gamma} = 0.013$ sec^{-1}. α, %; *v*, Pa·sec/min.

The (IPO + PAA + C_{60}) composite without heat treatment and upon prolonged low-temperature treatment has higher rates of increase in viscosity compared to the composite without fullerene. It may be suggested that in the melt fullerene acts as a plasticizer.

As mentioned above, the melt of the fullerene-containing composite preserves its low viscosity values for a long time. This is due to the fact that in the given samples, even upon prolonged drying, a considerable quantity of solvent remains. Therefore, at the beginning of the experiment on determination of the value of the melt viscosity of the composite with fullerene at 270°C the solvent comes out with simultaneous imidization (not registered), followed by the rapid completion of imidization with the plasticizing role of fullerene. The initial melt viscosity of the fullerene-free composites under low-temperature treatment is very high, which is why imidization is hindered and the rate of increase in the viscosity is low.

Heat treatment of the binder for 1 h at 220°C leads to the formation of a polymer composite with a high degree of imidization of both components, and in the fullerene-containing composite thereby it is higher (according to the data of the dielectric analysis, imidization is completed at lower temperatures) than in the fullerene-free composition. Therefore, the rate of increase in the melt viscosity of the fullerene-containing composite decreases, and the period of existence of the melt with a slightly varying viscosity increases to 80 min compared to the binder without fullerene (40 min) as a result of the formation of long and less defective (plasticizing effect of fullerene at imidization) polyamide chains formed from PAA.

Thus, in obtaining carbon-filled plastic for optimal impregnation of prepregs with the (IPO + PAA + C_{60}) binder, it is necessary to carry out a stepwise regime of heat treatment, keeping the final stage for 1 h at 220°C. This makes it possible to preserve at higher temperatures a sufficiently low value of the binder melt viscosity for a long time.

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NOTATION

$T_{\text{H.T}}$, temperature of heat treatment of the polymer mixture, °C; *v*, rate of increase in viscosity, Pa·sec/min; α, degree of imidization, %; $\dot{\gamma}$, rate of shear, sec^{-1}; η, melt viscosity, Pa·sec; η_0, initial melt viscosity, Pa·sec; τ, lifetime of melt, min; τ_0, time of the beginning of measurements, min.

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