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INFLUENCE OF THE LENGTH AND CONCENTRATION OF CARBON AND GLASS FIBERS ON THE PROPERTIES OF POLYPHENYLENE SULFONE

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The influence of the length and concentration of carbon (CF) and glass (GF) fibers on the rheological, physicomechanical and thermal properties of high-temperature polyphenylene sulfone thermoplastic with a filler content up to 40% (by mass) was investigated. Carbon and glass fibers 0.2- and 3-mm long were used as fillers. The introduction of CF and GF leads to a noticeable decrease in the melt flow index and the impact strength of polyphenylene sulfone, while the yield stress disappears on the stress-strain diagram, which is caused by a decrease in the material's ability to plastic deformations. With an increase in the fiber content, the elastic modulus and tensile strength of the composite increase both in bending and in tension. A significant increase in heat resistance occurs with an increase in the CF content, and samples with a CF content of 0.2 mm have a higher mass loss temperature. In the case of composites with GF, there are no significant changes in heat resistance.

The increasing fraction of carbon fibers and glass fibers in high-tech industries indicates the increasing interest of scientists and technologists in the development of new progressive and promising combinations of fibrous fillers and polymer matrices [1, 2]. To date, the search for new compositions and the selection of components for polymer blends has been carried out mainly based on knowledge and recommendations accumulated over many years of using thermosetting polymer-based systems. Despite the large amount of information available on the production and research of filled compositions, technologists still do not have enough scientific knowledge to develop carbon and glass plastics based on high-temperature thermoplastic polymers, which limits their effective use as binders for polymer composites.

This article discusses the effect of filler content – carbon fibers and glass fibers – and the geometric characteristics (length) of the fibers on the rheological, physicomechanical, and thermal properties of a high-temperature thermoplastic, polyphenylene sulfone (PPSU).

As the matrix for the production of composites with fibrous fillers, polyphenylene sulfone (PPSU) with optimally selected viscosity (reduced viscosity 0.4 dL/g) was used based on 4,4-dihydroxydiphenyl and 4,4-dichlorodiphenylsulfone, synthesized in the Advanced Polymers Laboratory at the Kabardino-Balkarian State university (KBSU) after Kh. M. Berbekov [3, 4].

Carbon fibers (CF) and glass fibers (GF) with a particle length of 0.2 and 3 mm manufactured by R&G (Germany) served as fillers. Since the fibers were pretreated with epoxy resin, prior to using them in this investigation, the fibrous materials were preheated to remove the resin, since the PPSU processing temperature is much higher than the decomposition temperature of epoxy resin.

Composites were obtained by melt blending on a Twin Tech (Great Britain) twin screw microextruder with L/D = 30. Samples for testing were obtained by injection molding on an SZS-20 machine manufactured by Haitai Machinery (China) with the material cylinder at 410-420 °C and the mold at 200 °C.

Mechanical uniaxial tension testing was performed on samples in the form of a double-sided blade with dimensions according to GOST 11262–80. Tests were carried out on a universal testing machine "Gotech Testing Machine CT-TCS

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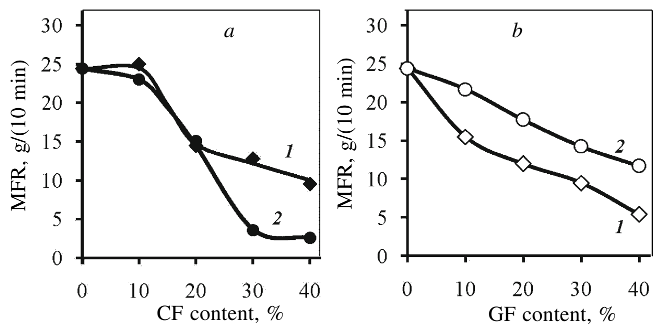

Fig. 1. PPSU MFR as a function of the content and length of CF (*a*) and GF (*b*) fibers: *1* – 0.2 mm; *2* – 3 mm.

Table 1. Physicomechanical Properties of Composite Materials Based on PPSU and CF

Composition	A_d, kJ/m^2		σ_y, MPa	ε_p, %
	w/o notch	notched		
PSSU	186	43	76.2	13.4
Particle length 0.2 mm				
PSSU + 10% CF	41.0	7.5	–	6.0
PSSU + 20% CF	41.0	9.6	–	4.6
PSSU + 30% CF	38.3	10.5	–	4.1
PSSU + 40% CF	40.6	9.5	–	3.0
Particle length 3 mm				
PSSU + 10% CF	39.8	9.3	–	5.0
PSSU + 20% CF	36.5	8.5	–	4.0
PSSU + 30% CF	38.0	8.5	–	3.8
PSSU + 40% CF	36.0	9.3	–	3.5

2000” (Taiwan) at 23 °C. Izod impact testing of notched and unnotched samples was carried out in accordance with GOST 19109–84 using a Gotech Testing Machine with a pendulum impact energy of 11 J, model GT-7045-MD (Taiwan).

The melt flow rate (MFR) was determined on a device for measuring the melt flow index IIRT-5 (Russia) at a temperature of 380 °C and under a 5 kg load. Heat resistance was determined by thermogravimetric analysis on a TGA 4000 instrument from Perkin Elmer (USA).

In order to study the influence of CF and GF with different particle lengths on the properties of PPSU, as well as to determine their optimal concentrations, composite materials were obtained containing 10 to 40% (by mass) fibrous fillers.

Rheological properties of fiber-filled composite materials were determined from the melt flow rate. Fig. 1a shows the dependence of the MFR on the content and length of the CF particles. It can be seen from Fig. 1 that an increase in the content of carbon fiber from 10 to 40% leads to a noticeable decrease in the MFR regardless of the length of the fibers. With a 20% content of CF, the MFR values for composites with long (3 mm) and short (0.2 mm) fibers are almost the same. Differences in the dependence of the viscosity of the composite melt on the fiber length are observed with the introduction of 30 and 40% carbon fiber. An increase in the content of CF from 20 to 40% has less effect on the MFR of composites containing short fiber (0.2 mm) filler material than of composites filled with 3 mm fibers. For the latter, the melt viscosity increases significantly at 30 and 40% content of fibrous filler, and the MFR values become very low.

The introduction of glass fibers is also accompanied by an increase in the viscosity of the PPSU melt, and with an increase in their content, the MFR decreases almost linearly (Fig. 1b). It should be noted that composites containing 3-mm long GF fibers have higher MFR values than similar composites containing 0.2-mm long GF fibers.

Thus, the introduction of fibrous fillers in both cases leads to a decrease in the melt flow index of the PPSU melt: rigid non-deformable filler particles prevent the flow of the polymer melt, increasing its viscosity. In the case of CF composites, melt flow becomes more difficult with increasing length of fibers. In the case of GF, on the contrary, composite melts with longer filler fibers flow better (have higher MFR). The reason for this phenomenon may be the destruction of fibers in the extrusion process due to the higher shear stress.

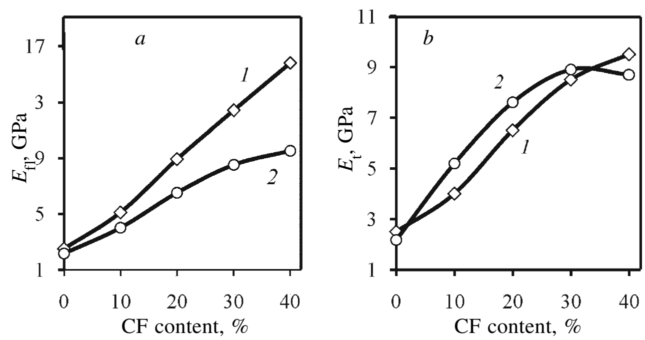

Fig. 2. Concentration dependences of the elastic modulus at three-point bending (flexural) (*a*) and uniaxial tensile stretching (*b*) of filled composites based on PSSU and CF: *1* – 0.2 mm; *2* – 3 mm.

Table 1 presents the results of measuring the deformation-strength characteristics of composites filled with CF. It can be seen in the Table that the introduction of fibrous filler leads to a significant reduction in impact strength (A_d) of PPSU, which, as is known, is an integral strength characteristic and is determined not only by strength (fracture stress), but also by plasticity of the polymeric material. The said effect of carbon fiber on impact strength means a decrease in the relative contribution of plastic deformation to the impact resistance of filled composites, i.e. the impact strength of the studied samples is determined to a greater degree by the strength of the composite and the resistance to the propagation of fracture.

It is noteworthy that an increase in the content of both longer and shorter hydrocarbons has little effect on the relative change in impact toughness of the notched and unnotched samples (approximately 4.5-fold change in both cases), however, some differences should be noted. The application of a notch reduces the impact strength of initial PPSU samples to 0.23 A_d. Unnotched carbon-filled composite samples (with a filler particle length of 0.2 mm) containing about 10–40% CF exhibit impact strength around 0.21-0.22 of the value A_d of the initial tested unnotched PPSU samples. It can be assumed that in this case the introduction of the filler and the application of the notch affect the ductility of the composite material similarly, equally suppressing it.

Notched samples of composites filled with CFs revealed a tendency for some increase in impact strength with increasing filler content, within the range of 0.17-0.24 of the values of A_d of the initial notched PPSU samples.

For unnotched samples containing CF fibers 3 mm in length, the impact strength is 0.19–0.21 of the corresponding value of the initial PPSU; for notched samples, this interval of relative reduction of A_d is 0.18-0.20.

Thus, 0.2-mm long carbon fibers used as a filler suppress the contribution of plastic deformation of the PPSU during impact testing less than 3-mm long carbon fibers.

As can be seen in Table 1, the same basic difference is found when comparing the fracture strain of sample compositions with different geometric characteristics of carbon fibers in uniaxial tension testing.

As for the quasistatic loading, with the introduction of CF at 10%, the decrease in the relative strain at fracture is more than doubled, and the yield stress disappears from the stress-strain diagram due to a decrease in the material's ability to plastic deformation. This effect (reduction of A_d and ε_d), more noticeable for samples with 3-mm long particles, is due to the high shape ratio of the fibrous fillers and their high rigidity, which limits plastic deformation of the polymer matrix under load [5-7].

As mentioned above, fibrous fillers, due to the high length-to-width ratio, have a reinforcing effect, increasing the strength and elasticity modulus of the material. The classic case of matrix reinforcement is the case (Fig. 2): the elasticity modulus during bending as well as stretching in quasistatic testing conditions monotonically increases with increasing content of CF. Composites prepared with longer fibers (3 mm) have a slightly higher tensile modulus, which is apparently due to a more efficient transfer of stress at the *polymer matrix – filler* interface, reducing the concentration of internal stresses and increasing the load resistance.

The decrease in the tensile modulus of a composite with a 40% content of CF with 3-mm long fibers, which is observed in Fig. 2b, is the result of a high melt viscosity, which led to underfilling of samples. In general, the increase in flexural rigidity with the introduction of 40% CF is 500-600%, and when stretched, it is about 330%.

Fibrous fillers also increase the tensile strength of the composite under uniaxial tension and at three-point bending (Fig. 3). The diagrams show a significant increase in strength both under tension and at bending with increasing

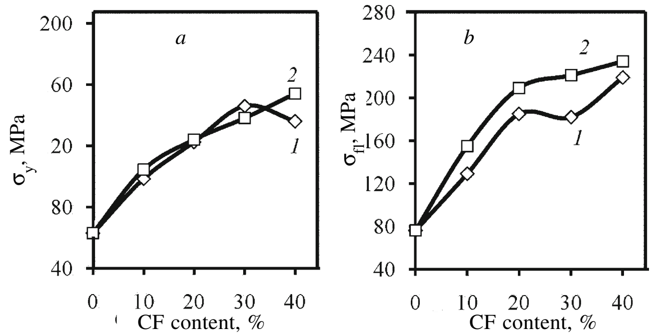

Fig. 3. Concentration dependences of ultimate strength under uniaxial tension (*a*) and three-point bending (*b*) of composites based on PSSU and CF: *1* – 0.2 mm; *2* – 3 mm.

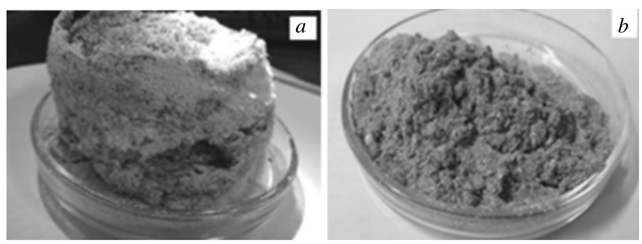

Fig. 4. Composites of PPSU + 20% CF with 3 mm (*a*) and 0.2 mm (*b*) long fibers.

filler content. At the same time, no significant difference was noted between the tensile strength of composites made with CF fibers 0.2- and 3-mm long. The difference is more apparent in bending tests: CF with 3-mm long fibers contributes better to increasing strength values.

The increase in the stress at fracture for composite containing 40% CF is about 140%, and during bending – slightly more than 200%.

Thus, it was found that in quasi-static tests, the modulus of elasticity, as well as strength – both for stretching and bending – increase with increasing filler content. At the same time, both types of CF (with 0.2- and 3-mm long fibers) composites with similar values describing physicomechanical properties, with a slight advantage of samples containing CF with 3-mm long fibers. However, the latter have a number of technological disadvantages:

- first, when mixed with the polymer, the fibers fray and form a cotton ball-like material (Fig. 4a), which significantly complicates the loading of the composite mixture into the extruder and adjusting thread diameter;

- second, the increased melt viscosity also makes processing difficult.

When using CF with 0.2-mm long fibers, the polymer mixture for extrusion is a fine powder that is easily processed, and the composites have a higher melt flow index (Fig. 4b).

Thus, the study of the influence of geometric dimensions of CF filler particles on the rheological and deformation-strength properties of PPSU led to the conclusion that the use of 0.2-mm long carbon fibers shows promise.

Table 2 presents the results of a similar study of the effect of glass fibers of various lengths and content on the properties of PPSU. It is clear from the table that the introduction of GF also leads to a decrease in impact strength of PPSU. However, in contrast to CF, wherein the impact resistance is almost constant for 10–40% content of CF, for GF the impact strength of the composite monotonically decreases with increasing content of GF, both for unnotched and notched samples. Similarly, as with the introduction of CF, the yield stress disappears and the relative deformation at break in uniaxial tension testing decreases.

With the exception of composites with a 10% GF content (with 0.2- and 3-mm long fibers), where the difference in the impact strength of the unnotched and notched samples is quite significant (and the yield stress is still found in the stress-strain diagram), the other composites have similar impact strength values regardless of the length of the filler fibers.

Table 2. Physicomechanical Properties of Composite Materials Based on PPSU and GF

Composition	A_d, kJ/m^2		σ_y, MPa	ε_p,%
	unnotched	notched		
PSSU	186	43	76.2	13.4
Particle length 0.2 mm				
PSSU + 10% GF	80.8	9.6	71.5	8.2
PSSU + 20% GF	36.0	8.2	–	4.4
PSSU + 30% GF	25.3	6.2	–	3.2
PSSU + 40% GF	14	5.1	–	2.3
Particle length 3 mm				
PSSU + 10% GF	43.4	8.2	–	5.7
PSSU + 20% GF	36.8	7.3	–	4.6
PSSU + 30% GF	27.2	5.8	–	3.2
PSSU + 40% GF	19.7	6.0	–	2.2

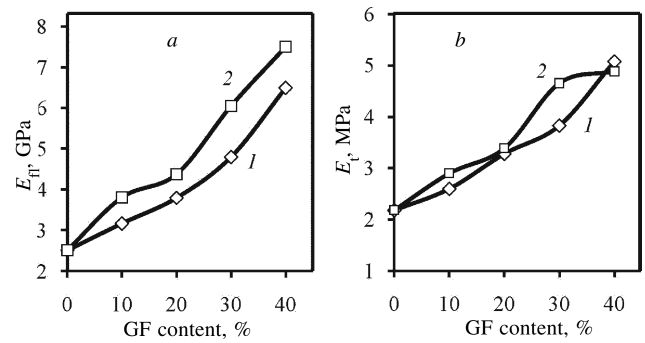

Fig. 5. Modulus of elasticity for bending (*a*) and stretching (*b*) of filled composites based on PPSU and GF as a function of concentration for various fiber lengths: *1* – 0.2 mm; *2* – 3 mm.

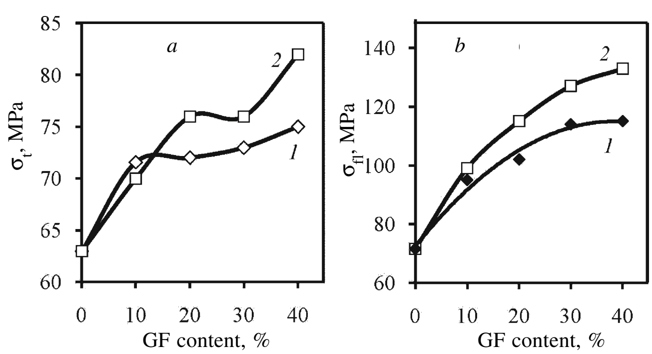

Fig. 6. Concentration dependences of ultimate tensile (*a*) and flexural (*b*) strength of filled composites based on PPSU and GF: *1* – 0.2 mm; *2* – 3 mm.

The results of quasi-static mechanical testing of composites based on PPSU and GF show that, as in the case of CF, the modulus of elasticity in bending and stretching increases in proportion to the content of the filler (Fig. 5). More clearly, the difference in properties depending on the length of the fibers is observed when testing for three-point bending: the introduction of with 3-mm long GF more significantly increases the elastic modulus. In tensile tests, the difference is less significant. In comparison with CF, the increase in the elastic modulus with the introduction of GF is much lower: at 40% content, the elastic modulus at bending is 160 and 200% higher than the corresponding

Table 3. Thermal Properties of Composite Materials Based on PPSU with CF and GF

Composition	$T_{2\%}$, °C	$T_{5\%}$, °C	$T_{10\%}$, °C
PSSU	504	529	550
	0.2-mm long CF		
PSSU + 20% CF	513	549	571
PSSU + 30% CF	536	562	580
PSSU + 40% CF	544	566	583
	3-mm long CF		
PSSU + 20% CF	516	554	575
PSSU + 30% CF	510	550	574
PSSU + 40% CF	525	558	579
	0.2-mm long GF		
PSSU + 20% GF	508	538	560
PSSU + 30% GF	511	539	562
PSSU + 40% GF	508	538	560
	3-mm long GF		
PSSU + 20% GF	515	547	567
PSSU + 30% GF	514	543	566
PSSU + 40% GF	517	545	564

value of the initial PPSU in the case of GF with 0.2- and 3-mm long fibers, respectively, and is 130% higher at stretching in both cases. For comparison, we recall that with the introduction of 40% CF, the modulus of elasticity at bending increased to 600%, and at stretching – to 330%.

The introduction of GF leads to an increase in the yield strength under uniaxial tension and three-point bending (Fig. 6). At 10% GF content, yield strength practically does not depend on the length of the fibers, however, a further increase in their content shows a more significant reinforcing effect of long fibers, and the higher the concentration, the more obvious the difference. On average, the superiority in strength of composites with long filler fibers is ~ 17% (at 40% content).

The increase in tensile strength after introducing 40% GF with 0.2- and 3-mm long fibers was 19 and 37%, respectively (and around 140% on average for CF); increase in flexural strength was about 62 and 87% (and about 200% for CF).

Thus, it was found that the introduction of GF also leads to a decrease in the plasticity of the composite. There is also an increase in stiffness and strength in quasistatic tests, but to a much lesser extent than when using CF. At the same time, the difference in properties when using GFs of various lengths is greater. Glass-filled composites with longer filler fibers (3 mm) have higher strength values.

Heat resistance is one of the most important operational and structural characteristics of structural materials. Carbon- and glass-fiber-filled composite materials based on PPSU were studied by the thermogravimetric analysis (TGA) in air at a heating rate of 10 °C/min. Heat resistance was estimated from the temperatures corresponding to mass loss of 2, 5 and 10%.

From the results of the study of the concentration dependence of heat resistance of composites with different lengths of carbon and glass fibers (Table 3), it can be seen that with increasing content of CF, there is a significant increase in heat resistance, and higher mass loss temperatures correspond to the samples containing 0.2-mm long CF.

In the case of composites containing 0.2-mm long GF, no significant changes in heat resistance with increasing filler content are observed. Higher values of heat resistance are demonstrated by composites filled with 3-mm long GF.

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