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EFFECTS OF LENGTH AND CONCENTRATION OF CARBON AND GLASS FIBERS ON POLYPHENYLENE SULFONE PROPERTIES

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The effects of length and concentration of carbon (CF) and glass fibers (GF) on the rheological, physicomechanical, and thermal properties of the high-temperature thermoplastic polyphenylene sulfone (PPSU) containing up to 40 wt% filler were studied. The fillers were CF and GF of lengths 0.2 and 3 mm. Addition of CF and GF decreased noticeably the melt flow index and PPSU impact viscosity so that the flowability limit disappeared in the stress—strain diagram because of the reduced ability of the material for plastic deformation. The elasticity modulus and strength of the composite for bending and tension increased with increasing fiber content. The heat resistance increased significantly with increasing CF content. Samples containing CF of length 0.2 mm had higher mass-loss temperatures. The heat resistance changed insignificantly for composites containing GF.

The increasing use of carbon- and glass-plastics in high technology sectors reflects the growing interest of scientists and technologists in developing new progressive and promising combinations of fibrous fillers and polymer matrices [1, 2]. Until now, new compositions were sought and components for polymer mixtures were selected mainly based on knowledge and recommendations accumulated by technologists over the course of multiyear practice with using similar systems based on reactoplasts. The volume of scientific knowledge is still insufficient to develop carbon- and glass-plastics based on high-temperature thermoplastic polymers despite the large amount of information on the design and study of filled composites. This limits their effective use as binders for polymer composites.

The present article examines the effects of the content and geometry (length) of filler, carbon and glass fibers, on the rheological, physicomechanical, and thermal properties of the high-temperature thermoplastic polyphenylene sulfone (PPSU).

The matrix for preparing the composites with fibrous fillers was PPSU with the optimal viscosity (intrinsic viscosity 0.4 dL/g) based on 4,42-dihydroxydiphenyl and 4,42-dichlorodiphenyl sulfones that were synthesized in the Laboratory of Progressive Polymers, H. M. Berbekov KBSU [3, 4].

Fillers were carbon (CF) and glass fibers (GF) with lengths of 0.2 and 3 mm (R&G, Germany). Fibers as received were coated with an epoxy resin that was removed by preliminary annealing because the PPSU processing temperature was significantly greater than the decomposition temperature of the epoxy resin.

Composites were prepared by melt mixing on a Twin-Tech twin-screw microextruder (Great Britain) with $L/D = 30$. Test samples were prepared by casting under pressure on an SZS-20 machine (Haitai Machinery, China) at cylinder temperature 410-420°C and form temperature 200°C.

Mechanical tests on a uniaxial tensile tester used two-sided paddle samples with dimensions according to GOST 11262-80. Tests were performed at 23°C on a CT-TCS 2000 Gotech Testing Machine (Taiwan). Izod impact tests with and without a notch were performed according to GOST 19109-84 using a Gotech Model GT-7045-MD Testing Machine with an 11-J pendulum (Taiwan).

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Table 1. Physicomechanical Properties of PPSU and CF Composites

Composition	A_p, кДж/м²		σ_{flow}, MPa	ε_p, %
	wo/n	w/n		
PPSU	186	43	76.2	13.4
Particle length 0.2 mm				
PPSU + 10% CF	41.0	7.5	–	6.0
PPSU + 20% CF	41.0	9.6	–	4.6
PPSU + 30% CF	38.3	10.5	–	4.1
PPSU + 40% CF	40.6	9.5	–	3.0
Particle length 3 mm				
PPSU + 10% CF	39.8	9.3	–	5.0
PPSU + 20% CF	36.5	8.5	–	4.0
PPSU + 30% CF	38.0	8.5	–	3.8
PPSU + 40% CF	36.0	9.3	–	3.5

Note: wo/n is without notch; w/n, with notch.

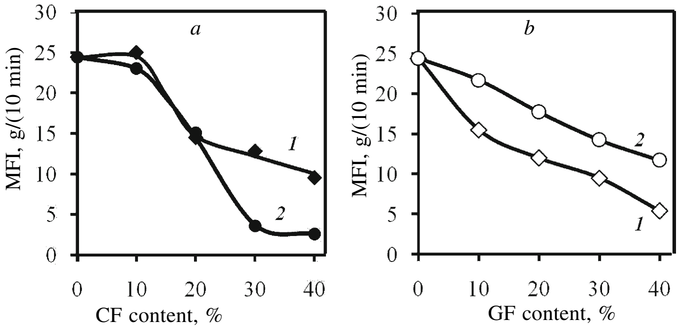

Fig. 1. Dependence of MFI of PPSU on content and length of CF (a) and GF (b): 0.2 (1) and 3 mm (2).

The melt flow index (MFI) were determined at 380°C and load 5 kg on an IIRT-5 instrument (Russia) for measuring the index of a melt. Heat resistance was determined using thermogravimetric analysis on a TGA 4000 system (PerkinElmer, USA).

Composites containing from 10 to 40% fibrous filler were produced to study the effects of CF and GF of different lengths on the PPSU properties and to determine their optimal concentrations.

The MFI was a metric of the rheological properties of the fiber-filled composites. Figure 1a shows the dependence of the MFI on the content and length of CF. The MFI decreased markedly regardless of the fiber length if the CF content was increased from 10 to 40%. The MFIs for composites with long (3 mm) and short fibers (0.2 mm) were practically identical with 20% CF. The dependences of the composite melt viscosity on fiber length showed discernable differences if 30 and 40% CF were added. Short fibers (0.2 mm) did not affect the MFI as significantly as long fibers (3 mm) if the CF content was increased from 20 to 40%. Long fibers at 30 and 40% contents increased the melt viscosity significantly so that the MFI values were very low.

GF also were associated with an increase of PPSU melt viscosity. The MFI values decreased almost linearly if their content was increased (Fig. 1b). It is noteworthy that composites containing long GF (3 mm) had greater MFI values than analogous composites with short GF (0.2 mm).

Therefore, the PPSU MFI decreased in both instances if fibrous fillers were added. Hard and rigid filler particles prevented the melt from flowing by increasing its viscosity. Melt flow was hindered more by the longer CF composites. Conversely, composites with longer GF had higher MFI values. The reason for this phenomenon could be fiber destruction during extrusion because of high shear stresses.

Table 1 presents the measured deformation and strength characteristics of CF-filled composites and shows that the PPSU impact viscosity (A_p) decreased if fibrous filler was added. The quantity A_p is known to be an integral strength characteristic determined not only by the breaking stress but also the polymer plasticity. The CF had this effect on the

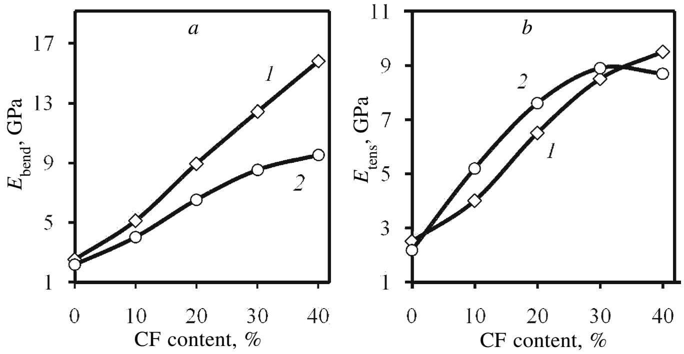

Fig. 2. Concentration dependences of elasticity modulus with three-point bending (a) and uniaxial tension (b) of filled PPSU and CF composites: 0.2 (1) and 3 mm (2).

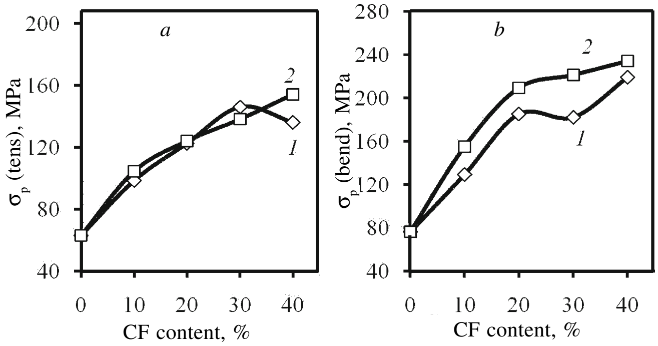

Fig. 3. Concentration dependences of uniaxial tensile (a) and three-point bending strength (b) of PPSU and CF composites: 0.2 (1) and 3 mm (2).

impact viscosity because the relative contribution of plastic deformation to the impact strength of the filled composites decreased, i.e., the impact viscosity of the tested samples was largely determined by the composite strength and the resistance to propagation of destruction.

It is noteworthy that the relative change of impact viscosity of samples with and without a notch (~4.5 times in both instances) was practically not affected by increasing the contents of long and short CF. However, let us focus on several differences. Notching decreased the impact viscosity of starting PPSU samples to $0.23 \cdot A_p$. Samples without a notch (with 0.2-mm filler) and 10-40% CF had impact viscosities of 0.21-0.22 of the A_p value of the starting PPSU samples without a notch. It could be proposed that in this instance, adding filler and notching had the same effects on the composite plasticity and suppressed it to equal extents.

CF-filled notched samples displayed a tendency for the impact viscosity to increase slightly with increasing filler content although in the range 0.17-0.24 of the A_p value of starting notched PPSU.

Unnotched samples with 3-mm CF had impact viscosities 0.19-0.21 of the corresponding value of starting PPSU. This range was 0.18-0.20 for the relative decrease of notched samples.

Thus, CF filler of length 0.2 mm suppressed the contribution of plastic deformation of PPSU during impact tests less than 3-mm CF.

Table 1 shows that the same difference was in principle observed when comparing the breaking bending of composites with different CF geometries in uniaxial tensile tests.

Quasi-static loading studies found that adding even 10% CF more than halved the relative breaking bending so that the flow limit disappeared in the stress—strain plot because the material was less capable of plastic deformation. This effect (reduction of A_p and ε_p) was stronger for samples with 3-mm CF and was due to the high form ratio of the fibrous fillers and their stiffness, which limited plastic deformation during loading of the polymer matrix [5-7].

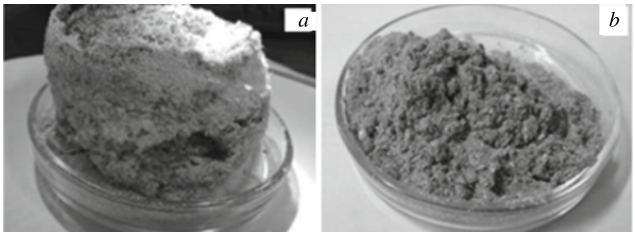

Fig. 4. PPSU composites with CF (20%) of length 3 mm (a) and 0.2 mm (b).

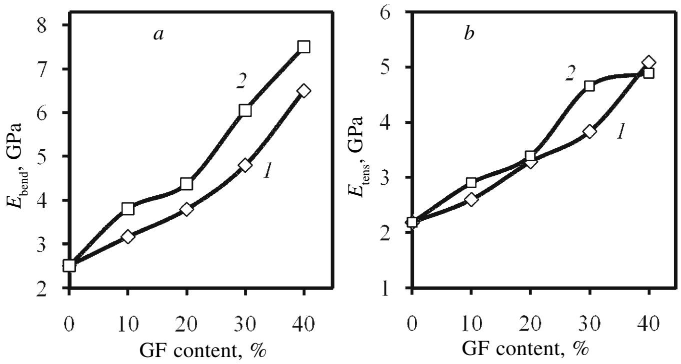

Fig. 5. Concentration dependences of elasticity modulus with three-point bending (a) and tension (b) of filled PPSU and GF composites: 0.2 (1) and 3 mm (2).

As mentioned above, the fibrous fillers acted as reinforcement and increased the strength and elasticity modulus of the material because of the high ratio of longitudinal to transverse dimensions. A classical case of reinforcement of the matrix of the filler occurred (Fig. 2). The elasticity modulus for bending and tension in quasi-static tests increased smoothly with increasing CF content. Composites with longer fibers (3 mm) had slightly greater tensile elasticity moduli. Apparently, more effective transfer of stress at the polymer-matrix—filler interface, the resulting reduced concentration of internal stresses, and an enhanced resistance to loads were responsible for this.

The decrease in the tensile elasticity modulus for the composite with 40% 3-mm CF (Fig. 2b) was a consequence of the high melt viscosity that led to incomplete filling of the test samples. In general, the bending strength increased by 500-600% after adding 40% CF; tensile strength, by ~330%.

Fibrous fillers also increased the uniaxial tensile and three-point strengths of the composite (Fig. 3). The plots show that the bending and tensile strengths increased considerably with increasing filler content. Also, the tensile strength of the composites with 0.2- and 3-mm CF did not differ noticeably. The difference was more obvious for bending tests where composites with 3-mm CF were stronger.

The gain of breaking stress for 40% CF was ~140%; bending stress, slightly greater than 200%.

Thus, the elasticity modulus and tensile and bending strengths in quasi-static tests increased with increasing filler content. Composites with both lengths of CF (0.2 and 3 mm) had similar physicomechanical properties with a slight advantage for samples with 3-mm CF. However, a disadvantage of these was the poorer performance:

-first, the fibers flocculated and formed wads during mixing with the polymer (Fig. 4a) that made their loading into the extruder and regulation of the thread diameter extremely difficult;

-second, the increased melt viscosity also hindered processing.

The extrusion mixture of 0.2-mm CF with polymer was a finely disperse powder that was easily reworked. The composites had high MFIs (Fig. 5b).

Thus, studies of the effect of CF filler geometry on the rheological and deformation-strength properties of PPSU led to the conclusion that 0.2-mm CF were promising.

Table 2. Physicomechanical Properties of PPSU and GF Composites

Composition	A_p, kJ/m^2		σ_{flow}, MPa	ε_p,%
	wo/n	w/n		
PPSU	186	43	76.2	13.4
Particle length 0.2 mm				
PPSU+ 10% GF	80.8	9.6	71.5	8.2
PPSU+ 20% GF	36.0	8.2	–	4.4
PPSU+ 30% GF	25.3	6.2	–	3.2
PPSU+ 40% GF	14	5.1	–	2.3
Particle length 3 mm				
PPSU+ 10% GF	43.4	8.2	–	5.7
PPSU+ 20% GF	36.8	7.3	–	4.6
PPSU+ 30% GF	27.2	5.8	–	3.2
PPSU+ 40% GF	19.7	6.0	–	2.2

Table 3. Thermal Properties of PVA and CF and GF Composites

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

Table 2 presents analogous results for the effects of GF of different lengths and contents on the PPSU properties and shows that adding GF also decreased the PPSU impact viscosity. The impact viscosity decreased smoothly for notched and unnotched composites with increasing GF content, in contrast with CF, where the impact resistance was practically constant for 10-40% CF. The flow limit disappeared and the relative uniaxial tensile breaking strain decreased, like for addition of CF.

The composites had similar impact viscosities regardless of filler fiber length, except for composites with 10% GF (0.2- and 3-mm lengths), where the difference in impact viscosities of notched and unnotched samples was significant (and a flow limit was still observed on the tension diagram).

Quasi-static mechanical tests of PPSU—GF composites showed that the bending and tensile elasticity moduli increased in proportion to the filler content, like for CF (Fig. 5). Three-point bending tests showed a more distinct difference in properties as a function of fiber length. The elasticity modulus increased much more after adding 3-mm GF. The difference was less in tensile tests. The gain of elasticity modulus after adding GF was much less than for CF. The bending elasticity modulus with 40% GF was greater by 160 and 200% than the corresponding value for starting PPSU for 0.2- and 3-mm GF, respectively. The tensile elasticity modulus increased by 130% in both instances. Recall for comparison that the bending elasticity modulus for 40% CF increased up to 600%; tensile, up to 330%.

Adding GF increased the uniaxial tensile and three-point bending strengths (Fig. 6). The strength was practically independent of fiber length for 10% GF. However, the more substantial reinforcing effect of the long fibers was evident if their contents were increased further. The higher the concentration was, the more obvious the difference was. Composites with long filler fibers were an average of ~17% stronger (with 40% content).

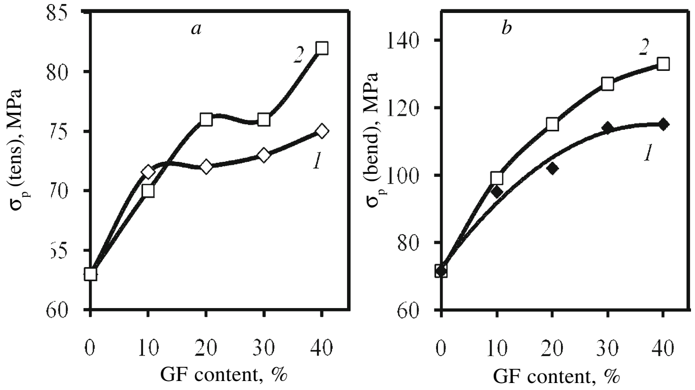

Fig. 6. Concentration dependences of tensile (a) and bending strength (b) of filled PPSU and GF composites: 0.2 (1) and 3 mm (2).

The tensile strength increased by 19 and 37% after adding 40% GF of lengths 0.2 and 3 mm, respectively (average 140% for CF). The bending strength increased by 62 and 87% (~200% for CF).

Thus, adding GF also decreased the composite plasticity. The stiffness and strength in quasi-static tests increased; however, much less than if CF were used. The properties differed more substantially if GF of different lengths were used. GF composites with long filler fibers (3 mm) had higher properties.

Heat resistance is one of the most important operating and structural characteristics of construction materials. CF and GF composites with PPSU were studied using thermogravimetric analysis (TGA) in air at heating rate 10°C/min. Heat resistance was estimated from the temperatures for loss of 2, 5, and 10% of the mass.

The heat resistance of composites with CF and GF of different lengths as a function of concentration (Table 3) showed that it increased significantly with increasing CF content. Samples with 0.2-mm CF had higher mass-loss temperatures.

The heat resistance of composites containing 0.2-mm GF essentially did not change with increasing filler content. Composites with 3-mm GF demonstrated higher heat resistance.

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