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DEVELOPMENT OF COMPOSITE MATERIAL BASED ON POLYPHENYLENE SULFONE FOR 3D PRINTING

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The effect of talc and various polymer additives on the basic mechanical properties of polyphenylene sulfone was studied. It was found that with an increase in the concentration of the filler, there is an increase in the elastic strength and a decrease in the plastic properties of polyphenylene sulfone. The physicomechanical properties of various polymer-polymer composites based on polyphenylene sulfone are considered. High efficiency of polycarbonate as a modifier of toughness is revealed. An efficient method has been developed for producing a composite with high values of impact strength and modulus of elasticity, based on the characteristics of the distribution of the filler in the polyphenylene sulfone polycarbonate binary system. It is shown that the concentration of the filler in the polycarbonate phase reduces the impact strength, whereas its concentration in the polyphenylene sulfone phase followed by the introduction of polycarbonate results in an impact-resistant and high modulus composite. Samples obtained by the 3D printing method exhibit high mechanical characteristics.

3D printing (or additive manufacturing, AM) is a rapidly growing industry with a constantly expanding market [1]. Additive technologies have made it possible to obtain objects of any degree of complexity and geometry, at times reducing the cycle time from an idea to a specific product.

Additive technologies are increasingly used not for prototyping, as at the initial stage of their development, but for obtaining specific working parts for various structures and assemblies. It is reported, for example, that the new Airbus A350 XWB airplane has more than 1,000 parts printed on a 3D printer [2].

A large number of different polymeric materials are currently produced by 3D printing: standard thermoplastics with operating temperatures of up to 100 °C (polylactides, acrylonitrile butadiene styrene, etc.), structural or engineering plastics with operating temperatures of up to 150 °C (polycarbonates, polyamides, polyethylene terephthalate) and superstructural polymers (polysulfones, polyetherketones, polyetherimides, etc.), which are capable of long-term operation at temperatures up to 200 °C and above.

Despite the excellent complex of physicomechanical properties of superstructural polymers, continuously developing production imposes ever greater demands on them, in particular, there is a need to develop new high-modulus and impact-resistant materials that can be processed by additive methods, in particular by layering the molten polymer strand (FDM-method). Intensive research has been conducted in this area in recent years [3-6].

The elastic-strength properties of superstructural polymers can be significantly increased by modification by fibrous fillers. However, the addition of fillers complicates manufacturability and often reduces impact resistance of such composites, especially when used in 3D printing [5]. Therefore, it is of interest to obtain composite materials with enhanced elastic-strength properties and at the same time high impact strength for use in 3D printing by the FDM method. One of the most widely used superstructural polymers for 3D printing by the FDM method is polyphenylene sulfone (PPSN), which has high chemical and radiation resistance, low water absorption, and low shrinkage during molding [7–9].

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Table 1. Physicomechanical Properties of Composites Based on PPSN and Talc

Composition	A_d, kJ/m^2		E_{fl}, GPa	E_t, GPa	σ_d, MPa	σ_y, MPa	ε,%
	unnotched	notched					
PPSN	163	17	2.63	2.14	72	87.6	13.6
PPSN + 5% talc	135	11	3.02	2.45	85	98.1	10.1
PPSN + 10% talc	112	–	3.56	2.94	90	97.5	8.7
PPSN + 15% talc	55	–	4.12	3.58	101	–	6.4

Notations: A_p – Izod impact strength, including; E_{fl} – flexural modulus; E_t is the modulus of elasticity under uniaxial tension; σ_p – fracture stress under uniaxial tension; σ_y – tensile yield strength; ε_p is the relative strain at fracture under tension.

The polymer matrix in this research was composed of polyphenylene sulfone based on 4,4-dihydroxydiphenyl and 4,4-dichlorodiphenyl sulfone, with characteristic viscosity of 0.45-0.50 dL/g, synthesized at the Laboratory of Advanced Polymers at KBSU using the previously described method [10, 11]. Talc from Imerys, Luzenac A7C (France) with an average particle size of 2 microns was used as the filler. Various polymer additives were used to increase the impact strength of the composites, including: polycarbonate (PC) based on 4,4-diphenylolpropane of the K-20 MRA brand from Carbotex (Japan), acrylonitrile butadiene styrene (ABS) of the 2020-31 brand produced by DPO Plastic (Russia), high-impact polystyrene (HIPS) of the 825ES brand produced by Nizhnekamskneftekhim (Russia).

Samples for testing were obtained by injection molding on a SZS-20 machine from Haitai Machinery (China) at a material cylinder temperature of 390 °C and a mold temperature of 180 °C.

Mechanical uniaxial tension testing was carried out on samples in the form of a double-sided blade with dimensions according to GOST 112 62-80. The tests were carried out on a universal testing machine “Gotech Testing Machine CT-TCS 2000” (Taiwan) at 23 °C. Izod impact testing was carried out on unnotched and notched samples according to GOST 19109-84 on a Gotech Testing Machine device, model GT-7045-MD, made in Taiwan, with a pendulum impact energy of 11 J.

Composites were obtained by melt blending in a TwinTech twin screw microextruder (UK).

At the first stage, the effect of different concentrations of the filler on the physicomechanical properties of PPSN was studied (Table 1). The data in Table 1 show that the mechanical properties of PPSN linearly depend on talc concentration: with increasing filler content, plastic properties monotonously decrease (toughness and elongation at break), while simultaneously, the elastic-strength characteristics increase (elastic moduli for bending and stretching, tensile yield strength and UTS). When the concentration of the filler is 15%, a significant decrease in impact resistance is observed along with an absence of plastic deformation (tensile yield strength does not manifest itself). At the same time, the elastic modulus and strength values become quite high (increasing by 55 and 15%, respectively, above the corresponding values for the initial PPSN).

To obtain both a high-modulus and impact-resistant composite, it is necessary to use a toughness modifier, which would level the negative effect of the solid filler on the plastic properties of the polymer. The rubbers commonly used for these purposes are not quite suitable for PPSN due to their low thermal properties and a significant decrease in the elastic modulus of the composite upon their introduction. In this regard, it was of interest to study the effect of high impact polystyrene (HIPS), acrylonitrile butadiene styrene (ABS) and polycarbonate (PC) on the impact resistance of PPSN to identify the most effective modifier for further production of talc-filled composites. Table 2 shows the properties of polymer-polymer composites based on PPSN and the specified impact strength modifiers.

The study of the possibility of using different polymers as toughness modifiers showed that PC rather effectively increases the impact resistance and ductility of PPSN. With the introduction of only 10% PC, unnotched PPSN samples are not destroyed during impact testing, and the rigidity of the initial polymer is not reduced.

As for HIPS and ABS, they are completely incompatible with PPSN: composite samples turn out heterogeneous, with stratification occurring already in the extrusion process. Respectively, their addition only leads to polymer embrittlement and a reduction of impact strength. As can be seen from Table 2, these samples have no yield strength under tension, which indicates the inability of the material to plastic deformations. Thus, PC has been found to be a sufficiently effective impact strength modifier of PPSN. It was chosen for further development of PPSN/Talc/PC ternary

Table 2. Mechanical Properties of Polymer-Polymer Composites Based on PPSN (Samples Obtained by Injection Molding)

Composition	MFI, g/10min	A_d, kJ/m^2		E_{fl}, GPa	E_t, GPa	σ_p, MPa	σ_y, MPa	ε,%
		unnotched	notched					
PPSN	5.0	150.0	16.5	2.66	2.20	66.0	88.0	14.0
PPSN + 10% ABS	8.0	84.1	9.0	2.76	2.67	76.8	–	5.2
PPSN + 20% ABS	6.6	18.2	9.3	2.61	2.53	71.3	–	5.0
PPSN + 10% HIPS	7.3	54.2	13.7	2.72	2.55	51.7	–	3.7
PPSN + 20% HIPS	6.6	21.2	11.5	2.70	2.50	45.7	–	2.6
PPSN + 10% PC	3.5	n/d	11.7	2.67	2.53	76.0	93.6	28.0
PPSN + 20% PC	2.4	n/d	14.0	2.63	2.55	73.0	82.5	79.0

Table 3. Mechanical Properties of PPSN/Talc/PC Composites Obtained by Various Methods (Samples Obtained by Die Extrusion))

Composition	A_d, kJ/m^2		E_{fl}, GPa	E_t, GPa	σ_d, MPa	σ_y, MPa	ε,%
	unnotched	notched					
PPSN	n/d (250)	20.1	2.49	2.22	72	87	17
PPSNT*	160	13.2	3.45	3.02	77	90.2	18.5
Mixing							
PPSNT + 5% PC	124	8.4	3.64	3.36	95	–	9
PPSNT + 10% PC	64	8.4	3.74	3.33	92	–	7.5
PPSNT + 20% PC	30	7.35	3.78	3.37	85	–	4
PPSN-based concentrate							
PPSNT + 5% PC	156	9.1	3.54	3.21	75	91.5	13
PPSNT + 10% PC	155	8.8	3.45	3.18	75	91	14
PPSNT + 20% PC	n/d (273)	12.5	3.30	3.07	70.0	89	13
PC based concentrate							
PPSNT + 10% PC	67.8	8.4	3.53	3.18	90.0	91	8
PPSNT + 20% PC	44	7	3.32	3.05	81.5	85	7

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*PPSNT – PPSN with the addition of talcum as filler.

composites with the aim of obtaining simultaneously hard and impact-resistant 3D printing materials. Composites were obtained by three methods:

- simultaneous mixing of all components and subsequent joint extrusion (mixing);
- preliminary extrusion of PPSN/talc with the subsequent introduction of PC (a PPSN-based concentrate);
- preliminary preparation of PC/talc concentrate and its subsequent introduction to PPSN followed by joint extrusion (PC-based concentrate); at the same time, the qualitative and quantitative composition of the composites remained unchanged.

The mechanical properties of PPSN/talc/PC composites obtained by various methods are given in Table 3. As can be seen from Table 3, the original PPSN has a high impact resistance. The addition of talcum filler leads to the expected changes in properties: a decrease in impact strength and an increase in the elastic modulus. The introduction of 5% PC in addition to talc to increase impact strength, in contrast, only aides in decreasing this property. A further increase in the concentration of PC is accompanied by an even greater loss of impact resistance. At 20% PC, the impact strength of the composite is more than 5 times lower than the corresponding value for the filled PPSN.

This effect, opposing the expectation, is apparently the result of the forming phase structure of this three-component composite. The introduction of the filler into the PPSN/PC polymer mixture, which is thermodynamically incompatible as confirmed by DSC (the presence of two glass transition peaks), may be accompanied by the concentration of the filler to a greater extent in one of the phases. This depends on the affinity of the filler for one or another component or on the rheological properties of the mixed polymers. When a mixture of three components is simultaneously loaded into the extruder (conventional mixing), the filler appears to concentrate in the PC phase, since at heat treatment

Table 4. Mechanical Properties of PPSN and PPSN/Talc/PC Composite (Samples Obtained by 3D Printing Using the FDM Method)

Composition	A_d, kJ/m^2	E_{fl}, GPa	E_t, GPA	σ_d, MPa
	unnotched			
PPSN	n/d (215)	2.55	2.12	79.7
PPSN/talc/PC	n/d (247)	4.08	3.15	70.1

temperatures its melt flow rate is significantly higher. This is accompanied by a loss of plastic properties and a decrease in the plasticity of the composite as a whole.

Composites obtained by pre-extrusion of PC-talc (PC-based concentrate) confirmed the proposition regarding filler distribution. Concentration of the filler in PC led to the production of samples with low impact strength, and the increase in the content of PC contributes to greater embrittlement of the material. A similar effect is observed when producing composites by ordinary mixing, as confirmed by the concentration of filler in the PC phase. The reduction in impact strength with increasing PC concentration in this case (in the case of three-component systems) can be explained by a reduction in the fraction of the impact-resistant polymer matrix due to an increase in the content of the non-plastic component (PC/talc blend). This leads to effects similar to those cause by the filling of a plastic matrix with hard additives: in accordance with the increase in their content, the ability for high-speed deformations decreases.

The sequence of introduction of the components can play a decisive role in the distribution of the filler in the binary system, so that it is possible to “forcibly” increase its content in one phase or another. This fact can significantly affect the mechanical properties of the composite [12]. On the basis of these considerations, composites of similar composition were obtained by preliminary extrusion of PPSN together with a filler, followed by the introduction of PC (PPSN-based concentrate). This made it possible to concentrate the filler in the PPSN phase, and the introduction of PC is already accompanied by an increase in impact strength. When the concentration of PC reaches 20%, unnotched samples are no longer destroyed, just like the starting PPSN.

Samples of composite yarns obtained by the developed method were printed using the FDM method. As can be seen in Table 4, the samples are characterized by high rigidity, 60% higher than the rigidity of pure PPSN, as well as by high impact strength.

Thus, it was found that the order of introduction of components in the PPSN/talc/PC system plays a crucial role in the formation of the structure and mechanical properties of the composite material. Concentration of hard filler in the PC phase leads to a loss of its modifying ability, which is accompanied by a decrease in the impact strength and plasticity of the composite as a whole, and with an increase in PC concentration, these effects increase. This is different from similar examples where low-modular thermoplastics or elastomers are used as impact strength modifiers. In their case, the encapsulation of a solid filler with an elastomer leads to an increase in the modifying capacity of the latter [13, 14]. With directed concentration of the filler in the PPSN phase, the PC again acts as a modifier of toughness, as is the case with the matrix PPSN.

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