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Bulk Properties and Application of Glass Fiber-Filled Polyphenylene Sulfides

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Abstract—Thermal, physicomechanical, and electro-, and thermophysical properties of glass fiber-filled polyphenylene sulfides were investigated, and their resistance to external acting and special factors was evaluated.

Keywords: glass fiber-filled polyphenylene sulfide, properties, external action, aging

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Increased requirements for operating performance and manufacturability, as well as weight and dimension characteristics of products being developed in almost all industry sectors have created the need for high-tech plastics with significantly improved technical and operational characteristics. These requirements are fully met by polymeric materials based on high-temperature thermoplastics such as polyetheretherketones, polyesterimides, and polyphenylene sulfides (PPS), whose use has become the main global trend in the modern plastics industry.

Composite materials based on high-temperature thermoplastics, due to their manufacturability making them suitable for fabrication of parts by high-throughput injection molding and extrusion methods and to serviceability up to 200–250°C, have already found extensive application in production of heavily loaded items in aerospace, military, automotive, electrical engineering, electronic, automotive, instrument-making, and other sectors.

The growth rate of high-temperature thermoplastics production and consumption was estimated at 10% per annum [1–3], which is more than twice the global plastics production as a whole. The demand, as well as the production and consumption growth rates are the highest for polyphenylene sulfides which combine in a unique way technological and operational properties such as high strength, hardness, and rigidity; low creep; inflammability; excellent electrical insulating properties; hydrolytic stability and chemical resistance, in particular, to automotive and aviation fuels; high resistance to climatic factors, UV and γ-radiation; and minimal permeability to most liquids and gases. Ready feedstock availability, relative ease of synthesis, and low cost have predetermined strong growth of PPSs, especially in Southeast Asia, where the growth rate is estimated at 30–40% per annum [2–7].

Currently, PPS-based materials are produced by more than 20 companies from different countries under the following brand names: Ryton (Chevron-Phillips, CPC), Fortron (Celanese, Ticona, Kureha, Polyplastics), Torelina (Toray, Japan), PPS (DIC Corp., Japan), Tedur (former brand of Bayer, now Albis Plastics), Craston (Ciba-Geigy), Primef (Solvay), etc., with brand assortment including more than 100 items [3, 4, 6–8]. In 2012, the global consumption of PPS-based compositions exceeded 135 thousand tons [7, 8], and already in 2015 their production reached 180 thousand tons, which in monetary terms (about 3.0 billion euros) exceeded that of many large scale-produced polymers. The projected

Table 1. Physicomechanical properties of glass-filled PPS [9, 26–29]

Run no.	Material characteristics		Tensile stress at break σ_b, MPa	Tensile modulus, MPa	Charpy impact strength, kJ/m^2	Heat deflection temperature, °C	Volume resistivity, Ω m	Dielectric strength, kV/mm
	Name, company name, country	Brand						
	Ryton®	BR 111[a]	159	12300	24	260	10^{13}	17.7
	Chevron-Phillips, USA	R-4	165	13700	25	260	10^{13}	19.7
		R-4-240BL	165	14500	40	265	10^{13}	21.7
		R-4-270NA	190	14500	45	265	10^{13}	20.0
	Fortron®	1140L4	195	12200	53	270	10^{13}	28
	Celanese, Ticona, Germany	1140E7	150	14700	28	270	10^{13}	28
		ICE 504L	170	–	51	262	10^{13}	30
		MT9140L4	190	13800	48	270	10^{13}	28
	Tedur®	L4510-1	180	–	45	260	10^{13}	25
	Albis Plastics, USA-Canada	L9107-1U	190	–	45	275	10^{13}	25
		L 9107-7	200	–	45	275	10^{13}	25
	PPS, DIC, Japan	PPS FZ-1140	180	15000	36	265	10^{13}	16
		PPS FZ-1140B2	170	15000	40	265	10^{13}	16
		PPS FZ-2140	180	14000	46	265	10^{13}	16
		PPS FZ-2140A1	190	15000	51	270	10^{13}	16
		PPS FZ-240	165	15000	53	265	10^{13}	16
	PPS Torelina,	A504CX1B	199	14500	55	260	10^{13}	24
	Toray Industries, Japan	A504CX90	200	15500	55	260	10^{13}	24
		A504CX95	190	15500	45	265	10^{13}	25
		A504FG1	165	15500	30	260	10^{13}	22
		A674M2[a]	150	12000	57	260	10^{13}	24

[a] Modified shock-resistant composition.

production of PPS-based materials in 2020 was 250 thousand tons.

The main consumers of injection-molded PPS-based plastics across the globe are electrical engineering and electronics, automotive and aerospace industries, as well as military equipment and other dynamically developing economy sectors [1, 3, 4, 6, 8–11].

Systemic studies focused on PPS were carried out in the USSR in 1970–1980 in the Nesmeyanov Institute of Organoelement Compounds, USSR Academy of Sciences [12–16]. Karbolit Research and Production Association (Kemerovo) even undertook efforts toward pilot production of PPS. However, after collapse of the Soviet Union all PPS-related research and development activities were stopped, and PPS has not been produced in the Russian Federation as yet.

In recent years the interest in PPS-based materials has significantly increased in Russia, and relevant studies have been conducted in research institutions, including All-Russian Research Institute of Aviation Materials [17], Interdepartmental Center for Analytical Research in Physics, Chemistry, and Biology, Presidium, Russian Academy of Sciences [17–21], POLYPLASTIC Research and Production Enterprise [18–22], and Prometey Central Research Institute of Structural Materials [23, 24]. Based on the available research results, pilot-scale production of the following developments has been implemented:

Table 2. Physicomechanical properties of glass-filled (40 wt %) Armoten PPS compositions

Quality parameter	Test method	Armoten SV 40	Armoten SV 30	Armoten SV 30-UP	Armoten SV 40-UP	Armoten SV MN 60
Density, g/cm^3	GOST 15139	1.66	1.58	1.51	1.62	1.91
Tensile stress at break, MPa	GOST 11262	206	181	166	196	158
Tensile modulus, MPa	GOST 9550	16693	12880	10900	15640	24770
Flexural stress at break, MPa	GOST 4648	302	259	246	289	258
Flexural modulus, MPa	GOST 4648	13100	10440	10200	12540	19500
Charpy unnotched impact strength (edgewise), kJ/m^2	GOST 4647	56	43	68	62	25
Heat deflection temperature (1.8 MPa), °C	GOST 12021	272	267	263	269	275
Dissipation factor (1 MHz)	GOST 22372	0.002	0.002	0.004	0.003	0.002
Dielectric constant	GOST 22372	4	4	4	4	5
Volume resistivity, Ω m	GOST 6433.3	6×10^{14}	6×10^{14}	6×10^{14}	6×10^{14}	2×10^{14}
Surface resistivity, Ω	GOST 6433.3	8×10^{16}	8×10^{16}	8×10^{16}	8×10^{16}	2×10^{16}
Dielectric strength, kV/mm	GOST 6433.3	34	30	27	30	27

—Prometey Central Research Institute of Structural Materials has set up and put into practice application of UPFS antifriction heat-resistant material based on Fortron polyphenylene sulfide and carbon fabric;

—POLYPLASTIC Research and Production Enterprise in 2018 launched production of the composite polymeric material based on PFS SV-40-1 polyphenylene sulfide, developed by the Interdepartmental Center for Analytical Research in Physics, Chemistry, and Biology, Presidium, Russian Academy of Sciences, and glass-filled injection-molded materials based on ARMOTEN and TERMORAN PPSs [25].

Analysis of the brand assortment of PPS-based materials [18–22] shows that the principal items are injection-molded compositions filled with 40 wt % glass fiber, which find application as high-strength structural materials (see Table 1 for selected properties of glass-filled PPSs from world's largest manufacturers).

Glass-filled PPS composites with a lower glass fiber content (≤30 wt %) have limited use because of poorer strength properties and higher cost compared to the 40 wt % glass fiber- reinforced compositions.

Composites with a higher degree of filling, mainly 60–70 wt % glass/mineral-filled ones, are characterized by very high stiffness (tensile modulus of 17000–21000 MPa) but have poor flow properties and low impact strength (20–25 kJ/m^2) and therefore are used mainly for the manufacture of thick-walled parts, predominantly for electrical engineering applications.

Since 2018, glass-filled PPS-based composite materials have been produced in Russia, among which Armoten materials are offered in a fairly wide brand assortment (Table 2) covering the main practical application areas. TERMORAN materials (Table 3) are represented by 2 brands: TERMORAN PFS SV-40 high-strength glass-filled polyphenylene sulfide and its shock-resistant analog TERMORAN PFS SV-40UP. Both material brands are produced either uncolored or spun-dyed black. TERMORAN materials are certified and passportized.

Composite polymer material PFS SV 40-1 is essentially polyphenylene sulfide filled with 40 wt % glass fiber, as well as with target additives; it is practically free of chlorine ions and is intended for electronic and electrical engineering and other special applications.

Tables 1–3 show that, in terms of the strength and electro- and thermophysical characteristics, the glass-filled materials produced in the Russian Federation are equal to the best foreign analogs, which concerns both basic and modified shock-resistant composites.

Comparative assessment of the level of the initial (basic) characteristics of materials undoubtedly provides valuable insights into the key advances made in this area, but these data are not sufficient for assessing the applicability of these materials for manufacturing particular products intended for specified operation conditions.

Table 4. Properties of TERMORAN glass-filled polyphenylene sulfides at different temperatures [30]

Run no.	Parameter	Test method	Parameter value for indicated brand		
			TERMORAN PFS SV-40	TERMORAN PFS SV-40UP	PFS SV 40-1
1	Tensile stress at break, MPa	GOST 11262	205	186	187
2	Tensile modulus, MPa	GOST 9550	15960	14500	15730
3	Flexural stress at break, MPa	GOST 4648	291	278	270
4	Flexural modulus, MPa	GOST 4648	14100	12620	12930
5	Charpy unnotched impact strength (edgewise), kJ/m^2	GOST 4647	53.0	63.0	55
6	Water absorption, 24 h, %	GOST 4650	0.02	0.02	0.02
7	Density, g/cm^3	GOST 15139	1.65	1.60	1.66
8	Volume resistivity, Ω cm	GOST 6433.2	6×10^{16}	6×10^{16}	4×10^{16}
9	Surface resistivity, Ω	GOST 6433.2	4×10^{16}	10^{16}	4×10^{16}
10	Dielectric strength, kV/mm	GOST 6433.3	28	32	31
11	Dissipation factor (10^6 Hz)	GOST 22372	0.0024	0.0026	0.003
12	Dielectric constant (10^6 Hz)	GOST 22372	4.0	3.9	4.0
13	Heat deflection temperature (1.8 MPa), °C	GOST 12021	271	265	266
14	Coefficient of linear thermal expansion, deg^{-1}	GOST 32618.2	14×10^{-6}	15×10^{-6}	15×10^{-6}
15	Thermal conductivity, W/mK	ISO 2207-2	0.36	0.35	0.36
16	Flammability (rating)	GOST 28157	PV-0	PV-0	PV-0
17	Glow wire flammability index	GOST 27483	960	960	960
18	Fungus resistance, points	GOST 9.049	0–1	0–1	0–1

From this perspective, the available marketing and scientific and technical, as well as advertising information on imported materials contains very scarce specific data on their resistance to operational and external factors and still less to special factors. Relevant information is typically limited to general phrases like "materials are characterized by high resistance to temperature, hydrolysis, climatic and other environmental effects."

In view of the above-said, we report herein the results from investigation of the main properties of domestic glass-filled polyphenylene sulfides TERMORAN PFS SV-40, TERMORAN PFS SV-40UP, and PFS SV 40-1 over a wide temperature range and from their testing for resistance to external acting, special, and operational factors using standard test procedures, as indicated in tables below.

Material Properties over a Wide Temperature Range

The patterns of changes in the strength characteristics with test temperature, displayed by both TERMORAN materials across a wide temperature range, proved to be identical for them, as well as for them and PFS SV 40-1. Specifically, in the low-temperature range the stiffness and strength tend to increase with an increase in the test temperature, and with rising the latter, the elasticity of the material shows an increasing trend (Table 4).

At low strains the materials exhibit brittle fracture, as is typical for filled polymer composites (see the stress-strain curves of the both brands in Fig. 1).

Excellent electrical insulating properties of the materials (Table 3) are retained throughout the operating temperature range. The dielectric strength of the materials ranges from 28 to 32 kV/mm (which exceeds that of the commonly used engineering thermoplastics) and remains practically unchanged with temperature rising to 220°C.

The volume resistivity under ordinary operating conditions is 10^{15}–10^{16} Ω cm, but at temperatures above the glass transition temperature of PPS, 90–120°C, it decreases by about 2 orders of magnitude.

The dielectric constant is almost independent of temperature, being 3.5–4.5.

The dissipation factor at 1 MHz under ordinary conditions is 0.002–0.003 but tends to increase slightly with decreasing frequency and increasing test temperature.

The respective thermal conductivities of TERMORAN PFS SV-40 and TERMORAN PFS SV-40UP of 0.36

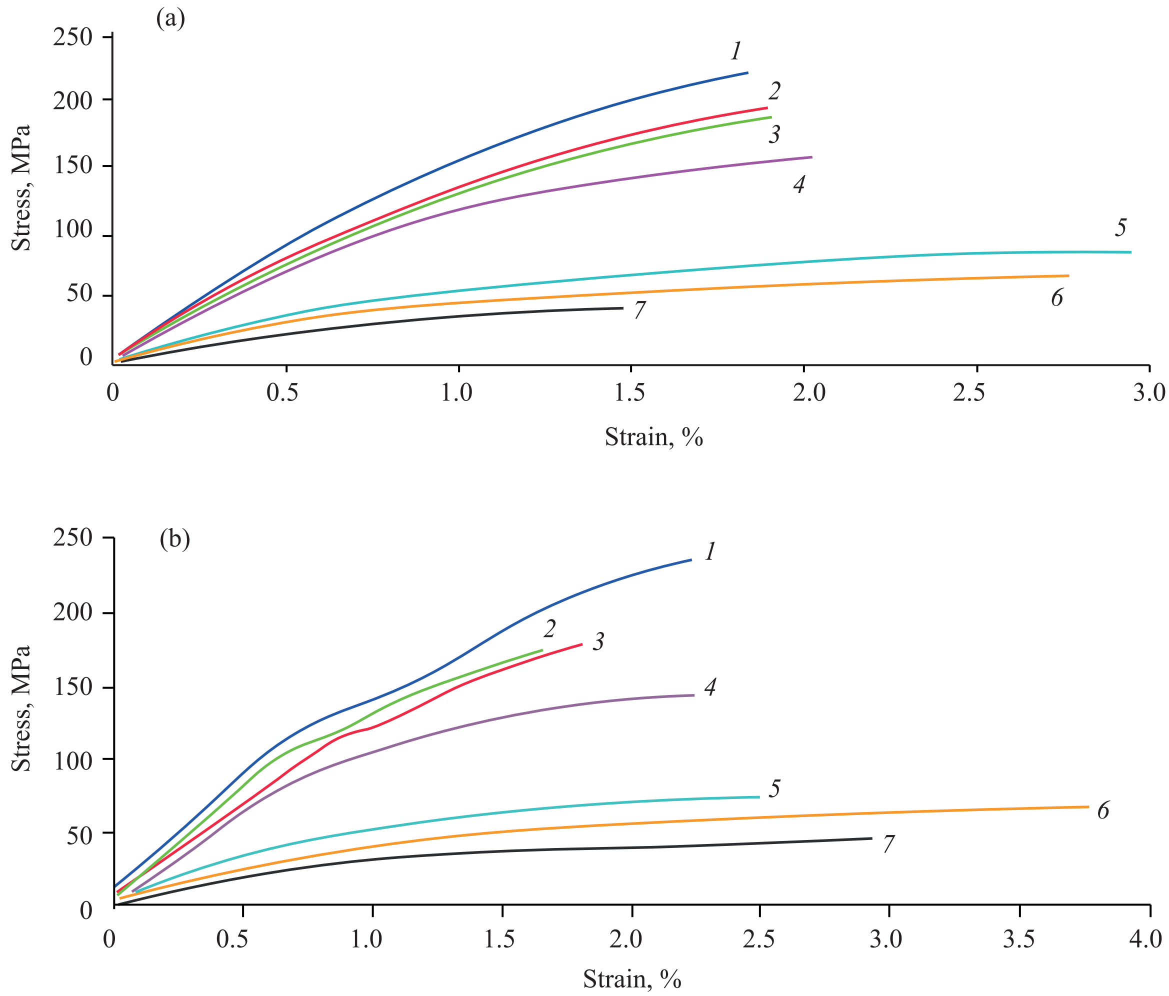

Fig. 1. Stress-strain curves for (a) TERMORAN PFS SV-40 and (b) TERMORAN PFS SV-40UP glass-filled polyphenylene sulfides, recorded at: (*1*) –40°C; (*2*) 23°C, (*3*) 40°C, (*4*) 80°C, (*5*) 130°C, (*6*) 180°C, and (*7*) 240°C.

and 0.35 W/mK tend to slightly increase on heating to 230–240°C.

The glass-filled polyphenylene sulfides exhibit fairly low coefficient of linear thermal expansion (CLTE), close to that of nonferrous materials (brass, bronze, etc.), stable over a wide temperature range, which affords strong leakproof metal-reinforced structures. A small inflection in thermomechanical curve, observed in the range of 90–110°C (Fig. 2), corresponds to the glass transition region of PPS.

As regards flammability, the glass-filled polyphenylene sulfides tested (Table 3) are rated PV-0 (which is the highest, most flame retardant, rating, corresponding to UL 94 V-0) due to the inherent inflammability without using flame retardant additives of the polymer matrix (limiting oxygen index of polyphenylene sulfide is 48).

A glow wire flammability index of 960°C, revealed by the fire resistance tests (Table 3), makes TERMORAN PFS SV-40, TERMORAN PFS SV-40UP, and PFS SV 40-1 glass-filled polyphenylene sulfides applicable in equipment exploited under permanent load in harsh operating conditions.

All these glass-filled polyphenylene sulfides (Table 3) exhibit high fungus resistance estimated at 0 and 1 point when tested according to method 1 (pure samples) and method 2 (infected samples) of GOST (State Standard) 9.049, respectively.

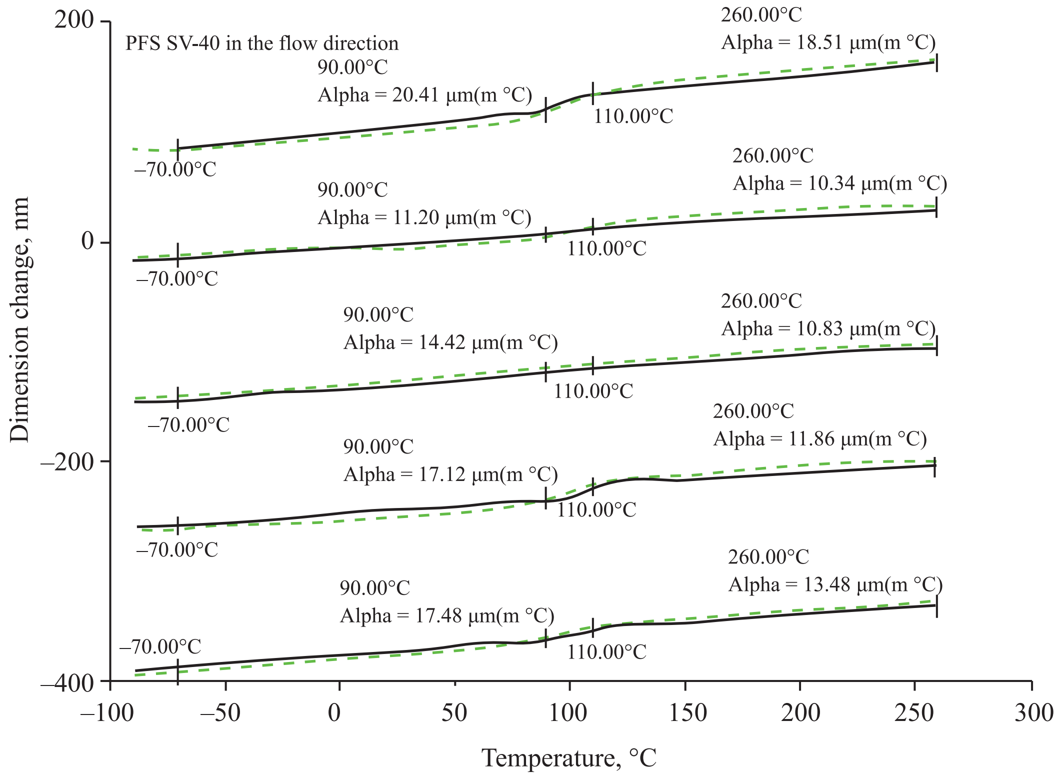

Fig. 2. Temperature dependence of CLTE of TERMORAN PFS SV-40 glass-filled polyphenylene sulfide.

RESISTANCE TO EXTERNAL ACTING FACTORS

Moisture and Water Resistance

Glass-filled polyphenylene sulfides are characterized by very low moisture absorption of 0.02 wt % as estimated for a material sample immersed in distilled water during 24 h at room temperature in accordance with GOST (State Standard) 4650.

Materials were tested according to GOST 10315 for moisture resistance by exposure of a sample (a disc (50±2) mm in diameter and (3.0±0.2) mm in thickness) at relative air humidity of (93+2)% at a temperature (23+2)°C in a climatic chamber and for water resistance by immersion in distilled water at a temperature of (23+0.5)°C. After a 12-months exposure the dimensions and weight of the samples remained practically unchanged (Tables 5–6). Specifically, the weight gain was as low as 0.032%, and the changes in the linear dimension do not exceed 0.025%, meeting the design documentation requirements for high-precision parts (accuracy class for dimensional tolerances “f” according to GOST 30893.1). Tables 5–6 show the testing results only for TERMORAN PFS SV-40, since they coincide with those for TERMORAN PFS SV-40UP and PFS SV 40-1.

Thermal Cycling Endurance

An informative indicator of the material response to the operating conditions is the thermal cycling endurance, with the thermal cycle test reproducing rapid changes in the operative, seasonal, and daily temperatures. Proceeding from the fact that products and equipment of various industry sectors can be operated in any of the climatic regions described in GOST 15150 and considering additional increases in the temperature of products due to heating by sunlight, the temperature range from –70 to +90°C was chosen for material testing. Thermal cycle testing of the glass-filled PPS was carried out in accordance with GOST RV 20.57.416 (method 205-1) by subjecting the samples to repeated cooling and heating cycles (a total of 25 cycles) in heating and cooling chambers at temperatures of –70°C and +90°C, respectively, for 4 h at each temperature.

Table 7 shows that, after testing, the physicomechanical and electrophysical properties of the materials remained

Table 5. Results of TERMORAN PFS SV-40 testing for moisture resistance

Parameter, unit	Test method	Parameter value during testing, month											
		1	2	3	4	5	6	7	8	9	10	11	12
Weight gain, %	GOST RV 20.57.416-98 (method 406-1)	0.020	0.025	0.028	0.027	0.030	0.028	0.025	0.030	0.034	0.034	0.030	0.032
Dimension change, %: —sample oriented in the flow direction	GOST RV 20.57.416-98 (method 404-1)	0.020	0.020	0.020	0.020	0.025	0.020	0.020	0.025	0.025	0.025	0.025	0.025
—sample oriented in the transverse direction		0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020

Table 6. Results of TERMORAN PFS SV-40 testing for water resistance

Parameter, unit	Test method	Parameter value during testing, month											
		1	2	3	4	5	6	7	8	9	10	11	12
Weight gain, %	GOST RV 20.57.416-98 (method 406-1)	0.038	0.047	0.052	0.067	0.065	0.066	0.068	0.071	0.078	0.082	0.083	0.080
Dimension change, %: —sample oriented in the flow direction	GOST RV 20.57.416-98 (method 404-1)	0.020	0.030	0.030	0.035	0.035	0.030	0.030	0.035	0.036	0.035	0.036	0.038
—sample oriented in the transverse direction		0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020

practically unchanged and met the requirements contained in the appropriate technical documentation.

As applied to the operating conditions for products of aerospace and other special equipment, the temperature range from –150 to +150°C was chosen for testing, with at least 10-min exposure at each temperature in the cycle and the total number of cycles of 100.

Table 8 shows that the indicators and characteristics of the glass-filled PPS remained practically unchanged from the initial level, evidencing high thermal cycling endurance.

Tests aimed to assess the resistance of the materials to salt fog were carried out in accordance with GOST RV 20.57.306, item 5.12. During the tests in a CORROSIONBOX1000 He salt fog chamber the samples were exposed to salt fog with dispersion of 1–10 μm (95% drops) and 2–3 g/m^3 water content at the temperature of 55± 2°C; the test duration was 7 days. As follows from the test results (Table 9), all brands of the materials tested are resistant to salt spray.

Also, all the glass-filled polyphenylene sulfide brands (Table 3) proved to be highly resistant to solar radiation (Table 10), as demonstrated by tests conducted in accordance with GOST RV 20.57-306 (item 5.10, method 1) in a Q-Sun Xe-3HSC weathering testing chamber Q at a temperature of (+45±2)°C and at an exposure time of 5 days.

Table 7. Results of thermal cycle testing of glass-filled polyphenylene sulfides in the range from –70 to +90°C

Parameter, unit	Test method	TERMORAN PFS SV-40		PFS SV 40-1	
		before testing	after testing	before testing	after testing
Tensile stress at break, MPa	GOST 11262	192	183	185	183
Tensile modulus, MPa	GOST 9550	15969	15686	–	–
Flexural stress at break, MPa	GOST 4648	285.4	287.1	271	273
Charpy impact strength, kJ/m^2	GOST 4647	55.8	54.6	61	60
Volume resistivity, Ω cm	GOST 6433.2	6×10^{16}	6×10^{16}	6×10^{16}	6×10^{16}
Dielectric strength, kV/mm	GOST 6433.3	34	34	–	–

Table 8. Results of thermal cycle testing of TERMORAN PFS SV-40 glass-filled polyphenylene sulfide in the range from –150 to +150°C

Parameter, unit	Test method	Parameter value	
		before testing	after testing
Tensile stress at break, MPa	GOST 11262	189.5	190.8
Flexural stress at break, MPa	GOST 4648	286.2	293.2
Compressive strength, MPa	GOST 4651	183.9	178.0

Table 9. Salt spray test results for the materials

Parameter, unit	Test method	Glass-filled polyphenylene sulfide brand					
		TERMORAN PFS SV-40		PFS SV 40-1		TERMORAN PFS SV-40UP	
		1[a]	2[a]	1[a]	2[a]	1[a]	2[a]
Tensile stress at break, MPa	GOST 11262	201	186	185.0	177.0	186	187
Tensile modulus, MPa	GOST 9550	16100	15560	16407	16030	14500	14410
Flexural strength at break, MPa	GOST 4648	291	293	271	263	278	272
Flexural modulus, MPa	GOST 4648	13700	13230	12930	13340	13620	12040
Charpy unnotched impact strength (edgewise), kJ/m^2	GOST 4647	54	54	50	45	63	58
Volume resistivity, Ω cm	GOST 6433.2	6×10^{16}	4×10^{15}	6×10^{16}	2×10^{16}	1×10^{16}	1×10^{16}
Surface resistivity, Ω	GOST 6433.2	6×10^{16}	2×10^{16}	6×10^{16}	2×10^{16}	6×10^{14}	6×10^{16}
Dielectric strength, kV/mm	GOST 6433.3	34	34	32	33	32	34

[a] (1) Before and (2) after testing.

Enhanced solar radiation resistance exhibited by the modified glass-filled material (TERMORAN PFS SV-40UP) deserves mentioning. The spun-dyed black material is characterized by even higher resistance.

Earlier [22], we revealed a reversible change in color of glass-filled polyphenylene sulfides when exposed to solar radiation and carried out a detailed study of the effect of photooxidation and photodegradation conditions on the materials of different composition [31, 32].

It is well understood that polyphenylene sulfide offers excellent chemical resistance [2–5, 8, 9, 11]. Specifically, it has no known organic solvents and is resistant to automotive and aviation fuels and fuels and lubricants, including methanol, hot engine oils, luboils, and antifreeze agent, which is crucial for special-purpose

Table 10. Results of the solar radiation resistance test for the materials

Parameter, unit	Test method	Glass-filled polyphenylene sulfide brand					
		TERMORAN PFS SV-40		PFS SV 40-1		TERMORAN PFS SV-40UP	
		1[a]	2[a]	1[a]	2[a]	1[a]	2[a]
Tensile stress at break, MPa	GOST 11262	201	187	185,0	170,2	186	185
Tensile modulus, MPa	GOST 9550	16100	15750	16407	16400	14500	14230
Flexural strength at break, MPa	GOST 4648	291	279	271.0	262.8	278	274
Flexural modulus, MPa	GOST 4648	13700	13650	12930	12950	13620	12312
Charpy unnotched impact strength (edgewise), kJ/m^2	GOST 4647	54	42	50.0	39.3	63	58
Volume resistivity, Ω cm	GOST 6433.2	6×10^{16}	$6\cdot0^{16}$	8×10^{15}	5×10^{15}	1×10^{16}	6×10^{16}
Surface resistivity, Ω	GOST 6433.2	6×10^{14}	2×10^{16}	6×10^{16}	6×10^{16}	6×10^{14}	1×10^{14}

[a] (1) Before and (2) after testing.

Table 11. Results of PFS SV 40-1 testing for resistance to electrolytes

Acceptance criterion parameter, unit	Test method	Acceptance criterion parameter value	
		before testing	after testing
Electrolyte 135 (N,N^I-dimethylformamide)			
Tensile stress at break, MPa	GOST 11262	185.0	180
Flexural strength at break, MPa	GOST 4648	271	253
Flexural modulus, MPa	GOST 4648	12930	12860
Charpy impact strength, kJ/m^2	GOST 4647	50	36
Dielectric strength, kV/mm	GOST 6433.3	32	27
Surface resistivity, Ω	GOST 6433.2	8×10^{15}	2×10^{15}
Volume resistivity, Ω cm	GOST 6433.2	6×10^{16}	2×10^{14}
Electrolyte P-4 (γ-butyrolactone)			
Tensile strength at break, MPa	GOST 11262	185,0	189
Flexural strength at break, MPa	GOST 4648-2014	271	264
Flexural modulus, MPa	GOST 4648-2014	12930	12930
Charpy impact strength, kJ/m^2	GOST 4647	50	40
Dielectric strength, kV/mm	GOST 6433.3	32	27
Surface resistivity, Ω	GOST 6433.2	8×10^{15}	6×10^{15}
Volume resistivity, Ω cm	GOST 6433.2	6×10^{16}	2×10^{15}

machinery, as well for as aircraft and automobile construction applications.

The PFS SV 40-1 material was tested for resistance to harsh chemical environments, including liquid capacitor electrolytes, in accordance with GOST 12020 at a temperature of 110°C during 96 h. As seen from Table 11, the strength and electrophysical properties of PFS SV 40-1 remained practically unchanged from the initial level, except for the Charpy impact strength and dielectric strength, both of which decreased by 15–20%.

Long-Term Thermal Stability

Long-term isothermal aging of TERMORAN PFS SV-40 and PFS SV 40-1 glass-filled PPS samples at 150°C for 2000 h in air caused no changes in their physicomechanical and electrophysical characteristics, which evidences their high thermal stability.

Table 12. Change in the physicomechanical and electrophysical properties of TERMORAN PFS SV-40 at 220°C

Parameter	Time of testing at 220°C, h				
	0	48	120	288	720
Tensile stress at break, MPa	194	198	193	184	156
Tensile modulus, MPa	16540	17100	17050	17210	17200
Flexural strength at break, MPa	292	290	286	265	239
Flexural modulus, MPa	13640	14230	14120	14250	14390
Charpy unnotched impact strength (edgewise), kJ/m^2	54	46	45	38	31
Dissipation factor (1 MHz)	0.0025	0.0024	0.0032	0.0023	0.0028
Dielectric constant	4.1	4.0	4.1	4.1	4.1
Volume resistivity, Ω cm	4×10^{16}	5×10^{16}	6×10^{16}	4×10^{15}	3×10^{15}
Surface resistivity, Ω	6×10^{16}	7×10^{16}	8×10^{16}	4×10^{16}	6×10^{15}

Table 13. Change in the physicomechanical and electrophysical properties of TERMORAN PFS SV-40 at 240°C

Parameter	Time of testing at 240°C, h				
	0	48	120	288	720
Tensile stress at break, MPa	194	189	183	178	179
Tensile modulus, MPa	16540	17265	17390	17380	17420
Flexural strength at break, MPa	292	281	268	254	228
Flexural modulus, MPa	13640	13790	13800	14850	14670
Charpy unnotched impact strength (edgewise), kJ/m^2	54	49	46	36	28
Dissipation factor (1 MHz)	0.0025	0.0026	0.0023	0.0027	0.0030
Dielectric constant	4.1	4.1	4.0	4.0	4.2
Volume resistivity, Ω cm	4×10^{16}	2×10^{16}	5×10^{16}	6×10^{15}	4×10^{15}
Surface resistivity, Ω	6×10^{16}	4×10^{16}	4×10^{16}	6×10^{16}	7×10^{15}

With an increase in the isothermal aging temperature to 220–260°C, TERMORAN PFS SV-40 exhibited changes in its properties level. Specifically, the tensile modulus and flexural moduli (stiffness) increased, and ≤ 25% decreases in the tensile stress at break and flexural stress at break at 240°C compared to those of 220°C were observed (Tables 12–13). Aging at a temperature of 260°C led to further, but not critical (by ≤50%) reduction of the material properties (Table 14). Notably, the general patterns, nature, and level of changes in the properties of the glass-filled polyphenylene sulfide PFS SV 40-1 were almost identical to those in the case of TERMORAN PFS SV-40.

It is noteworthy that both the deterioration of the main physicomechanical characteristics and the enhancement of the material stiffness tended to reach certain equilibrium (limiting) values that were independent of the test temperature. This indicates the predominance of physical aging processes occurring in the material, driven by a change in the crystalline component of the PPS under the isothermal aging conditions [20]. This is indirectly evidenced by the fact that the electrophysical parameters of the materials remained practically unchanged from the initial level (Tables 12–14).

Resistance to Climatic Aging

One of the most important characteristics determining broad applicability of polymeric materials in technical products is their real service life, since plastics are subject to aging, i.e., their useful properties undergo irreversible changes caused by a combination of chemical and physical transformations occurring during their processing, storage, and operation [33, 34].

The service life of glass-filled polyphenylene sulfides when stored in unheated warehouses under equiprobable location across the territory of the Russian Federation was estimated for TERMORAN PFS SV-40 material based on the results of accelerated climatic aging tests by the

Table 14. Change in the physicomechanical and electrophysical properties of TERMORAN PFS SV-40 at 260°C

Parameter	Time of testing at 260°C, h				
	0	48	120	288	720
Tensile stress at break, MPa	194	179	166	157	138
Tensile modulus, MPa	16540	17580	17745	17850	17755
Flexural strength at break, MPa	292	263	262	245	221
Flexural modulus, MPa	13640	13850	14320	14640	14830
Charpy unnotched impact strength (edgewise), kJ/m^2	54	43	38	34	27
Dissipation factor (1 MHz)	0.0025	0.0026	0.0022	0.0027	0.0029
Dielectric constant	4.1	4.2	4.1	4.0	4.0
Volume resistivity, Ω cm	4×10^{16}	3×10^{16}	6×10^{16}	6×10^{15}	4×10^{15}
Surface resistivity, Ω	6×10^{16}	2×10^{16}	3×10^{15}	1×10^{15}	3×10^{16}

Table 15. Change in the physicomechanical and electrophysical properties of TERMORAN PFS SV-40 during accelerated climatic aging test

Material quality parameter	Test method	Material quality parameter value during accelerated storage conditions, year									
		0	1	2	3	5	10	15	20	25	30
Physicochemical properties											
Tensile stress at break, MPa	GOST 11262	194.0	201.1	201.4	202.2	205.0	200.7	198.4	197.3	195.0	195.6
Tensile modulus, MPa	GOST 9550	16540	16860	16840	16800	16670	16580	16220	16190	16370	16140
	GOST 4648	292.2	298.6	298.4	302.3	299.8	294.4	290.7	288.0	291.1	290.5
Flexural modulus, MPa	GOST 4648	13640	14770	14870	14850	14910	14930	14860	14400	14320	14360
Charpy unnotched impact strength, kJ/m^2	GOST 4647	54.1	51.0	50.7	51.2	52.4	51.5	51.5	47.9	46.8	47.3
Electrophysical properties											
Dielectric strength, kV/mm	GOST 6433.3	32	31	32	34	34	34	33	32	32	–
Surface resistivity, Ω	GOST 6433.2	6×10^{16}	4×10^{15}	6×10^{15}	1×10^{16}	8×10^{15}	3×10^{15}	4×10^{15}	2×10^{15}	1×10^{15}	–
Volume resistivity, Ω cm	GOST 6433.2	4×10^{16}	4×10^{16}	3×10^{16}	4×10^{16}	4×10^{16}	4×10^{16}	4×10^{16}	2×10^{16}	2×10^{16}	–
Dielectric constant	GOST 22372	4.10	4.02	4.02	4.02	4.02	4.02	4.02	4.02	4.03	–
Degree of crystallinity, %	–	47	47	53	51	56	47	50	49	–	43

method developed in accordance with GOST 9.707. As a property retention (storability) criterion served a ≤25% change in the physicomechanical and electrophysical properties of the material.

As applied to the above-listed storage and operation conditions, the climatic aging factors include the temperature (both positive and negative) and its daily and seasonal changes, as well as air humidity. The

Table 16. Change in the physicomechanical and electrophysical properties of PFS SV 40-1 during accelerated climatic aging test

Acceptability criterion parameter, unit	Determination method	Acceptability criterion parameter value from accelerated climatic aging test, year							
		0	1	3	5	10	15	20	25
Tensile stress at break, MPa	GOST 11262	185	191	191	191	194	190	189	187
Flexural strength at break, MPa	GOST 4648	271	277	274	280	277	273	272	267
Charpy unnotched impact strength, kJ/m^2	GOST 4647	50	47	45	47	47	47	45	43
Surface resistivity, Ω	GOST 6433.2	8×10^{15}	5×10^{15}	8×10^{15}	1×10^{16}	9×10^{15}	4×10^{15}	6×10^{15}	4×10^{15}
Volume resistivity, Ω	GOST 6433.2	6×10^{16}	6×10^{16}	6×10^{16}	6×10^{16}	6×10^{16}	6×10^{16}	6×10^{16}	1×10^{16}
Dielectric strength, kV/mm	GOST 6433.3	32	31	32	35	34	33	33	32

absolute hydrophobicity of TERMORAN PFS SV-40 [30] allows neglecting the humidity factor when developing accelerated climatic aging regimes.

In accordance with GOST 9.707, the minimum positive test temperature should be equal to or higher than the absolute maximum storage temperature of the material, and the maximum temperature, equal to or less than the onset temperature of the phase, structural, or chemical transformations of the material. The practically significant phase transformations of PPS are melting and transition from glassy to high elastic state. The melting point of polyphenylene sulfide is 280–290°C, and the glass transition temperature range, from 90 to 120°C. As defined in GOST 16350, the maximum positive air temperature in the territory of the Russian Federation does not exceed +45°C, and the negative temperatures may be as low as –60°C. Therefore, +90°C was taken as the maximum positive temperature, and –60°C, as the negative temperature for the accelerated aging tests.

Based on the isothermal aging data (Tables 12–14) and in accordance with GOST 9.707 (method 2), the accelerated testing regimes for TERMORAN PFS SV-40 climatic aging were calculated: the testing cycle equivalent to one year of storage to be applied as 318-h of holding at a temperature of +90°C, followed by cyclic loading with holding at –60°C for 3 h and at +60°C for 2 h, repeated in triplicates.

In a similar way, the regimes of accelerated testing of PFS SV 40-1glass-filled polyphenylene sulfide for property retention under conditions of long-term storage in heated warehouses were calculated.

Tables 15 and 16 summarize the results of the accelerated aging tests for TERMORAN PFS SV-40 and PFS SV 40-1 brands of glass-filled PPS. It is seen that these materials are highly resistant to climatic aging. Specifically, the main strength characteristics and indicators of the electrophysical properties of the materials changed negligibly. The sole indicator that exhibited a >10% reduction was the Charpy impact strength, and then only after 20 testing cycles (by 11.5%). However, these changes were significantly smaller compared to the specified criterion (25%), even after longer tests (12.5% after 30 cycles).

Thus, the service life of TERMORAN PFS SV-40 glass-filled PPS under conditions of storage in unheated warehouses provided equiprobable location across the territory of the Russian Federation was estimated at ≥30 years, and that of PPS SV 40-1, at ≥25 years under conditions of storage in heated warehouses under equiprobable location across the territory of the Russian Federation.

Thermogravimetric analysis of both material brands was carried out on a TGA Q50 instrument (TA Instruments) in accordance with GOST 9.715 (heating rate 10°C/min, air). It revealed no changes in the nature and quantitative indicators of the degradation process during the accelerated testing procedure, which evidences good thermal stabilization of the materials.

The DSC analysis of the materials during the accelerated aging tests revealed processes leading to changes in the degree of crystallinity as calculated from the enthalpy of melting of PPS (using the enthalpy of melting of crystalline PPS of 112 J/g [19] as a reference). The DSC thermograms of melting of the material samples were measured on a Perkin Elmer DSC 6000 instrument using the methods described in GOST 55134

(ISO 11357-1:2009) and GOST R 55135 (ISO 11357-2:1999). However, the revealed structural changes were insignificant, since they caused no substantial alterations in the strength properties.

Overall, the changes exhibited by the indicators of the material properties during the accelerated aging tests (Tables 15 and 16), in our opinion, are expectable for glass-filled materials based on crystallizing thermoplastics, being due to the occurrence of additional crystallization of the polymer in the material and to the accumulation of damages at the polymer-glass fiber interface, leading to higher defectiveness (porosity) of glass-filled materials [35]. In the initial stage of aging, additional crystallization and enhancement of the degree of crystallinity of PPS prevail as impact strength reduction factors. At longer aging times (>15 years), under continuing structural rearrangements in PPS, the accumulation of damages at the polymer-filler interface due to seasonal and daily temperature drops becomes the dominant factor, responsible for reduction of the impact strength and for deterioration of some other properties of the materials.

Radiation Resistance

Testing TERMORAN PFS SV-40 and PFS SV 40-1 glass-filled polyphenylene sulfides for radiation resistance was carried out in accordance with GOST 9.706: radiation source ^{60}Co, average gamma ray energy 1.25 MeV, temperature (25±5)°C, air as medium, gamma radiation dose rate up to 5000 Gy/h (500 krad/h).

Control of the determining and characteristic indicators of the radiation resistance of the materials tested (tensile stress at break, tensile modulus, flexural stress at break, flexural modulus, and impact strength) showed that, at the radiation absorbed dose of 10 Mrad, they decreased by ≤8%, and at an absorbed dose of 100 Mrad, by <12% from the initial level. Therefore, TERMORAN PFS SV-40 and PFS SV 40-1 materials meet the requirements for radiation resistance in accordance with GOST 25645.331.

Combined with the previously published data [18–22, 30–32], the present results provide a fairly comprehensive insight into the strength, processing, and operational characteristics of TERMORAN brand materials and into their resistance to thermal, climatic, and other acting factors. This allows taking well-informed decision on their applicability for producing particular products intended for operation under specified conditions.

Based on their high strength and electro- and thermophysical characteristics, TERMORAN and PFS SV 40-1 domestic glass-filled polyphenylene sulfides can be recommended for manufacturing various parts of aerospace and special equipment, as well as of items in oil and gas production, automotive, electrical engineering, and other industry sectors, intended for operation under severe conditions and over a wide temperature range.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

1. Darienko, I.N., *Ekspertn. Soyuz*, 2012, no. 3.
2. *Evraz. Khim. Rynok*, 2008, no. 3(39), pp. 14–21.
3. Johaenning, F., *Polym. Mater*., 2012, no. 2, pp. 40–44.
4. Mikhailin, Yu.A., *Termoustoichivye polimery i polimernye materialy* (Heat-Resistant Polymers and Polymer Materials), St. Petersburg: Professiya, 2006.
5. Mikhailin, Yu.A., *Spetsial'nye polimernye kompozitsionnye materialy* (Special Polymer Composite Materials), St. Petersburg: Nauchnye Onovy i Tekhnologii, 2009.
6. *The Chemical Journal*, 2005, October–November, pp. 73–74.
7. *Evraz. Khim. Rynok*, 2013, no. 10(109), pp. 24–30.
8. Zhukova, I., *International Trade Fair Plastics and Rubbers Interplastica*, 2017, Moscow, January 24–27, 2017. www.plasinfo.ru.
9. FORTRON® Polyphenylene Sulfide (PPS) Product Brochure, Ticona, 2015.
10. Properties of DIC.PPS, DIC Product Catalog. http://www.dic-global.com/eu/en/products/pps/pdf/dic_pps_property.pdf.
11. Bieksha, J., *Elektron. Bull*., 2014, no. 1(47), pp. 24–27.
12. USSR Inventor's Certificate no. 525717, appl. December 4, 1974, publ. August 25, 1976.
13. USSR Inventor's Certificate no. 627141, appl. April 4, 1977, publ. October 5, 1978.
14. USSR Inventor's Certificate no. 730721, appl. January 1, 1978, publ. April 30, 1980.
15. USSR Inventor's Certificate no. 627141, appl. March 23, 1986, publ. September 15, 1990.
16. Nedel'kin, V.I., Zachernyuk, B.A., and Andrianova, O.B., *Ross. Khim. Zh*., 2005, vol. 49, no. 6, pp. 3–10.
17. Petrova, G.N. and Beider, E.Ya., *Ross. Khim. Zh*., 2010, vol. 54, no. 1, pp. 34–40.
18. Ekimov, A.I., Kalugina, E.V., Samoryadov, A.V., Bitt, V.V., and Prikazshchikov, A.V., *Tekhnologii i materialy dlya ekstremal'nykh uslovii: Materialy 11-oi Vserossiis-*

koi konferentsii (Technologies and Materials for Extreme Conditions: Proc. 11All-Russian Conf.), Moscow, November 8–13, 2016, Moscow: Mezhved. Tsentr Anal. Issled. v Oblasti Fiziki, Khimii i Biologii pri Prezidiume Rossiiskoi Akdemii Nauk, 2016, pp. 4–9.

19. Bitt, V.V., Kudryavtseva, M.V., Ivanov, A.N., Samoryadov, A.V., Prikazshchikov, A.V., and Kalugina, E.V., *Polymer. Truby*, 2017, no. 1(55), April, pp. 52–59.

20. Bitt, V.V., Borisova, O.V., Kudryavtseva, M.V., Kalugina, E.V., and Samoryadov, A.V., *Tekhnologii i materialy dlya ekstremal'nykh uslovii: Materialy Vserossiiskoi konferentsii* (Technologies and Materials for Extreme Conditions: Proc. All-Russian Conf.), Zvenigorod, December 10–14, 2018, Moscow: Mezhved. Tsentr Anal. Issled. v Oblasti Fiziki, Khimii i Biologii pri Prezidiume Rossiiskoi Akdemii Nauk, 2018, pp. 227–235.

21. Samoryadov, A.V. and Usenko, E.S., *Materialy i tekhnologii novogo pokoleniya dlya perspektivnykh izdelii aviatsionnoi i kosmicheskoi tekhniki: IV Vserossiiskaya nauchno-tekhnicheskaya konferentsiya* (New-Generation Materials and Technologies for Advanced Aerospace Products: Proc. IV All-Russian Sci. and Tech. Conf.), Moscow, August 26, 2019, Moscow: Vseross. Nauchno-Issled. Inst. Aviats. Mater., 2019, pp. 164–177.

22. Ivanov, V.B., Bitt, V.V., Solina, E.V., and Samoryadov, A.V., *Polymers*, 2019, vol. 11, no. 10, pp. 1579–1584. DOI:10.3390/polym11101579.

23. Lishevich, I.V., Bakhareva, V.E., Sargsyan, A.S., and Skobeleva, E.L., *Vopr. Materialoved.*, 2009, no. 1(57), pp. 111–115.

24. Lishevich, I.V., *Cand. Sci. (Tech.) Dissertation*, St. Petersburg, 2015.

25. Feofanov, B.N., *Presentation of report*, Army-2019, Moscow, August 18–20, 2019. https://plastinfo.ru/information/news/42512_02.07.2019/.

26. *Polyfenylenesulfide Resins*, Brochure, Product Catalog Phillips Petroleum Corp., 1992.

27. Properties of DIC.PPS, DIC Product Catalog. http://www.dic-global.com/eu/en/products/pps/pdf/dic_pps_property.pdf.

28. Barvinskii, I.A. and Barvinskaya, I.E., *Spravochnik po lit'evym termoplastichnym materialam* (Handbook on Injection-Molded Thermoplastic Materials). www.barvinsky.ru.

29. *Baza polimerov* (Polymer Base). www.plasinfo.ru.

30. Samoryadov, A.V., Kalugina, E.V., and Bitt, V.V., *Plast. Massy*, 2019, nos. 7–8, pp. 52–56.

31. Ivanov, V.B., Solina, E.V., and Samoryadov, A.V., *Vse materialy: Entsiklopedicheskii spravochnik* (All Materials: Encycloped. Ref. Book), 2019, no. 11, pp. 32–37. https://doi.org/10.31044/1994-6260-2019-0-11-32-37

32. Ivanov, V.B., Solina, E.V., and Samoryadov, A.V., *Polymer Sci., Ser. D*, 2020, vol. 13, no. 3, pp. 353–357. https://doi.org/10.1134/1995421220030089

33. Emanuel', N.M. and Buchachenko, A.L., *Khimicheskaya fizika stareniya i stabilizatsii polimerov* (Chemical Physics of Aging and Stabilization of Polymers), Moscow: Nauka, 1982.

34. Karpukhin, O.N., *Usp. Khim.*, 1980, vol. 49, no. 8, pp. 1523–1553.

35. Samoryadov, A.V. and Parshikov, Yu.G., *Ross. Khim. Zh.*, 2016, vol. 60, no. 4, pp. 64–79.