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Grafted interpenetrating polymeric systems based on cross-linked siloxaneurethanes

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A series of cross-linked polysiloxaneurethanes with different functional groups in the nodal organosilicon fragment and related grafted interpenetrating polymeric systems with poly(methyl methacrylate) were synthesized, and their structural relaxation and mechanical properties were studied. Specific features of microphase separation and the mechanism of molecular mobility in these systems were considered.

Key words: interpenetrating polymeric systems, polysiloxaneurethanes, organosilicon compounds, triatomic alcohols, oligosiloxanediols, molecular mobility, dielectric relaxation, microphase separation, compatibility, mechanical properties.

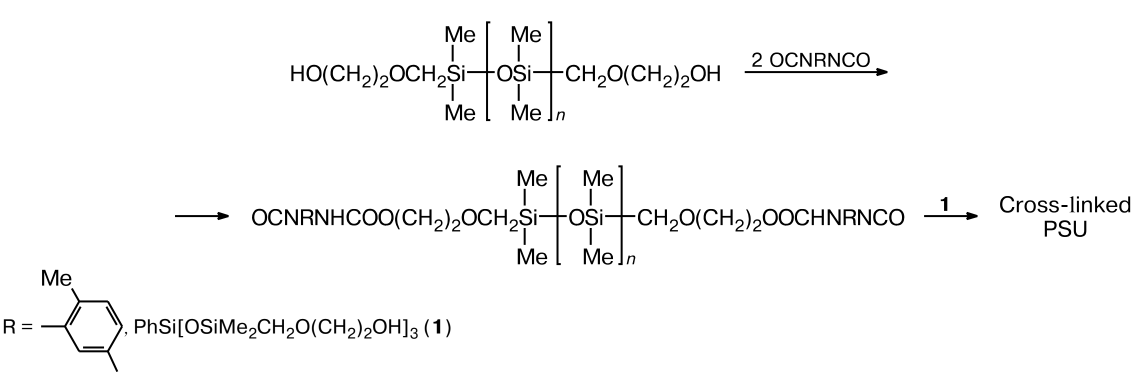
The problem of compatibility of heterogeneous polymers in the creation of multi-component polymeric systems is one of the central tasks of the chemistry and physics of polymers, especially in the case of systems based on organosilicon and organic polymers.

Since polyorganosiloxanes and organic polymers are virtually completely incompatible thermodynamically, which appears as a great difference in their solubility parameters, and conditions of mixing of heterogeneous components should be controlled, we synthesized a series of cross-linked polyorganosiloxaneurethanes (PSU) with the block copolymer structure and more complex related interpenetrating systems (IPS) with poly(methyl methacrylate) (PMMA) (Fig. 1). This made it possible to improve the conditions of mixing for the components as a result of both the formation of chemical bonds between heterogeneous blocks and the topological restrictions introduced by a network of chemical bonds. The introduction of high-polarity urethane fragments, capable of manifesting strong intermolecular interactions, into the structure of such systems contributed additionally to interactions between the components of the system under study.

Results and Discussion

Cross-linked PSU were prepared by the transformation of oligosiloxanediol**1** into macrodiisocyanate and the reaction of the latter with a polyatomic alcohol**2** *via* Scheme 1.

Scheme 1



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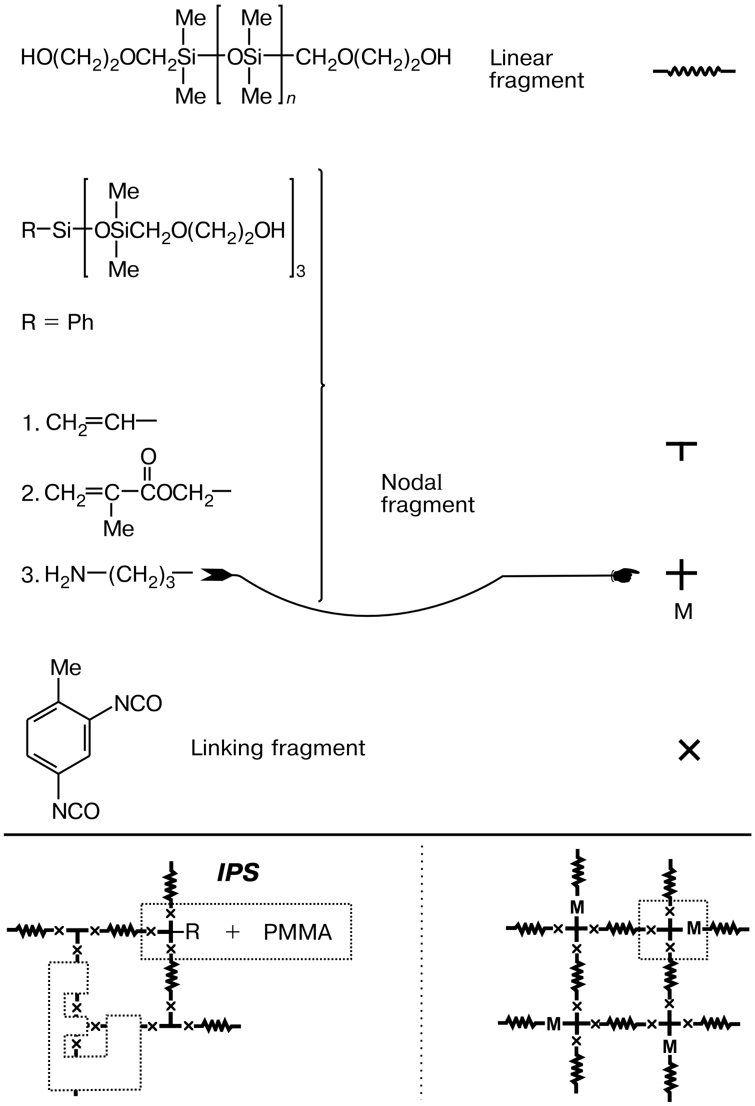


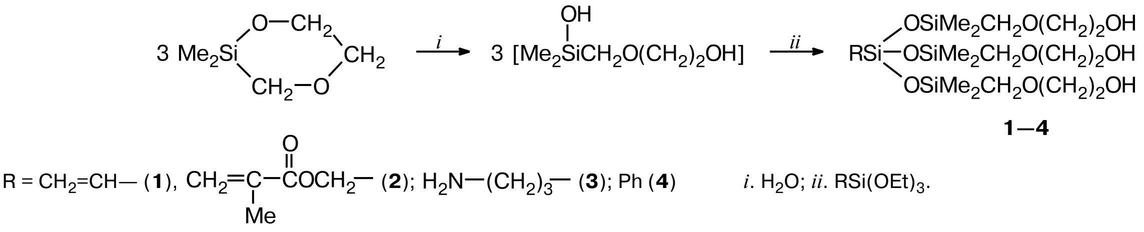
Fig. 1. Structural scheme of constructing cross-linked PSU and IPS.

Polyatomic organosilicon alcohols **1—3** were synthesized by the condensation of the hydrolysis product of 1,1-dimethyl-1-sila-2,5-dioxacyclohexane with organotriethoxysilane (Scheme 2).

We have synthesized previously[2] polyatomic alcohol **4**. Other alcohols **1—3** were synthesized for the first time.

Compound **3** is tetrafunctional toward macrodiisocyanates, and the nodal fragment of the related cross-linked PSU can exert a remarkable effect on the structure and properties of resulting polymers. The functionality of triol **2** is three; however, the presence of methacrylate group capable of polymerization provides additional pos-

Scheme 2



sibilities for variation of the properties of polymers. Interpenetrating systems of this type with chemical bonds between heterogeneous networks were named grafted IPS.[3,4]

Polyatomic alcohols formed *via* Scheme 2 can be isolated only as bottoms after ethanol was distilled off, because even distillation in high vacuum produces a polymer due to the dehydration of ethylene glycol groups of triols.

A complex approach based on the simultaneous control of several parameters was used for controlling the phase structure and properties of a multi-component polymeric system based on incompatible organosilicon and organic (especially carbon-chain) polymers.

1. We monitored the number of high-polarity groups introduced directly in the siloxane chain and capable of manifesting strong intermolecular interactions both between each other to form associates and with polar groups of organic polymers. The associates formed acted as thermally labile physical nodes. The optimum concentration of the polar groups has been determined earlier.[5,6]

2. Cross-linked structure, a block copolymer structure of PSU, and a possibility of fine variation of the component ratio and lengths of organic and organosilicon blocks were used.[5,6]

3. We took into account the chemical nature and the structure of a nodal fragment of the PSU network, which plays a key role in the formation of the phase structure and morphology of the system, including a possibility to control the functionality of the network, and in the efficient control of the number of chemical links for grafted IPS.

The data on the dielectric relaxation of cross-linked PSU and related grafted IPS with PMMA are presented in Figs. 2 and 3. All polymers under study are characterized by two relaxation regions with the corresponding peaks in the temperature plot of the electrical loss tangent tanδ and respective steps in the temperature plot of the dielectric constant ε´ caused by an increase in ε´ upon defreezing the molecular mobility. The temperature position and values of activation energies E_a^{app} (Table 1) of the transitions under consideration make it

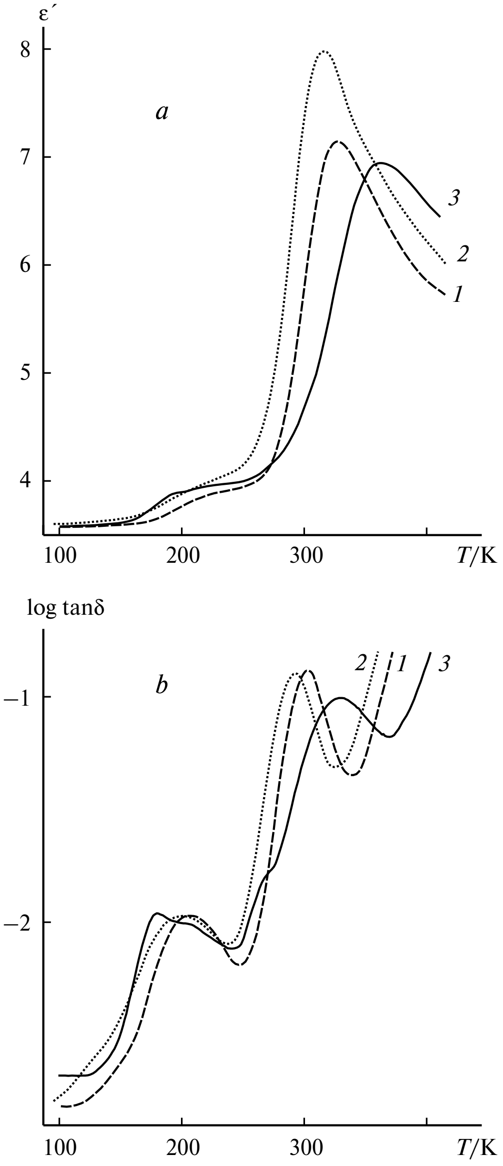


Fig. 2. Temperature plots of the dielectric constant ε′ (*a*) and the dielectric loss tangent tanδ (*b*) of the starting PSU with different functional groups in the nodal fragment: *1*, vinyl; *2*, methacryloxymethyl; and *3*, aminopropyl.

Table 1. Temperature of maxima (1 kHz) and activation energies of the fundamental α-relaxation transitions for PSU and related grafted IPS with PMMA

Compound	R	PSU				PSU—PMMA (75/25 wt.%)			
		PDMS phase*		Urethane phase		PDMS phase		Urethane—PMMA phase	
		T/K	E_a^{app} /kJ mol^{-1}	T/K	E_a^{app} /kJ mol^{-1}	T/K	E_a^{app} /kJ mol^{-1}	T/K	E_a^{app} /kJ mol^{-1}
1	CH_2=CH—	207	105±5	303	160±5	186	800±5	337	175±5
3	H_2N—$(CH_2)_3$—	181	80±5	329	145±5	—	±5	328	145±5
2	CH_2=CMeCOOCH$_2$—	200	85±5	292	185±5	174	8—	—	—

* PDMS is polydimethylsiloxane.

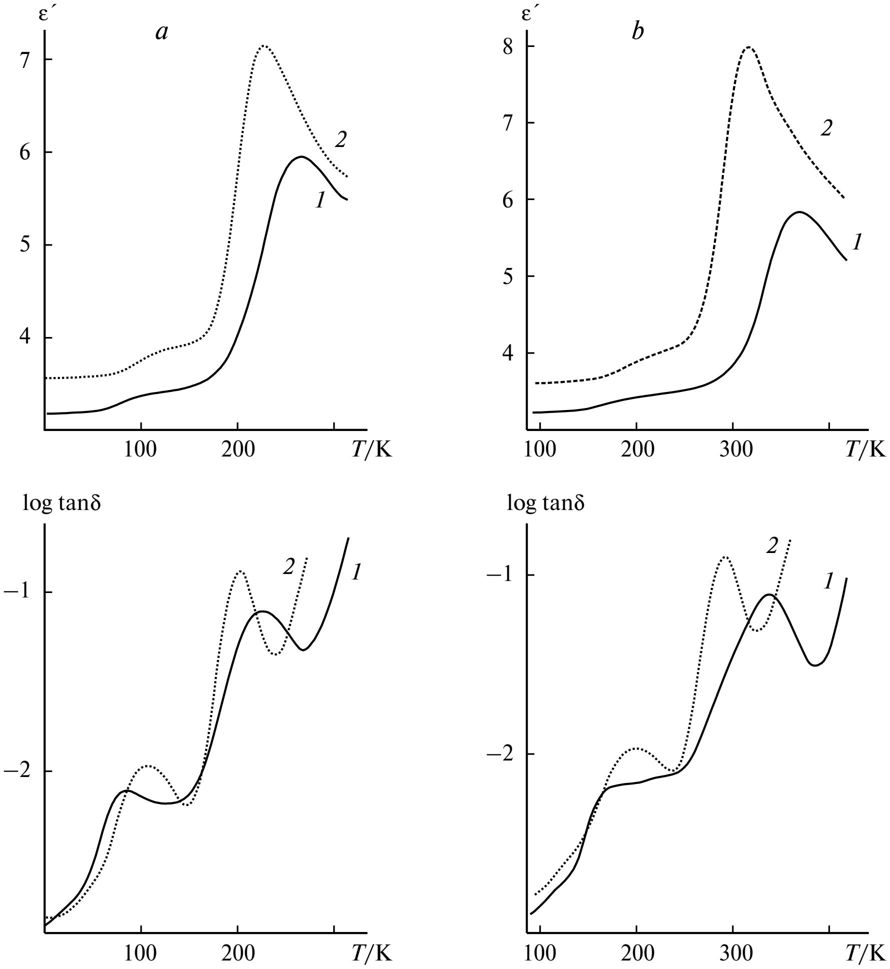


Fig. 3. Temperature plots of the dielectric constant ε′ and the dielectric loss tangent tanδ of the starting PSU (*1*) with vinyl (*a*) and methacryloxymethyl (*b*) functional groups in the nodal fragment and related grafted IPS with PMMA (*2*).

possible to assign them to the fundamental α-relaxation processes.

For PSU (see Fig. 2), the low-temperature α-relaxation transition corresponds to defreezing of the molecular mobility in the organosilicon microphase, and the high-temperature transition is related to defreezing of the molecular mobility in the so-called "urethane microphase." In the case of grafted IPS (see Fig. 3), a low-temperature α-transition related to the mobility in the organosilicon microphase is observed, and only one high-temperature α-transition between the α-peaks of PSU and PMMA corresponds to defreezing of the mobility in the combined urethane—PMMA microphase.

We have previously found[5—7] a similar mechanism of microphase separation with close temperature activation parameters for a series of cross-linked block copolymer trifunctional PSU with a Ph group in the nodal organosilicon fragment.

A decrease in the temperature of the low-temperature α-transition and its increase for the high-temperature transition observed for tetrafunctional PSU (see Fig. 2, curve *3*) can be related to weakening of the influence of the nodal fragment on the mobility in the organosilicon microphase. Thus, the appearance of a high-polarity carbamide group (with the close chemical affinity to the urethane moiety) in the organosilicon nodal fragment facilitates the transition of at least some organosilicon nodal fragments to the urethane microphase, which changes basically the mechanism of microphase separation of PSU. This assumption is favored by a noticeable expansion and shift to higher temperatures of the high-temperature α-transition. A similar regularity was observed[6] for PSU with organic nodal fragments.

Grafted IPS exhibit only one high-temperature α-transition with the temperature between the corresponding values for PSU (see Table 1) and PMMA (390 K). This assumes the formation of a combined PSU—PMMA phase (more exactly, urethane—PMMA phase). However, a substantial expansion of this relaxation region (see Fig. 3) indicates only a partial compatibility of the IPS components. A question arises whether the partial compatibility of the IPS components is related only to chemical bonds between them or an additional mechanism is possible? The latter is favored by the decrease in the temperature of the low-temperature α-peak maximum in the temperature plots of tanδ for grafted IPS by 21—26 K relatively to the corresponding values for PSU. This suggests that some restrictions of molecular mobility in the organosilicon phase are eliminated due to the partial replacement of strong intermolecular interactions between the urethane fragments by the interaction of the urethane groups of PSU with the ester groups of PMMA.

The extension curves of PSU and grafted IPS agree well with the results of relaxation measurements. It can be seen that the aforementioned features of the behavior of the high-temperature relaxation are reflected as substantially higher values of the rupture strength σ and the Young modulus *E* for grafted IPS compared to those for the starting PSU and higher values for tetrafunctional PSU than those for trifunctional PSU. For tetrafunctional PSU and grafted IPS based on PSU with a vinyl group in the nodal fragment, a relative elongation upon rupture increases substantially simultaneously with an increase in σ and *E*. A yield stress appears and a neck is formed for grafted IPS based on PSU with a methacryloxymethyl group in the nodal fragment.

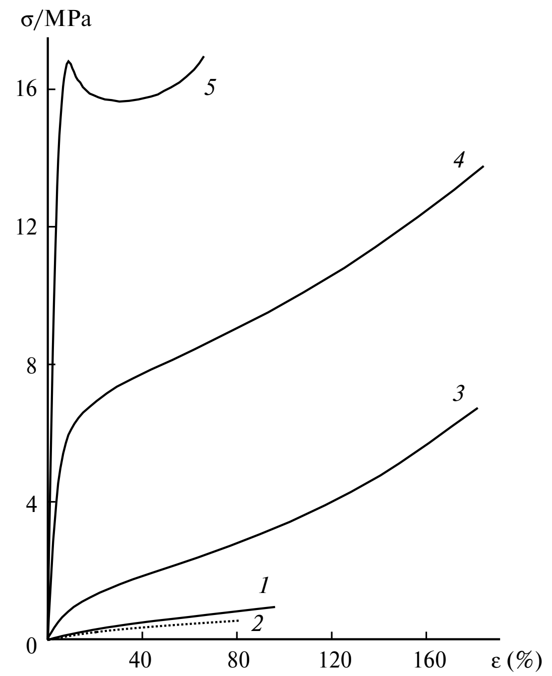


Fig. 4. Extension curves of the starting PSU with vinyl (*1*), methacryloxymethyl (*2*), and aminopropyl (*3*) groups in the nodal fragment and PSU-based grafted IPS with vinyl (*4*) and methacryloxymethyl (*5*) groups in the nodal fragment and PMMA.

Thus, the studies of the structural relaxation and physicomechanical properties of a series of cross-linked siloxaneurethane polymers and related IPS with PMMA showed a possibility of a purposeful control of microphase separation processes in both the starting cross-linked PSU, depending on the structure of the nodal fragment, and related grafted IPS with PMMA. A possibility of transition of an organosilicon nodal fragment from the organosilicon microphase to the urethane microphase was accomplished for the first time. This occurs when a high-polarity urea group is inserted into the nodal fragment.

The relaxation spectra of grafted IPS are characterized by the low-temperature α-transition in the PDMS microphase and the high-temperature region of α-relaxation corresponding to defreezing of the molecular mobility in the combined PSU—PDMS microphase. A partial compatibility observed for PSU and PMMA is related to the presence of chemical bonds and specific molecular interactions between heterogeneous networks. A possibility of controlling the phase structure and mechanical properties of PSU and IPS was shown. Cross-linked polymers with the physicomechanical properties variable in a wide range were synthesized.

Experimental

Mechanical tests of the obtained films were carried out under the stretching conditions with a tensile velocity of $1 \cdot 10^{-4}$ m s^{-1} on a 2166R-5 stretching setup (Tochpribor, Ivanovo). Dielectric measurements were performed using an R5083 multi-frequency (50—$1 \cdot 10^5$ Hz) bridge (Tochelektropribor, Kiev) in an interval of 80—800 K in air and *in vacuo* (1.33 Pa) for samples 25 mm in diameter and 0.05 mm thick.

^{1}H NMR spectra were recorded on a Bruker WP-200SY spectrometer (200 MHz) in CCl_4 using Me_4Si as internal standard.

Tris[(2-hydroxyethoxy)methyl(dimethyl)siloxy]vinylsilane (1). 2,2-Dimethyl-1,4-dioxa-2-silacyclohexane (SCH) (7.94 g, 0.06 mol) was mixed with ammonia water (pH 10, 1.08 g, 0.06 mol), and vinyltrimethoxysilane (2.96 g, 0.02 mol) was added after 30 min. The mixture was stored for 24 h at 20 °C, and then methanol was distilled off on a rotary evaporator. Compound **1** (10.0 g, 99%) was isolated as a colorless transparent viscous liquid, n_D^{20} 1.4545. Found (%): C, 40.66; H, 8.31; Si, 22.15; OH, 10.64. $C_{17}H_{42}Si_4O_9$. Calculated (%): C, 40.60; H, 8.42; Si, 22.34; OH, 10.14. ^{1}H NMR, δ: 0.35 (s, 6 H, Me_2Si); 3.25 (s, 2 H, CH_2Si); 3.60 (t, 2 H, CH_2O); 3.75 (t, 2 H, CH_2O); 3.42 (s, 2 H, CH_2=C).

Tris[(2-hydroxyethoxy)methyl(dimethyl)siloxy]methacryloxymethylsilane (2) was obtained similarly from SCH (15.14 g, 0.114 mol), methacryloxymethyltriethoxysilane (10 g, 0.038 mol), and H_2O (2.06 g, 0.114 mol). Compound **2** was isolated in 99% yield (21.65 g). Found (%): C, 40.93; H, 7.80; Si, 18.94; OH 8.70. $C_{20}H_{46}Si_4O_{11}$. Calculated (%): C, 41.79; H, 8.06; Si, 19.54; OH, 8.87. ^{1}H NMR, δ: 0.30 (s, 6 H, Me_2Si); 1.95 (s, 3 H, MeC); 3.12 (s, 2 H, CH_2Si); 3.40 (t, 2 H, CH_2O); 3.62 (t, 2 H, CH_2O); 4.63 (s, 2 H, CH_2=C).

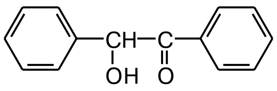
Table 2. Ratio of components in the synthesis of PSU and related grafted IPS with PMMA

Compound	Triol		MDIC		MMA /g
	g	mmol	g	mmol	
1*	1.84	3.34	6.01	5.01	2.61
2	1.60	3.34	6.01	5.01	2.54
3	2.00	3.32	5.98	4.98	2.66

* In the case of triol **1**, 2 wt.% of the cross-linking agent (triethylene glycol dimethacrylate ether) were added to MMA.

Tris[(2-hydroxyethoxy)methyl(dimethyl)siloxy]-γ-aminopropylsilane (3) was synthesized similarly from SCH (19.83 g, 0.15 mol), γ-aminopropyltriethoxysilane (11.07 g, 0.05 mol), and H_2O (2.7 g, 0.15 mol). Compound **3** was isolated as a viscous colorless liquid, n_D^{20} 1.4618. Found (%): C, 39.75; H, 8.84; Si, 19.95; OH, 9.05. Calculated (%); C, 40.49; H, 8.87; Si, 21.04; OH, 9.55. ^{1}H NMR, δ: 0.15 (s, 6 H, Me_2Si); 0.90 (s, 2 H, CH_2Si); 1.43 (s, 2 H, CH_2); 2.50 (s, 2 H, CH_2N); 3.00—3.03 (d, 2 H, OCH_2Si); 3.31 (t, 2 H, CH_2O); 3.47 (t, 2 H, CH_2O).

Cross-linked polysiloxaneurethanes (PSU) and interpenetrating systems (IPS). To prepare cross-linked PSU, macrodiisocyanate (MDIC) based on OKD-8 and 2,4-toluylenediisocyanate was mixed with the corresponding triol in ratios indicated in Table 2. The mixture was evacuated for 5 min, and 0.4 wt.% tin diethyl dicaprylate was added. Then the mixture was evacuated for 5 min, poured into a glass mold, and stored for 3 days to complete urethane formation. To obtain IPS, methyl methacrylate containing a dissolved photosensitizer (benzoin) was added (0.1 wt.% of the MMA weight) to a mixture of components of polyurethane (MDIC, triol, tin diethyl dicaprylate). The resulting mixture was evacuated for 5 min and poured in glass molds. After the complete formation of a PSU gel (3 days), the molds were irradiated for 7 h with the light from a PRK-4 lamp, which was remote from the molds at a distance of 25 cm. The loads are presented in Table 2.



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