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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Materials with Controllable Plasticity Based on Low Molecular Weight Organosilicon Rubber

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Abstract—Modification of SKTN-A low-molecular-weight rubber with layered compounds, silicon-containing fillers, and boric acid was studied. Changes in the plasticity of organosilicon rubber samples in relation to the concentration and composition of modifying additives were determined. Changes in the ductility and viscosity of the modified composites were analyzed.

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Polymers and polymeric composites exhibiting various functional characteristics, including plastic properties, attract increased researchers' interest [1]. Abramchuk et al. [2–4] examined new highly elastic magnetic materials for gaskets and dampers. The plastic characteristics of polymers in relation to their structure were studied in [5, 6]. Wang et al. [7, 8] studied how these characteristics depend on the degree of cross-linking. Thus, search for various ways to control the plasticity of polymeric composites by introducing plasticizers, polymers of other nature, and/or fillers is of both scientific and practical interest.

Our goal was the development of materials with controllable plasticity on the basis of SKTN-A low molecular weight organosilicon rubber, modified with fillers of various classes: layered compounds, silicon-containing fillers, and boric acid.

As layered fillers we used clay (bentonite) intercalated with alkylbenzyldimethylammonium, molybdenum disulfide (MoS_2), and graphite modified with acids. A specific feature of such fillers is the possibility of immobilization of macromolecular fragments in their interlayer spaces [9, 10].

As silicon-containing fillers we used silicon particles, porous quartz, and Aerosil. In this case, interaction of a polymer with filler particles is mainly due to adsorption forces. Enhancement of intermolecular interaction due to hydrogen bonding and cross-linking can lead to a decrease in the flexibility of macromolecules and to enhancement of the material strength.

Changes in the relative strain depending on time (sample creep at gradual development of strain in the loading–unloading mode) allowed comparison of the effect exerted by fillers of different nature on the mechanical properties of materials based on SKTN-A organosilicon rubber.

EXPERIMENTAL

SKTN-A low molecular weight organosilicon rubber [GOST (State Standard) 13835–73], a colorless viscous liquid with a molecular weight of $(2–10) \times 10^4$, having the structure $HO–[Si(CH_3)_2–O]_n–H$, was used as binder in preparation of composites. The materials were prepared by mixing the components in the required proportions, followed by pressing at 2 MPa in a demountable cylindrical stainless steel mold (length 2 cm, plunger diameter 1 cm) at room temperature.

Some characteristics of the fillers are given in the table. Molybdenum disulfide MoS_2 and particles of intercalated clay were added to rubber in concentrations from 51.2 to 68.4 and from 51.9 to 73.3 wt %, respectively. Particles of thermally expanded graphite (TEG) were mixed with rubber in concentrations of up to 4 wt %. To prepare composites, we also used

Some characteristics of fillers used

Filler	Interlayer spacing, nm	Bulk density, g cm^{-3}	Particle size, μm	Specific surface area, m^2 g^{-1}
Bentonite	3.400	0.512	–	–
Thermally expanded graphite	0.336	0.007	~200	20
Molybdenum disulfide	0.320	0.466	3–5	5
Porous quartz	–	1.683	2–10	–
Silicon	–	0.206	1–10	–
Aerosil	–	0.058	10–25	286

silicon, PKN-200 silica gel, porous quartz particles, and Aerosil (AS-300). The filler concentrations in the low molecular weight rubber (wt %) were as follows: Si 59.8–79.1, PQ 26.5–40.7, and AS 15.1–21.2 wt %.

The ductility of the filled composites was measured on a modified Kargin's balance by penetration of a spherical indenter [11–13]. The balance design allowed variation of the load from 0.1 to 50 g. The error in measuring the deformation was 0.001 cm. The ductility I, which is a quantitative measure of creep, was calculated by the Hertz formula [11, 12] deduced for penetration of a spherical indenter into a solid surface:

$$I = (16/3)h^{3/2}r^{1/2}F^{-1}, \quad (1)$$

where h is the penetration depth; r, radius of the sphere; and F, force.

These relationships are valid if the sample height is at least five times greater than the indenter radius. From the curve of ductility variation with time, it is possible to obtain a series of mechanical characteristics of a material, including elastic strain, creep, and viscosity [14]. The dynamic viscosity of composites was determined from the experimental dependences of the ductility on time at a constant load after attainment of a steady-state flow mode, from the cotangent of the slope of the linear portion of the curve.

As we found in [15], the creep of a composite depends on the time passed before the measurements. Therefore, the viscosity and ductility for some composites were measured at room temperature several hours and 2 days after the sample preparation.

Electron micrographs of TEG were taken with a Supra scanning electron microscope (Carl Zeiss, Germany).

The microviscosity and micrononuniformity of filled systems were analyzed by the ESR spectra of a spin probe, stable tetramethylpiperidine-1-oxyl (TEMPO) radical [16, 17]. Probes were introduced into samples from the gas phase to a concentration of 10^{17}–10^{18} spin cm^{-3}. After introducing the probe, samples were kept at room temperature for 24 h to ensure its uniform distribution. The ESR spectra were recorded on a Bruker EMX ESR spectrometer (Germany) in the X-range of frequencies at UHF power of 5 mW and modulation amplitude of 0.1 G. The correlation time of probe rotation was determined from the experimental spectra by comparing them with the theoretical spectra calculated in [18].

Composites with layered fillers. The initial SKTN-A is a Newtonian liquid with a dynamic viscosity of about 0.6 Pa s. Introduction of layered fillers leads to an increase in the viscosity by several orders of magnitude. The strongest effect on the viscosity is exerted by TEG. With this filler, even at low degrees of filling (4 wt %), the viscosity of the system increases to $\eta = 0.7 \times 10^7$ Pa s, whereas with MoS_2 and bentonite the same viscosity is attained only with 50 wt % filler. Apparently, the strong effect of TEG on the viscosity of the composite is due to specific features of adhesion interactions of SKTN and TEG, complex shape of TEG particles, and splitting of graphite layers.

Figure 1 shows the creep curves of composites containing MoS_2 or bentonite. In bentonite-containing composites, considerably greater plastic strain is developed, although the difference in the viscosity of the systems is insignificant. For example, for the composite containing 50 wt % MoS_2, the viscosity was $\eta = 0.6 \times 10^7$ Pa s, and for the composite containing the same amount of bentonite, it was $\eta = 0.9 \times 10^7$ Pa s. In the composites containing more than 60 wt % MoS_2

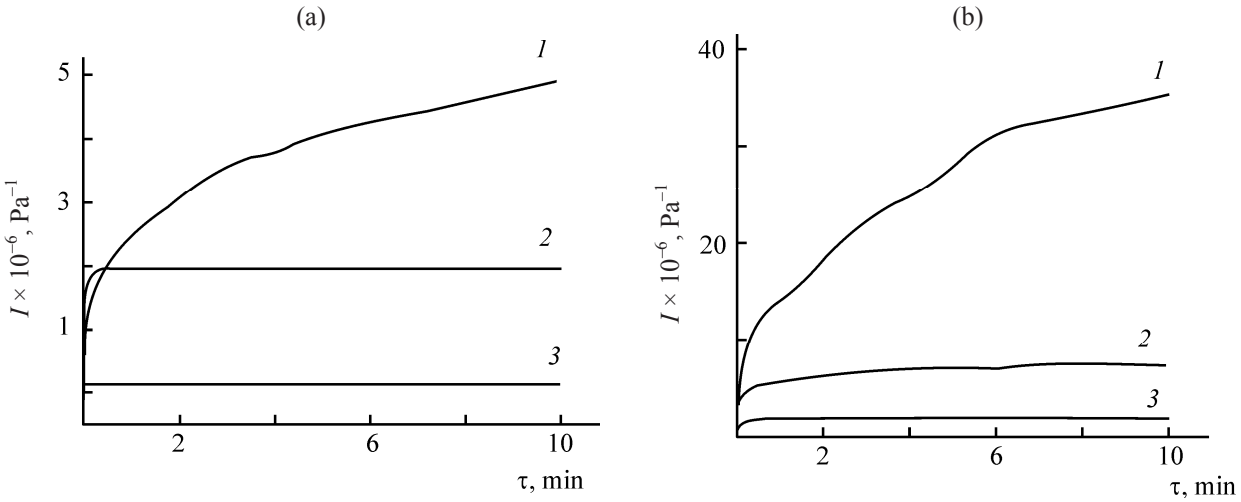

Fig. 1. Creep (I) curves of (a) SKTN-A–molybdenum disulfide and (b) SKTN-A–bentonite composites. (τ) Time; the same for Figs. 2–4; (a) MoS_2 content, wt %: (*1*) 50, (*2*) 60, and (*3*) 70. (b) Bentonite content, wt %: (*1*) 50, (*2*) 70, and (*3*) 90.

or bentonite, the flow does not develop, and after attainment of a certain ductility it does not increase further. Apparently, the absence of flow is associated with a relatively strong three-dimensional framework formed by interaction with each other of filler particles separated by thin rubber layers.

In a composite material containing solid particles, polymer and filler layers are shifted under an external load. At low degrees of filling, the composites are highly fluid, and at high degrees of filling SKTN molecules can be distributed over the solid phase surface and be immobilized in interlayer areas. It was shown previously that adsorption of rubber macromolecules sharply restricts their segmental mobility, up to glass transition [19, 20]. In this case, the polymers exhibit lower fluidity because of stronger adsorption interactions of molecular chains of the polymer with the surface of interlayer areas of filler particles.

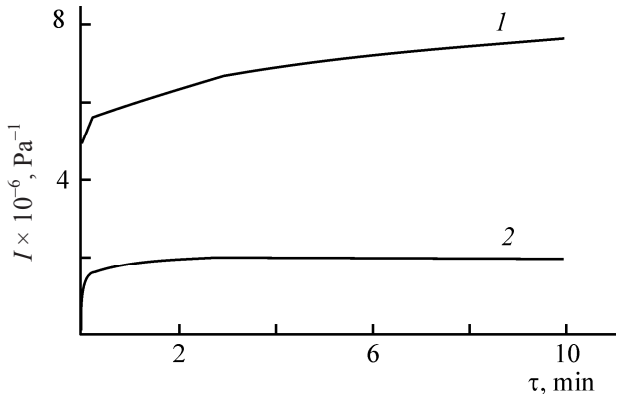

Fig. 2. Creep (I) curves for SKTN samples modified with (*1*) 15 and (*2*) 21 wt % Aerosil particles.

Composites with silicon-containing fillers. Filling with silicon particles does not lead to the formation of plastic materials even at a high degree of filling. For the composite containing 80 wt % Si, the dynamic viscosity does increase relative to SKTN by 4 orders of magnitude to 0.6×10^4 Pa s, but the yield point is lacking.

Composites based on porous quartz exhibit properties of plastic bodies at a filler concentration exceeding 60 wt %. However, at lower filler concentrations, the composites are fluid systems without yield point. The systems with porous quartz considerably exceed in viscosity those with silicon. For example, the viscosity of the composite with 33 wt % of porous quartz is $\eta = 6.7 \times 10^4$ Pa s.

Composites with Aerosil filler show much more promise for the development of materials with controllable plasticity. Figure 2 shows that, although irreversible strain is developed in a composite with 15 wt % AS, the viscosity is relatively high, 0.8×10^7 Pa s, and with 21 wt % AS the composite exhibits the properties of a plastic material.

Thus, the most effective fillers for SKTN-A are active fillers TEG and AS, which ensure strong interaction of the polymer with filler particles. It was found in [21] that, with an increase in the filler surface area (the BET specific surface area of Aerosil A-300 is 286 $m^2\ g^{-1}$), the concentration of adsorption points increases, and the major contribution to the network

structure is made by polymer–filler topological nodes. It was shown that the molecular mobility of adsorption layers of macromolecules is considerably decreased [19, 20]. However, the use of porous fillers with insufficiently developed surface can also favor formation of materials with a high plasticity.

It is known [22, 23] that interaction via hydroxy groups of macromolecules of a low molecular weight rubber with compounds like boric acid (BA), containing OH groups, results in structurization of the material, accompanied by an increase in viscosity. Formation of waxy compounds was observed in interaction of dimethyldichlorosilanes with BA [24, 25]. Therefore, in this study we also used boric acid as structuring agent.

It was shown previously [26] that, with an increase in the boric acid concentration in SKTN (from 5 to 40 wt %) and in the time of preliminary keeping of the composites before tests, their viscosity increased. This phenomenon was considered as a way to control the plasticity of composite materials. Figure 3 shows the creep curves of composites into which different amounts of boric acid were added. As seen from Fig. 3, the larger the amount of boric acid added, the lower the creep. The viscosity calculated from the linear portions of the curves increases with an increase in the amount of boric acid added. The steady-state flow is developed not at once. All the creep curves are characterized by relatively extended portions corresponding to the development of elastic strain. On removing the load, a noticeably elastic aftereffect is observed, and a part of ductility is reversible. The irreversible part of compliance, associated with the flow of the composite, decreases with an increase in the boric acid content.

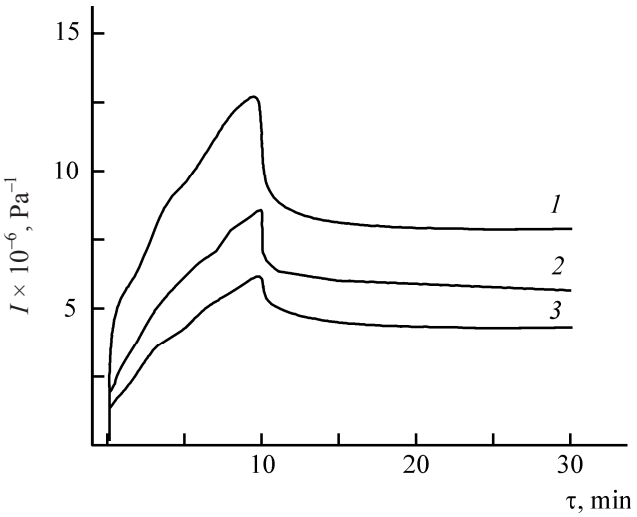

Fig. 3. Variation of the creep (I) curves with an increase in the boric acid content in SKTN samples containing 25 wt % porous quartz particles. BA content, wt %: (*1*) 7, (*2*) 13, and (*3*) 18.

Boric acid was additionally introduced into composite materials containing porous quartz, silica gel, Aerosil, and TEG. With such modification, despite the fact that the amount of the low molecular weight filler increased, the viscosity of the composite decreased. On adding BA to composites filled with TEG (Fig. 4a) or AS (Fig. 4b), the compliance sharply increased, the viscosity decreased, and the residual strain increased. The viscosity of composites filled with 4% TEG decreased on adding BA by an order of magnitude,

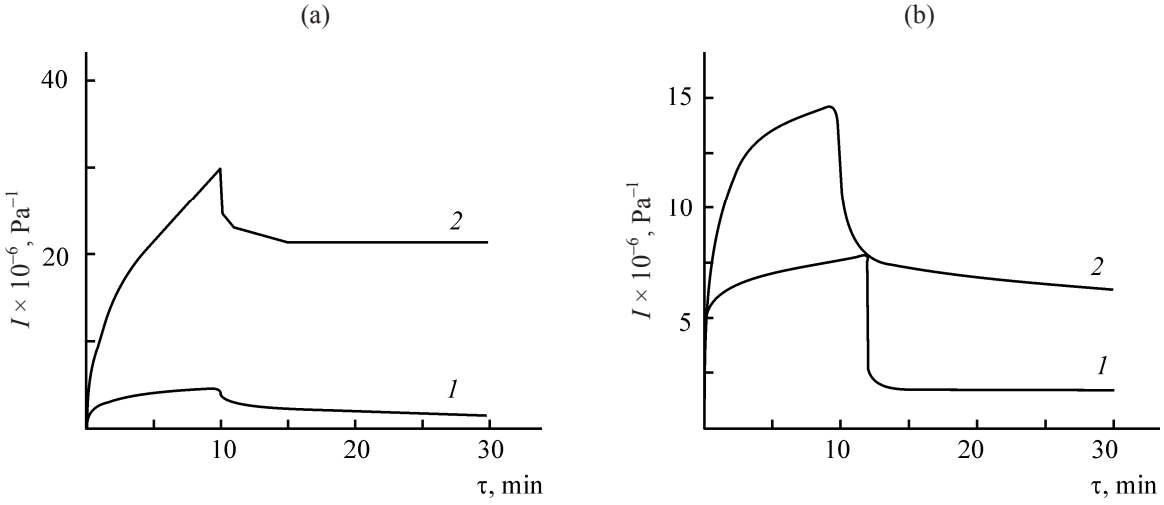

Fig. 4. Creep (I) curves of composites filled with (a) 4% TEG and (b) 15% AS, (*1*) without BA and (*2*) with addition of BA.

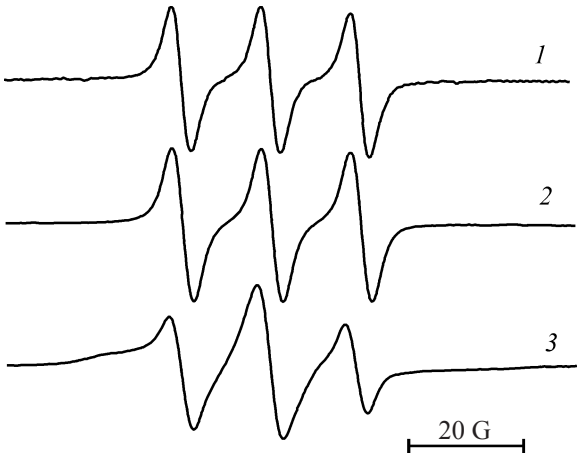

Fig. 5. ESR spectra of TEMPO probe in SKTN-A rubber. Filler: (*1*) none, (*2*) 30 wt % BA, and (*3*) 10 wt % Aerosil (T = 293 K).

from 7×10^6 to 0.6×10^6 Pa s. Apparently, BA prevents formation of a rigid structure resulting from interaction between filler particles. The effect is particularly strong with TEG. For the composites filled with 15% AS, the viscosity on adding BA decreased by a factor of less than 2, from 8×10^6 to 5×10^6 Pa s. Apparently, with AS, which is an active filler, BA is incapable of breaking adsorption bonds between SKTN macromolecules and AS particles. Thus, although addition of BA to SKTN does lead to an increase in the viscosity, for materials filled with inactive fillers BA is a compound decreasing interaction between filler particles.

The results of ESR measurements of the mobility of spin probes in rubber samples modified with BA and AS particles also show that the microviscosity of areas of the material and the extent of its heterogeneity increase. Let us consider data obtained by the spin probe method. The correlation time of the spin probe rotation τ characterizes the microviscosity of the system. In unfilled SKTN-A samples, the lines have the same intensity (Fig. 5, spectrum *1*). This pattern suggests high molecular mobility with $\tau \leq 0.1$ ns.

Introduction of up to 30 wt % boric acid into the rubber does not noticeably affect the probe mobility (Fig. 5, spectrum *2*). However, on adding 10 wt % Aerosil, the ESR spectrum changes essentially: The lines of the triplet become asymmetrically broadened, and additional broad low-field lines appear (Fig. 5, spectrum *3*). These changes are indicative of the system heterogeneity. The spectra can be interpreted assuming the existence of two groups of areas differing in the correlation time of the probe rotation: $\tau \approx 0.6$ ns for the more mobile areas and $\tau \approx 7$ ns for the less mobile areas. Larger τ corresponds to the molecular mobility in the region of glass transition. However, as shown in [19, 20], with an increase in the distance from the filler particle surface, the correlation time continuously decreases. Hence, it will be more correct to analyze the ESR spectra taking into account the continuous distribution function with respect to τ. The spectra calculated at Gaussian distribution with respect to τ are given in [18]. Good agreement of the calculated and experimental probe spectra in the SKTN–Aerosil system is observed at the following parameters: mean value $\tau = 5$ ns, half-width at $1/e$ part of height 3 orders of magnitude.

At statistically uniform distribution of probes in a sample, the ratio of the mobile and "rigid" regions is approximately equal. Adsorption of rubber macromolecules on fillers sharply restricts the segmental mobility of the macromolecules, up to the glass transition [19, 20]. The thickness of the interphase layer modified by the surface of filler particles is no less than 10 layers. The data obtained by the spin probe method show that introduction of 10 wt % Aerosil into SKTN leads to a decrease in the molecular mobility of all the macromolecules of the matrix. About half of them are in the state close to the glassy state.

The developed approaches to controlling the viscosity of low molecular weight rubber can be applied to the development of conducting composites based on TEG.

Thus, our study demonstrated the principal possibility of developing materials with controllable plasticity by modification of SKTN-A low-molecular-weight rubber with various classes of fillers. Fillers affect the viscosity properties of composites to different extents. The strongest effect is attained on adding adsorption-active fillers.

Among layered fillers, TEG exerts the strongest effect. In the composites containing bentonite, considerably greater plastic strain is developed than in the composites with MoS_2, although the viscosities of these composites differ insignificantly. The absence of flow is apparently due to fairly strong three-dimensional framework formed by interaction with each other of filler particles separated by thin rubber layers.

In the case of nonlayered fillers, the effects observed are also different. For example, filling with silicon particles does not lead to the formation of

plastic materials even at a high degree of filling. Composites with porous quartz exhibit properties of plastic bodies at a filler concentration exceeding 60 wt %. The composites filled with Aerosil particles show much more promise for the development of materials with controllable plasticity.

CONCLUSIONS

(1) The most effective fillers for SKTN-A are active fillers, thermally expanded graphite and Aerosil, ensuring strong interaction between polymer and filler particles.

(2) Introduction of boric acid into the composites leads to a decrease in their viscosity. For the materials filled with inactive fillers in which the pore system is not developed, boric acid decreases the interaction of filler particles.

(3) The ESR method is fairly informative for determining the microviscosity and heterogeneity of the systems under consideration.

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