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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Influence of the Ratios of Natural and Butadiene–Styrene Rubbers on the Viscosity of Rubber Blends and Fragmentary Mobility of Macromolecules

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Abstract—The structural states of macromolecules of natural and butadiene–styrene rubbers in their blends were studied by evaluating the spin–lattice relaxation times of carbon nuclei. The relationship between the viscosity of rubber blends and fragmentary mobility of macromolecules was examined.

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The dependences of the viscosity of blends of natural (NR) and butadiene–styrene (BSR) rubbers on the elastomer ratio are reported and analyzed in numerous papers [1–3]. The dependences given by different authors are essentially different.

The diversity of the trends observed is apparently due to different conditions of compounding and different degrees of NR plasticization in its compounding with other rubbers. It is known that compounding of rubbers of different nature results in formation of predominantly heterophase systems in which the components are separated by a layer of segmental solubility and by thicker boundary layers of phases, consisting of macromolecules with altered supramolecular organization. The density of the layer of segmental mutual diffusion is lower than the additive value [1, 2]. The density of the boundary layers depends on the nature of the contacting polymers. Changes in the supramolecular structure and density of macromolecule arrangement in the interphase area can be manifested in changed mobility of carbon atoms and separate atomic groups of the macrochains. These atoms and groups can differently respond to contact between two different polymers.

In this study we examined changes in the mobility of chain fragments arising when rubbers of different chemical structures are compounded. This characteristic can offer important information on the structural state of macromolecules and of the system as a whole.

EXPERIMENTAL

The mobility of the atomic groups in macromolecules of rubbers and their blends was evaluated by ^{13}C nuclear relaxometry. To study the rheological aspect of compounding of NR blends differing in the degree of plasticization with SKMS-30ARK rubber, we determined the viscosities of the systems obtained. The composition dependence of the viscosity is plotted in Fig. 1. NR–SKMS-30ARK rubber blends were prepared under the same conditions, both for individual rubbers and for their compounds, on 320–160/160 laboratory rollers to eliminate the effect of the blending time on the viscosity. Filled rubber stocks containing (wt proportion) [4] rubber 100, stearin 2.5, sulfenamide Ts 0.1–1.2, sulfur 2–2.5, and P-324 carbon black 50 were prepared in a 4.2-l rubber mixer with oval rotors at a rotation rate of 40 rpm for 12 min.

Experiments with increasing content of the vulcanization accelerator and decreasing sulfur content in the blend were performed with an increase in the BSR amount in NR–BSR compounds, so as to equalize the vulcanization kinetics and attain equal degree of cross-linking with further vulcanization of rubber stocks. Two cases of variation of the viscosity of NR–BSR blends were considered. In the first case (Fig. 1a),

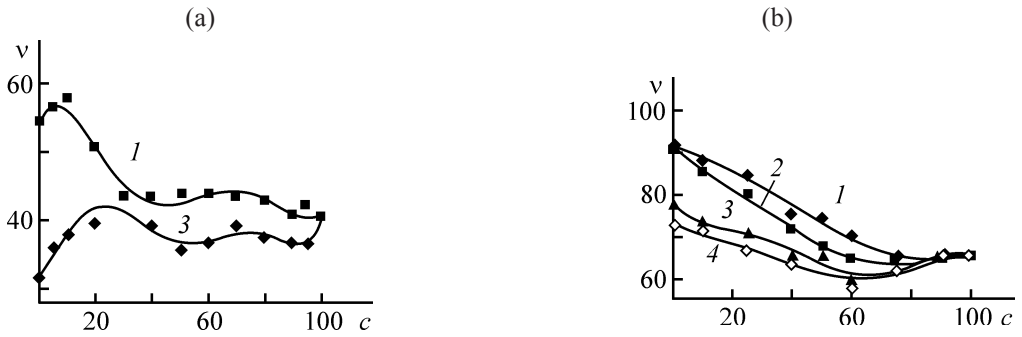

Fig. 1. Mooney viscosity ν of (a) rubber blends and (b) rubber stocks filled with carbon black, as a function of the SKMS-30ARK weight fraction c in NR–SKMS-30ARK blends. Samples prepared (a) on rollers and (b) in rubber mixer. NR plasticate: (*1*) P1, (*2*) P2, (*3*) P3, and (*4*) P4.

the viscosity of rubber blends passed through extrema. On adding BSR to NR, the viscosity of the blends increased even when the viscosity of the BSR added was lower than that of the NR (Fig. 1a, curve *1*). The minimal viscosity was observed in the region of phase inversion, at ratios close to 50 : 50. Similar trend in the viscosity was observed on adding 20 wt % NR. For the filled blends (Fig. 1b), the viscosities were below the additive values. With an increase in the degree of NR plasticization, the viscosity of rubber stocks decreased.

To rationalize differences in the viscosity of NR–BSR blends in the unfilled and filled states, we examined the effect exerted on the viscosity by changes in the fragmentary mobility of rubber macromolecules. A specific feature of the structure of polymer blends is enhancement of the intermolecular interaction, which should be manifested in changes in the relaxation times of carbon atoms, caused by the polymer interaction.

The mobility of atomic groups in macromolecules of rubbers and their blends was evaluated by ^{13}C nuclear relaxometry [5, 6].

The spin–lattice relaxation times T_1 of the ^{13}C nuclei in polymers were measured by the method of inversion followed by recovery, using the 180–τ–90–T pulse train. The time τ was varied from T to 0.025 s, and T was taken longer than $5T_1$ for complete relaxation of the ^{13}C nuclei [7]. This method allows selective measurement of the spin–lattice relaxation time T_1 of nonequivalent nuclei giving separate signals in the spectrum.

We obtained the ^{13}C NMR spectra of NR–SKMS-30ARK blends with component ratios of 0 : 100, 5 : 95, 15 : 85, 50 : 50, 80 : 20, 90 : 10, and 100 : 0 at 30°C. When determining the spin–lattice relaxation time of each carbon atom, we took into account the number of protons boded to it. The spin–lattice relaxation times of various fragments of carbon chains of natural *cis*-1,4-polyisoprene compounded with butadiene–styrene in various ratios are given in Table 1.

It can be seen that the relaxation time of the most mobile methyl carbon atom decreases to the greatest extent. The methine –CH= and methylene $–CH_2–$ groups are less mobile. The relaxation time of the quaternary carbon atom decreases in going to 1 : 1 blend of NR with BSR from 0.814 to 0.301 s. However, the relaxation mechanism for the quaternary carbon atom may differ from the dipole–dipole mechanism because of long distance to other paramagnetic centers. At the same time, it should be noted that the quaternary carbon atom is chemically bonded to the methine, methylene, and methyl carbon atoms whose relaxation time decreases on compounding of NR with BSR. A decrease in the mobility of the atoms surrounding the quaternary carbon atom leads to its braking. Thus, it can be concluded that compounding of NR with BSR leads to a decrease in the mobility of the whole polymer chain of polyisoprene.

At the NR : BSR ratio of 50 : 50, the signals of nuclei 1, 2, and 3 are not separated because of increased content of SKMS-30ARK and superposition of the signals from methylene and methine groups of butadiene in the butadiene–styrene copolymer. The spin–lattice relaxation times of the carbon chain fragments of polybutadiene in a blend with *cis*-1,4-polyisoprene at various component ratios are given in Table 2.

Table 1. Relaxation times of the ^{13}C nuclei of *cis*-1,4-polyisoprene in a blend with SKMS-30ARK[a]

Content of *cis*-1,4-polyisoprene, wt %	Relaxation time, s			
	1	2	3	4
100	0.078	0.140	0.126	1.083
95	0.074	0.126	0.114	0.804
90	0.071	0.112	0.118	0.948
80	0.06	0.120	0.120	0.849
50	–	–	–	0.600

[a] Assignment of *cis*-1,4-polyisoprene signals: (1) –CH=, (2) –*C*H_2–C=, (3) –*C*H_2–CH=, and (4) –CH_3.

Table 2. Relaxation times of the ^{13}C nuclei of butadiene in a blend of butadiene–methylstyrene with *cis*-1,4-polyisoprene[a]

Content of *cis*-1,4-polyiosprene, wt %	Relaxation time, s	
	1	2
0	0.160	0.182
5	0.131	0.172
15	0.139	0.164
50	0.103	0.132

[a] Assignment of butadiene signals: (1) –CH=*C*H– and (2) –CH_2–.

It can be seen that the most mobile are the butadiene carbon atoms linked by the double bond. The methylene carbon nuclei in the fragments formed by *cis*-1,4-addition are less mobile. With an increase in the content of NR in the blend, the relaxation times of all the butadiene nuclei decrease. In this case, it was difficult to distinguish the relaxation time of styrene carbon nuclei because under our measurement conditions the signals were weak and broadened. On the whole, compounding of NR with BSR leads to a decrease in the spin–lattice relaxation time and in the mobility of chains of both rubbers.

The data we obtained allow a conclusion that contact of *cis*-1,4-polyisoprene with butadiene–styrene copolymer is accompanied by a relatively strong intermolecular interaction. Presumably, owing to higher cohesion energy density of styrene, which is distributed in the macromolecule not only randomly but also in definite sequences (only 30% of styrene units are isolated, 40% form pairs, and the other may show tendency to adjacent arrangement [8]), some of isoprene units of NR are selectively adsorbed on boundary surfaces on styrene sequences of BSR, which decreases their mobility and leads to their denser arrangement. At the same time, butadiene sequences of BSR units, which have lower cohesion energy than NR isoprene units [9], are adsorbed on the latter units, becoming less mobile and acquiring higher packing density. The existence in NR of associated structures, e.g., in the form of trans conformers [10], increases the probability of such adsorption in rubber compounding. Intermolecular attraction occurring in rubber compounding leads to mutual restriction of the mobility and densification of macromolecules in boundary layers, favoring formation of a common composite system. It should be noted that, owing to the two-phase structure, the number of macromolecules directly participating in the contact is small relative to their content in the bulk, and the spin–lattice relaxation time of the carbon nuclei of the chains of both rubbers appreciably decreases. The intermolecular interaction is long-range. As follows from Tables 1 and 2, in the blends densification of macromolecules in boundary layers prevails over their loosening in the layer of mutual segmental diffusion.

Changes in the structural state of a part of macromolecules in boundary layers and in the layer of segmental solubility may be responsible for changes in the viscosity of the blends. As the content of BSR in the natural rubber matrix is increased, the viscosity starts to increase, which is consistent with a decrease in the mobility and spin–lattice relaxation time of carbon atoms of the isoprene units prevailing in the blend. In the region of phase inversion, a minimum in the viscosity is observed, caused by an increase in the total area of the phase boundary of the components near the phase inversion and to an increase in the volume the macromolecules located in the loose layer of mutual segmental diffusion. An increase in the butadiene–styrene content after phase inversion leads to an increase in the viscosity owing to braking of butadiene chains under the action of cis-1,4-polyisoprene. Similar trends in viscosity variation are observed with increasing NR content in the BSR matrix and then after phase inversion.

Thus, the denser structure of boundary layers of different phases and the loosened structure of the layer of mutual segmental diffusion exert competing effects on the viscosity of the blends, the first factor increasing, and the second, decreasing the viscosity. In

the presence of a carbon filler in the rubber blend, its intermolecular interaction with the elastomers considerably prevails over the interaction of the elastomers with each other, and the volume content of the interphase layer in the system exerts a decisive effect on the viscosity. As a result, the viscosity curve lies below the additive values (Fig. 1b).

CONCLUSIONS

(1) Experiments on compounding natural and butadiene–styrene rubbers revealed a decrease in the spin–lattice relaxation time of the carbon nuclei of the polymer chains, suggesting strong intermolecular interaction, decreased mobility, and densification of macromolecules in the boundary layers of the contacting phases.

(2) A change in the structural state of macromolecules in boundary layers is manifested in specific dependence of the viscosity of the blend on the component ratio.

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