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Fig. 1

Figure 1: Fig. 1

Abstract

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LOW-TEMPERATURE RELAXATION PROCESSES IN RUBBER-LIKE POLYMERS

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Although relaxation phenomena in polymers were first studied in rubber-like polymers (1,2), in solid polymers the processes of molecular relaxation have been investigated incomparably better. Usually (3) high-temperature (upon transition from the highly elastic to the elastic-solid state) and low-temperature maxima of mechanical losses (m.m.l.) are observed. Corresponding to them (4) are maxima of dipole-elastic and dipole-radical dielectric losses (d.l.). A correlation has been established between the action of mechanical and electrical alternating fields (3,5). The molecular mechanisms of the high-temperature and low-temperature maxima are usually associated with changes in the mobility of segments and side groups of the chain.

Fig. 1. Temperature dependences of the coefficient of mechanical losses χ at a frequency of 0.1 oscillations/min for sulfur vulcanizates of rubbers:
1 –NK, 2 –SKS-30, and 3 –SKN-40

In rubber-like polymers analogous relaxation processes occur at low temperatures; therefore the corresponding maxima in rubber-like polymers should appropriately be called the main and the secondary. The existence of the main maximum, as also in solid polymers, is explained by a change in segmental mobility (6–8). The secondary maximum, however, was not detected in measurements carried out in electric fields (8). Investigations at low temperatures were mainly limited to the study of the problem of frost resistance (9,10). The glassy state itself of rubber-like polymers has not been systematically investigated.

In order to establish the relationship between structure, molecular mobility, and the macroscopic relaxation properties of rubber-like polymers, we carried out a series of studies, some results of which are reported in this article. Natural and synthetic rubbers were investigated, as well as sulfur, thermal, and radiation spatially structured (or network) polymers obtained on their basis. Measurements were made by dynamic mechanical methods at low mechanical and sonic

Fig. 2. Temperature dependences of the tangent of the dielectric loss angle $\mathrm{tg}\,\delta_{\mathrm{el}}$ for sulfur vulcanizates of rubbers: 1 –SKS-30 and 2 –SKN-40 at frequency $\nu = 50$ Hz

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frequencies in the range 10^{-3}-10^{2} Hz and over a broad temperature interval from −180 to +25°. For comparison of the processes of mechanical and dielectric relaxation, temperature dependences of dielectric losses were recorded. The structural features of rubber-like polymers and the character of their molecular mobility were additionally studied by means of IR and NMR methods.

The main m.m.l., observed in the structurally liquid state of the polymer ([9]), is determined by the type of rubber (Fig. 1) and, for relatively sparse spatial networks, does not depend on the degree of cross-linking.

Polar nitrile rubbers with high internal friction have the greatest height of the m.m.p. The principal m.d.p. also have the greatest magnitude in sulfur vulcanizates based on polar rubbers; for nonpolar rubbers* they have a noticeably smaller height and are observed at lower temperatures (Fig. 2).

The m.d.p. of nonpolar and, especially, polar polymers, in comparison with the m.m.p., were observed even at comparable frequencies at higher temperatures, and the activation energies of the processes of dielectric relaxation, as compared with mechanical relaxation, proved to be larger by 2-6 kcal/mole. The incomplete correlation between the processes of dielectric and mechanical relaxation in the region of the principal maxima is due to the difference in the sizes of the kinetic units and in the character of their thermal motion. The mechanical field acts mainly on segments of the main chains, whereas the electric field acts on polar side substituents. In the first case the side substituents are free, while in the second the force field acts through them on chain segments; i.e., in the case of an electric field the sizes of the kinetic units and the activation energy increase somewhat. In the region of the principal m.m.p. and m.d.p. there is observed a sharp change in the line width and of the second moment, NMR, and also a change in the absorption intensities of a number of principal bands in the IR spectra.

Fig. 2. Temperature dependences of the tangent of the dielectric loss angle $\mathrm{tg}\,\delta_{\mathrm{el}}$ for sulfur vulcanizates of rubbers: 1 –SKS-30 and 2 –SKN-40 at frequency $\nu = 50$ Hz

Secondary m.m.p. are observed for all rubbers, and their order of position differs from that of the principal maxima (Fig. 1). The secondary m.m.p., apparently, are caused by looseness of the molecular packing, as a result of which the presence of free volume makes it possible to preserve mobility both of side groups and of atomic groups in the main chains. The greater flexibility and regularity of the arrangement of NR molecules determine its more perfect molecular ordering, and therefore in it the secondary m.m.p. is observed at a higher temperature and has a smaller magnitude. At the same time, the presence of branching and the asymmetry of SCS molecules, the irregularity of SKB, and the lesser flexibility of parts of SKN molecules lead to the presence of less ordering, promoting loosening of the structure, increasing the free volume, and creating the possibility of greater mobility of atomic groups (methyl CH_3, vinyl $-CH{=}CH_2$, phenyl C_6H_5, and nitrile $-C{\equiv}N$). NMR and IR spectra show that in the glassy state there is also some mobility of the CH_2 atomic groups, characteristic of rubbers, in the main chain.

With increasing frequency, the secondary m.m.p. shift toward higher temperatures more rapidly (Fig. 3) than the principal ones, as a result of which at high frequencies they almost completely merge with the principal ones. This is due to the fact that the secondary m.m.p. are associated with the motion of smaller kinetic units and with lower (by a factor of 1.5-2) activation-energy values than the principal ones.

* Noticeable dielectric losses of nonpolar polymers appear in connection with the presence in them of side groups, double bonds, nonrubber inclusions and partial oxidation, and also owing to the orientation of dipoles caused by the difference in polarizability of C—H bonds with the primary, secondary, or tertiary position of the carbon atom, characteristic of the polymer structure ([12]). Only the combination of these causes can at present explain the presence of dielectric losses in nonpolar polymers.

Secondary m.d.p. were observed only for polar SKN rubbers. Their appearance is associated with the presence of polar nitrile groups —C N and with their mobility, due to the loose packing of atactic nitrile rubbers. The weakly polar side substituents of nonpolar rubbers are practically not affected by electric fields, whereas in mechanical fields side substituents having a certain mass take part in the relaxation process. For the secondary m.d.p. a sharper shift toward higher temperatures with increasing frequency is also characteristic than for the main maxima (Fig. 3). In the region of the secondary maxima, the activation energies of mechanical and dielectric relaxation processes are close, but also do not coincide, which indicates some difference in polar rubbers in the sizes of the kinetic units or in the conditions of their motion. As in the case of mechanical fields, so also in the case of electric fields, the degree of shift of the main and secondary maxima along the temperature scale with increasing frequency can be estimated from formulas of the form (13)

$$\frac{1}{T_M} = A - B \lg \nu,$$

where the constants A and B are inversely proportional to the activation energy and have different values for mechanical and electric fields. In this case the degree of shift of the main and secondary maxima is determined by the

Figure 3

Figure 3: Figure 3

Fig. 4

Figure 4: Fig. 4

corresponding constants B. The smaller the activation energy, the greater the value of the constant B and the greater the shift of the maxima. Consequently, secondary maxima with lower activation energy should shift more rapidly with increasing frequency. This is in agreement with the fact that in polar rubbers, for which a larger value of the activation energy is characteristic, the degree of shift is smaller than in nonpolar ones.

Fig. 3. Dependence of the temperature of the m.m.p. and m.d.p. on the frequency of the external action for a sulfur vulcanizate of SKN-18 rubber in coordinates $\frac{1}{T_M}$, $\lg \nu$: 1, 3—respectively for the main and secondary m.m.p.; and 2, 4—for the main and secondary m.d.p.

Thus, for polar rubber-like polymers both main and secondary m.m.p. and m.d.p. are observed, whereas for nonpolar polymers secondary m.d.p. are practically not observed. This is due to the fact that nonpolar polymers are characterized by extremely small dielectric losses, and the accuracy of the methods does not permit the detection of secondary m.d.p. at low temperatures. In addition, the main m.m.p. of polar and nonpolar rubbers differ only slightly (Fig. 1), whereas the main m.d.p. differ sharply (Fig. 2), which is also due to the lower dipole moments of nonpolar polymers. In this connection, in studying the relaxation properties of weakly polar rubber-like polymers, dynamic mechanical methods prove more effective; therefore, the influence of supramolecular structures on the relaxation properties of rubber-like polymers was studied by us in alternating mechanical fields.

The study of low-temperature molecular relaxation processes in rubber-like polymers is of particular interest in connection with the molecular ordering found in them (14). It was expected that at low temperatures the mechanical properties of rubbers and vulcanizates would not differ. Indeed, the maxima of pure NR and of its sulfur vulcanizate in the glass-transition region are practically identical (Fig. 4). However, the secondary m.m.p. of a sulfur vulcanizate of NR with a sparse network of cross-

is appreciably greater than in pure NR. The type of vulcanizate also has a substantial effect on the magnitude of the secondary maximum. Thus, in the radiation vulcanizate of SKB the main and secondary mechanical-loss maxima are noticeably smaller than in the sulfur vulcanizate with the same network density, and this phenomenon is expressed even more distinctly for the secondary maxima than for the main ones.

Fig. 4. Temperature dependences of the coefficient of mechanical losses χ for pure NR *(1)* and its sulfur vulcanizate *(2)* with a sparse spatial network ($E_\infty = 8$ kgf/cm^2) at a frequency of 0.1 oscillations/min

The decrease in the magnitude of the mechanical-loss maximum in the radiation vulcanizate of SKB is connected with its greater molecular ordering.

These facts may be explained by the difference in the supramolecular structures formed under different crosslinking conditions. Bundles of chains in rubber-like polymers are unstable; therefore, under the action of thermal motion they break up and arise again. At high temperatures the structure of rubber is close to a picture of disordered, chaotically entangled chains. Transverse bonds formed at elevated temperatures hinder the packing of chains into bundles; therefore, on cooling, the high-temperature structure of the rubber is fixed. A radiation vulcanizate is obtained as a result of γ-irradiation (with a Co^{60} source) at 20°, and spatial structuring is not accompanied by destruction of the already existing molecular ordering.

The greater difference between the secondary mechanical-loss maxima of radiation and sulfur vulcanizates of SKB, in comparison with the main maxima, apparently indicates molecular ordering that continues with decreasing temperature and is due to the mobility of small kinetic units, which are aggregates of atomic groups.

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