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Abstract

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On the Nature of Bonds and the Gas Permeability of Spatially Structured Polybutadiene

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The influence of spatial structuring on the gas permeability of polymers has previously been studied by a number of investigators. One of the practically important cases of structuring is the formation of spatial networks in rubber through the addition of sulfur during vulcanization. Barrer and Skirrow (^{1}) showed that the gas permeability of rubber decreases nonlinearly with an increase in the amount of sulfur bound by the rubber. An increase in the density of the spatial network leads, at the same time, to a decrease in the constants of diffusion and of gas solubility in the polymer, and therefore the permeability constant, which is the product of these two quantities, is a highly sensitive indicator in the study of polymer structuring. In addition to the general decrease in gas permeability, an increase in the network density in a polymer in the high-elastic state is accompanied by an increase in the apparent activation energies of permeability and diffusion, as well as in the constants D_0, which characterize the temperature dependence of permeability and diffusion (^{1}).

A decrease in permeability and an increase in the activation energy of permeability were also observed during the oxidation of rubber (^{2}), under the action of short-wave radiation on polyethylene (^{3}), and in other cases of spatial structuring of polymers. An increase in the number of nodes of the spatial network in a polymer is accompanied by an increase in the glass-transition temperature of the polymer. If one takes into account that the glass-transition temperature and the gas permeability of a polymer depend on the flexibility of the chain molecules, then the changes in these quantities during polymer structuring must be in a definite relationship. This relationship may be expressed as a dependence between the logarithm of the gas permeability and the glass-transition temperature, which for sulfur vulcanizates of rubber has a linear character (^{4}).

The specific properties of spatially structured polymers depend on the density, regularity of arrangement, and chemical nature of the cross-links (^{5}). Determining the dependence of gas permeability on the amount of bound sulfur in rubber does not make it possible to answer unambiguously the question of the influence of the density of cross-links, since it is known that sulfur, in addition to forming intermolecular bonds, can also add intramolecularly. The groups formed as a

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

result of sulfur addition—$-S-S-$, $H-S-$, and others—possess high polarity, which promotes the development of intermolecular forces and a reduction in gas permeability. Indeed, linear polymers containing a considerable amount of sulfur, both in the main chain—thiokols (6)—and in the form of sulfur attached to the main chain (7), are characterized by reduced gas permeability. Ebonite (8)—a spatially structured product of the combination of rubber with sulfur—also has low gas permeability. The possibility of clarifying the separate influence of bridge covalent and intermolecular bonds on gas permeability is of great interest.

To solve this problem, we studied spatially structured polybutadienes differing in the chemical nature of the cross-links, the density of which was characterized by the value of the equilibrium high-elastic modulus, determined by the method of (^9).

Fig. 1. Dependence of the nitrogen permeability of polybutadiene at 20° on sulfur content. **1**—dissolved sulfur, **2**—intramolecularly bound sulfur, **3**—vulcanizate with sulfur and diphenylguanidine

The formation of spatial networks in polybutadiene (SKB-40) was achieved by heating in a press at 220°; by exposure to Co^60 radiation; by heating with sulfur and diphenylguanidine; and by heating with sulfur and thiuram. The density of the networks was varied both by the duration of heating or irradiation and by changing the content of vulcanizing agents. It was assumed that at high temperature (220°) spatial structuring proceeds predominantly through the opening of double bonds; under Co^60 irradiation, bonds of the type —C—C—arise; upon vulcanization with thiuram, monosulfide bonds arise; and with diphenylguanidine, predominantly polysulfide bonds (^10, ^11). The objects of the study were specimens 80 mm in diameter and 0.5 mm thick, obtained by hot pressing. Gas permeability was determined on a thermostatted Shuman apparatus (^12). Nitrogen (99.6% N_2) from a cylinder was used as the gas; before entering the apparatus it was subjected to preliminary drying. The gas permeability values P were expressed in cm^3 (N.T.P.) sec^{-1} cm^{-1} atm^{-1}, and the equilibrium modulus E_∞ values in kg cm^{-2}.

To estimate the influence of additional intermolecular forces, arising when sulfur is introduced into rubber, on the change in gas permeability, a preliminary study was made of the gas permeability of polybutadiene rubber containing dissolved, intramolecularly bound, and cross-linking sulfur.

Fig. 2. Change in the equilibrium modulus and nitrogen permeability of polybutadiene during heating (220°)

The results obtained are shown in Fig. 1. Dissolved sulfur, the concentration of whose supersaturated solutions in polybutadiene at 20° does not exceed 2%, has no substantial influence on the nitrogen permeability of the rubber. A small change in permeability is also observed in the case of intramolecularly bound sulfur (curve 2—for the product of the interaction of dienes with mercaptan). The greatest effect in lowering the permeability of polybutadiene is produced by sulfur that promotes the formation of a spatial structure (curve 3—sulfur vulcanizate with diphenylguanidine). Thus, cross-linking sulfur bonds arising between the chain molecules of the polymer exert a stronger influence on the reduction of gas permeability than an equivalent amount of sulfur-containing groups attached intramolecularly.

The existence of a dependence of gas permeability on the concentration of the nodes of the spatial network makes it possible to establish a relation between gas permeability and the equilibrium high-elastic modulus.

As an example, Fig. 2 shows the characteristic dependence of the equilibri-

of the equilibrium modulus and nitrogen permeability on the heating time of polybutadiene at 220°. The decrease in gas permeability observed in the process of spatial structuring is accompanied by an inversely proportional increase in the equilibrium modulus. The relation between gas permeability and the equilibrium modulus may be expressed by the simple dependence:

$$\lg P = \lg P_1 - kE_\infty,$$

where P and P_1 are the gas permeabilities of the vulcanizate and the rubber, respectively, E_∞ is the equilibrium high-elastic modulus, and k is a proportionality coefficient. The dependences of $\lg P$ on E_∞ at various temperatures are shown in Fig. 3. As follows from the data obtained, the chemical nature of the bond does not exert a substantial influence on the change in the gas permeability of polybutadiene during spatial structuring. At one and the same value of the high-elastic modulus, the value of $\lg P$ remains approximately constant for networks of different chemical nature. However, this conclusion can be drawn only with respect to fairly loose networks (up to $E_\infty = 30$–40 kg cm^{-2}), since in denser networks an individual influence of the nature of the bonds on the gas permeability of polymers is possible. In the case of loose networks, the principal role in reducing the flexibility of chain molecules and decreasing permeability belongs to the cross-linking bond, in comparison with which the intermolecular forces determined by the chemical nature of this bond are, to a first approximation, of no substantial significance.

Fig. 3. Dependence of the logarithm of nitrogen permeability on the equilibrium modulus. *a*—irradiation with Co^{60}, *b*—heating with sulfur and diphenylguanidine, *v*—heating with sulfur and thiuram, *g*—heating at 220°.

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