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Investigation of the Properties of Rubber Structures Reinforced through Interaction with Carbon Blacks

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At the present time, the nature of the reinforcing action of active rubber fillers remains, to a considerable extent, still unclear. Two mechanisms of the action of a filler on a polymer are assumed: 1) adsorptive interaction and the development of a spatial structure in the polymer under the influence of the surface of particles of the active filler ($^{1-6}$), and 2) densification of the vulcanization network near the filler particles (carbon black) as a result of the catalytic influence of the latter on the vulcanization processes (^{7,8}). The first mechanism appears to be more general. We have obtained data on the formation of a double, mutually interconnected structural network of the polymer and of aggregates of carbon-black particles (^{6}). For the reinforcing effect to appear, the "reinforced" polymer structure that forms must permeate the entire volume of the system, being closely connected with the structural network consisting of particles (aggregates) of carbon black. According to these ideas, the "reinforced" structures determine the increase in the strength of rubber. Their formation must be accompanied by a decrease in the free energy of the system. The character of the structure is evidently determined by the intensity of the adsorptive interaction, i.e., by the nature of the polymer and the surface of the carbon-black particles. It may be assumed that the "reinforced" polymer structure arises in the process of introducing carbon black into it; moreover, we believe that such a structure can gradually attain a certain quasi-equilibrium state, to which the greatest mechanical strength of the system corresponds, as occurs in the case of concentrated suspensions of carbon black in rubber solutions ($^{2-6}$). However, in rubbers the quasi-equilibrium state of the reinforced structures is not actually achieved, owing to the imperfection of mixing methods and the high viscosity of the medium.

In the present work, rubber—carbon-black systems, both unvulcanized and vulcanized, were investigated. The vulcanizates were prepared according to a "standard" formulation with the vulcanization accelerator sulfenamide BTs (SKD and BSK) and captax (NK); 50 parts by weight of carbon black were introduced per

100 parts by weight of rubber. The rubbers used were butadiene-styrene (BSK), grade—

Table 1

Physicochemical characteristics of carbon blacks

Carbon black	Specific surface, m^2/g (from electron-microscopy data)	Oil number, ml/g (dibutyl phthalate absorption)	pH of aqueous suspension	Content of unpaired spins, $10^{-19}/m^2$ (by ESR method)*	C	H	O	S
I Vulcan-3	76	1.03	8.1	1.07	98.1	0.22	0.9	0.88
II Vulcan-3 graphite-treated	76	1.04	7.0	0.00	99.9	0.1	0.0	–

* Investigations by the ESR and NMR methods were performed by O. V. Nikitina in the radiospectroscopy laboratory of the Kazan Branch of the Academy of Sciences of the USSR and at Kazan University.

rubbers: Yuropen-1500; natural rubber (NR)—smoked sheet; stereoregular polybutadiene (SKD)—Yuropen-cis; carbon blacks: active furnace black—Vulkan-3 (I) and the same black, partially graphitized for 24 h at 2600° (II). The physicochemical characteristics of the blacks are given in Table 1.

The blacks were introduced into the rubbers on laboratory rolls. The mechanical characteristics of the unvulcanized mixes were determined: plastic strength (limiting shear stress) and viscosity on a Kanavets shear plastometer in the range 60–120°. The activation energy of viscous flow was calculated by the method of Bartenev (^{9}).

Fig. 1. Thermogram of mixes: rubber—black I and rubber—black II

Fig. 2. Change in the quasi-equilibrium modulus E'_∞ of rubbers based on BSK (at 50% elongation) as a function of temperature: H—unfilled rubber (H), I—containing black I, II—containing black II

In parallel, the thermography method was used with a Kurnakov pyrometer. Thermograms were recorded in the interval 20-200°, with unfilled rubber serving as the standard. Fig. 1 presents thermograms of BSK mixes with blacks I and II.

In the next series of experiments vulcanizates were studied; the rate of stress relaxation, the quasi-equilibrium modulus (in the range 20–110°), and tensile strength were determined on a Polanyi dynamometer. In addition, the vulcanizates were studied by the NMR method on a "SPIN-ECHO" instrument: the spin–spin relaxation time was determined. The results obtained are given in Table 2 and in Fig. 2.

Table 2

Characteristics of the systems studied

Characteristic	Without black	Without black	Without black	With black I	With black I	With black I	With black II	With black II
	SKD	NR	BSK	SKD	NR	BSK	SKD	BSK
U, kcal/mol	7.0	9.0	11.5	–	–	–	–	–
P_m, kg/cm^2	0.179	–	0.543	1.51	–	1.12	0.60	0.89
τ, kg/cm$^2 \cdot$ min	0.30	0.22	0.25	0.09	0.11	0.12	0.28	0.22
P, kg/cm^2	32	184	45	170	272	263	108	107
T_2, μsec	1180	610	400	940	610	380	1030	–

Note. U—activation energy of rubber flow; P_m—limiting shear stress of the unvulcanized mix at 60° and shear-rate gradient $2.54 \cdot 10^{-2}$ s^{-1}; τ—average rate of stress relaxation of the vulcanizate at 20° and 50% deformation over the time interval from 1 min from the start of the experiment to the point at which the stress-relaxation curve becomes linear; P—tensile strength of vulcanizates (specimens 0.5 mm thick); T_2—spin-spin relaxation time.

According to Fig. 2, in filled vulcanizates, within a certain temperature interval—70-110° with black I and 70-92° with black II—changes in structure are observed: the destruction of a certain set of bonds, stronger than the intermolecular bonds in the unfilled polymer. According to the thermograms in Fig. 1, an endothermic process is observed in the same temperature interval. Comparing these data, it is easy to understand that, in this temperature region, destruction of the "reinforced" structures occurs. The indicated destruction may be likened to a kind of phase transition. The more active carbon black I also forms more stable (stronger) structures. This is related to the well-known fact that the surface of carbon black I contains more active centers for hydrocarbon adsorption than the surface of carbon black II. The heats of adsorption of the model hydrocarbon—butene-1—on carbon blacks I and II were studied earlier [10]. Graphitization of carbon black, which leads to a decrease in surface heterogeneity as a result of the disappearance of the most active adsorption centers (defects of the crystalline lattice of the carbon black), should narrow the temperature interval of the structural transition because of the absence of more stable (stronger) bonds.

These results are in agreement with the data in Table 2. The tensile strength P of the vulcanizate and the plastic strength P_m of the unvulcanized compound are substantially higher in the case of carbon black I than in the case of carbon black II; the rate of stress relaxation, greatest in the case of the unfilled system, decreases to some extent in the presence of carbon black II and, to an even greater extent, in the presence of carbon black I. This is quite evident, since the mobility of polymer chains should decrease as the stability (strength) of the "reinforced" structure increases. This conclusion is also consistent with the change in the time T_2 of spin-spin relaxation, which decreases as the strength of the "reinforced" structures increases.

Comparison of the magnitude of the reinforcing effect caused by introducing carbon blacks I and II into different rubbers shows that the weaker the forces of intermolecular interaction in the polymer (qualitatively characterized by the activation energy of viscous flow), the more readily "reinforced" structures are formed and the greater the difference in mechanical properties between filled and unfilled systems. This regularity also holds when comparing crystallizing and noncrystallizing polymers, independently of the well-known influence of polymer crystallizability on the strength properties of rubbers.

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Note: Figure translations are in progress. See original paper for figures.