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Abstract

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Study of the Structure of Rubbers and Vulcanizates by the Replica Method

In previous investigations ($^{1-3}$), electron-microscopic study of the structure of a number of rubbers revealed that rubbers are ordered systems whose structural elements are "ribbons" with a thickness on the order of 1000 Å.

These structures were initially found in thin films of rubbers, i.e., under rather artificial conditions for preparing specimens for the electron microscope. It was then necessary to establish whether similar structures exist in real blocks of rubber and whether they change during vulcanization, since in that case one could judge the relation of these structures to mechanical properties. The objects chosen for study were isotactic polyisoprene (SKI) and polybutadiene (SKD) rubbers, sodium-butadiene rubber (SKB), vulcanizates of these rubbers with 3% thiuram, 5% zinc oxide, and 1% stearic acid, and NR vulcanizates of the same composition with different degrees of vulcanization (5, 40, and 110 min). The structure of rubbers and of vulcanizates based on these rubbers was studied with an electron microscope by the replica method. In the case of vulcanizates, single-stage carbon replicas were prepared, and in the case of rubbers, two-stage lacquer–carbon replicas.

The rubber was first frozen in liquid nitrogen, after which it was split according to a method that had been developed (^{4}). The surface formed upon splitting is produced as a result of a spontaneously propagating crack and should pass predominantly along the boundaries of supramolecular structures.

A solution of collodion in amyl acetate was applied to the fractured surface of the rubber. After evaporation of the solvent, the collodion film was mechanically separated from the rubber. Onto the resulting lacquer replica, previously shadowed with palladium, a layer of carbon was deposited at a right angle. After dissolution of the collodion, the carbon replica was examined in the electron microscope.

For vulcanizates, replicas were taken from surfaces formed after rupture and splitting of rubber disks. The disk was split by the same method as for the rubber. The single-stage carbon replica was separated from the surface of the vulcanizate with the aid of gelatin, after which the latter was dissolved in hot water.

Replicas of SKI and SKD rubbers are shown in Fig. 1a, b. The structure of these rubbers is clearly visible: against a background of fine formations covering the entire field of the microphotograph, rather large spherulite-like particles are scattered. Comparing these figures with previously obtained data ([1],[2]), one may observe that the fine formations are ribbon-like structures. It should be noted that in polyisoprene the structures are finer (Fig. 1a) than in polybutadiene (Fig. 1b).

Thus, examination of rubber in the bulk confirms the presence in elastomers of structural formations in the form of randomly arranged ribbons. Moreover, it is interesting to note that spherulite-like structures are observed in rubbers that have been previously cooled, whereas in earlier work, in films prepared at room tem-

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

temperature, only ribbon structures were observed. Apparently, lowering the temperature promotes the occurrence of crystallization processes in these rubbers.

The study of vulcanizates based on SKI and SKD showed that the structures existing in the rubber are preserved in the process of vulcanization. With 40-minute vulcanization, ribbon structures are clearly visible (Fig. 1, *v*; Fig. 3), and in the case of the polybutadiene vulcanizate they are more widely distributed over the entire field of view (Fig. 3).

Next, the influence of the degree of vulcanization on the character of the supramolecular structures for NR was investigated (Fig. 2). Vulcanization was carried out under the same conditions as for SKI and SKD. At 5 min (Fig. 2*a*) and 40 min (Fig. 2*b*) of vulcanization, ribbon formations are clearly visible. With further vulcanization up to 110 min (Fig. 2*v*), one can observe the destruction of the ribbon formations and the disordered distribution of individual structural elements of rather large size. Investigation of the structure of SKB and its vulcanizate (Fig. 4) showed that in this case structures analogous to the structures of SKI and SKD are observed.

With 5-minute vulcanization under the same conditions, ribbon structures are clearly visible (Fig. 4*a*). As the vulcanization time is increased to 50 min, one can observe the disappearance of the ribbon structures—only remnants of ribbon formations are visible (Fig. 4*b*).

Thus, by applying the replica method, it was possible to show that the structures observed in blocks of rubbers are analogous to the structures obtained in thin films.

We come to the conclusion that rubbers and rubber vulcanizates are not some kind of exception, and that the creation of the required supramolecular structures is just as necessary for ensuring stable mechanical properties as it is for any other type of polymer material (films, fibers, plastics). It is also evident that the widespread conception of rubber vulcanizates as homogeneous systems consisting of randomly entangled molecular chains joined by chemical bonds is only the first and, apparently, a very rough approximation. The presence of structures naturally necessitates a reconsideration of these conceptions, and first of all of the mechanism of vulcanization.

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Fig. 1. Replica from the fracture surface of polyisoprene rubber (*a*), the same for polybutadiene rubber (*b*), the same for a torn vulcanizate of polyisoprene rubber (*v*).

Fig. 2. Replicas from the surface of torn vulcanizates of natural rubber. Vulcanization time: *a*—5 min, *b*—40 min, *v*—110 min.

Fig. 3. Replica from the fracture surface of a vulcanizate of polybutadiene rubber.

Fig. 4. Replicas from the tear surface of vulcanizates of sodium-butadiene rubber: *a*—5 min, *b*—100 min vulcanization.

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

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