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Abstract

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ELECTRON-MICROSCOPIC STUDY OF STRUCTURAL CHANGES OCCURRING DURING THERMAL VULCANIZATION OF CHLOROPRENE RUBBERS

Recently it has been found that even in rubber-like polymers there exist well-pronounced structures, ranging from amorphous ribbon-like formations to spherulites and single crystals in crystallizing rubbers ([1,2]). It is quite natural that the whole approach to studying the behavior of structured systems must be different from that for structureless ones. When elastomers are processed into products, they undergo vulcanization; therefore the question arises of the structure of vulcanizates.

Vulcanization is usually carried out at temperatures considerably exceeding the melting temperatures of rubbers; therefore, in the process of vulcanization the supramolecular structures present in rubbers are destroyed. It was of interest to determine how ordering processes can proceed in vulcanizates, and whether they can occur at all. This was the subject of the present study. Crystallizing chloroprene rubbers—nairit A and neoprene AC—were chosen as the objects of investigation. Vulcanization was carried out by the thermal method, which is the most severe method and at the same time makes it possible to carry out vulcanization without introducing any additives. The studies were performed with the aid of an electron microscope. The samples were prepared in the form of thin films on the surface of water; the films were then caught on grids, after which thermal vulcanization was carried out both in vacuum and in air at a temperature of 153°, the duration of vulcanization being varied from 5 to 60 min. The density of the network formed was determined by the swelling method on a sample of nairit A film (the film was taken thicker than that examined in the microscope) in benzene; the calculation was carried out from nomograms compiled by Schwartz ([3]). It turned out that vulcanization in air for 10 min does not lead to formation of a network, whereas upon vulcanization for 20–60 min the network density changes from $0.82 \cdot 10^{20}$ to $1.7 \cdot 10^{20}$ bonds/g. Vulcanization in vacuum leads to the formation of a denser network; thus, samples vulcanized for 20 and 60 min possess a network with a density of $1.8 \cdot 10^{20}$ bonds/g, while those vulcanized for 10 min have 10^{19} bonds/g.

Figure 1a presents a typical picture of a freshly prepared film of the rapidly crystallizing neoprene AC. It is seen that the entire film is permeated by well-formed needle-like formations. Figure 1b gives a microphotograph of a sample of the same rubber vulcanized for 5 min in air. It is clearly seen that after vulcanization the observed crystalline formations are less perfect than in the freshly prepared rubber film. In the microphotograph, mainly ribbon-like structures are visible, and only partly formed spherulite-like formations. With increasing vulcanization time, the ability of neoprene AC to crystallize decreases, and after 20 min of vulcanization no structures are observed in the film.

The vulcanization process was studied in greater detail on nairit A. A freshly prepared film of this rubber has a ribbon-like structure, and upon standing for 24 hours crystallization occurs with the formation of charac-

structures (^{4}). A typical microphotograph is shown in Fig. 2a. During vulcanization in vacuum for 5 min, only ribbon-like structures are formed in the rubber film. A typical picture is shown in Fig. 2b. With an increase in the vulcanization time, no structures are observed in the film.

For comparison, samples of nairite A were vulcanized in air. It was found that in this case the crystalline structures are also destroyed; however, immediately after vulcanization the formation of planes of hexagonal shape was observed (Fig. 3). Their formation proceeds best at a vulcanization duration of 20 min, whereas at a vulcanization time of 50–60 min no ordered formations of any kind are observed in the samples. It should be noted that vulcanization is carried out at a temperature considerably above the melting point of the rubbers; therefore at this temperature all existing crystalline formations melt. After vulcanization in vacuum, in the relatively slowly crystallizing nairite A, no formation of any structures occurs. However, in the case of vulcanization in air for 20 min, planes of hexagonal shape arise immediately; i.e., structure formation in the vulcanizate proceeds more rapidly than in the initial rubber. The difference in structure formation in vulcanizates obtained in air and in vacuum is apparently explained by the formation of a looser network during vulcanization in air. At short vulcanization times for neoprene AC in air, immediately after vulcanization a partial restoration of the structure occurs, owing to the fact that the crystallization rate of neoprene AC is considerably greater than the crystallization rate of nairite A.

It was then of interest to trace how crystallization processes proceed in rubbers after their vulcanization during storage. Samples of nairite A vulcanized in vacuum for 10 min, when stored in air, give the picture shown in Fig. 4a. In the photograph one can observe the appearance of needle-like formations, which are more ordered in comparison with the initial ribbon-like structures. With prolonged vulcanization, more than 20–30 min, the vulcanizate loses its ability to crystallize, and during storage for a month no ordered formations of any kind arise. A vulcanizate prepared in air behaves differently. Fig. 4b shows the picture of nairite A vulcanized for 5 min and stored in air for 10 days. Sheaf-like and other structures are visible in the field of view. Fig. 4c shows more perfect structures that arose during storage of a sample vulcanized for 20 min. Here it is clearly visible that spiral growth of crystals occurs on the initially formed plane. Samples vulcanized for 50–60 min or longer do not crystallize within a month.

Thus, thermal vulcanization destroys the initial structure of chloroprene rubbers, and subsequent structuring is slowed as the vulcanization time increases; moreover, during vulcanization in vacuum the capacity for subsequent crystallization is expressed much more weakly than during vulcanization in air. Study of the structural changes during vulcanization in air of nairite A showed that there is an optimum time of thermal vulcanization (20 min), at which crystallization proceeds much faster than in the initial sample and leads to the forma-

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Fig. 1. Film of neoprene AC: freshly prepared (a) and after vulcanization in air for 5 min (b)

Fig. 2. Film of nairite A after crystallization for 24 hours (a) and after vulcanization in vacuum for 5 min (b)

Fig. 3. Crystallized film of nairite A after vulcanization in air for 20 min

Fig. 4. Film of nairite A: vulcanized in vacuum for 10 min (a); vulcanized in air for 5 min (b); vulcanized in air for 20 min (c). After vulcanization, storage for 3 weeks

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Figure 1

Figure 2

Figure 3

Figure 4

the formation of the most perfect structures. The network formed in this case corresponds to crosslinks located across chain segments with an average number of carbon atoms of 400.

With such a degree of branching, it is extremely difficult to imagine the onset of crystallization of any linear polymer, especially when the question concerns the emergence of higher structural forms. A contradiction arises between this generally known proposition and the results obtained on the crystallization of vulcanized rubbers.

We believe that the possibility of crystallization is created by the nonuniformity of the distribution of vulcanization bonds in the polymer mass. Structural studies in recent years have shown that most polymers, including rubbers, are not homogeneous systems in the structural sense of the word, but form more or less clearly expressed structures. If, at the temperatures of rubber vulcanization, some structures are preserved in it, then it is quite natural that any chemical processes, including vulcanization, will proceed first of all on the surface or, more precisely, at the interfaces of these structures. Only at high degrees of vulcanization will such bonds begin to arise within the structural elements as well.

In this case, the initial vulcanization processes should not lead to the loss of the rubber' s ability to crystallize with the formation of higher supramolecular forms, which is what was observed in this work.

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REFERENCES

[1] V. A. Kargin, V. G. Zhuravleva, Z. Ya. Berestneva, DAN, 144, 1089 (1962).
[2] S. H. Andrews, Proc. Roy. Soc., A270, 134, 232 (1962).
[3] A. G. Shvarts, *Kauchuk i rezina*, 7, 31 (1957).
[4] V. G. Kalashnikova, M. V. Kazhdan et al., *Vysokomolek. soed.*, 6, 5, 906 (1964).

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