Reports of the Academy of Sciences of the USSR

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1962

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1962. Volume 144, No. 5

PHYSICAL CHEMISTRY

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ELECTRON-MICROSCOPIC STUDY OF THE STRUCTURE OF RUBBERS

In a number of works devoted to the electron-microscopic study of the structure of amorphous polymers ([1]), it was established that they prove to be well-ordered systems and that the short-range order in a number of polymers can be expressed so clearly that, as a result, structures having a regular geometric form are produced. On the basis of the study of a whole series of objects it was shown that the structural elements in solid amorphous polymers are globules and fibrillar formations, called by the authors bundles of chains. It remained unclear what change occurs in the structural elements of amorphous polymers when the flexibility of the molecular chains is increased—on passing to elastomers—and, in general, whether any ordered structures exist in elastomers. At the same time, it is known that in low-molecular liquids with asymmetric particles ordered regions exist as a result of fluctuations; in addition, in natural rubber, when it is stretched, the process of crystallization readily takes place. It is therefore natural to assume that in rubbers which are in the amorphous state, ordered regions must also exist.

There are several works in the literature devoted to the electron-microscopic study of the structure of rubbers ([2]-[8]). In these, one usually observes the picture either of a structureless film or of droplets of different size. When films are torn, long thin threads with elliptical or spherical thickenings are formed, or networks with the same kind of thickenings.

These observations are not entirely convincing, since under the action of surface-tension forces the relief of the mobile elastomer is smoothed out, with the formation either of droplets or of a flat surface. This circumstance constitutes the main difficulty in the electron-microscopic study of elastomers.

In order to eliminate these difficulties in studying the structure of rubbers, various methods of preparing specimens were used. Different solvents, or mixtures of them, were employed in order to worsen the solubility of the rubbers and thereby create conditions for a better manifestation of the structural elements.

Fig. 1

Figure 1: Fig. 1

In addition, preparation of specimens at reduced temperature also promoted the detection of a finer structure. Finally, a method of stretching the films was used with the aim of partially destroying their structure, which would make it possible to observe both changes and separate structural elements. To increase contrast, the specimens were shadowed with palladium.

Figure 1 gives the picture of a film of natural rubber, on which, in contrast to the photographs cited in the literature, a clearly expressed structure can be observed. A similar picture is given by the synthetic rubber SKB-30 (Fig. 1). Here too the structure of the film is visible. One might have thought that the inhomogeneous structure of the film is due to folds formed under the action of tensions arising during drying of the film, since in the electron microscope we observe the surface relief. To obtain—

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Fig. 1. **A**—Microphotograph from a film of natural rubber on a carbon substrate (5000×); **B**—the same from an SKB-30 film on a carbon substrate (7000×); **V**—the same from an n.r. film obtained from a solution in chloroform (5600×); **G**—the same from an n.r. film, slightly stretched (2300×); **D**—the same from an n.r. film stretched by 150% (40000×); **E**—the same from an n.r. specimen applied at −5° (5000×).

To obtain more clearly expressed details of the film structure, films were prepared from a number of different solvents; in preparing films from a solution in chloroform, the picture shown in Fig. 1 B was obtained, where a torn piece of film is visible, at the edges of which one can observe the ends of the "ribbons" composing the film; fragments of these ribbons are scattered irregularly over the entire field of view. Consequently, what is visible on the film are not folds, but elements of the film structure.

In addition, changing the substrate (carbon, collodion, and quartz) produces no change in the picture. All this indicates that the electron-microscopic image does indeed reflect the structure of the rubber film.

The film consists, as it were, of randomly arranged ribbons about ∼ 1000 Å wide. The details of the film structure are seen more distinctly in Fig. 1 B. In contrast to the structural elements of crystalline polymers (bundles, ribbons, strips), the ribbons forming the rubber film have no boundary of separation. This fact becomes clear if one takes into account that, when ribbon-like structures arise, no phase transition has yet occurred.

With a very slight stretching of the film of natural rubber (on the order of a few percent), a microphotograph was obtained (Fig. 1 G) in which it is seen that thin threads are drawn out from the ribbons; these apparently represent the elementary structural units of rubber—bundles of chains. Since the stretched threads are arranged perpendicular to the direction of the ribbons, it may be assumed that the bundles of chains in the ribbons have the same arrangement. If the rubber film is stretched more strongly (by 100-200%), an almost complete destruction of the ribbons practically occurs, with the formation of bundles 100-200 Å thick (Fig. 1 D). It might have been assumed that, when the temperature is lowered, ordered structures should appear more distinctly. Indeed, when a specimen was prepared from a dilute solution at a solution and substrate temperature of −5°C, more clearly expressed structural elements were obtained, as is seen in Fig. 1 E. Here there is a picture of very thin, parallel threads (bundles of chains), the aggregation of which gives rise to larger ribbon-like structures.

Thus, in contrast to existing ideas about elastomers as systems consisting of entangled molecular chains, the investigation of thin films of natural rubber has revealed that they consist of randomly arranged ribbons. When the film is stretched, thinner elementary structures are observed, formed upon destruction of the ribbons (bundles). When the temperature is lowered, more ordered structures are formed. Consequently, in rubbers, as in other amorphous polymers, structural order exists.

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Received
1 III 1962

CITED LITERATURE

1. V. A. Kargin, J. Pol. Sci., **30**, 247 (1958).
2. G. F. Shun, *Chemistry and Technology of Polymers*, No. 5, 61 (1961).
3. C. E. Hall, E. A. Hauser et al., Ind. and Eng. Chem., **36**, 7, 634 (1944).
4. E. A. Hauser, Rubber Age, **78**, 6, 881 (1956).
5. E. A. Hauser, Rubber Age, **78**, 5, 713 (1956).
6. K. A. Peshkovskaya, *Kauchuk i rezina*, **3**, 12 (1959).

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