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On the Question of the Crystallization of Natural Rubber

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In the analysis of thermomechanical curves of natural rubber obtained under the continuous action of a load on an automatic recording apparatus (¹), a number of features caused by crystallization processes are revealed. These processes, which substantially affect the mechanical properties of the polymer, are naturally reflected in the character of the thermomechanical curves as well. Earlier (²) it was shown that a "step" is observed on the thermomechanical curve of natural rubber at 0°C. Its appearance was associated with the melting of the crystalline phase formed in the rubber during its freezing, preceding the experiment in which the thermomechanical curves were recorded.

The appearance and disappearance of crystallites in the polymer causes changes in its deformability. Such changes can be observed especially clearly by recording the thermomechanical curve under alternating increase and decrease of the load. (Let us recall that under the continuous action of a load, what is recorded on the thermomechanical curve is not the deformability, but the total accumulation of deformation during heating of the polymer.)

Figure 1 presents the thermomechanical curve of natural rubber recorded on the same apparatus with a device for automatic periodic loading. Here and below only portions of the curves are shown—up to temperatures of 50-60°. The experiment was carried out in a nitrogen atmosphere at a heating rate of 2 deg/min. The magnitudes of the loads were 0.64 and 3.2 kg/cm, and the duration of action of each was 2 min. The curve shows a sharp increase in deformability at 0°, caused by melting of the crystallites. Also noteworthy is the noticeable decrease in the amplitude of the oscillations (in other words, the deformability of the specimen) in the temperature region from −35° up to the melting point of the crystallites. This circumstance is explained by the fact that, in the very course of the experiment in which the thermomechanical curve is recorded, in the indicated region, close to the temperature of optimum crystallization of natural rubber (−25°), additional crystallization occurs, leading to strengthening of the rubber.

We established that thermostating specimens at −25° increases, on the thermomechanical curve, the magnitude of the step at 0° owing to an increase in the amount of the crystalline phase, which is practically not deformed under the ap-

Fig. 1 and Fig. 2: thermomechanical curves

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plied load values on the specimen (3.2 kg/cm^2). In Fig. 2, 1, one of the curves obtained in this way is shown. During cooling of the rubber from room temperature to a temperature below the glass-transition point (under our conditions about one hour), crystallite formation occurs practically only at the crystallization optimum, since crystallization at other temperatures requires considerably more time.

If, however, the freezing time of the specimen is sharply reduced, crystallization in the rubber does not occur at all. In Fig. 2, 2, the thermomechanical curve is presented for a specimen of natural rubber immersed in liquid nitrogen. On the curve there is a complete absence of the step corresponding to melting of the crystalline phase at 0°. The melting temperature of the crystallites depends on the tem-

temperatures of their formation; at 0° crystallites formed at −25° melt.

To obtain appreciable amounts of crystallites in rubber melting below or above 0°, it is necessary, as Wood indicates (3), to keep the samples at the appropriate temperatures from several hours to many days and even years. By prolonged thermostating at −10° we obtained a rubber sample whose thermomechanical curve is shown in Figs. 2, 3. The rise corresponding to the melting of the crystalline phase occurs here at a higher temperature than for the sample frozen at −25°, namely at +10°.

Fig. 1. Thermomechanical curve of NR under periodic loading. Large load 3.2, small 0.64 kg/cm^2; change of loads every 2 min.

Fig. 2. Thermomechanical curves of NR (constant load 3.2 kg/cm^2). **1** –thermostated 1.5 h at −25°, **2** –frozen in liquid nitrogen, **3** –thermostated 7 h at −10°.

We had at our disposal a sample of natural rubber that had been stored for several years at room temperature (20-25°). Under these conditions crystallization also occurs in the rubber; moreover, according to Wood' s data, the crystallites formed usually melt at about 40°. Such rubber is called "hardened" rubber.

In Fig. 3, 1 the thermomechanical curve of "hardened" natural rubber is presented. As can be seen, it differs considerably from the thermomechanical curve of rubber crystallized at low temperatures. At the same load, the "hardened" rubber has a significantly smaller deformability in the highly elastic state, but a sharp jump in deformability appears at 45-48°. This rise on the thermomechanical curve evidently corresponds to the melting of crystallites formed in the rubber during storage under room-temperature conditions. A small step at 0° is retained on the curve, corresponding to the melting of crystallites that arose during freezing.

Fig. 3. Thermomechanical curves of NR (constant load 3.2 kg/cm^2). 1 —initial "hardened" rubber; 2 —the same rubber, heated to 53°; 3 —same as 2, thermostated for 6 hours at −25°.

Figure 2: Fig. 3. Thermomechanical curves of NR (constant load 3.2 kg/cm^2). 1 —initial "hardened" rubber; 2 —the same rubber, heated to 53°; 3 —same as 2, thermostated for 6 hours at −25°.

Fig. 4. X-ray patterns of natural rubber. Designations are the same as in Fig. 3.

Figure 3: Fig. 4. X-ray patterns of natural rubber. Designations are the same as in Fig. 3.

Heating the rubber above 50° should lead to the elimination of crystallinity. Indeed, in rubber heated to 53° (the sample thereby became transparent), a sharp increase in deformability at 45° is no longer observed (Fig. 3, 2), whereas the deformability upon transition to the highly elastic state (around −60°) is increased to a considerable extent in comparison with the initial rubber.* It is characteristic that on the thermomechanical curve taken immediately after heating to 53°, the step of crystallite melting at 0° is also absent. True, under thermostating such rubber for 1.5 hours at −25°, crystallization occurs, and a step appears on the thermomechanical curve at 0°. In a sample that has been heated and held for 70 days, low-temperature crystallization occurs under the conditions of the ordinary freezing regime of the sample, without preliminary thermostating. On this basis one may suppose that the crystalline phase formed at room temperature plays the role of a "seed" on which crystallization of rubber occurs at low temperatures.

For a more convincing proof of the conclusions drawn from the analysis of the thermomechanical curves concerning the crystallization of natural rubber, it seemed expedient to us to supplement them by means of the X-ray method.

Fig. 3. Thermomechanical curves of NR (constant load 3.2 kg/cm^2). 1 —initial "hardened" rubber; 2 —the same rubber, heated to 53°; 3 —same as 2, thermostated for 6 hours at −25°.

Fig. 4. X-ray patterns of natural rubber. Designations are the same as in Fig. 3.

X-ray examination of natural rubber was carried out on a URS-50I ionization apparatus in reflection from a cut surface, and also by the photographic method

* Another similar sample, after heating, was stored at room temperature for 70 days. On the thermomechanical curve of this sample there again appeared a step near 45°, indicating the formation, under storage conditions at room temperature, of a crystalline phase melting at 45°.

with copper and iron radiation. On the ionization apparatus we were able to record X-ray patterns of samples at temperatures from room temperature down to −40° and lower, by blowing the sample with a stream of cold nitrogen (^{4}). From the X-ray pattern of "hardened" rubber (Fig. 4, 1) it is seen that reflections caused by partial crystallinity of the sample are superimposed on the broad diffuse halo of the amorphous phase of rubber. When the sample is heated to 53°, these reflections disappear (Fig. 4, 2), and only the diffuse halo characteristic of the amorphous phase remains.

To study the "low-temperature" crystalline phase, which passes into the amorphous state at 0°, two identical rubber samples were heated to 53°. Having made sure that the crystalline phase was absent in them, we thermostated them for 6 hours at −25°. After this the samples were cooled below the glass-transition temperature of rubber. From one of these samples a thermomechanical curve was recorded; from the other, X-ray patterns were taken at −25° and then at room temperature. On the thermomechanical curve obtained (Fig. 3, 3) for such rubber, a rise is observed near 0°, reflecting the transition of the crystalline phase into the amorphous state. The X-ray pattern recorded at −25° is similar to the X-ray pattern of "hardened" rubber, although some differences are observed (Fig. 4, 1, 3) in the intensities of the reflections. On the X-ray pattern of the same sample, but recorded at room temperature, there is only a diffuse halo.

From this it may be concluded that the crystalline phases arising during prolonged storage at room temperature and at −25° are ident-

*···although they have "their own" melting temperatures, differing by 40–45°. It seems to us that this fact can be explained as follows. Natural rubber has only one crystalline phase. Rubbers crystallize at different temperatures in one and the same lattice, but at −25°, as Wood and Treloar note (7), owing to the high rate of crystallization, nonequilibrium crystallites are obtained. In this case, large internal stresses arise in the crystalline polymer, shifting the melting temperature toward lower temperatures (8). The low melting temperature of crystallites formed under conditions of rapid crystallization may also be explained by the abnormally small sizes of the crystallites, as, for example, Doll (9) indicates for the case of melting of annealed and quenched samples of polyethylene terephthalate and polyethylene sebacate.

Thus, the study of the thermomechanical properties of natural rubber in the temperature interval in which its crystallinity can be observed clearly indicates the appearance and disappearance of the crystalline phase. At the same time, crystalline formations arising under different conditions are distinguished. The results obtained from analysis of the thermomechanical curves are compared with X-ray structural-analysis data and mutually complement one another. The methods used may be useful in the study of other polymers.

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* The calculation and indexing of the X-ray diffraction patterns agree well with the results of Bunn (5) and Fischer (6) for stretched natural rubber.

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

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