B. Ya. TEITELBAUM, E. F. GUBANOV

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Abstract

Full Text

B. Ya. TEITELBAUM, E. F. GUBANOV

ON THE INFLUENCE OF A FORCE FIELD ON STRUCTURAL TRANSFORMATIONS IN NATURAL RUBBER

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In studying the thermomechanical properties of natural rubber, we encountered the fact that the force used in the method for recording thermomechanical curves (TMC) has a substantial effect on the change in its properties. It is known from the literature that low-temperature crystallization is accelerated by preliminary stretching of a rubber or vulcanized-rubber specimen ([1–3]). The oxidative processes observed at higher temperatures ([4,5]) are also activated in a field of mechanical stresses ([6,7]).

One can discern a certain common feature in such different processes occurring here as crystallization and thermo-oxidative structuring, if they are considered from the standpoint of changes in the mechanical properties of the polymer. In both cases its hardening occurs (owing to the formation of a crystalline phase or of cross-linked structures) as a consequence of the action of a mechanical field.

The purpose of the present work was the direct observation of changes in the deformability of natural rubber under the action of a mechanical force at the temperature of optimum crystallization (−25°) and at temperatures at which oxidative structuring of rubber is observed. By determining the change in deformability of a specimen with time, it is possible to follow the course of the indicated processes.

Fig. 1. Deformability curves of NR specimens at −25°. Duration of action of alternating loads of 7.04 and 0.64 kg/cm^2, in min.: *a* –3 and 1; –2 and 2; –1 and 3.

The isothermal deformability curves were recorded automatically on an apparatus for recording TMC ([8]) under the action of a periodically applied load

([9]). The recording of deformation (the depth of penetration of a punch into the specimen) takes place on an electronic potentiometer in the same way as in the case of TMC, but the sweep along the abscissa axis is set by a linearly increasing voltage taken from a special sensor.

Figure 1 shows one of the deformability curves of smoked-sheet rubber (molecular weight 769,000), recorded at -25°. The isothermal deformability curve consists of a series of peaks, the left (ascending) branches of which indicate the deformability of the specimen under the action of the larger load, while the right (descending) branches indicate the magnitude of the reversible deformation during the "rest" period (action of the small load).

It is evident that, with time, both the deformability and the elasticity of the rubber gradually decrease until, finally, after approximately 2.5 hours, the specimen becomes completely nondeformable under the applied load. If heating is then begun and the recording is continued under periodic loading in the TMC removal regime, then at a certain temperature the deformability abruptly reaches values close to the initial one. This temperature 0° corresponds, as was established earlier ([10]), to the melting of the crystalline phase formed in NR at -25°, which undoubtedly indicates a connection between the loss of deformability and crystallization. It is necessary, however, to know whether the observed phenomenon is an indication of a process taking place in the rubber at a given temperature independently of mechanical actions, or whether it is caused by the periodically applied force. In works ([11,12]) the influence of periodic loads on the crystallization of polycarbonates and polyethylene terephthalate was noted. It seemed of interest to determine to what extent this is characteristic of NR.

It turned out that after thermostating the specimens at -25° without load for a time during which the rubber, judging from the deformability curves, completely hardens, they still retain a considerable ability to deform. Hence follows the conclusion that mechanical forces have an activating effect on the crystallization of rubber.

Experiments were carried out to determine the influence of the loading regime of a specimen on its ability to crystallize. The complete cycle, as before, was 4 min, but the ratio of loading time to "rest" time was, respectively, $3:1$ and $1:3$ (Fig. 1 *a* and *c*). It is not difficult to see that the horizontal section after loss of deformability is situated differently for all three curves in Fig. 1: at the level of the initial loading (upper dashed line) in the case of three-minute loading; somewhat lower, though close to it, for two-minute loading; and still lower, approximately midway between the levels of loading and rest (lower dashed line), for one minute of action of the load. This circumstance indicates that polymer crystallization proceeds most effectively while a load is acting on it.

Deformability curves recorded under a regime of equal duration of rest and loading, but with different total cycle lengths (2, 4, and 8 min), are similar to one another both in the position of the horizontal section and in the time of hardening of the specimen (about 2.5 hours in all cases). Thus, no influence of

Fig. 2

Figure 2: Fig. 2

the frequency of application of the load on the crystallization rate of NR was observed. This does not, of course, exclude the possibility of detecting such influences at considerably greater changes in loading frequency.

Let us now turn to consideration of the processes occurring at higher temperatures.

In the TMC of natural rubber, a characteristic "hump" is observed in the region 55—120°. We have shown that at these temperatures thermooxidative structuring takes place in the rubber. It was of interest to clarify the influence on this process of those mechanical stresses under which the polymer is found during the removal of the TMC.

For this purpose, isothermal deformability curves were obtained at 60 and 80°. The method of recording them and the method of thermostating the specimen are the same as at −25°, but because of the greater deformability of rubber under these temperature conditions, the magnitudes of the loads were reduced.

Figure 2 gives the deformability curve of NR recorded at 60°. Despite the fact that crystallization at this temperature is excluded, the deformability of the specimen decreases with time to a certain value, after which it practically does not change. The decrease in deformability in this case is apparently caused by the formation of interchain bonds in the rubber, while the presence of a definite limit is possibly connected with the nonrenewable consumption of oxygen dissolved in the rubber in the processes of thermooxidative structuring (the experiment was carried out in a nitrogen atmosphere).

Since the formation of crosslinked structures hinders the development of viscous flow, this should be reflected in the temperature of the end of penetration (T_k) of the corresponding TMCs. Indeed, if the TMCs of the original rubber and of the same material after the procedure of recording the deformability curve shown in Fig. 2 are compared, it turns out that T_k increased from 180 to 190° (Fig. 3, curves 1 and 2). The plateau of the elastic state on curve 2 is strictly horizontal, whereas the deformation in the corresponding portion of curve 1 increases noticeably owing to a certain plasticity of the rubber in the highly elastic state. On curve 2 the effect at 0° is absent, which indicates a reduced capacity for low-temperature crystallization.

Fig. 2. Deformability curve of NR at 60°. Alternation of loads 2.56 and 0.032 kgf/cm^2 every 1 min.

The facts of a decrease in deformability in the highly elastic state (as evidenced by the decrease in the height of the rise of curve 2 in Fig. 3 at T_c), as well as a decrease in the plasticity and crystallizability of the rubber, are undoubtedly

Fig. 3

Figure 3: Fig. 3

associated with the development of structuring processes, which apparently have a mechanochemical character.

Mechanical activation of oxidative reactions in rubber leads to their proceeding at a noticeable rate even at room temperature. The deformability curve recorded under these conditions is similar in character to the curves obtained at 60 or 80°. The deformability of the specimen also decreases with time to a certain constant value, but much more slowly—over 6-7 h.

The processes of degradation and formation of crosslinked or branched structures can be studied by measuring viscosity. For this purpose, for viscometric determinations (13) that part of the specimen which was directly under the tip of the loaded punch was cut out. To obtain the required amount of material (0.05-0.1 g), a series of analogous experiments was carried out. The prepared solutions (in toluene) were filtered; in all cases the residue did not exceed 3.5% of the weighed sample, and this value was taken into account when calculating the solution concentration.

Fig. 3. TMCs of NR specimens: 1 —original specimen, 2 —after recording the deformability curve of Fig. 2, 3 —after extraction in acetone.

As follows from the data of Table 1, when rubber is heated to 80° in the TMC recording regime (but without a load), the intrinsic viscosity practically does not increase. But if heating is carried out under conditions of action—

tension on the specimen, and especially when the loaded polymer is held at 80° for 1 hour, a sharp increase in the values of $[\eta]$ is observed. An increase in $[\eta]$, although somewhat smaller in magnitude, can also be noted under the action of a load on NR specimens at room temperature.

All this undoubtedly indicates that the structuring processes proceed most intensively in the loaded polymer, and thus the effects on the thermomechanical curves of rubber at 55–120° are due not only to changes in deformability with temperature, but also to the action of those mechanical stresses to which the specimen is subjected during the experiment.

Table 1

Characteristic viscosity $[\eta]$ of NR specimens

	Without load	Static load, 3.2 kg/cm^2
At room temperature	4.2	6.0*
Heated to 80° in the T.M.C. recording regime	4.3	6.5
Thermostated at 80° for 1 hour	5.2	6.8

* For 1 hour.

The thermoreactivity on the T.M.C. of NR specimens from different batches manifests itself with different intensity. It was natural to suppose that this is explained by the nature and concentration of the natural antioxidants present in them. To test this assumption, the latter were removed from the specimens by extraction with acetone for 100 hours at room temperature. The solvent residues were distilled off in vacuum until constant weight was reached.

The T.M.C. of the rubber after such treatment is shown in Fig. 3 (curve 3). Attention is drawn to the increase in the "hump" in the region 55–120° in comparison with the original specimen (curve 1), which indicates a greater tendency toward structure formation of the specimen subjected to extraction. This can evidently also explain the fact of the increase in the temperature of the end of penetration T_k on curve 3 to 195°.

The results of the present work, using the study of natural rubber as an example, show that the mechanical actions applied in recording thermomechanical curves not only reveal the structural transformations occurring in the polymer (crystallization, formation of spatial structures), but also actively influence the course of these transformations.

Institute of Organic Chemistry
Academy of Sciences of the USSR
Kazan

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