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Abstract

Full Text

PHYSICAL CHEMISTRY

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THERMOGRAPHIC INVESTIGATION OF THE PROCESS OF LOW-TEMPERATURE CRYSTALLIZATION OF NATURAL RUBBER

(Presented by Academician B. A. Arbuzov, 30 XII 1963)

Crystallization of elastomers is a phase transition, and its investigation can be effectively carried out by well-known methods of phase analysis. Among the latter, the method of differential thermal analysis—thermography—is undeservedly little used. Meanwhile, the thermal effect of melting of crystalline phases should be clearly manifested on differential heating curves. From the magnitude of the corresponding peak on the thermogram one can estimate the amount of crystalline phase and, by carrying out such observations in time, study the kinetics of crystallization. Investigations of this kind were carried out by us for crystallizing synthetic polychloroprene rubber—nairite (^{1}).

Recently a paper (^{2}) was published in which the melting of crystalline phases in gutta-percha, balata, natural rubber, and a number of synthetic rubbers was studied by the thermographic method. However, the results obtained for NR are rather indefinite. In another paper, also recently published (^{3}), several rubbers, including NR, were investigated. It was found that the form of the curves obtained depends on the "thermal history" of the specimen; however, this question was not specially studied. Nor were sufficiently clear thermograms of NR obtained there.

Fig. 1. Thermograms of smoked-sheet natural rubber: **a** —specimen stored for several years at room temperature; **b** —the same specimen, examined again after cooling and thermostating at −25° for 1 hour.

In the present work the aim was set to investigate the manifestation of the presence of crystalline phases on thermographic curves of NR and to try to

Figure 2

Figure 2: Figure 2

use the differential-thermal method of analysis for observing the course of the crystallization process.

The recording of thermograms was carried out on a Kurnakov pyrometer of type PK-52 with chromel-alumel thermocouples. As a reference it proved convenient to use synthetic rubber of the SKBM or SKD type, which has no thermal effects in the temperature region studied. The specimen and reference, weighing about 0.7 g, were made in the form of cylinders 8 mm in diameter and placed in glass test tubes. Heating (as well as thermostating) of these test tubes was carried out in a massive cylindrical aluminum block, equipped with a long extension for immersion in a Dewar vessel with liquid nitrogen (during cooling) and with a heating winding on the generatrix surface. Heating was carried out according to a linear program with a specified rate. The design of the block and the heating regime of the specimen are similar to those used in the apparatus for recording thermomechanical curves.

(ˆ4), which makes it possible to compare the results of the present investigation with the data of thermomechanical tests (ˆ5).

It is known (ˆ6) that crystallization of rubber* can occur over a rather broad temperature range, but at very different rates. The optimum crystallization temperature is −25°. This process ("hardening" of NR) also proceeds at room temperature, although it lasts for months and even years. The melting point of the crystallites formed depends, according to dilatometric and some other studies, on the temperature conditions of crystallization.

Before recording the thermogram, the specimen must be cooled below the region of phase transformations. In this process crystallization may occur, the more intensively the more slowly the cooling is carried out and, in particular, the more time is spent in passing through the temperature of optimum crystallization. Generally speaking, one should bear in mind the possibility of crystallization also in the course of heating—on approaching the point of optimum crystallization from the low-temperature side, after which melting of the crystallites formed should be observed.

Fig. 2. Thermograms of NR at various heating rates. In all experiments the specimen was preliminarily thermostated for 5 h at −25°.

Figure 1a shows a thermogram obtained by us for natural smoked sheet rubber that had been stored for several years at room temperature. On the thermogram two endothermic peaks are clearly visible, with minima respectively at 0 and 40°: the larger of them may be attributed to melting of the crystalline phase formed at room temperature, whereas the smaller one corresponds to crystallites that arose during cooling. To confirm this interpretation, the same specimen was

Figure 3

Figure 3: Figure 3

cooled again and deliberately held at −25° (thermostating for 1 h), after which the thermogram was recorded again.

On the differential curve obtained (Fig. 1b), the effect at 40° is practically absent. This is quite understandable, since the specimen was heated above the indicated temperature, and new crystallites with the same melting point could not form during the short time of the experiment. At the same time, the peak at 0° became more pronounced, in accordance with the increased exposure of the specimen at −25°. Thus, the nature of the indicated peaks may be considered established. Moreover, from their magnitude it appears possible to estimate the content of one or another type of crystallites.

The thermograms presented were recorded at a sufficiently high heating rate. With slower heating, especially if thermostating at −25° was sufficiently prolonged, it is found that the endothermic peak with a minimum near 0° is complex. On the descending branch of the peak a "shoulder" appears, which, with still slower heating, turns into a small exothermic maximum between two endothermic peaks. With further slowing of the heating, the first endothermic peak and the exothermic maximum following it become very diffuse and almost indistinguishable.

* Crystallization occurring as a result of stretching of rubber is not considered here.

As follows from the results of dilatometric determinations (ˆ6), melting of the crystals formed at −25° begins when the temperature is raised by 4-6° and occupies a rather considerable temperature interval, ending at about 0° and even somewhat higher. If the crystals are melted by heating to 0°, then, following melting, crystallization begins again. In our opinion, the formation of new crystallites may begin not only after the melting of the entire existing mass of crystals, but also during heating, immediately as successive fractions of crystallites melt. A kind of recrystallization takes place, which well explains the considerable length of the melting interval, as well as the fact that on thermomechanical curves of NR the melting is noted in the form of a rather sharp jump near 0°. The crystallites formed under large supercooling are replaced by increasingly more equilibrium ones (with a higher melting point). This process proceeds with a positive thermal effect. True melting, i.e., the complete transition of the crystalline phase into the amorphous phase, occurs in a considerably narrower interval.

Fig. 3. Dependence of the melting interval (*a*) and of the values of the peak areas on the thermogram (*b*) on the heating rate

In order for the process under consideration to be detected by the thermographic

Figure 4

Figure 4: Figure 4

method, it is necessary that the heating rate during recording of the thermograms be commensurate with the rate of recrystallization.

Figure 2 shows a series of thermograms recorded at different heating rates, illustrating the considerations presented above. The specimen was thermostated at −25° for 5 h.

Fig. 4. Dependence of the magnitude of the peak area on the thermogram, proportional to the content of the crystalline phase, on the thermostating time of NR at −25°

The slower the heating, the wider the temperature interval from the beginning to the end of melting. The corresponding points are indicated on the thermograms, and their difference ΔT is shown as a function of the heating rate in Fig. 3. The same graph shows the values of the areas found from the thermograms presented (the boundaries of the indicated areas are marked on them by dotted lines).

It is noteworthy that the magnitude of the peak area remains practically constant (within $±$10%). All subsequent experiments were carried out with one definite heating rate—about 2 deg/min.

It is known that the areas of endothermic peaks on the thermogram are proportional to the amount of absorbed heat (^7) and, consequently, in the case under consideration, to the amount of crystalline phase. This circumstance was used by us to observe the course of crystallization at −25°. Test tubes with the NR specimen and the standard were introduced into the cylindrical channels of a thermal block thermostated at −25°*. After 10 min the temperatures of the specimen and the block practically became equal. In this state the specimen was kept for a definite time from 1 to 8 h; intensive crystallization of NR takes place. After this one may proceed

* Before each experiment the specimen was heated to 50-60° for its complete amorphization.

for recording the thermogram. It proved useful, however, in order to ensure that a steady heating regime had been established by the time the thermographic peak appeared, after thermostating first to cool the specimen to −50, −60° and only then to begin recording the thermogram.

The results of experiments at a heating rate of about 2 deg/min for unvulcanized rubber are presented in Fig. 4. The kinetic curve obtained shows that the content of the crystalline phase during thermostating at −25° increases with time, approaching a certain limit after 8-9 h. The curve is analogous to the corresponding graph obtained by the thermographic method for nairite (^1).

It is also of interest to compare these results with studies of crystallization of

NR under the action of a mechanical load. By observing deformations under periodic application of a load during thermostating at −25°, it was found (^8) that, under the loading regimes tested, the stiffening of rubber as a result of its crystallization is completed after 2–2.5 h, i.e., much more rapidly. The differences are due to the activating influence of the force field on the crystallization process.

It should be noted that clear thermograms were obtained by us in a regime that by no means exhausted the sensitivity of the apparatus. This makes it possible to hope to detect and study crystallization processes not only in pure NR, but also in various rubber mixtures and rubbers, in weakly crystallizing rubbers and other polymers.

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