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Structural and Mechanical Study of Elastomers under Plane Deformation[1]

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Abstract—The plane shrinkage of various elastomers [natural rubber, synthetic isoprene rubber, and plasticized poly(vinyl chloride)] at room temperature has been studied via direct microscopic observations. Prior to deformation, the surface of polymer samples is decorated with a thin (several nanometers) metallic layer. Further deformation leads to formation of the surface relief in the coating. An analysis of the formed microreliefs allows one to visualize and characterize the induced stress field in the sample. The shrinkage of poly(vinyl chloride) samples is accompanied by development of the uniform surface relief over the whole surface of the deformed polymer. This fact suggests a homogeneous character of the stress field and, hence, a homogeneous structure of the polymer sample. In the case of crosslinked rubbers (natural rubber and synthetic isoprene rubber), their plane shrinkage leads to the development of an irregular pattern on the polymer surface. In addition to the folded surface relief that is typical of the poly(vinyl chloride) structure, one can observe 20- to 50-μm "islands," which are characterized by their own morphological features. Information on structural inhomogeneity of rubbers that is obtained by scanning electron microscopy correlates with the data of DSC measurements. The advantages of electron microscopic procedure for studying structural rearrangements in polymers during strain recovery of elastomers are demonstrated.

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INTRODUCTION

Investigation of structural features of the deformation of rubbery polymers is of both fundamental and applied importance. However, the problem concerning gaining adequate information on structural rearrangements taking place in rubbery polymers during their deformation is far from being solved. First, let us mention that rubbers are amorphous materials; therefore, their study by traditional structural methods based on phase-contrast phenomenon (X-ray analysis, electron diffraction analysis, and microscopy) appears to be ineffective.

In our recent publications [1–3], a new microscopic procedure for visualization of structural rearrangements in polymers during their deformation has been worked out and experimentally substantiated. To visualize the above structural rearrangements, the polymer sample prior to its deformation (shrinkage) is decorated with a thin rigid coating. Deformation of the polymer support entails dramatic changes in the surface relief of both the deposited coating and the adjacent polymer layer. Surface relief formation in the coating can be easily detected by direct microscopic observations. This procedure makes it possible to gain important information on the character and distribution of mechanical stresses in the deformed polymer sample. Evidently, stress distribution is directly related to structural features of the deformed solid. The above procedure can be applied for studying deformation of polymers in any physical and phase states.

This study presents pioneering attempts for studying the plane deformation and shrinkage of rubbery polymers by direct microscopic observations.

EXPERIMENTAL

In this study, we investigated films based on crosslinked synthetic isoprene rubber (SIR) and crosslinked natural rubber (NR) with a thickness of 500 μm. Prior to vulcanization, the initial non-crosslinked rubbers were subjected to mastication in an RVD-180 rubber grinding machine for 4.5 min at 150°C and a rotation speed of 30 rpm. Then, the rubber samples were rolled for 8 min and repeatedly treated in the grinding machine for 3.5 min. The crosslinked samples were prepared by vulcanization of the ground mixture with 1 phr of dicumyl peroxide per 100 phr of raw rubber. The mixture containing the crosslinking agent was rolled at 70 ± 5°C. Vulcanization was carried out at

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150°C for 50 min. The crosslinked samples were extracted with acetone for 1 day and dried in air at room temperature. In addition, we studied 100-μm-thick commercial films based on PVC containing 60% plasticizing agent dioctyl phthalate (DOP). According to DSC measurements, the glass transition temperature of the plasticized PVC was –15°C. The measurements were performed on a Mettler TA 4000 thermal analyzer equipped with a DSC30 unit; the heating rate was 20 K/min.

Plane stretching of polymer films was carried out according to the following procedure. A polymer film was fixed in an O-ring framework. Stretching was performed with a movable plunger that was pushed toward the window of the O-ring framework in the direction normal to the film plane. As a result, the film sample was stretched by a given strain. After stretching, the polymer sample was fixed in a circular framework and its surface was decorated with a thin (10 nm) platinum layer by ionic plasma deposition. Then, the samples were released from the framework and their surface was examined with a Hitachi S-520 scanning electron microscope. In all cases, when the samples were released from the framework, they fully recovered their initial dimensions.

Mixtures based on the crosslinked rubber and the crystalline hydrocarbon *n*-octadecane ($C_{18}H_{38}$, T_m = 28.2°C) were prepared via swelling of NR samples in the hydrocarbon melt at 50°C. The swollen samples were cooled in ice-water to temperatures below the crystallization temperature of octadecane. For light scattering measurements, we prepared dilute (1%) solutions of plasticized NR in heptane or toluene. A microgel was separated from NR solutions via a Beckmann preparative ultracentrifuge at a rotation speed of 40000 rpm. The dimensions of microgel particles in dilute solutions were estimated by inelastic light scattering via an ALV SP-81 goniometer.

RESULTS AND DISCUSSION

Figure 1 presents the electron micrographs of the samples based on the plasticized PVC after their stretching by different strains, deposition of a thin (10 nm) metallic (platinum) layer, and shrinkage. As follows from the corresponding SEM images, the metallic coating deposited onto the polymer surface loses its stability and acquires a regular microrelief. The character of this surface microrelief is quite similar to the morphology of other systems prepared under the same conditions [4–8]. As follows from Fig. 1, this microrelief is seen as densely packed and randomly curved folds that uniformly cover the whole surface of the polymer sample. The width of the above folds is quite uniform and can be directly measured from the corresponding SEM images. In particular, when the plane compression (shrinkage) is 10% (Fig. 1a), the fold width is ~1.35 μm.

When the degree of plane compression is increased from 14 to 27%, no marked changes in the morphology of the formed microrelief are observed (Figs. 1b, 1c). However, the fold width changes. As was shown in [9], the number of folds is independent of the compression ratio of the polymer support. At the initial instant of stability loss, a fixed amount of folds is nucleated, and further compression of the polymer support does not entail any increase in their density. In this case, one can only observe compression of the formed microrelief by analogy with compression of harmonica folds. Evidently, with increasing the compression ratio, the microrelief period (the fold width) decreases. The above decrease in the microrelief period is observed at all compression ratios of the PVC support. Hence, the plane shrinkage of the plasticized PVC decreases the polymer surface area and, according to the known laws [4–8], the deposited coating loses its stability and acquires a regular microrelief. Let us mention that this relief is uniform throughout the entire polymer surface. This result suggests a homogeneous (affine) character of the stress field responsible for shrinkage of the deformed polymer and, hence, a relative homogeneity of the polymer structure.

Let us now discuss the results obtained for classical elastomers (crosslinked rubbers NR and SIR) prepared under similar conditions. Figure 2 presents the SEM images of NR samples. As is well seen, at relatively low ratios of plane compression, the polymer surface acquires a regular microrelief that is similar to that as observed for the PVC samples (cf. Figs. 1 and 2a). However, at higher compression ratios (Fig. 2b), one can observe new morphological features of the formed microrelief. In addition to the regions of irregular folds, the polymer surface contains regions with an ordered arrangement of folds. The length of the above regions is 20–40 μm, and they are separated by regions with irregular folds with similar dimensions. Nevertheless, the regions of irregular and disordered location of folds constitute a continuous medium, whereas the ordered regions are seen to be discrete and involved in the disordered matrix.

The above structural features are even better pronounced for SIR samples after their plane shrinkage. As follows from Figs. 3a and 3b, regions with ordered arrangement of folds appear even at a compression ratio of 5%. The dimensions of the above regions achieve 50 μm. Within the above regions, the folds are arranged in a regular and parquetlike order. A similar pattern is also observed at higher plane compression ratios of the rubber support (Figs. 3c, 3d). Let us mention that, within the above ordered regions, all folds are parallel to each other; however, the location of ordered regions on the polymer surface is random.

An analysis of regular microrelief patterns formed upon deformation (shrinkage) of polymers with a thin coating allows one to visualize stress fields responsible for the occurrence of the above processes. According to

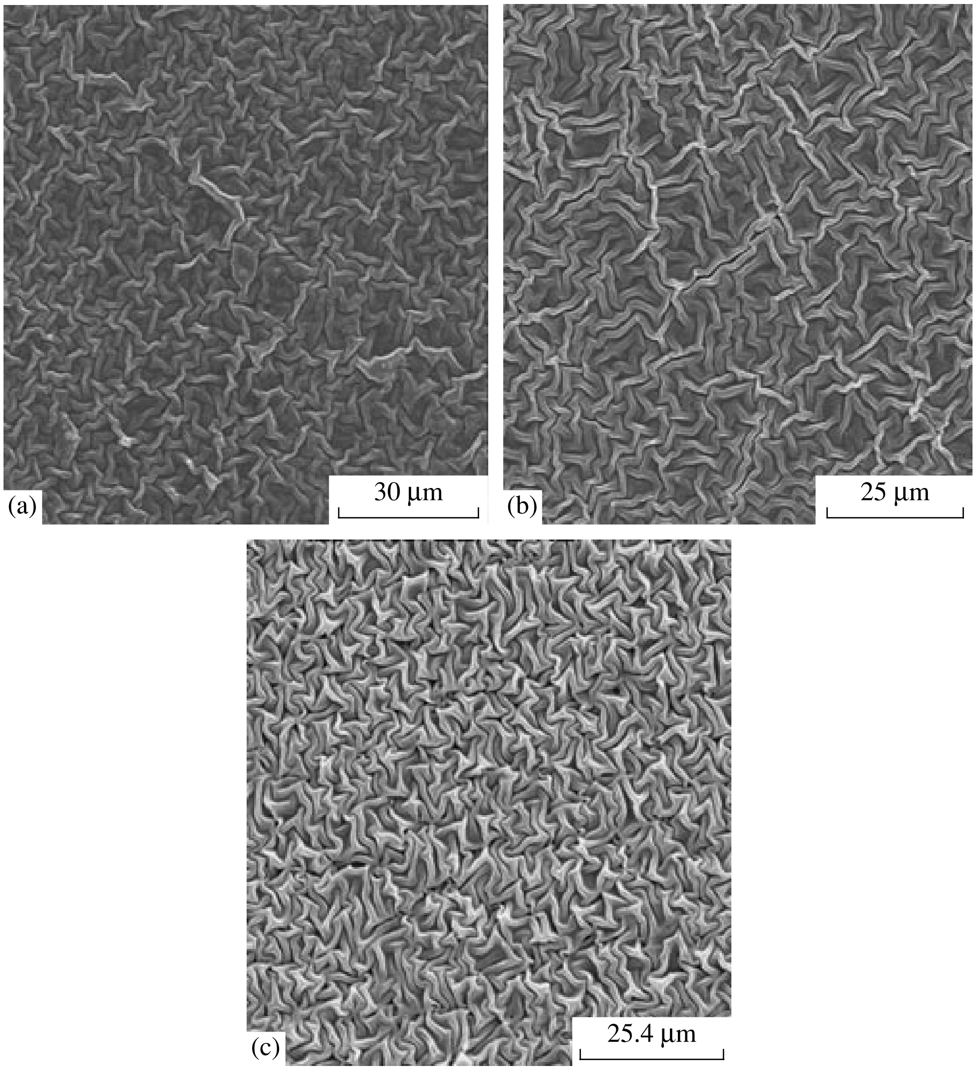

Fig. 1. Scanning electron micrographs of the samples based on plasticized PVC after their plane deformation by (a) 10, (b) 14, and (c) 27%, subsequent deposition of a thin (10 nm) platinum layer, and strain recovery.

the adopted ideas, at least for rubbers, such stress fields are assumed to be homogeneous (affine). This fact serves as a basis for the statistical theory of rubber elasticity [10]. The homogeneous character of a microrelief formed as a result of compression of the coating on the soft support apparently reflects the homogeneous character of induced stress fields. As was shown above, this pattern is observed for the samples of the plasticized PVC after their plane shrinkage. At the same time, the shrinkage of rubbers makes it possible to reveal two morphological types of the regular microrelief: irregular and regular location of folds (Figs. 2, 3). In other words, the stress field responsible for the polymer shrinkage is inhomogeneous; hence, this fact attests that three-dimensional structure of rubbers is inhomogeneous as well. Furthermore, the above procedure provides a means of visualization and estimation of dimensions of the above structural inhomogeneities (20–50 μm). A different character of surface structuring has been earlier observed for the plasticized PVC and crosslinked rubbers after their uniaxial stretching (shrinkage) [11].

A question concerning the mechanism of the above behavior arises: What is the reason for different microrelief patterns formed upon the shrinkage of the plasticized PVC and chemically crosslinked rubbers? Here, it is important to mention that PVC is formed by linear unbranched macromolecules. The degree of crystallinity of commercial PVC samples is low. This fact is explained by a low content of syndiotactic sequences in its chains. Nevertheless, the presence of short regular sequences of repeating units provides for possible local interchain crystallization of the polymer. This crystallization is sufficient for formation of the three-dimensional network of macromolecules connected by crystalline junctions in solutions [12]. Therefore, one can compare this polymer with classical elastomers (high

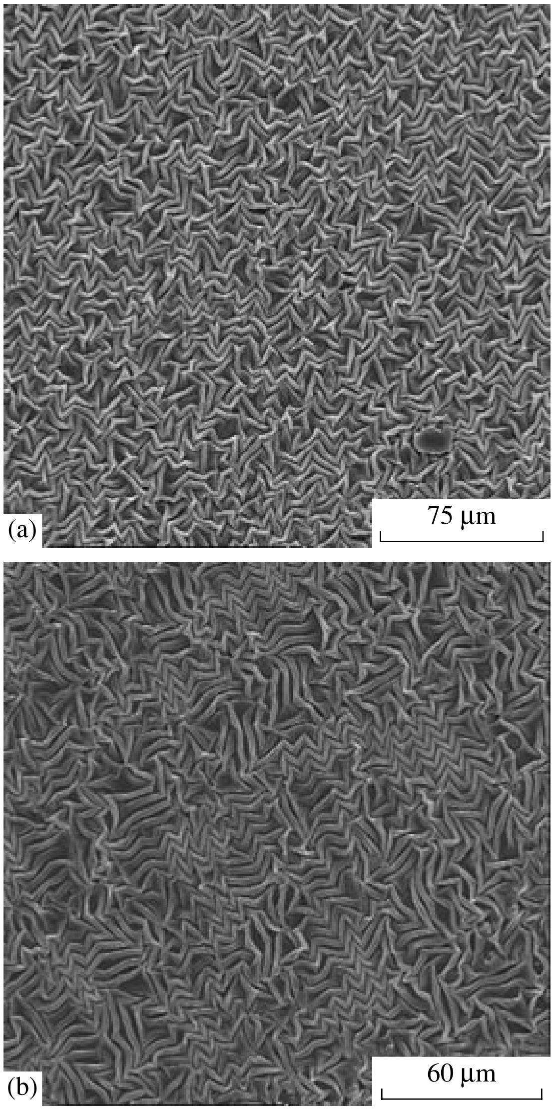

Fig. 2. Scanning electron micrographs of the NR-based samples after their plane deformation by (a) 5 and (b) 20%, subsequent deposition of a thin (10 nm) platinum layer, and strain recovery.

strain recovery). The data presented in Fig. 1 lead us to conclude that the formed network of crystallites is spatially homogeneous.

At the same time, the experimental results do not allow one to consider classical elastomers (crosslinked natural and synthetic rubbers) as topologically homogeneous networks. In particular, theoretical results presented in [13] make it possible to understand the mechanism of inhomogeneous swelling and resultant inhomogeneous stress and strain distributions in network polymers. The microheterogeneous structure of *cis*-isoprene rubber has been confirmed by direct X-ray studies (both SAXS and WAXS) [14]. The heterogeneous structure of peroxide and sulfur vulcanizates of NR has been revealed by scanning electron microscopy [15].

According to speculations reported in [16], one of the reasons for network inhomogeneity may be the presence of inhomogeneities in the system even prior to vulcanization. As was shown in [17], NR contains both sol and gel fractions. The molecular mass of macromolecules in the gel fraction is higher than 10^6. This system also contains the aggregates of linear macromolecules that appear owing to the presence of polar oxygen-containing groups. The amount of this gel is not constant and depends on the prehistory of the test sample [17–19]. As was shown in [20, 21], the mastication of NR, which is used to improve its properties, is likewise accompanied by formation of the gel fraction, which apparently exists in the form of slightly crosslinked rubber particles.

Therefore, mastication prior to the chemical crosslinking (vulcanization) of rubbers leads to formation of the product of inhomogeneous composition. This three-dimensional inhomogeneous structure is fixed by further vulcanization via chemical bonds.

To gain insight into the nature of structural inhomogeneity of the rubber samples under study, the content of the gel fraction in NR plasticates was quantitatively estimated. To this end, NR plasticate solutions in toluene and heptane were studied by light scattering. As was found, this solution contains a certain amount of swollen polymer microgels with dimensions of 2–3 μm. The above microgel particles were separated from the noncrosslinked fraction by the ultracentrifuge, and their content was estimated to be 25–30% with respect to the overall weight of NR. This value agrees with the data reported in [22]. As was shown in [22], the mastication of rubbers is accompanied by the breakdown of the longest macromolecules and their partial crosslinking. Depending on the regime of mastication, the content of the gel fraction may achieve 60% with respect to the weight of the initial NR.

Hence, the NR plasticate contains a linear polymer and a fraction of crosslinked microgels (the gel fraction). Evidently, further vulcanization can entail the development of additional structural inhomogeneities in the polymer network, which are provided by the inhomogeneous distribution of the crosslinking agent [23]. Evidently, this inhomogeneous character of rubber network exerts a certain effect on stress–strain characteristics of the resultant materials and their swelling behavior, sorption properties, permeability, and many other parameters. Therefore, information concerning structural inhomogeneity of rubber networks seems to be very important. With allowance for the fact that rubber networks are amorphous systems, their investigation by means of traditional structural methods based on the phase contrast of objects under study (X-ray analysis and electron diffraction method) appears to be ineffective.

Therefore, the search for new approaches to studying this challenging problem is crucial. For example, one approach [24] is based on a certain version of the

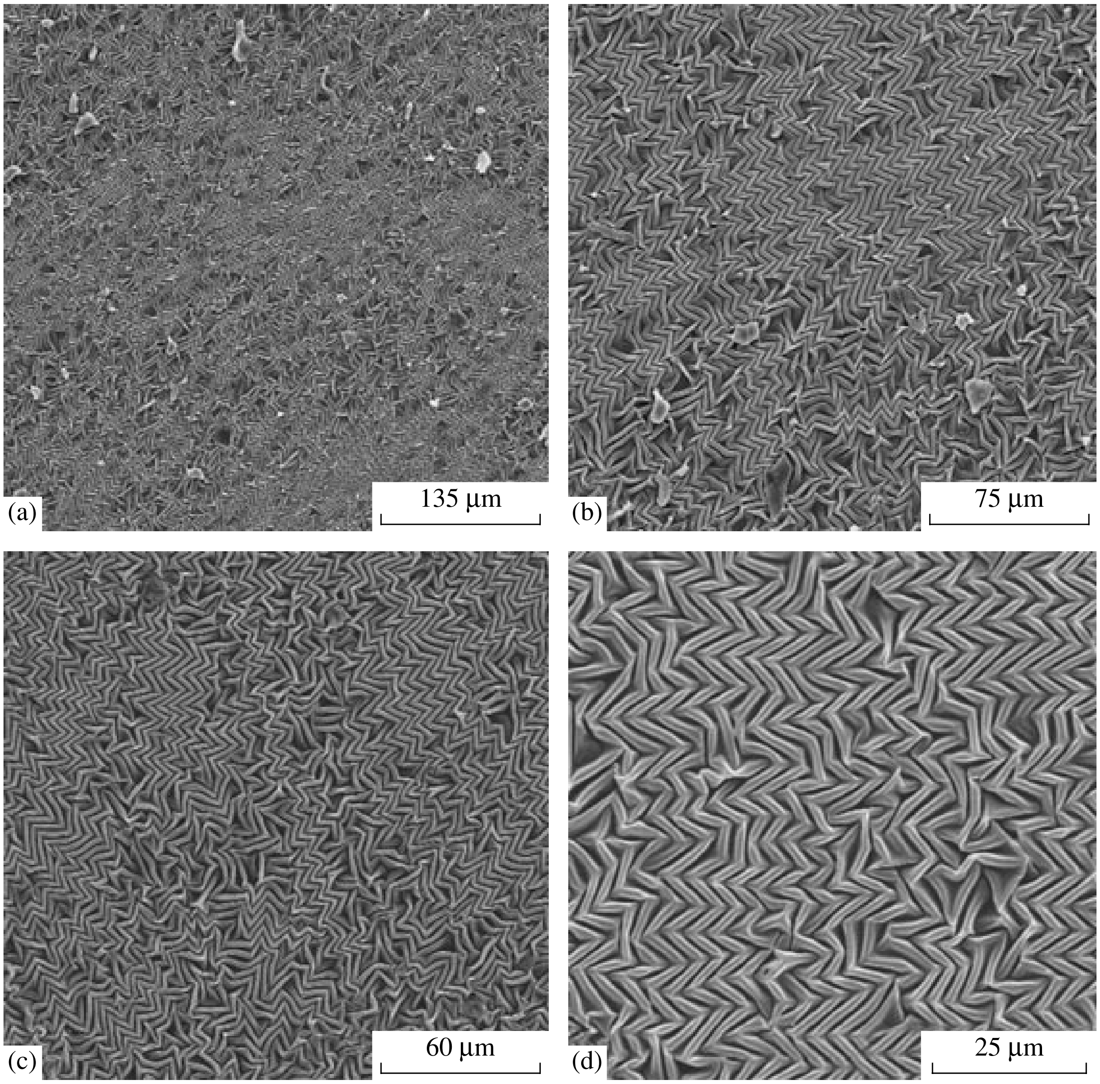

Fig. 3. Scanning electron micrographs of the SIR-based samples after their plane deformation by (a, b) 5 and (c, d) 14%, subsequent deposition of a thin (10 nm) platinum layer, and strain recovery. Comments are given in text.

method of molecular probes. The idea behind this approach concerns the fact that investigation of the structure and properties of a crystallizable sample presents a far simpler problem as compared with studying the structure and properties of amorphous compounds. The use of this method for rubber polymers requires addition of a solvent—a low-molecular-mass compound—to polymers via swelling, and this component should be capable of further crystallization in the polymer bulk. The in situ investigation of this crystalline component allows one to gain knowledge of the polymer structure. It is important that the melting temperature of the added low-molecular-mass component should be higher than room temperature in order to provide for its crystallization in the polymer bulk on cooling.

In this study, we used *n*-octadecane as a crystallizable low-molecular-mass component. The melting temperature of this linear hydrocarbon is 28.2°C. Figure 4 presents the DSC scans of pure *n*-octadecane (curve *1*) and *n*-octadecane added to NR via swelling (curve *2*). As is well seen, at the selected heating rate, the melting temperature of pure *n*-octadecane is 32.8°C. At the same time, the polymer matrix shows two well-pronounced melting temperatures of *n*-octadecane that are observed at temperatures below the melting temperature of pure *n*-octadecane. A depression in the phase transition temperature of a solvent in the presence of a polymer is a well-known fact. In particular, the dependence of the melting temperature of solvent on the composition of the swollen polymer may be calculated in terms of the theory of polymer solutions through the Flory equation [25]:

$$1/T_{\mathrm{m}} - 1/T_0 = -R/\Delta H[\ln(1 - \varphi_{\mathrm{p}}) + (1 - N^{-1})\varphi_{\mathrm{p}} + \chi\varphi_{\mathrm{p}}^2],$$

where T_{m} is the melting temperature of a solvent in the presence of NR, T_0 is the melting temperature of a pure

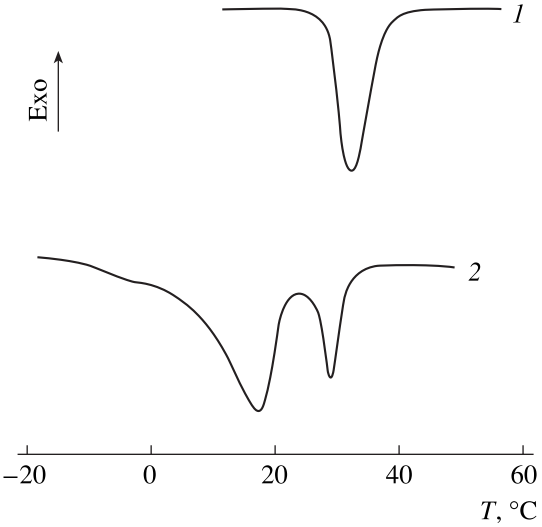

Fig. 4. The DSC scans of (*1*) pure *n*-octadecane and (*2*) the NR sample containing 0.31 volume fractions of *n*-octadecane.

solvent, ΔH is the fusion heat of a solvent (*n*-octadecane), N is the degree of polymerization of NR, φ_p is the volume fraction of a polymer, and χ is the interaction parameter. As is seen, the melting temperature of the solvent decreases with an increase in the polymer concentration in the system.

The above two phase transition temperatures may be related to the presence of two polymer fractions with different compositions in the system. Indeed, the equilibrium degree of swelling of a network polymer is known to be controlled by its degree of crosslinking. The existence of two melting temperatures suggests that the resultant NR network contains two fractions with different degrees of crosslinking and, hence, different contents of the low-molecular-mass component. On the one hand, this network involves gel fractions or, in other words, the crosslinked fraction prior to vulcanization. On the other hand, treatment with dicumyl peroxide leads to crosslinking of the whole system, including the fraction of linear macromolecules (the sol fraction) that exists in the rubber prior to vulcanization. As a result, this process leads to formation of the "bicomponent" inhomogeneous network. This fact is confirmed by two phase transition temperatures of the low-molecular-mass probe.

As is seen, the results obtained by both methods (DSC and electron microscopy) are in fair agreement. The proposed microscopic procedure allows one to visualize structural features of deformation of rubber polymers and appears to be very sensitive to structural (three-dimensional) inhomogeneity of the deformed elastomer. This procedure makes it possible not only to ascertain structural (topological) inhomogeneity of the rubber network but also to estimate the dimensions and localization of structural inhomogeneities.

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