

# Structural Features of Deformation of Rubbery Polymers<sup>1</sup>

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Received November 5, 2003;

Revised Manuscript Received March 10, 2004

**Abstract**—A direct microscopic procedure was used for studying the mechanism of deformation of rubbery polymers. To visualize structural rearrangements in the deformed polymer, it is sufficient to decorate its surface with a thin rigid coating prior to deformation. As a result of deformation and related changes in the surface area of the test polymer sample, the formed relief is changed in the coating and in the adjacent polymer layer. Direct microscopic examination and an analysis of the specific features of the induced microrelief allow one to gain important information concerning the mechanism of deformation of a polymer support. It is found that the deformation and shrinkage of a plasticized poly(vinyl chloride) (PVC) and a crosslinked isoprene rubber (SKI) are accompanied by appreciably different structural rearrangements. The tensile drawing and shrinkage of the plasticized poly(vinyl chloride) proceed along with the formation of morphologically similar structures in the surface polymer layer with the deposited metallic coating. In the case of SKI, one may observe a marked difference in patterns corresponding to direct (stretching) and reverse (shrinkage) deformation processes. It is assumed that this effect is related to the difference in the molecular mobility of crosslinked (SKI) and non-crosslinked (PVC) polymers.

## INTRODUCTION

In our recent works [1–3], a new microscopic procedure for the visualization of structural rearrangements taking place during the deformation of polymers was advanced and experimentally justified. In the general case, the procedure for the visualization of structural rearrangements is based on a fundamental property of solids. As a rule, all solids change their surface area during deformation. While the volume of a body may remain invariable, its surface area is always changed. The sign of this change may be different: surface increases during tensile drawing (uniaxial and plane) and decreases during shrinkage. The advanced procedure for the visualization of structural rearrangements is based on this particular property of polymers.

For the visualization of structural rearrangements in the deformed polymer, it is sufficient to decorate its surface with a thin rigid layer prior to deformation. As a result of deformation and concomitant changes in the polymer surface area, the surface relief is changed in the coating and in the adjacent polymer layer. A direct microscopic examination and an analysis of specific features of the formed microrelief allow one to gain important information concerning the mechanism of deformation of the polymer support. Actually, in this

case, we are dealing with the visualization of structural rearrangements during deformation and/or shrinkage of the deformed polymer.

In particular, the application of this procedure makes it possible to advance new speculations concerning the mechanism of deformation of glassy polymers, which are based on direct microscopic observations [2, 3].

This procedure is applicable for studying the processes of deformation of polymers in various physical and phase states (rubbery, viscous, crystalline, etc.). It is worth mentioning that the deformation of rubbery polymers is accompanied by marked changes in their surface area. However, this effect is virtually neglected when considering and analyzing the mechanism of their deformation.

In this work, an attempt was made to study deformation and shrinkage processes in rubbery polymers by using the direct microscopic procedure [1–3].

## EXPERIMENTAL

In this work, we used films of a synthetic isoprene rubber with a thickness of 500  $\mu\text{m}$ . This rubber was crosslinked by 1.5 phr of dicumyl peroxide per 100 phr of a raw rubber at 150°C (SKI). We also used commercial PVC films containing 60% of a plasticizing agent (dioctyl phthalate, DOP) with a thickness of 100  $\mu\text{m}$ . The glass transition temperature of the plasticized PVC estimated by the DSC method was equal to  $-15^\circ\text{C}$ . The measurements were performed on a Mettler TA 4000 thermal analyzer equipped with a DSC 30 unit; the

<sup>1</sup> This work was supported by the Russian Foundation for Basic Research (project nos. 02-03-32492 and 03-03-32748), the special-purpose federal program "Integration" (grant no. I-0429), and the program "Leading Scientific Schools" (grant VSh-602.2003.3).

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heating rate was 20 K/min. The films were cut into dumbbell-shaped specimens with a gage size of  $6 \times 22$  mm. Before and after tensile drawing, the surface of the test samples was decorated by a thin (11 nm) platinum layer using the method of ionic plasma deposition. The tensile drawing of the samples to given tensile strains was carried out using hand-operating clamps. Electron-microscopic observations were performed on a Hitachi S-520 scanning electron microscope.

## RESULTS AND DISCUSSION

At room temperature, the plasticized PVC exists above its glass transition temperature; as a result, after tensile drawing and shrinkage, its initial dimensions are fully recovered. This recovery is accompanied by a complete relaxation of the surface microrelief, which is induced during deformation; the development of the surface microrelief is provided by the deformation and fragmentation of the deposited metallic coating [4]. In this connection, to study the process of surface structuring in PVC, it is necessary to fix the dimensions of the sample after its deformation.

Figure 1 presents the typical results of this study. As is clearly seen (Fig. 1a), at low tensile strains (10%), the metallic coating breaks down into fragments with almost similar dimensions (20–30  $\mu\text{m}$ ). At the same time, a regular wavy microrelief with a period of  $\sim 3$   $\mu\text{m}$  is formed on the polymer surface. At this stage of deformation, the formed microrelief is not very regular. Many elements of this microrelief are poorly pronounced: separate nucleated folds do not span from one side of the coating to another, their length is small, and, finally, they fade away.

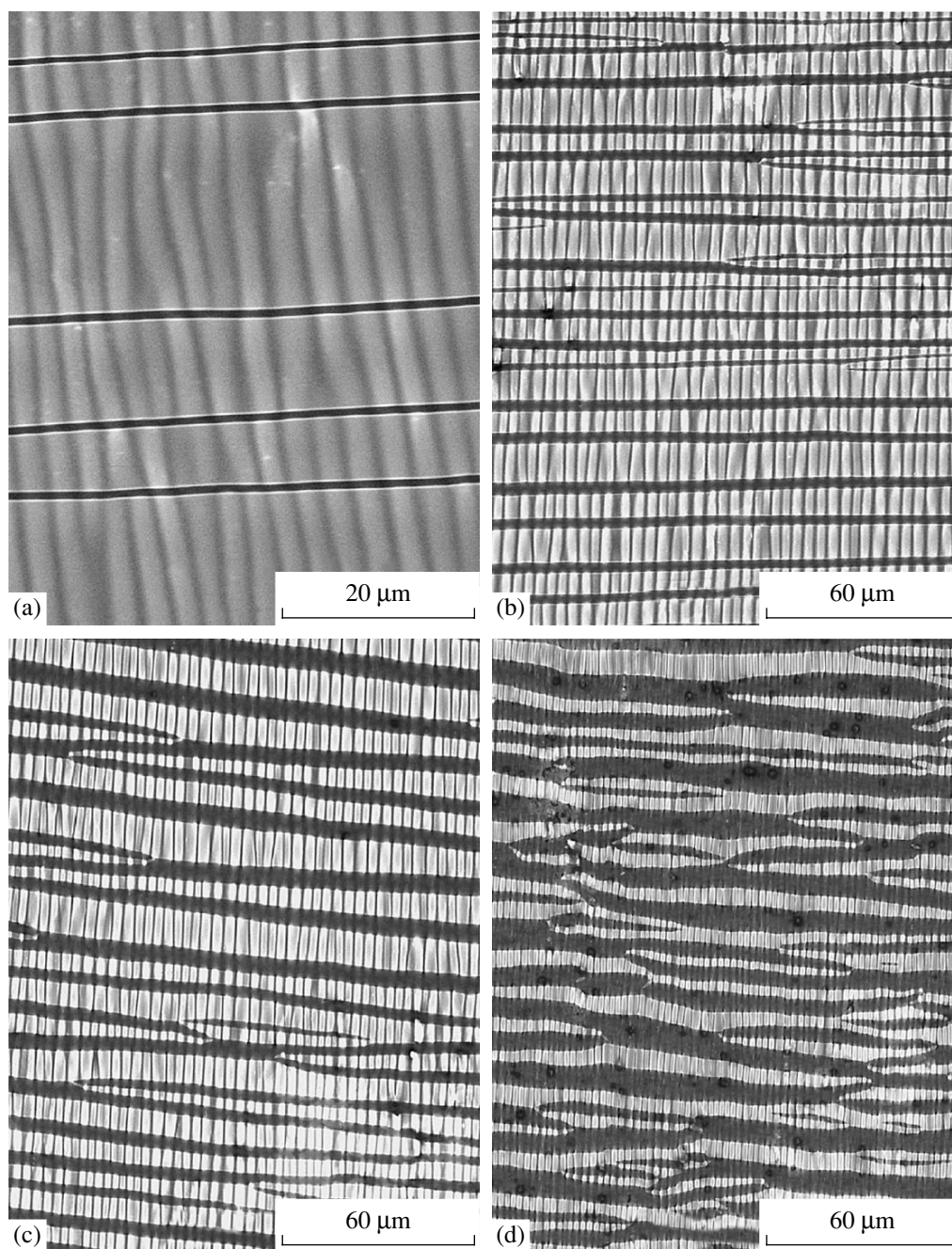
As the tensile strain is increased to 50% (Fig. 1b), the number of cracks in the coating markedly increases. The dimensions of the fractured fragments decrease down to  $\sim 12$   $\mu\text{m}$ . In this case, the microrelief period slightly changes. With the increasing tensile strain to 100 (Fig. 1c) and 200% (Fig. 1d), progressive disintegration of the coating takes place, the microrelief becomes more perfect, and its period decreases.

The above evolution of the microrelief during deformation of the polymer support is fully identical to the corresponding process, which is observed during deformation of a thermoplastic polymer (PET) with a thin metallic coating [5, 6]. The deformation of the plasticized PVC with a thin metallic coating is accompanied by the same surface structuring as that in “a rigid coating on a soft support” systems. The basic features of such structuring involve the development of the regular microrelief, the regular fragmentation of the coating, and the regular changes in the parameters of microrelief and the dimensions of the fractured coating fragments with varying the tensile strain of the polymer film support. A detailed description of the mechanism of the above phenomena (the progressive disintegration of coating and changes in the microrelief period) is given in [4].

However, as compared with the microrelief in the nonplasticized PVC, the microrelief formed during deformation of the plasticized PVC [7] is unstable. Let us remember that this microrelief exists until the dimensions of the stretched sample are fixed. Really, the glass transition temperature of the plasticized PVC (see EXPERIMENTAL) is below room temperature; therefore, if after stretching the sample is released from the stretching clamps, the initial dimensions of the sample are fully recovered, the coating surface is flattened, and the formed microrelief disappears. In the case of thermoplastic films, such as PET, PVC, and PS, polymer films with a stable microrelief may be prepared by stretching the coated polymer samples at temperatures above the glass transition temperature. Then, the coated polymer samples with the formed surface microrelief are cooled down to temperatures below the glass transition temperature and released from the stretching clamps. It is this cooling of the polymer sample below its glass transition temperature that allows one to fix surface structures and to prepare polymer films with a stable microrelief.

Nevertheless, there is a simple and efficient means of imparting a stable surface microrelief to polymer films in the rubbery state (above the glass transition temperature). To this end, a polymer film should be stretched to a given tensile strain; then, a thin rigid coating should be deposited onto the surface of the sample with fixed dimensions. Evidently, a subsequent stress release leads to a complete shrinkage of the sample, because the polymer exists in its rubbery state. During shrinkage, the geometric dimensions and surface area of the polymer sample are fully recovered. In this case, the coating deposited prior to shrinkage would be exposed to the action of tensile and compressive stresses [4]; inevitably, this would affect the pattern of the surface relief. Obviously, the formed microrelief would be stable because, due to complete relaxation after deformation, the dimensions of the film sample are stable, and no spontaneous changes in the surface area are allowed.

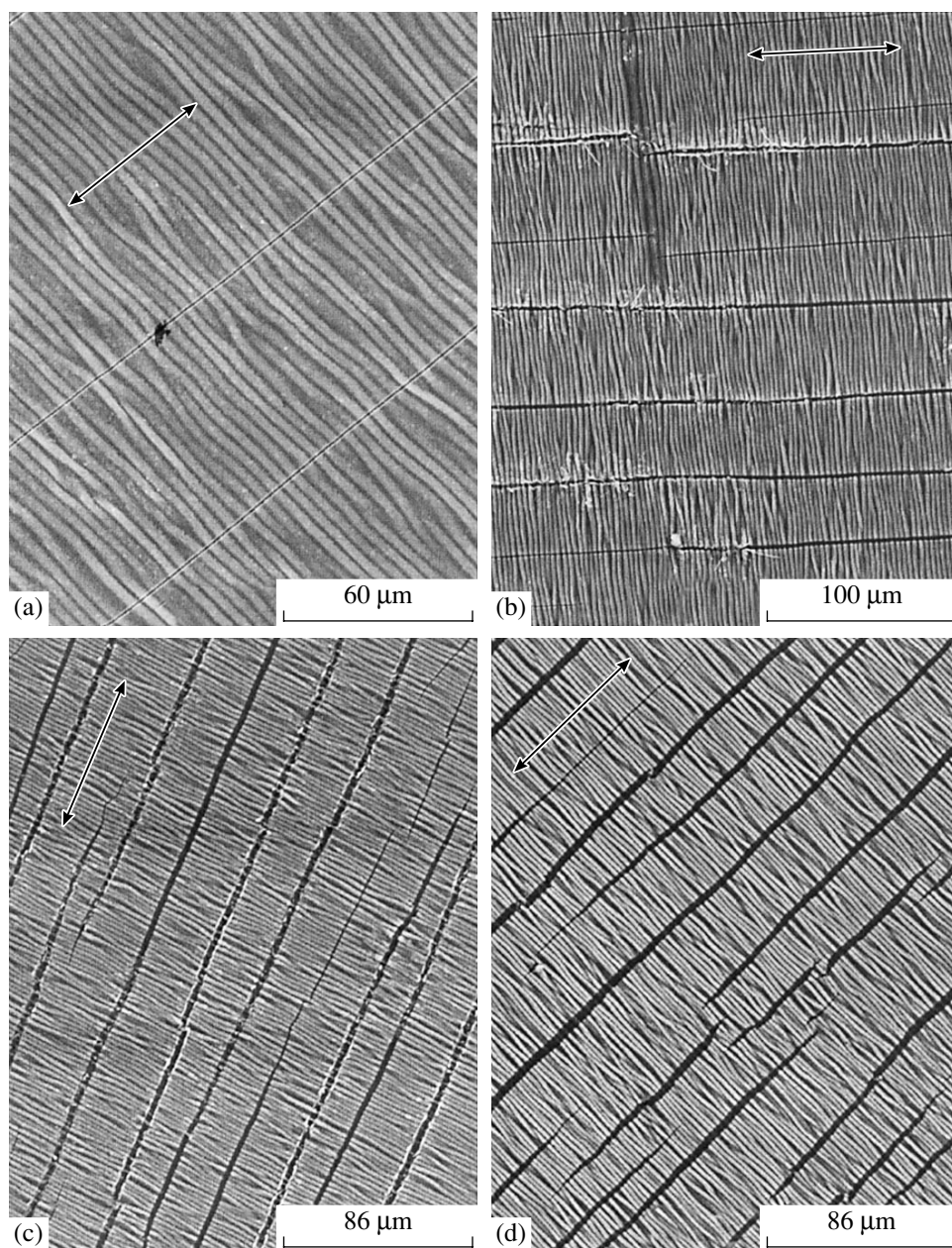
Such experiments were performed, and the related results are presented in Fig. 2. As is seen, the surface of the plasticized PVC during shrinkage is covered by the microrelief, which is fully identical to that formed during “direct” stretching of the polymer sample (Fig. 1). Really, deformation entails the development of a regular microrelief and rather regular fragmentation of the coating (Fig. 2a). With the increasing tensile strain in the PVC samples (the samples were stretched prior to coating deposition), the number of cracks in the coating increases and the microrelief wavelength decreases (Figs. 2b–2d). However, the relief, formed during shrinkage of the plasticized PVC samples, is markedly different from that formed during “direct” stretching of this polymer. As compared with the relief formed during the “direct” stretching of polymer samples, the pattern of this microrelief is turned by  $90^\circ$  with respect to



**Fig. 1.** Scanning electron micrographs of platinum-coated PVC samples stretched by (a) 10, (b) 50, (c) 100, and (d) 200%. The direction of tensile drawing is vertical.

the stretching axis. This fact seems to be quite clear because the polymer film under its uniaxial drawing is subjected to the parallel action of two different modes of deformation: elongation in one direction is accompanied by contraction in the perpendicular direction. This implies that the solid coating on the film surface also experiences two modes of deformation: compression and stretching. As was shown in [4], it is the compression of the coating that is responsible for the development of the regular microrelief, whereas stretching pro-

vides its regular fragmentation. As is known, during stretching of rubbery polymers, their volume remains virtually unchanged, but this process is accompanied by a marked side contraction, which entails the compression of the coating in the direction perpendicular to the axis of tensile drawing and the development of the corresponding relief. In the case of shrinkage of the preliminarily stretched sample, the directions of stretching and compression coincide. In other words, in the two cases above, the directions of compression of



**Fig. 2.** Scanning electron micrographs of PVC samples stretched by (a) 10, (b) 50, (c) 100, and (d) 200%, decorated with platinum coating, and allowed to shrink down to their initial state. The arrows show the direction of deformation.

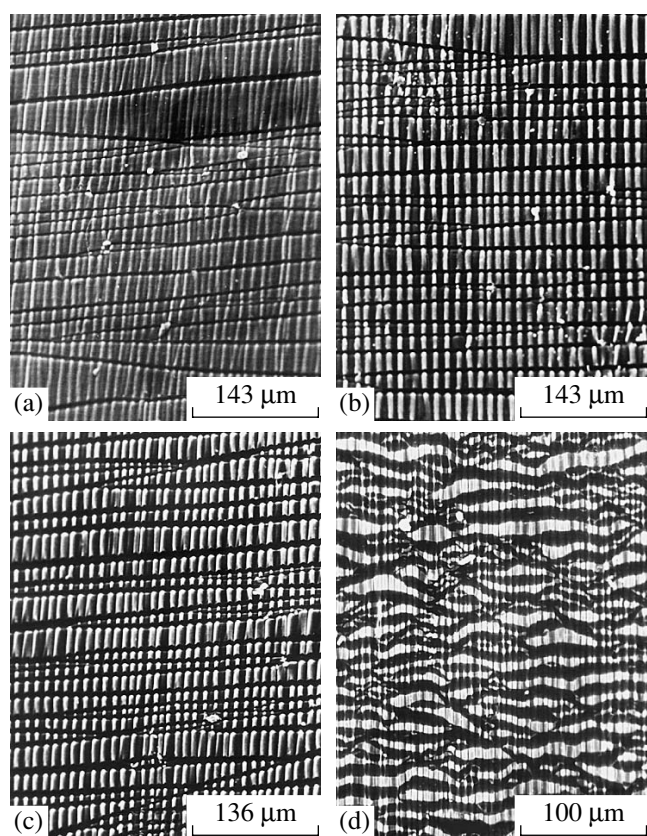
the polymer surface are perpendicular to each other with respect to the axis of tensile drawing of the polymer sample; this is the reason why the directions of the formed microreliefs are mutually perpendicular. Nevertheless, an evident similarity between microreliefs induced by “direct” stretching (the forward process) and shrinkage (the reverse process) of the plasticized PVC allows one to conclude that deformation is fully reversible.

In conclusion, one may state that the above surface structuring in the metallic coating corresponds to the homogeneous (affine) deformation of the polymer sup-

port. Speculations concerning this particular mode of deformation in the polymer support make it possible to advance a fair description and prediction of structural and mechanical behavior of such systems [4, 5].

It is necessary to mention that the analysis of the microrelief formed during direct stretching and shrinkage of the plasticized PVC allows one to characterize the mechanism of deformation and shrinkage of a polymer without any stable chemical crosslinks [8] even though its deformation is reversible.

Let us now consider the structural rearrangements in the crosslinked polymer in its rubbery state. To this end,



**Fig. 3.** Scanning electron micrographs of the samples of crosslinked isoprene rubber with platinum coating stretched by (a) 25, (b) 50, (c) 100, and (d) 400%. The direction of tensile drawing is vertical.

let us perform a microscopic examination of the deformation of films based on the crosslinked SKI with the deposited thin (11 nm) platinum surface coating. Let us recall that, to this end, the surface of the rubbery sample was decorated by a metallic coating; then, the samples were stretched to a given tensile strain, and their dimensions were fixed. The as-prepared samples were studied on a scanning electron microscope. The results of microscopic observations are presented in Fig. 3. As is clearly seen, the specific features of the “direct” stretching of SKI samples are similar to those of the deformation of other “rigid coating on a soft support” systems [4]. Over the interval of tensile strains under study, deformation leads to the development of a regular microrelief and a regular coating fragmentation. As the tensile strain is increased, the period of the regular microrelief decreases, and the mean dimensions of the fractured coating fragments go down; this behavior fully agrees with our earlier speculations [4, 5].

The development of the stable microrelief on the surface of the crosslinked rubber makes it possible to reveal certain unknown but universal features (Fig. 4). As in the earlier experiments (Fig. 2), the polymer sample was stretched to a given tensile strain and its dimen-

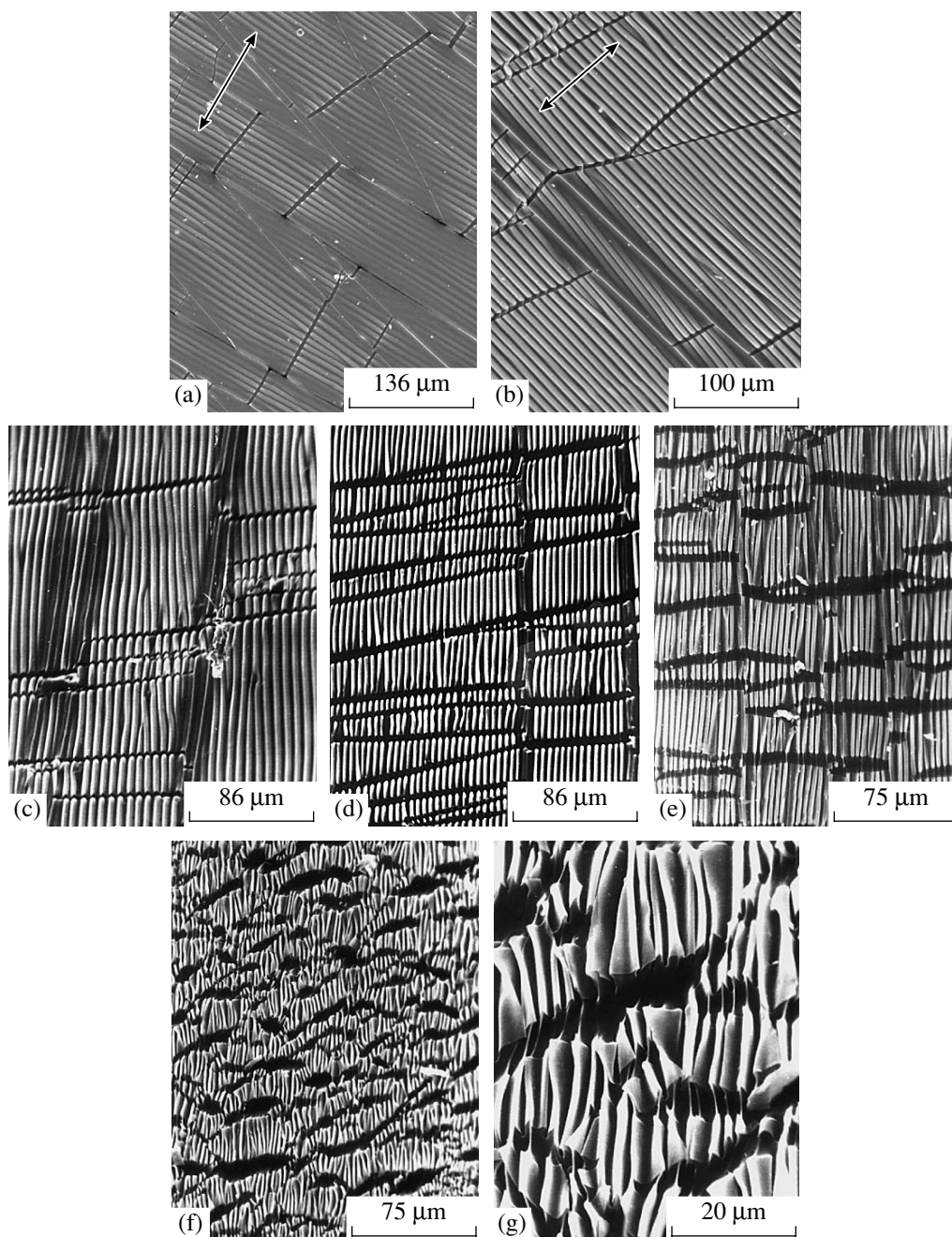
sions were fixed; then, the metallic coating was deposited, and the sample was released from the clamps. Due to stress release, the initial dimensions of the sample are fully recovered, and this process is accompanied by the development of the microrelief in the deposited coating.

As was found, this relief is noticeably different from microreliefs, which were earlier observed upon the deformation of other “rigid coating on a soft support” systems. These earlier unknown specific features of surface structuring are mostly pronounced at low tensile strains. Figure 4a presents the SEM micrograph of the rubber sample after its stretching by 10%, coating with a metallic layer, and stress release. As a result, the sample underwent a complete size contraction. As is clearly seen (Fig. 4a), in this case, the formed surface microrelief is composed of several structural elements. First, this concerns parallel folds that, as in other cases, are arranged into a regular microrelief. The folds are collected into well-defined “stacks.” Inside “stacks,” the folds are regular and parallel to each other. However, in each separate case, the orientation of folds is somewhat different from the orientation in neighboring “stacks.” As a result, a certain “parquet” structure on the polymer surface is formed.

The “stacks” of folds are likely to span from one to another side of the sample. We did not notice that the above “stacks” are interrupted or change their structure anywhere on the surface of the sample. Between the above “stacks,” other structural elements are located. Such structural elements involve relatively smooth and relief-free bands. These regions may contain individual folds or certain primordial structures of the regular relief. The above folds are different from the regular relief because they are not wide and regularly arranged elements with a sinusoidal cross section. These folds are very narrow and straight. The structure of the folds makes it possible to conclude that, within such regions, the metallic coating is drawn into the polymer volume. In other words, as compared with the above-mentioned case of the plasticized PVC, the surface of the coated polymer during its shrinkage decreases in, at least, two different ways: via formation of the regular microrelief and via retraction of a coating in the narrow rectilinear zones between regions of the regular microrelief. Let us mention that the regions where the coating retraction takes place are also rather regular.

The fragmentation of the coating during shrinkage of the crosslinked rubber is characterized by several specific features. In this case, in contrast to the above structuring during the shrinkage of the plasticized PVC (Fig. 2), the cracks do not propagate in straight lines over large distances or even from one to another side of the test sample. As is clearly seen, the cracks in the coating are primarily located in the regions with the regular microrelief. When a growing crack encounters the bands where the coating is drawn into polymer volume, its growth is arrested. A further fragmentation





**Fig. 4.** Scanning electron micrographs of the samples of crosslinked isoprene rubber stretched by (a) 10, (b) 20, (c) 50, (d) 100, (e) 200, and (f, g) 400%, decorated with platinum coating, and allowed to shrink to their initial state. The arrows show the direction of deformation.

proceeds via nucleation and growth of a new crack at the opposite side of the above region. Usually, this crack is nucleated in the vicinity of the preceding crack. It is important to mention that, as compared with the above case of the plasticized PVC, the direction of the propagation of some cracks in the coating is not perpendicular to the orientation of the regular microrelief. As follows from Fig. 4a, many cracks are inclined at a certain angle, even though the above cracks are unable to

cross the whole cross section of the coated polymer surface. As a rule, these inclined cracks are also terminated in the regions of the polymer surface, where the coating is drawn into the volume.

When the initial tensile strain is increased to 20%, no marked changes in the surface structuring of the coating are observed. As is clearly seen (Fig. 4b), as a result of shrinkage, a system of regions with a regular microrelief is formed on the polymer surface. These

regions are separated by deeper and narrower regions, where the coating is drawn into the polymer volume. A marked improvement of the microrelief pattern is evident. The folds in each region become more pronounced and better ordered with respect to each other. Furthermore, regular folds located in the neighboring regions separated by deeper and narrower regions, where the coating is drawn into polymer, appear to be almost parallel to each other. As follows from the comparison of Figs. 4a and 4b, a parquet structure is not observed during shrinkage of the polymer sample, which was stretched by 20% prior to its deformation.

With increasing the preliminary tensile strain to 20%, the character of the coating fragmentation also remains virtually unchanged. As is clearly seen, due to the polymer shrinkage, cracks in the coating primarily propagate in direction perpendicular to direction of the regular microrelief. As in the above case, the growing cracks are unable to overcome regions where the coating is retracted into the polymer. The cracks are terminated once they achieve the above regions and renucleate at its opposite side. Let us mention that the number of cracks that deviate from the direction perpendicular to the direction of the regular microrelief is markedly decreased as compared with the case of the shrinkage of the polymer sample with a tensile strain of 10%.

As the preliminary tensile strain is increased to 50%, new features in the surface structuring of the coating are observed (Fig. 4c). Nevertheless, in this case, the basic morphological forms of the induced structures are preserved. As is clearly seen, the shrinkage of such samples is accompanied by the formation of continuous regions with a regular wavy relief. As earlier, these regions are separated by certain zones on the polymer surface, where the coating is retracted inside the polymer by an appreciable distance. As above, cracks in the coating, which propagate perpendicularly to the direction of the formed regular microrelief, are unable to surmount the regions where the coating is retracted into polymer. Once such regions are achieved, the cracks are terminated but renucleate at the opposite side. Along with this process, new structural elements in the coating relief appear. As is seen in the SEM images at a higher magnification (Fig. 4d), rectilinear narrow cracks are formed in the coating and such cracks cross the regions with the regular relief at an angle of  $\sim 45^\circ$ . Such cracks are also observed in the samples deformed by 20%. However, in this case, these cracks are rather scarce. It is interesting to note that these narrow, inclined cracks are also unable to overcome the regions where the coating is retracted into the polymer volume. The appearance of the inclined cracks likely attests to the fact that, during shrinkage, marked shear stresses are developed in the polymer support.

As the preliminary tensile strain is increased further (to 100%), the pattern of structuring in the sample during its shrinkage remains virtually the same. As follows from Fig. 4d, a rather perfect relief with a period of

$3.6 \mu\text{m}$  is formed on the polymer surface. One may easily distinguish well-pronounced and regular regions where the coating is retracted into the polymer volume. The direction of such regions coincides with the direction of the regular microrelief. The cracks in the coating are still unable to overcome such regions and, usually, their growth ceases.

With increasing the tensile strain to 200%, the morphology of the formed relief is somewhat changed (Fig. 4e). At this tensile strain, the regular relief becomes more perfect. Its period decreases to  $2.5 \mu\text{m}$ , and this decrease is likely related to an increase in the degree of compression of the coating. In this case, the regions where the coating is retracted to the surface gradually fade away and become less pronounced. As follows from Fig. 4e, the cracks in the coating start to surmount these regions and cross them without any termination.

As the preliminary tensile strain is increased to 400%, the pattern of surface structuring is markedly changed again (Fig. 4f). As is clearly seen, the regions where the coating is fully retracted into polymers disappear. In this connection, the regular relief covers the whole surface of the test sample in a rather uniform way. The disappearance of the above regions entails changes in the character of fracture in the coating. Cracks in the coating propagate in a rather free mode; they do not terminate in any particular regions and have quite a different length. Many cracks propagate by rather long distances so that, using a microscope, one may hardly follow the sites of their termination; one might even think that they fully cross the surface of the test sample. Stress in the support that controls the direction of crack growth slightly deviates from the direction perpendicular to the direction of the regular microrelief. As a result, the regular fragmentation of the coating, which is typical of lower preliminary tensile strains, is not observed; cracks twist and appear to be not rectilinear.

At higher magnifications, the surface structuring shows another earlier unknown feature (Fig. 4g). At certain sites of the polymer surface that are exposed due to crack widening in the coating, the polymer also acquires a certain regular microrelief. Each fold in the coating "initiates" the formation of a fold with a well-pointed tip in the exposed rubber.

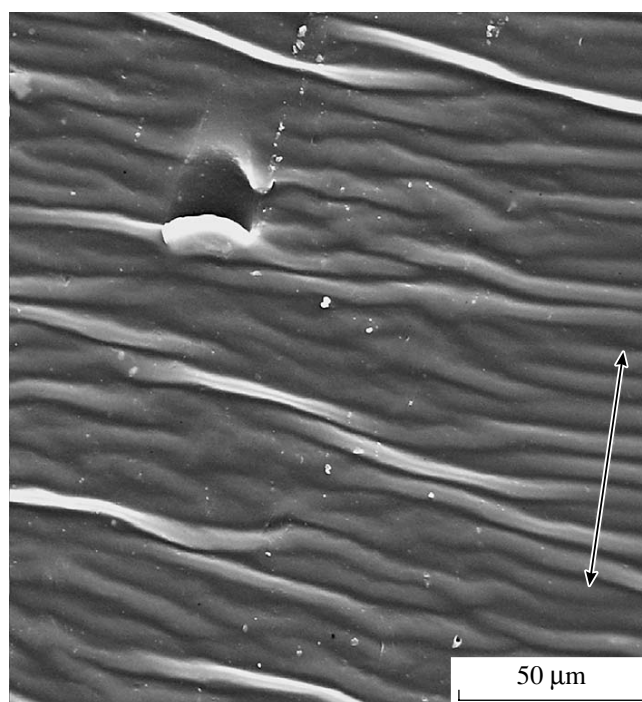
Let us mention that, during the direct stretching of the polymer sample with the same coating (cf. Figs. 3 and 4), both regular fragmentation of the coating and the development of the regular relief appear to be substantially different. In this case, the propagation of rectilinear cracks is observed, no inclined cracks are formed, and regions where the coating is retracted into the polymer are absent.

The question arises of why the morphological features of the coated polymer after its deformation to a small tensile strain (10–20%) and subsequent shrinkage are so different from the corresponding results obtained

for the noncrosslinked polymer (the plasticized PVC). Furthermore, at low tensile strains, the mechanism of shrinkage of the crosslinked rubber is substantially different from the mechanism of shrinkage of the same rubber but stretched to higher tensile strains (cf. Figs. 4a and 4e). Let us recall that, in the other polymer-rigid coating systems [4, 5], no marked difference between the morphologies of the formed surface structures of the samples with different tensile strains was observed. In the systems studied in earlier works, the regular microrelief was formed in the sample at low tensile strains, and further deformation of the polymer support entailed only its improvement and perfection, as well as gradual changes in the microrelief period and the mean dimensions of the fractured coating fragments.

The analysis of the results shown in Fig. 4 leads us to suspect that the mechanism of deformation of the crosslinked rubber appears to be markedly different at high and low tensile strains. According to the statistical theory of rubbery elasticity [9], the deformation of the crosslinked rubber network is affine at different stages of deformation and does not experience any changes during stretching. For the crystallizable rubber, this situation takes place at tensile strains below  $\sim 250\text{--}300\%$ . At higher tensile strains, orientational crystallization commences. Possibly, the morphological features of the samples after their stretching by 200–400% and subsequent shrinkage are related to the fact that, during recovery of the initial dimensions, the rubber changes its structure. As is well known, in the case of crystallizable rubber stretched to high tensile strains, stress release is accompanied not only by the recovery of its structure, but also by the reverse transition from a crystalline to amorphous state [10].

The procedure of the visualization of structural rearrangements in the deformed polymer [1–3] makes it possible to study the mechanism of polymer shrinkage by fixing the level of recoverable deformation and varying the initial level of its deformation. In other words, the same level of polymer shrinkage can be achieved in polymer samples with different initial tensile strains. This possibility is illustrated by the following experiment. The polymer sample was stretched to a relatively high tensile strain (100%), and its dimensions were fixed; then, its surface was coated with a thin metallic layer. As compared with earlier experiments and related results (Fig. 4), the shrinkage of this sample is not complete but is equal to 10%. Therefore, one may compare the surface structuring for the two different samples but with the same shrinkage (10%). A difference between the samples is the following: their preliminary tensile strain is equal to 10 or 100%, respectively. As was found, the results appear to be strikingly different. Structuring in the surface layer of the sample stretched by 10% was discussed above (Fig. 4a). This sample contains a whole set of morphological forms, and many of them were unknown. In the second case (Fig. 5), the shrinkage of the polymer sample leads to the development of a rather imperfect but still regular microrelief



**Fig. 5.** Scanning electron micrographs of the sample of crosslinked isoprene rubber stretched by 100%, decorated by platinum coating, and allowed to shrink by 10%. The arrow shows the direction of deformation.

with a wavelength of  $7.5\ \mu\text{m}$ . As is seen, the surface of the polymer sample is rather uniformly covered by this microrelief. The single specific feature of this relief is that some folds in several regions are somewhat higher than other folds. The fact that there are no cracks in the coating also seems to be rather surprising.

Therefore, the applied procedure of the visualization of structural rearrangements in the deformed polymer illustrates a gradual change in the mechanism of rubber deformation with increasing its tensile strain. The advanced approach is insufficient for detailed description of the mechanism of polymer deformation; however, this procedure allows one to detect and visualize the induced stress fields in the deformed polymer.

Really, the action of compressive stresses is responsible for the development of the regular microrelief [4, 5]. The nucleation of cracks in the coating is likely to be related to the action of tensile stresses. It is this combination of regular microrelief and rectilinear cracks observed during the direct stretching of the polymer sample (Figs. 1, 2) that is provided by the polymer nature of the support. To preserve its constant volume, the polymer sample during its elongation in one direction is inevitably compressed in the perpendicular direction. In essence, the analysis of the corresponding patterns presents the visualization of stresses acting in the polymer sample. By studying the relief pattern, one may easily distinguish the directions of compression



and tensile drawing. Let us emphasize that, during the deformation of the rubbery polymer, various stresses (compressive, tensile, shear stresses) are induced, and such stresses may be easily identified by the procedure of the surface deposition of thin rigid coatings onto the polymer sample (Fig. 4).

This procedure makes it possible to visualize another important process during polymer deformation. This concerns changes in the polymer surface area during deformation of the polymer sample. Depending on the mode of deformation, the polymer surface may either increase (tensile drawing) or decrease (shrinkage). This increase in the surface area is inevitably accompanied by the carryover of the polymer material from the volume (bulk) to the surface; during shrinkage, the reverse process is likely to occur. The procedure advanced in this work also makes it possible to characterize this process. The contraction of the interfacial surface is well detected, in particular, by the appearance of the above-mentioned polymer regions, in which the coating is drawn into the polymer bulk. The regular microrelief also characterizes the contraction of the polymer surface area. This procedure also allows one to follow an increase in the polymer surface area during deformation. The cracks in the coating are likely to be filled with the material that is carried onto the polymer surface from the bulk during deformation.

Therefore, the above experimental data suggest that the deformation and shrinkage of the crosslinked rubber are accompanied by several earlier unknown features. In this case, surface structuring in the rubber-metallic coating systems appears to be substantially different during the tensile drawing of the coated polymer sample and during the shrinkage of the same polymer on which the coating is deposited in its deformed state (compare Figs. 3 and 4). The latter fact attests that the advanced procedure makes it possible to ascertain the following: under the experimental conditions used in this work, the deformation of rubber is not equilibrium. This observation is proved by different patterns obtained during direct (tensile drawing) and reverse (shrinkage) processes of polymer deformation. At the same time, during deformation and shrinkage of the plasticized PVC, the differences are not that dramatic; this fact attests that the deformation of this polymer is closer to equilibrium.

The above results of direct microscopic observations of structuring during tensile drawing and shrinkage of rubbery polymers with a thin rigid coating entail several problems. First, why do the surface structuring during deformation and shrinkage of the crosslinked rubber appear to be so different? Second, what is the reason behind the morphological differences detected during the shrinkage of crosslinked (SKI) and

uncrosslinked (PVC) polymers? These problems may be clarified in further studies.

Now, one may only assume that, in PVC that is not a crosslinked rubber, the molecular mobility is likely to be enhanced, and the relaxation of stresses induced during deformation proceeds at a relatively high rate. As a result, a comparatively fast equalization of the stress field takes place, and its relaxation approaches the level close to equilibrium. Therefore, during direct and reverse processes, virtually identical patterns of the surface microrelief are observed.

In the crosslinked rubber, the molecular motion is not as free as that in PVC. Furthermore, the stress-induced crystallization of SKI is likely to impart certain specific features to the mechanism of deformation (shrinkage). As a result, the routes of deformation during direct and reverse processes and induced stress fields do not coincide, and they manifest themselves as different microrelief patterns.

Therefore, the procedure of visualization of structural rearrangements advanced in [1–3] appears to be efficient for studying the mechanism of deformation of rubbery polymers. This experimental procedure by itself is unable to provide exhaustive answers to all the stated problems; however, its value lies in its ability to raise the challenge.

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