

Visualization of Structural Rearrangements Responsible for Temperature-Induced Shrinkage of Amorphous Polycarbonate after Its Deformation at Different Conditions¹

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Abstract—Structural rearrangements during the temperature-induced shrinkage of amorphous polycarbonate after its tensile drawing below and above the glass transition temperature, rolling at room temperature, and solvent crazing have been studied with the use of the direct microscopic procedure. This evidence demonstrates that the character of structural rearrangements during the temperature-induced shrinkage of the oriented amorphous polymer is primarily controlled by the temperature and mode of deformation. In the case of the polymer sample stretched above the glass transition temperature, the subsequent temperature-induced shrinkage is shown to be homogeneous and proceeds via the simultaneous diffusion of polymer chains within the whole volume of the polymer sample. When polymer deformation is carried out at temperatures below the glass transition temperature, the subsequent temperature-induced shrinkage within the volume of the polymer sample is inhomogeneous and proceeds via the movement of rather large polymer blocks that are separated by the regions of inelastically deformed polymer (shear bands or crazes).

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INTRODUCTION

Inelastic deformation of glassy polymers is known to be accompanied by the mutual orientation of macromolecules. The above changes are observed in all cases, independently of the mode of loading (tensile drawing, compression, shearing, or rolling) and of the temperature interval where deformation is carried out (below or above the glass transition temperature T_g). When the oriented samples are annealed above the glass transition temperature, the reverse process takes place: namely, the geometric dimensions of the sample are recovered and, as a result, complete polymer disorientation occurs. One can expect that, despite the formal similarity between the above processes of temperature-induced strain recovery of the deformed amorphous samples (a complete recovery of initial geometric dimensions and mutual disorientation of macromolecules), the character of this strain recovery should depend on the mode of inelastic deformation.

However, there are currently no direct experimental data that allow one to characterize structural rearrangements taking place during transition of the deformed polymer sample to its initial state during annealing. In general, it is difficult to control and investigate the tem-

perature-induced shrinkage of oriented polymer samples because, first, there is no external force acting on the sample that can be directly measured. Second, the inhomogeneous structure of amorphous polymers shows fluctuation nonequilibrium rather than a phase character [1–4]. This fact is associated with marked experimental difficulties for studying the mechanism of structural rearrangements in amorphous polymers. These difficulties are related to the fact that all traditional and well-known structural methods based on the phase contrast of the test samples (X-ray analysis and electron-diffraction analysis) appear to be inapplicable. At the same time, it is quite evident that high strains of amorphous polymers are associated with a well-pronounced process of mass transfer. Even though the importance of the above mass-transfer process for understanding the mechanism of polymer deformation on the whole seems to be quite evident, this phenomenon is far from being well studied and characterized.

In our recent publications, a new universal microscopic procedure for studying the structural rearrangements during deformation of solid polymers has been proposed [5–8]. In this case, a procedure for the preparation of the test samples is rather simple and involves the following stages. Prior to the tensile drawing or contraction of the polymer sample, its surface is decorated with a thin (10–15 nm) metallic coating. As a result of subsequent deformation of the polymer sup-

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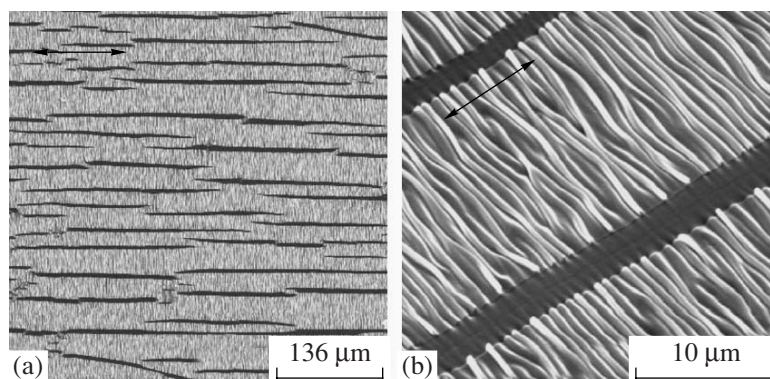


Fig. 1. SEM images of the surface of the PC sample deformed by 50% at a temperature of 160°C. The deformed sample with fixed dimensions was cooled to room temperature; then, its surface was decorated with a thin (10 nm) platinum coating, and the coated sample was annealed at 155°C. Here and in Figs. 2 and 3, the direction of tensile drawing is shown by arrows.

port, the deposited coating experiences structural rearrangements that are associated with processes taking place in the polymer sample. The above structural rearrangements provide information concerning the mechanism of deformation of the polymer support and the distribution of stresses that are responsible, in particular, for its shrinkage. Let us emphasize that the proposed procedure [5–8] is the first to allow characterization (visualization) of the process of mass transfer in the course of the temperature-induced shrinkage of amorphous polymers after their deformation via different deformation modes with the aid of direct microscopic observations.

The objective of this study is focused on the use of the direct microscopic procedure for the visualization of structural rearrangements that are responsible for the temperature-induced shrinkage of the amorphous polycarbonate (PC) after its deformation via different deformation modes.

EXPERIMENTAL

We studied the commercial unoriented films of the amorphous PC ($M_w = 8 \times 10^4$) with a thickness of 250 μm . The test samples with a gage size of 6 \times 22 mm were deformed by tensile strains on an Instron 1122 universal tensile machine at room temperature and at 160°C. The PC samples were rolled at room temperature on hand-operated rollers. The PC samples were stretched by 17% at room temperature in the presence of an adsorptionally active liquid environment (AAL) (ethanol). The solvent-crazed PC samples were placed into a narrow gap between two glasses and annealed in a thermostated chamber at a given temperature. Changes in the linear dimensions of the samples were measured on a KM-6 cathetometer with an error no higher than 0.03%. Some samples were prepared as described in [5–8]. All samples were examined on a

Hitachi S-520 scanning electron microscope. Thermo-mechanical studies were carried out on a Mettler TA 4000 thermal analyzer that makes it possible to obtain a high-accuracy temperature dependence of changes in the film thickness.

RESULTS AND DISCUSSION

The amorphous polymer was deformed under different conditions. Some samples were stretched by 50% at 160°C, which is 15°C higher than the glass transition temperature of PC (145°C). After stretching, the sample with fixed dimensions was cooled down to room temperature and released from the clamps of the stretching device. The PC samples were deformed also at room temperature via necking. Furthermore, the PC samples were subjected to rolling at room temperature, so that the length of the samples increased by 40%. Finally, the PC samples were deformed via the mechanism of solvent crazing at room temperature.

In all cases, all polymer samples experience a complete recovery of their linear dimensions and initial structure after annealing above the glass transition temperature (155°C). Evidently, in all the above-mentioned cases, the mechanisms of polymer deformation are different. Hence, one can expect that the processes of shrinkage of the deformed polymer samples during annealing should be different also. To gain information concerning the mechanism of shrinkage of the oriented PC, the deformed samples were decorated with a thin (10 nm) metallic coating prior to annealing.

Let us consider in detail direct microscopic data that provide an opportunity to visualize structural rearrangements taking place during the temperature-induced strain recovery of the PC samples after their deformation by different mechanisms. Figure 1 shows the SEM images of the PC sample after its deformation above the glass transition temperature, deposition of a

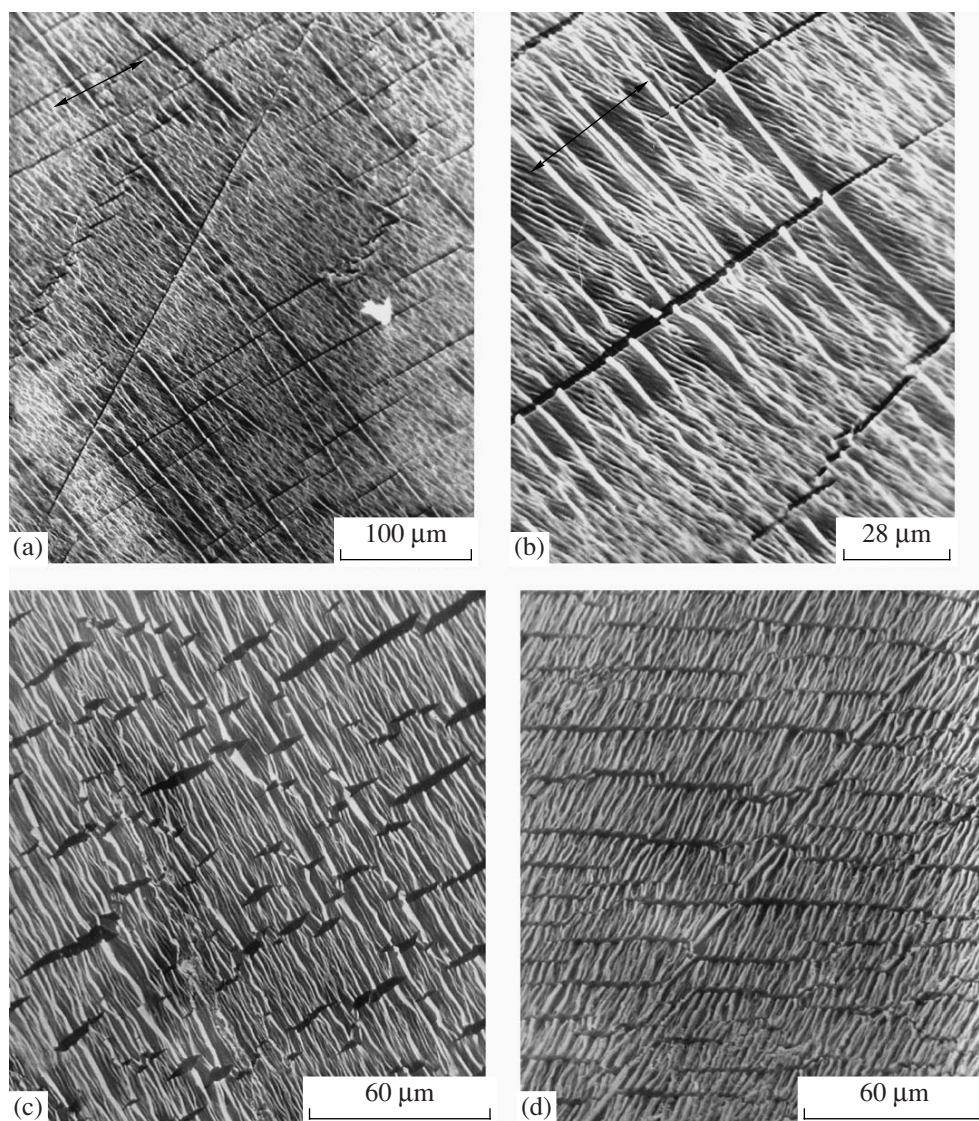


Fig. 2. SEM images of the PC sample after its deformation at room temperature via necking. The surface of the deformed sample was decorated with a thin (10 nm) platinum coating, and the coated sample was annealed at (a, b) 130, (c) 140, and (d) 155°C.

thin metallic coating on its surface, and annealing. As is seen, the shrinkage of the deformed sample is accompanied by at least two types of surface structuring. First, one can observe a profuse and rather regular fragmentation of the deposited coating. Second, a wavy and periodic surface microrelief is formed. The development of the regular microrelief is provided by the compression of the coating due to the shrinkage of the polymer sample. During annealing, the length of the sample decreases but its width in the direction normal to the axis of tensile drawing increases. It is this stress that leads to the breakdown of the coating and to the formation of a set of rectilinear or straight cracks. The mechanism of the above phenomena has been described in detail in [9–12].

Let us consider some specific features of the PC samples since this polymer has been used as a polymer support for the first time. First, note that the formed microrelief appears to be very regular. Indeed, all cracks in the coating are rectilinear and regular. The wavy microrelief also shows a well-pronounced regular character (Fig. 1b). The microrelief period is about 1 μm . This period is seen to be the same over the whole surface of the sample. The above specific features of the formed microrelief suggest that the field of inner stresses responsible for the temperature-induced shrinkage of polymers is highly homogeneous.

Let us consider structural rearrangements during shrinkage of the glassy PC after its deformation at room temperature via necking. Figure 2a shows the SEM

image of the PC sample after its deformation at room temperature (the region of the necked polymer), deposition of a thin (10 nm) platinum coating, and annealing below the glass transition temperature (at 130°C). At moderate magnifications, one can easily identify at least three types of morphological forms of the surface microrelief. First, this microrelief contains the folds that are oriented in the direction normal to the axis of tensile drawing (and shrinkage) of the polymer sample; second, it contains the rectilinear cracks in the coating that are formed owing to the expansion of the oriented polymer in the direction normal to the axis of tensile drawing. Both morphological features are typical of the shrinkage of the PC sample deformed at temperatures above T_g . Finally, on the surface of the polymer sample, one can observe long straight lines that intersect the entire surface of the sample and each other at different angles. The above lines are shear bands that are formed in the glassy polymer at the early stages of deformation. The presence of the above shear bands can be visualized in the samples with the coating after their shrinkage [7]. However, in the PC sample deformed above the glass transition temperature, annealing does not lead to formation of the shear bands (cf. Figs. 1, 2).

Note that the character of the relief formed during annealing of the polymer sample deformed below the glass transition temperature appears to be different from the surface pattern observed for the polymer sample oriented above the glass transition temperature. As is well seen at high magnifications (Fig. 2b), the folds of the surface microrelief have different widths and, probably, different heights. Some folds are oriented strictly along the direction normal to the axis of tensile drawing of the polymer sample. The above folds are located at different distances from each other (ranging from 1 to 40–50 μm). Between the above folds, one can observe the development of another surface microrelief with numerous folds, and a distance between these folds is 0.5–1 μm . These folds do not span long distances across the sample but are located at a certain angle with respect to longer folds. It is important that, in this case, a regular character in the arrangement of folds and cracks in the coating is less pronounced as compared with that in the polymer sample after its deformation above the glass transition temperature. The causes of the above difference in the morphological forms produced during shrinkage of the amorphous polymer sample with the metallic coating after its deformation above and below glass transition temperature T_g were described in [4–8].

When the oriented polymer sample is annealed near the glass transition temperature (140°C) (Fig. 2c), it experiences further shrinkage. However, this treatment does not markedly change the pattern of surface structuring. As in the above-mentioned cases, one can observe irregular folds with different heights and cracks in the coating. It is worth mentioning that, at this

stage of shrinkage, the coating starts to flake from the polymer surface.

When the oriented polymer sample is annealed above its glass transition temperature (155°C), one can observe a complete recovery of its initial geometric dimensions. In this case, the process of exfoliation of the coating from the polymer support becomes more pronounced and the regular character of surface structuring appears to be fully disturbed (Fig. 2d). On the whole, one can conclude that the field of stresses stored by the polymer sample during its deformation below the glass transition temperature is far more inhomogeneous than that developed during deformation of the sample above the glass transition temperature. This fact implies that the process of cold drawing is extremely inhomogeneous and proceeds not at the molecular level, as in the case of deformation above the glass transition temperature (Fig. 1), but is accompanied by the movement of large fragments of the material. Evidently, in this case, the molecular orientation in this material is likewise inhomogeneous and changes from one to another point in the volume of the polymer sample.

Let us consider the consequences of annealing for the PC sample after its preliminary rolling at room temperature. The deformation of glassy polymers via rolling, especially PC, has specific features that are different from those that appear during deformation of the same polymers under different conditions [13, 14]. The shrinkage (the recovery of initial dimensions) of glassy polymers after their rolling below the glass transition temperature and subsequent annealing is poorly studied, especially from the structural standpoint. Similarly to the other modes of inelastic deformation of glassy polymers, the rolled samples are known to recover their initial dimensions during annealing. This fact is quite expected because the inelastic deformation of the polymer sample changes the conformational set, which the polymer sample tends to recover once a sufficient molecular mobility is attained. Nevertheless, it seems evident that each mode of inelastic deformation of the polymer sample is accompanied by the characteristic structural rearrangements that should be studied in order to construct the general character of deformation of glassy polymers.

As a result of rolling, the surface of the rolled sample is seen to contain certain irregularities that are oriented along the direction of rolling (Fig. 3a). This relief apparently appears owing to surface irregularities printed by the metallic rollers on the smooth surface of the PC film.

At low magnifications, one can hardly identify any structural changes in the surface layer of the polymer sample after its annealing at 100°C (Fig. 3b). The relief on the surface of the polymer sample is similar to that in the sample without any annealing (cf. Figs. 3a

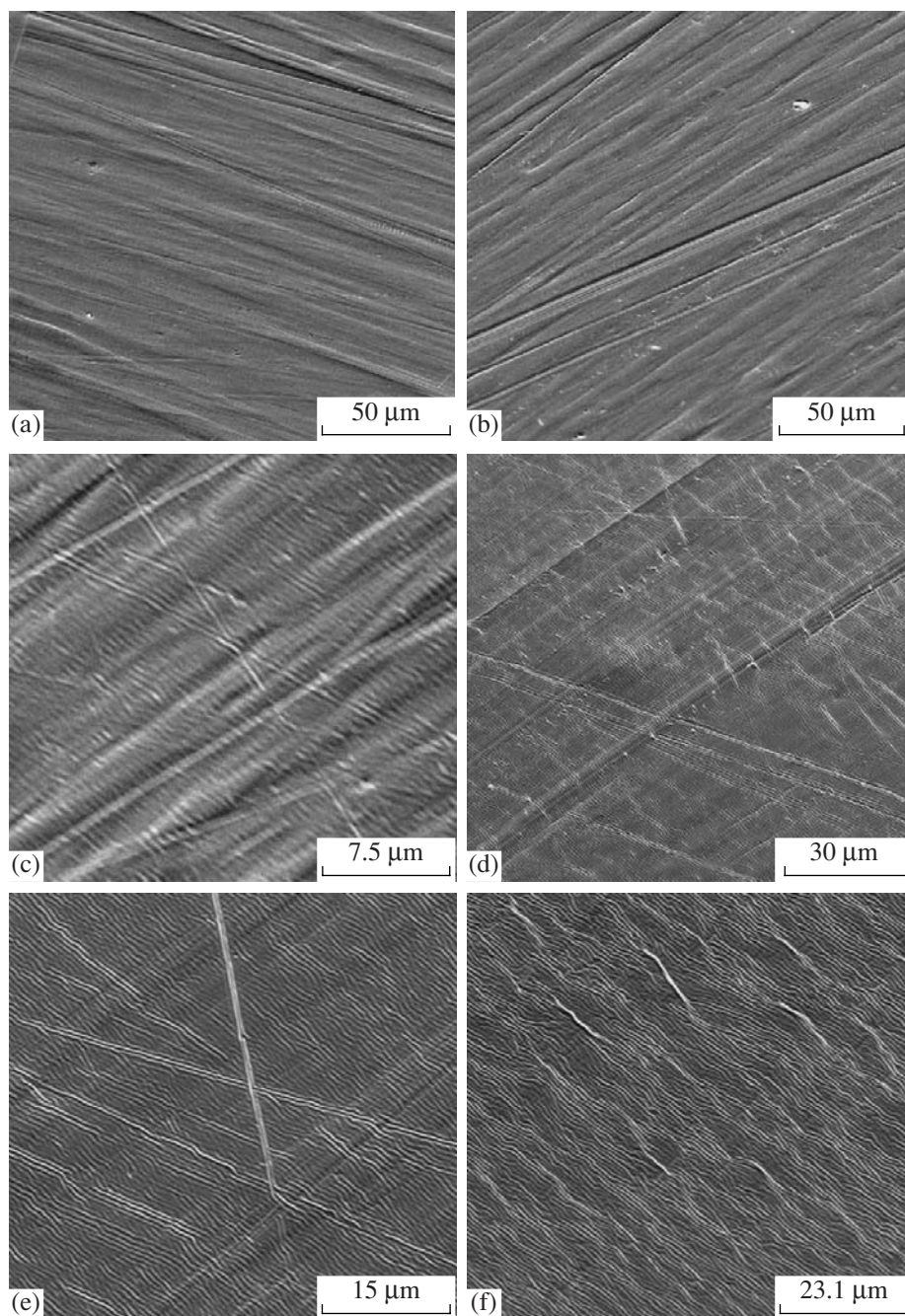
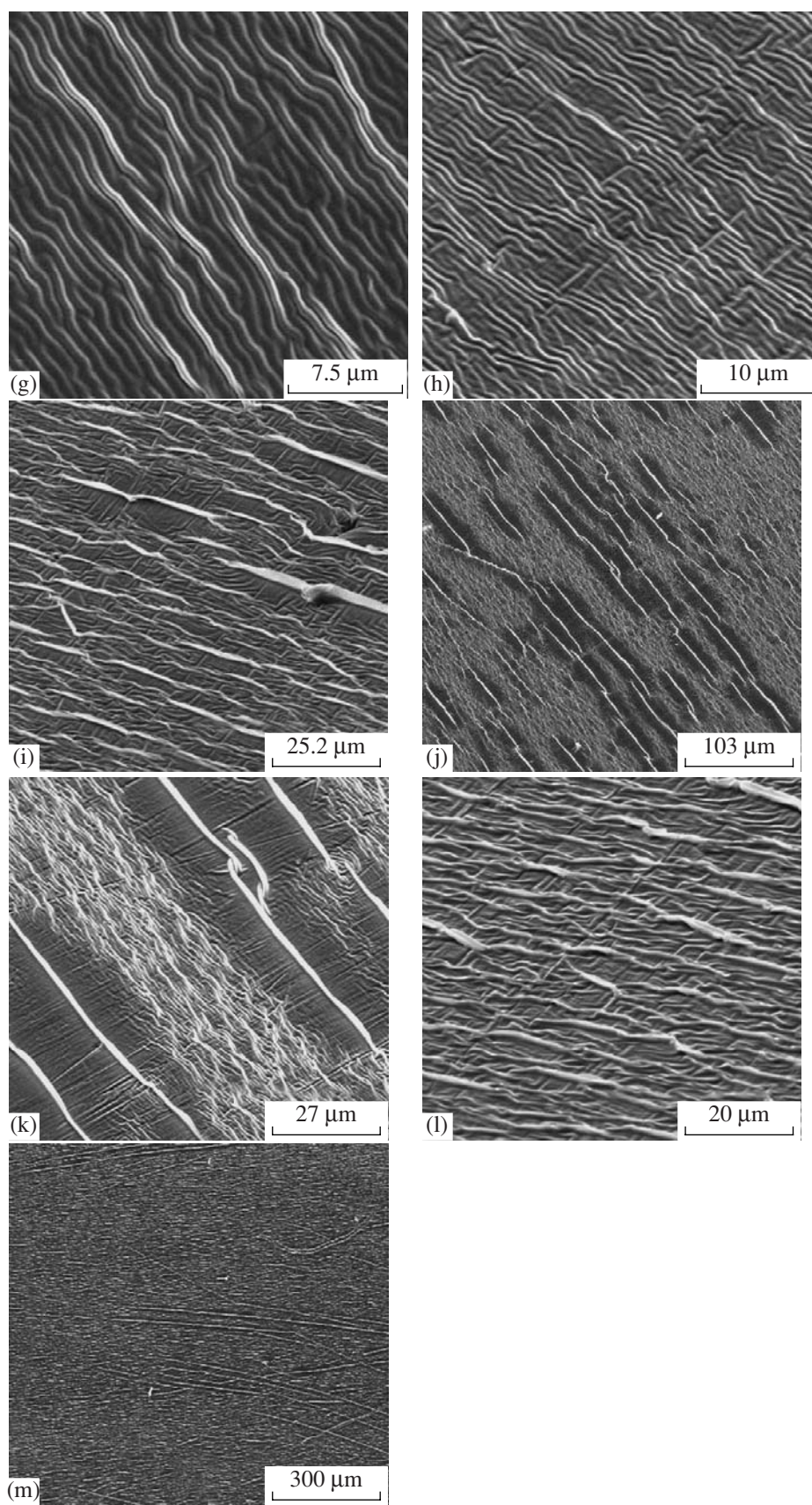


Fig. 3. SEM images of (a) the PC sample after its deformation at room temperature via rolling and (b) of the same sample decorated with a thin (10 nm) platinum coating after annealing at (b, c) 100, (d, e) 110, (f–h) 120, (i) 130, (j, k) 140, and (l, m) 155°C.

and 3b). However, at higher magnifications (Fig. 3c), one can reveal at least two features of surface structuring at the surface of the polymer sample with the metallic coating after its annealing at 100°C, namely, a regular wavy microrelief oriented in the direction normal to the axis of rolling and rectilinear bands that intersect the polymer sample at a certain angle with respect to the axis of rolling. In [4–8], the above bands are identi-

fied as shear bands. For the rolled sample, the period of the microrelief formed at this stage of annealing is small and equal to $\sim 0.4 \mu\text{m}$.

As is seen, the PC sample after its rolling at room temperature is capable of certain molecular rearrangements that take place at temperatures 50°C lower than the glass transition temperature.

**Fig. 3.** (Contd.)

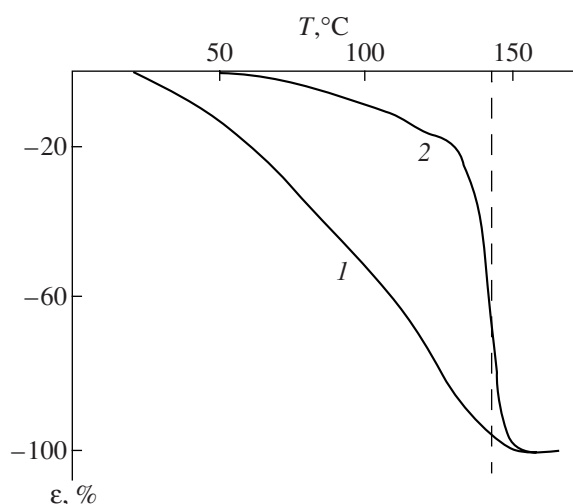


Fig. 4. Temperature dependence of the recovery of the linear dimensions of the PC samples after their uniaxial stretching via the mechanisms of (1) solvent crazing and (2) tensile drawing in air via necking. The dashed line corresponds to the glass transition temperature of PC.

As the annealing temperature is increased to 110°C, the pattern of surface structuring is markedly changed, even though this temperature is much lower than the glass transition temperature. As follows from Fig. 3d, even at small magnifications, one can reveal numerous rectilinear shear bands at the surface of the polymer sample that are oriented at a certain angle to the axis of rolling. At higher magnifications (Fig. 3e), one can easily identify a regular wavy relief in the deposited coating that demonstrates the shrinkage of the polymer sample along the direction of rolling. This relief is more pronounced than the relief formed during the annealing of the sample at 100°C (cf. Figs. 3c and 3e).

As the annealing temperature is increased to 120°C, a folded microrelief becomes more perfect and its folds are oriented in the direction normal to the axis of rolling (Fig. 3f). The folds of this relief become rather long and closer to perfect, even though it contains certain irregularities. At the same time, between the regular folds of the above surface relief, one can reveal the raised folds which are seen to be lighter (Fig. 3g). A detailed microscopic examination additionally allows one to identify new elements in the surface microrelief. As is seen, when the polymer sample is annealed at 120°C, its surface is covered by few folds that are oriented in the direction normal to the direction of primary folds or, in other words, along the direction of rolling (Fig. 3h).

When the PC sample with the deposited coating is annealed at 130°C after its rolling at room temperature, the formed surface microrelief involves two mutually perpendicular structures (Fig. 3i). This relief represents a set of regular folds that are oriented, as in the earlier

case, perpendicularly to the direction of rolling. Some folds have higher height. They are higher than other folds and seen in the corresponding SEM images as white bands that are oriented in the normal direction with respect to the axis of rolling. However, let us mention that the relief shown in Fig. 3i is likewise characterized by a well-pronounced system of numerous folds that are perpendicular to the direction of primary folds or, in other words, oriented along the direction of rolling.

As the annealing temperature is increased to 140°C, the whole pattern of the surface relief breaks down into individual well-separated regions seen as asymmetric structures with appreciably different orientations (Fig. 3j). At moderate magnifications, one can easily distinguish the raised folds that are oriented perpendicular to the axis of rolling (continuous light bands in Fig. 3j). The above folds are surrounded by dark regions, and their structure will be discussed below in more detail. The remaining surface of the polymer sample is covered with a folded structure with a smaller period. At higher magnifications, one can study this structure in detail (Fig. 3k). Regular folds oriented in the perpendicular direction with respect to the axis of rolling have an irregular configuration and small length. They are located in the regions between big (high) and continuous folds of a nearly rectilinear shape. At the same time, the whole surface of the polymer sample is covered with rectilinear folds that are oriented along the direction of rolling. The above folds intersect all other structural elements of the surface relief.

Note that the above-mentioned variety of morphological forms is formed in the PC sample during its annealing below the glass transition temperature or, in other words, when the polymer exists in the glassy state. This observation suggests that, within this temperature interval, certain large-scale modes of the molecular motion come into play. During annealing, the relaxation of the above modes of the molecular motion entails a complicated evolution of internal stresses, which can be recognized by using the proposed procedure for the preparation of the test samples for microscopic studies.

Finally, when the PC sample with the deposited coating is annealed above the glass transition temperature (155°C) after its rolling at room temperature, the whole surface of the test sample appears to be covered with a regular microrelief that involves two mutually perpendicular structures (Fig. 3l). It is worth mentioning that, at this annealing temperature, the polymer sample completely recovers its initial dimensions. In addition to the structure shown in Fig. 5l, at low magnifications, one can distinguish that the numerous shear bands induced in the structure of the polymer sample upon cold rolling preserve their individual character in the surface relief that is visualized with the use the samples with the deposited metallic coating (Fig. 3m).

The above experimental evidence clearly shows that the annealing of the PC samples after their rolling at room temperature is accompanied by complicated and multistage structural rearrangements. Remember that, in the above-mentioned case of uniaxial compression, linear dimensions of the polymer sample in the direction perpendicular to the axis of tensile drawing tend to decrease (the transverse contraction). This contraction entails cracking in the deposited coating because, during annealing and subsequent shrinkage, the oriented polymer sample not only decreases its length but also increases its dimensions in the direction normal to the axis of tensile drawing (shrinkage). This widening of the sample appears to be responsible for the profuse cracking in the coating. One of the specific features of the deformation of the polymer sample via cold rolling concerns an increase in the linear dimensions of the sample: both the length (the direction of rolling) and the width of the sample are increased. As a result of annealing, both the length and width of the rolled sample tend to decrease. Since the annealing does not lead to an increase in the linear dimensions of the polymer sample, the deposited coating does not break down and its temperature-induced shrinkage is not accompanied by the formation of cracks.

The proposed procedure allows one to visualize the structural rearrangements during the shrinkage of the polymer sample after its deformation via cold rolling. First, note that the oriented PC sample shows a highly inhomogeneous level of reversible deformation. Microscopic data shown in Fig. 3 make it possible to identify some unknown features in the structural mechanical behavior of the PC samples deformed via cold rolling at room temperature. First, practically all inelastic deformation of the PC samples can relax below the glass transition temperature. Second, this relaxation can be resolved into two components. The first component of strain relaxation proceeds in the direction along the axis of rolling. The relaxation of this component commences at about 100°C. When the annealing temperature is increased to 130°C, the second component of strain relaxation comes into play. The direction of this component is normal to the direction of the first component and to the axis of rolling. As the annealing temperature is increased further, both components of strain relaxation are observed, and this conclusion is confirmed by the development of two mutually perpendicular morphological forms of the microrelief in the metallic coating. This experimental evidence does not answer the question why the rolled samples show only two mutually perpendicular components of inelastic deformation, one of which coincides with the direction of rolling. This result is not evident, because, during rolling, the polymer film is free in all directions along its perimeter and there are no limitations for its orientation in any direction. Nevertheless, this result follows

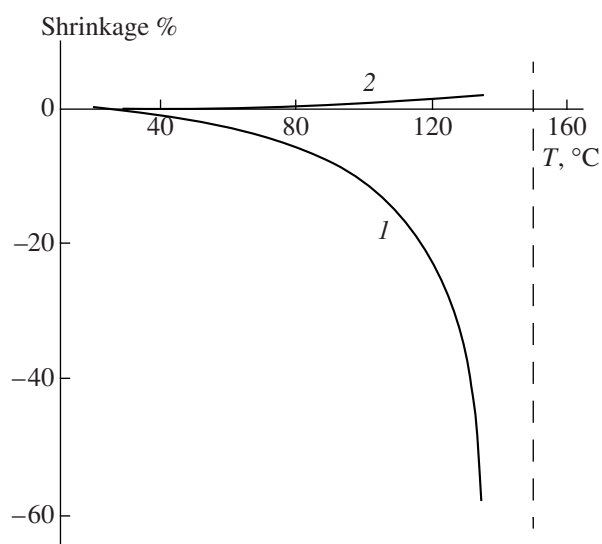


Fig. 5. Temperature dependence of relative changes in the linear dimensions of (1) crazes and (2) unoriented regions between crazes along the direction of tensile drawing of the solvent-crazed PC samples. The dashed line corresponds to the glass transition temperature of PC.

from the direct microscopic observations and seems to be undisputed.

The solvent crazing of polymers in the presence of liquid environments is also accompanied by the molecular orientation of polymers. This mode of inelastic deformation has characteristic features that are different from all other modes of deformation. The point is that, in this case, deformation proceeds via the nucleation and growth of microscopic regions containing the oriented fibrillar material (crazes). As a result, the deformed polymer is characterized by an inhomogeneous structure, in which crazes coexist with fragments of the undeformed bulk polymer. Nevertheless, as in all above-mentioned cases, the annealing of the crazed sample leads to complete recovery of the initial polymer structure. It seems impossible to characterize this process by the dependence of the thickness of the deformed polymer sample plotted against annealing temperature, because the crazed sample contains fragments of the undeformed polymer. For this reason, the length of the deformed sample was plotted against the annealing temperature.

Figure 4 shows this dependence for the PC samples after their deformation in the presence of AALE via the mechanism of classical solvent crazing (curve 1). For comparison, this figure shows also the thermomechanical curve for the PC sample after its tensile drawing in air via necking (curve 2). As is expected, the polymer oriented in air fully restores its initial linear dimensions in the temperature region of glass transition, which is shown by the dashed line in Fig. 4. When the sample is

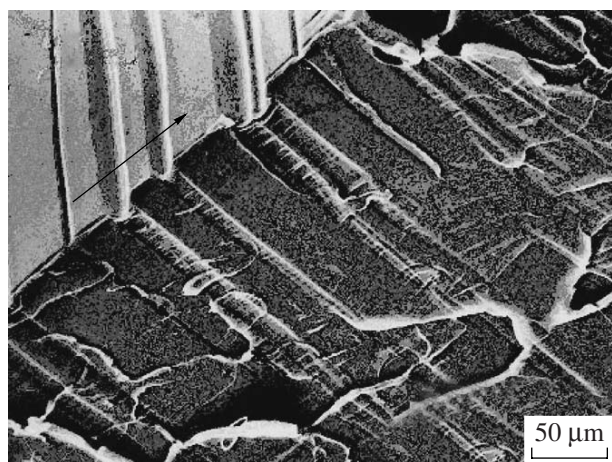


Fig. 6. SEM images of the solvent-crazed PC sample at room temperature in an AALE by 15%. Here and in Figs. 7 and 8, the direction of tensile drawing is shown by arrows.

annealed below the glass transition temperature, one can observe its partial shrinkage (by ~15%). The mechanism of this low-temperature contribution to the temperature-induced shrinkage of a glassy polymer has been described in detail in [15–17].

At the same time, the shrinkage of the solvent-crazed PC sample commences practically at room temperature; when the glass transition temperature T_g is attained, all crazes are fully healed and the initial polymer structure is recovered [18]. Evidently, the temperature-induced shrinkage of the solvent-crazed PC is provided by the processes taking place in crazes. The data shown in Fig. 5 directly confirm this conclusion. Figure 5 shows also the temperature dependence of a distance between the walls of an individual craze (curve 1) and the dimensions of a fragment of the undeformed polymer located between the crazes (curve 2). As is seen, the craze walls start to approach each other at temperatures well below the glass transition temperature of PC, which is shown in Fig. 5 by the dashed line. At the same time, with an increase in the annealing temperature, the dimensions of the fragment of the undeformed material between crazes appear to be somehow increased owing to its thermal expansion. It is of importance that a similar low-temperature shrinkage is observed for the solvent-crazed samples based on other glassy polymers [19].

Unusual thermomechanical properties of the solvent-crazed amorphous polymers can be easily explained by the fact that, in the highly dispersed oriented material of crazes, the glass transition temperature is depressed. This observation is confirmed by the experimental data obtained in the past decade [20, 21]. As was shown in the above publications, in thin films and in thin surface layers (tens and hundreds of nanometers) of bulk polymers, an enhanced large-scale ther-

mal motion takes place. Furthermore, according to some authors [22, 23], all glassy polymers at room temperature are enveloped by a thin layer of devitrified rubbery polymer.

Hence, the low-temperature shrinkage of the solvent-crazed glassy polymers (including PC) is provided only by the entropy-driven contraction of craze fibrils bridging the opposite craze walls. This contraction takes place once its local glass transition temperature is attained. However, many details of this process remain vague. In this case, the adopted standpoint is the following: during annealing of the solvent-crazed PC samples, craze walls approach each other; once T_g is attained, crazes appear to be completely healed, and the polymer sample recovers its initial structure and properties. Let us use the proposed procedure for the preparation of the test samples [4–8] for the direct microscopic studies in order to gain additional information concerning the mechanism of structural rearrangements taking place during annealing of the solvent-crazed PC samples.

Figure 6 shows the SEM image of the solvent-crazed PC sample. In this case, crazes are seen to intersect the whole cross section of the sample. The surface of crazes and fragments of the unoriented polymer has a well-pronounced smooth relief. To reveal (visualize) structural rearrangements taking place during annealing of the solvent-crazed PC sample, its surface was decorated with a thin (10 nm) metal coating; then, the coated sample was annealed below (70°C) and above T_g (155°C). For microscopic studies, the samples were fractured in liquid nitrogen and examined on a scanning electron microscope.

Figure 7a shows the SEM image of the solvent-crazed PC sample after its annealing at 70°C. At this annealing temperature, one can observe a certain depression on the surface of the polymer sample that is typical of the structure of a craze from which the AALE is removed. The fracture surface of the test sample is smooth. Nevertheless, one can observe a fibrillar porous structure of crazes, which spans inside the volume of the polymer sample. Shrinkage of the solvent-crazed samples during annealing is accompanied by structural rearrangements that can be identified by studying the surface of the craze, which isolates its internal structure from the outer space (Fig. 7b). The craze surface has a folded relief that is oriented along the axis of a craze. The above folds are formed when the opposite craze walls approach each other during annealing. The arrangement of the folds on the craze surface is irregular, and this observation suggests that the character of shrinkage of the crazed material is inhomogeneous.

The efficacy of the proposed procedure for the preparation of the test sample is most pronounced during study of the structure of the solvent-crazed PC samples

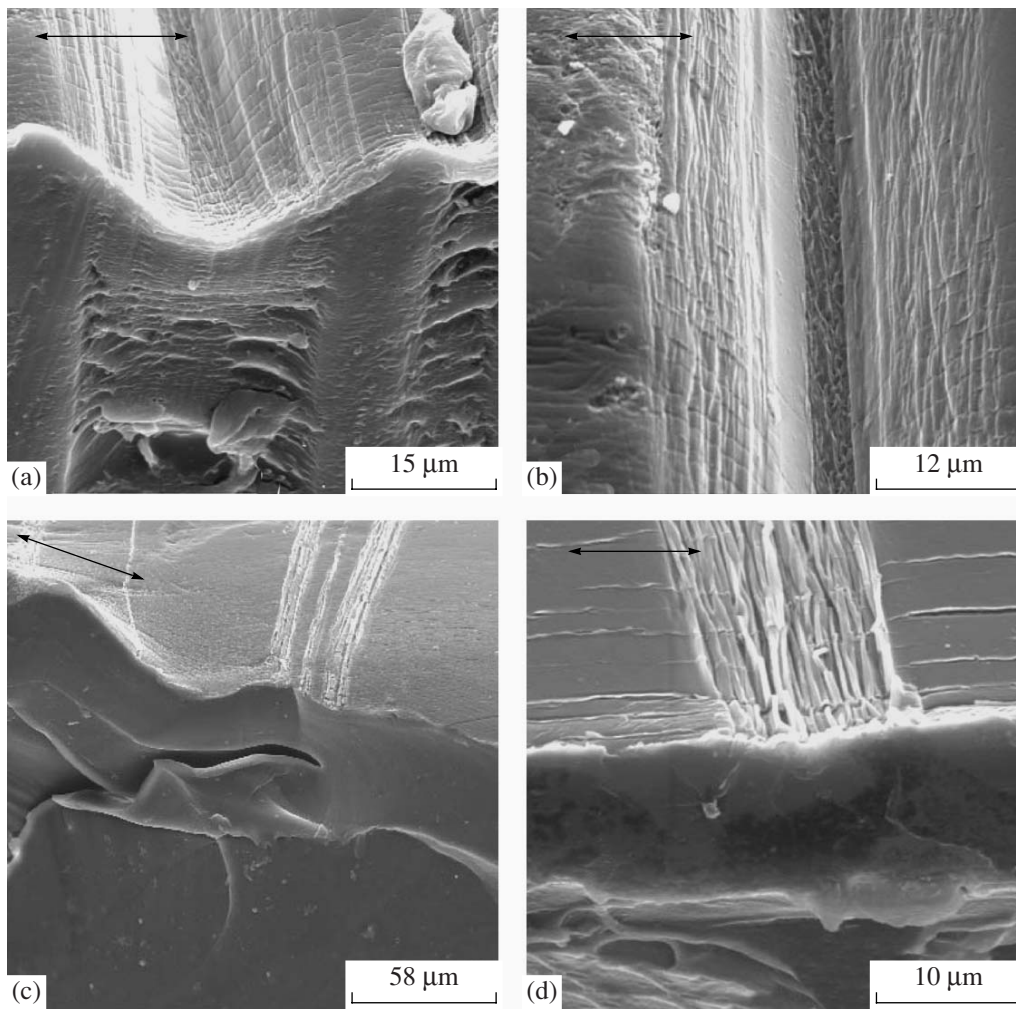


Fig. 7. SEM images of the solvent-crazed PC samples after their tensile drawing by 17% at room temperature in the presence of an AALE and annealing at (a, b) 70 and (c, d) 155°C.

after annealing above the glass transition temperature (155°C). As was mentioned above, at this annealing temperature, complete healing of the crazed structure takes place. However, the deposited coating makes it possible to recognize the sites where the crazes were located before the annealing (Fig. 7c). Within these regions, the coating acquires a well-pronounced folded relief. At the same time, at the fractured surface, one can observe a smooth relief without any traces of crazes. This observation does not imply that, within the volume of the polymer sample, crazes experience no healing which is observed on the surface of the sample owing to the deposited coating.

If the procedure of the preparation of test samples is modified, the processes taking place within the volume of the polymer sample can be visualized. Figure 8a displays the SEM image of the sample with a temperature–stress prehistory similar to that of the sample shown in Fig. 7a. The only difference between the test samples is

the following. The solvent-crazed PC sample was fractured at low temperatures; then, the fractured surface was coated with a thin metallic layer and the coated sample was annealed under the same annealing conditions as the sample shown in Fig. 7a. As is seen, as a result of this treatment, the folded relief is formed not only on the surface of the sample annealed at 70°C but also across its cross section (at the fractured surface). This observation indicates that the shrinkage of the crazed materials in the PC sample takes place in the whole volume, not only in the surface layer of crazes. Furthermore, the fractured surface contains regular folds that characterize the fine features of the temperature-induced low-temperature shrinkage of the crazed material.

The solvent-crazed PC samples after their annealing above the glass transition temperature (155°C) likewise contain regions of the folded relief not only on the surface of the sample but also in its volume (Fig. 8b). This

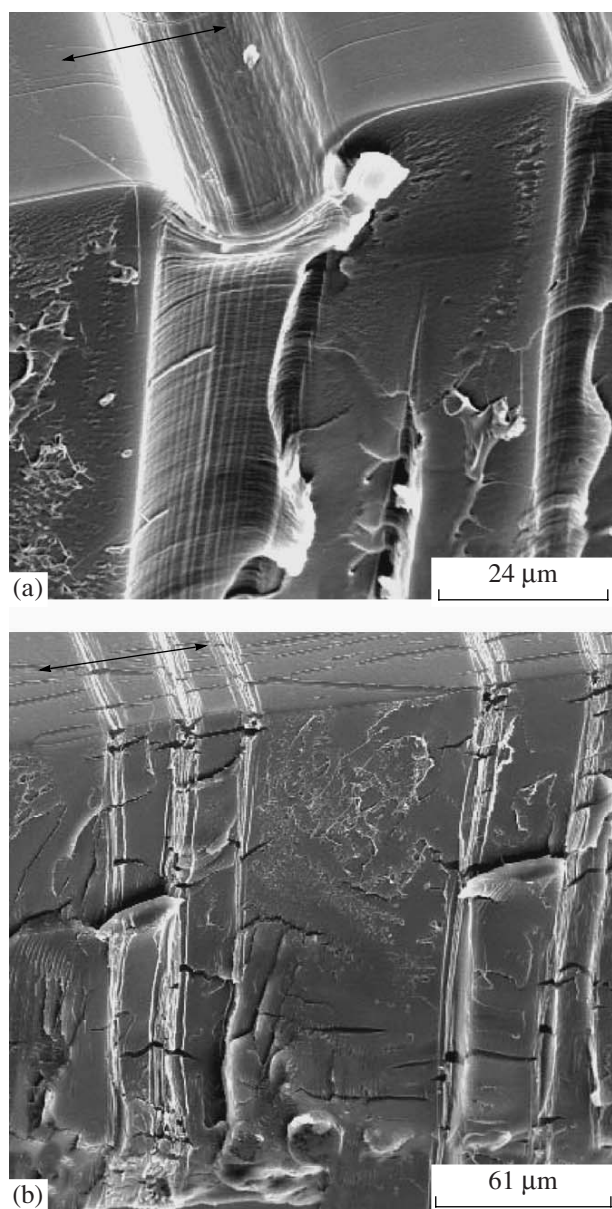


Fig. 8. SEM images of the solvent-crazed PC samples after their tensile drawing at room temperature in the presence of AALE by 17% and annealing at (a) 70 and (b) 155°C. A thin metallic coating was deposited onto the test sample after their low-temperature fracture.

evidence allows one to visualize the location of crazes at the surface and in the volume of the PC samples, even though annealing leads to the complete healing of crazes. At higher magnifications, one can see that the closure of craze walls (Fig. 7d) provides a very dense packing of the folds in the coating.

The advantages of the proposed procedure are the following. As a result of inelastic deformation of the polymer sample, its surface area is changed. The tensile drawing, rolling, and solvent crazing of polymers are accompanied by an increase in the surface area. The

reverse process (shrinkage of the oriented polymer) decreases the surface area. Evidently, changes in the surface area are provided by the transport of the polymer material from or into the volume of the sample. An analysis of the above microscopic data (Figs. 6, 7) leads us to conclude that the shrinkage is accompanied by the transfer of the polymer material into the volume of the sample via diffusion, so that the surface of the sample remains smooth at all stages. In this context, direct microscopic observations do not allow one to localize sites where the mass transfer from and into the volume of the polymer sample occurs. The deposited coating makes it possible to visualize the above sites and the direction of acting stresses. This circumstance is likely related to the fact that the deposited material is incompatible with the polymer and can not “follow” it on its way inside the volume of the sample.

The above experimental evidence demonstrates a high efficacy of the procedure of the preparation of the samples based on amorphous polymer for studying the structural features of its deformation by direct microscopic observations. These results suggest that the character of the structural rearrangements during the temperature-induced shrinkage of oriented amorphous polymer is primarily controlled by both the temperature interval of deformation and the mode of deformation. In particular, when the polymer sample is deformed above the glass transition temperature, its further temperature-induced shrinkage is homogeneous and proceeds via the cooperative diffusion of polymer chains in the whole volume of the polymer sample. When the polymer sample is deformed below the glass transition temperature, its temperature-induced shrinkage appears to be inhomogeneous and proceeds via the movement of rather large polymer blocks that alternate with the regions of inelastically deformed polymer (shear bands or crazes).

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