

Structural Tomography of Poly(methyl methacrylate) Deformed by Uniaxial Compression¹

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Abstract—A special procedure for studying structural rearrangements in polymers under their uniaxial compression was proposed. A cylindrical polymer sample commonly used in deformation tests was composed of thin polymer layers. After deformation, this sample was disassembled into individual layers, and their structure and properties were examined (the structural tomography). As was shown for PMMA, this procedure allows one to gain new information concerning the deformation mechanism of a glassy polymer. Using the method of atomic force microscopy, contributions from bulk and surface components of the polymer structure upon uniaxial compression were ascertained. In particular, upon annealing, the structural relaxation of the deformed glassy polymer was found to proceed in a complex way, thus revealing the two components of temperature-induced shrinkage: low-temperature (the surface component) and high-temperature (the bulk component).

INTRODUCTION

In our recent papers [1–3], a new mechanism of inelastic deformation of glassy polymers was proposed. According to this approach, at the early stages of deformation (below the yield point and in the yield region), one may observe polymer transition to an oriented state in the thinnest surface layers, which are localized in shear bands separating the regions of the initial undeformed polymer. It is important to mention that the glass transition temperature in surface layers is known to be markedly depressed [4]. As a result of inelastic deformation, the polymer acquires a complex structure, which is composed of two components and one component is characterized by a reduced glass transition temperature. It is this structural inhomogeneity of the deformed glassy polymers that provides a plausible explanation of some still unclear features of their behavior, including the mechanism of low-temperature shrinkage upon annealing [5, 6]. Noteworthy is that the proposed mechanism is based on direct microscopic observations obtained using a new universal procedure [1–3] and, thus, is almost free of any experimentally unjustified assumptions.

The objective of this work involves further development of the advanced novel procedure for the visualization of structural rearrangements during deformation of

glassy polymers. We studied PET and PMMA; PMMA is a glassy polymer that has been comprehensively studied from the viewpoint of the mechanism of its inelastic deformation. In this work, the procedure proposed in [1, 3] was compared with well-developed and common methods for polymer deformation under uniaxial compression [5, 6].

EXPERIMENTAL

In this work, we studied the commercial films of a biaxially oriented PET with a thickness of 20 μm and commercial sheets of an unoriented PMMA with a thickness of 1 mm. In the case of PET, the film surface was decorated with thin (15 nm) platinum layers using the method of ionic plasma deposition; the films were then annealed at 150–230°C. Commercial PMMA sheets were cut into circular samples with a diameter of 8–10 mm. After the as-prepared test samples were subjected to uniaxial compression at room temperature; their surface was coated by thin (15 nm) platinum layers using the method of ionic plasma deposition, and the samples were annealed at 50–130°C. Some samples were assembled into multilayered cylinders. To this end, circular samples cut from the PMMA sheet with a thickness of 1 mm were collected into a cylinder with a height-to-diameter ratio of 2 : 1. The as-prepared cylinder was placed between compressing surfaces in a testing machine and subjected to uniaxial compression by 30% at room temperature. After deformation, this cyl-

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inder was disassembled into individual layers. Each layer was coated with thin (15 nm) platinum layers using the method of ionic plasma deposition, and the as-prepared samples were annealed at 50–130°C. The surface of all the test samples was examined by a Nano-scope-3 atomic force microscope (Digital Instruments, Santa Barbara) under the regime of contact forces. The probe–sample interaction force was maintained at a level of 10^{-9} N in the scanning mode. Thermomechanical studies were performed on a Mettler TA 4000 thermal analyzer. Deformation of the samples under uniaxial compression was conducted on an Autograph AGS-10kNG tensile machine (Shimadzu) at a strain rate of 4.8 mm/min.

RESULTS AND DISCUSSION

As was mentioned above, one of the main objectives of this work concerns the visualization of structural rearrangements during inelastic polymer deformation. In the general case, the procedure for visualization of structural rearrangements first used in [1–3] is based on a fundamental property of solids. During their deformation, all solids change their surface area. While their volume may stay unchanged, their surface area always changes. The sign of this change may be different: the surface increases in tension (either uniaxial or plane) and decreases upon compression.

The proposed procedure for the visualization of structural rearrangements is based on this property of polymers. To apply this procedure, it is necessary to conduct deformation of the polymer sample so that one can follow changes in its surface area. The key trick in the preparation of the test samples for this procedure of the visualization of structural rearrangements is the following. In [5, 6], the polymer sample was subjected to the uniaxial compression when a tight cohesion between the polymer sample and the compressing surface took place; as a result, the sample became barrel-shaped. For direct microscopic observations, the deformation of the polymer sample was carried out under the conditions where it was able to slide freely along compressing surfaces. Given this, the height of the sample decreases due to an increase in its surface area which is in contact with compressing surfaces. It is these surfaces that change their area during either deformation or shrinkage. Evidently, this increase in the surface area is provided by a carryover of some polymer material from bulk to the surface during deformation or, vice versa, by polymer transfer from the surface to bulk. The surface area changes may be easily estimated and controlled by varying the diameter of the test sample before and after deformation (shrinkage).

When the above surface is covered with a thin coating prior to its deformation (shrinkage), this coating would display structural rearrangements in the deformed support upon its further deformation (shrinkage). The deformation (shrinkage) mechanism of the support controls the pattern of surface structuring of the

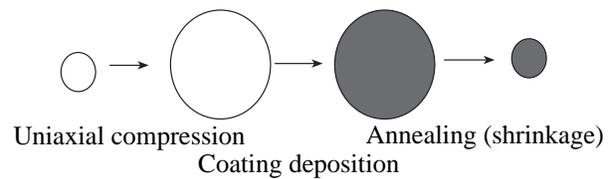


Fig. 1. Schematic representation of the experimental procedure for the visualization of structural rearrangements during temperature-induced shrinkage of the polymer sample after its deformation via uniaxial compression.

coating. In turn, the surface structuring of the coating provides information concerning the mechanism of polymer deformation. Relief formation in the coating may be easily studied by direct microscopic observations. Preparation of the test samples for such examination is schematically presented in Fig. 1.

Let us consider the character of structural rearrangements during a uniform affine deformation of polymer in its rubbery state. This mode of polymer deformation is well studied, and its mechanism is fairly described in terms of the statistical theory of high elasticity. To this end, it seems convenient to use the commercial film of the biaxially oriented PET. As is known, such films are prepared by a biaxial drawing of PET in the temperature interval above its glass transition temperature (85–95°C) and subsequent thermal stabilization at 180–210°C [7]. Annealing of this film at 180–230°C leads to its plane shrinkage [8–10]. When this film is coated with a thin metallic layer before annealing (shrinkage), the as-developed pattern in the coating corresponds to a uniform plane compression of the polymer support. Figure 2 presents the microscopic image of this PET sample after its plane shrinkage by 16% upon annealing at 200°C. As a result of the compression of the coating on the surface of the polymer sample after its shrinkage, one may observe the development of a strikingly regular and beautiful relief, which uniformly covers the entire polymer surface; this relief is characterized by regular folds with almost similar dimensions.

The mechanism behind the development of the regular relief during the compression of a rigid coating on the surface of a soft support was described in [11, 12]. The development of such a regular relief presents a certain mode of the Euler stability loss in anisodiametric solids upon their uniaxial compression. This phenomenon is observed upon the uniaxial compression of an anisodiametric solid (fiber, film, membrane). When a certain critical stress is achieved during compression, anisodiametric solids lose their stability and acquire a half-wave shape. If an anisodiametric solid (including, a thin rigid coating) is strongly attached to a soft support (substratum), the whole pattern of the stability loss in the coating is dramatically changed. At a certain critical compressive stress, the body is unable to assume a half-wave shape because, upon its deviation from a rec-

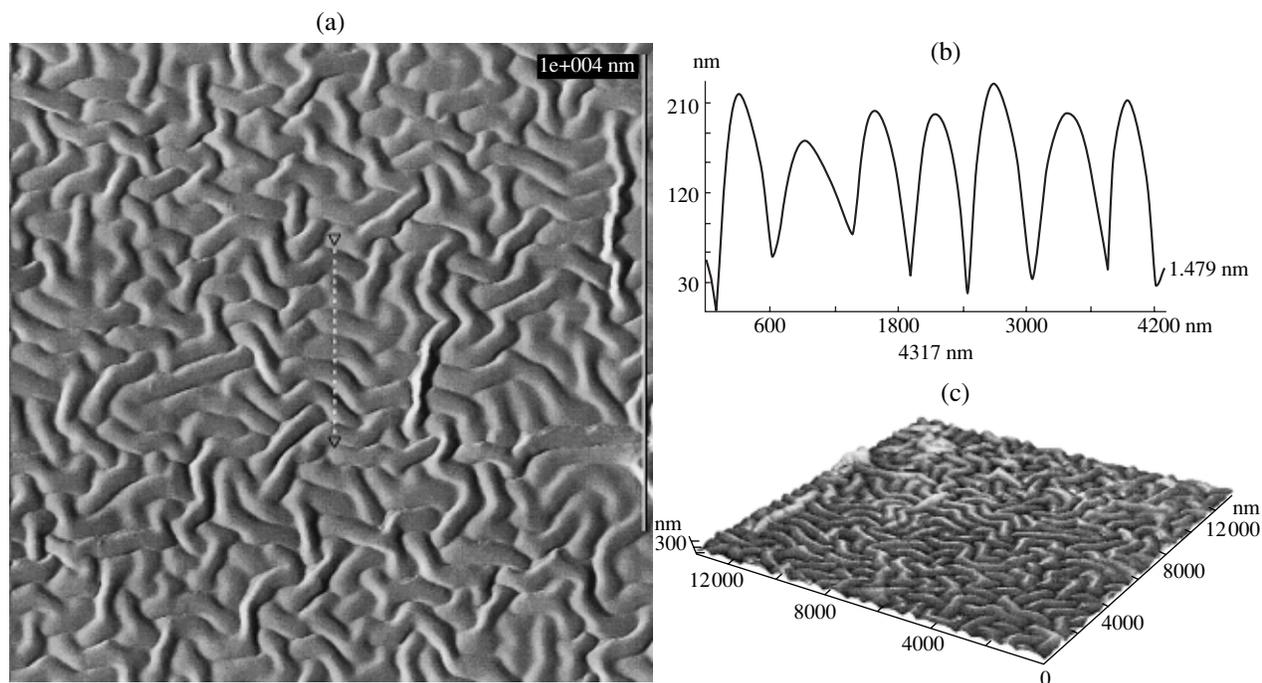


Fig. 2. (a) AFM image, (b) surface profilogram, and (c) 3D reconstruction of AFM image of the biaxially oriented PET sample coated with a thin (15 nm) platinum layer after its annealing at 210°C.

tilinear form, it would be affected by the restoring force acting from the support; this force is proportional to the deviation. As a result of such an interaction between the external applied stress and the as-induced inner resistance from the support, the coating inevitably folds like a folded rule and assumes a sinusoidal shape with a certain constant wave period.

From the viewpoint of the subject of the present work, it is important to mention only the following aspect. The affine uniform compression of a rubbery polymer support assists the development of a peculiar microrelief in the rigid coating. A typical example of this relief is shown in Fig. 2. Naturally, the pattern of the as-induced microrelief is almost independent of the nature of either coating or support [8–10].

Let us consider the effect of shrinkage of the polymer sample deformed at temperatures below its glass transition temperature on the surface structuring in the polymer–rigid coating system. Figure 3 presents several AFM images of the surface of PMMA samples with a thin metallic coating after their shrinkage upon annealing. The test samples were preliminarily deformed by 20% under uniaxial compression. Different values of strain recovery were achieved by varying the annealing temperature. As is well seen (Fig. 3a), at low annealing temperatures (50°C), polymer shrinkage proceeds in a rather nonuniform way. Polymer surface area decreases via retraction of the surface material into the polymer bulk in narrow rectilinear regions (shear bands), which intersect each other and the surface at different angles.

As the annealing temperature (the level of shrinkage) is increased to 70°C, the density of shear bands increases (Fig. 3b). It is important to mention that the polymer located between the shear bands is virtually not involved in shrinkage, as the coating surface in these regions remains smooth and flat. If the deformed PMMA sample is annealed at temperatures close and above the glass transition temperature (90°C) when its shrinkage exceeds 50%, the surface structuring pattern is changed noticeably (Fig. 3c). As is well seen, in addition to rectilinear shear bands, one may observe a marked transformation in regions between them. Almost the entire polymer surface acquires a folded relief whose morphology is similar to that of the relief induced upon uniform shrinkage of the rubbery polymer (cf. Figs. 2 and 3c). Let us note that these results fully agree with the earlier experimental data for polystyrene and PET [1–3]. The latter fact attests that the mechanisms of temperature-induced shrinkage and deformation of glassy polymers are common in nature.

Despite the above-mentioned common nature behind the mechanisms of inelastic deformation of various glassy polymers, the methods of preparing the test samples used in this work are somewhat different from those applied in numerous earlier studies [13–16]. Usually, the deformation of polymers under uniaxial compression is performed for cylindrical samples. As a result, the polymer sample becomes barrel-shaped. A reverse process of the temperature-induced strain recovery is studied by measuring the height recovery of the deformed samples upon their annealing. Let us

remember that, in [1–3], the process of surface structuring in the samples with the deposited coating was investigated as follows. The test disc-shaped samples with a diameter of 10 mm were sandwiched between two discs based on a plastic metallic alloy (an eutectic lead–tin alloy with a finely grained crystalline structure compared with that in pure metals, and a high plasticity); the diameter of metallic discs was 13 mm, and their thickness was 1 mm. Metallic discs and sandwiched polymer samples were simultaneously squeezed at room temperature. Evidently, under these conditions, the necessary degree of polymer compression can be easily achieved; however, one cannot record the uniaxial compression curve because, in this case, the mechanical response is related to both the polymer and the material of pads, which provide a free slide of the sample with respect to compressing surfaces. This fact somehow impedes the interpretation of the results, especially, when, for example, a difference in structural rearrangements in the polymer upon its deformation below and above the yield point is probed because, in this case, any definition of the yield point becomes rather ambiguous.

To circumvent the above problem, we propose a new simple and vivid procedure for studying structural rearrangements in the deformed polymer. For this purpose, we prepared a full analog of the sample, which is traditionally used in the mechanical studies of polymer response under uniaxial compression [5, 6]. The test sample was a cylinder with a diameter of 9–12 mm and a height of 18–24 mm. However, in contrast to traditional samples, this cylinder was composed of discs with a thickness of ~1 mm (Fig. 4). The uniaxial compression of this sample not only allows one to record the traditional stress–strain curve of uniaxial compression. After deformation, this sample may be disassembled into individual layers, and each layer may be studied using the above procedure of direct microscopic observations. Actually, this approach presents the means for structural tomography of the deformed polymer.

Deformation of the as-prepared samples entails two aspects, which make it possible to perceive that this tomographic procedure does not introduce any serious consequences to the deformation mechanism on the whole. First, under the action of uniaxial compression, a multilayered sample (its structure is shown in Fig. 4) deforms as a single unit; as a result, a cylindrical sample becomes barrel-shaped in full agreement with shape changes during the deformation of a monolithic sample. Second, the stress–strain curve of the multilayered sample under uniaxial compression is consistent with the corresponding uniaxial compression curve of a monolithic polymer.

This approach allows one to obtain new important information concerning the deformed polymer, which is similar to information extracted using the tomographic method. Figure 5 presents the strain of each individual polymer layer plotted against its location

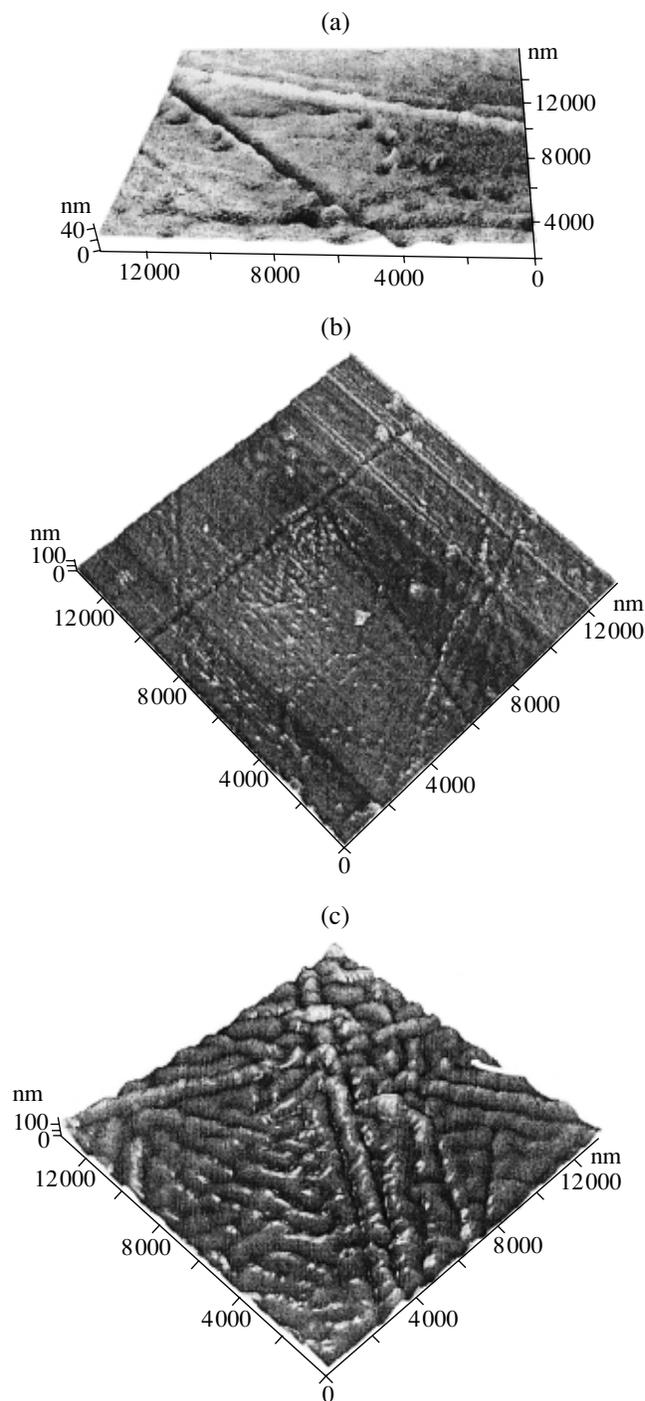


Fig. 3. AFM images of PMMA samples after their uniaxial compression by 20% and annealing at (a) 50, (b) 70, and (c) 90°C after deposition of thin (15 nm) platinum coating.

(distance) with respect to the compressive surface. The experimental data shown in Fig. 5 suggest that the structure of the polymer sample after its uniaxial compression is highly heterogeneous. Actually, the PMMA sample after its uniaxial compression by 30% contains regions with quite different local strains. First 3 to 4

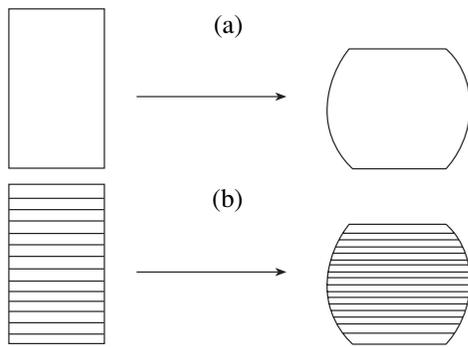


Fig. 4. Schematic representation of uniaxial compression tests of the polymer sample, which was (a) described in [5, 6] and (b) used in this work.

layers adjacent to compressing surfaces virtually contain no residual strain. At the same time, in the central part of the barrel-shaped polymer sample, the strain exceeds 70%.

The proposed procedure enables one to study the temperature-induced recovery of the dimensions of each layer from the above barrel-shaped sample. In Fig. 6, these data are presented as the absolute values of height recovery of each layer from the barrel-shaped sample as a function of the annealing temperature. As is well seen, depending on the location of each layer in the entire structure of the sample, three different modes of thermomechanical behavior are observed. Layers 1–3 with respect to their location relative to compressing surfaces slightly change their dimensions upon annealing. Their thermomechanical behavior is almost similar to that of the initial undeformed PMMA (the lower curve); in this connection, these data are not shown in Fig. 6. Sample 4 shows a well-pronounced low-temper-

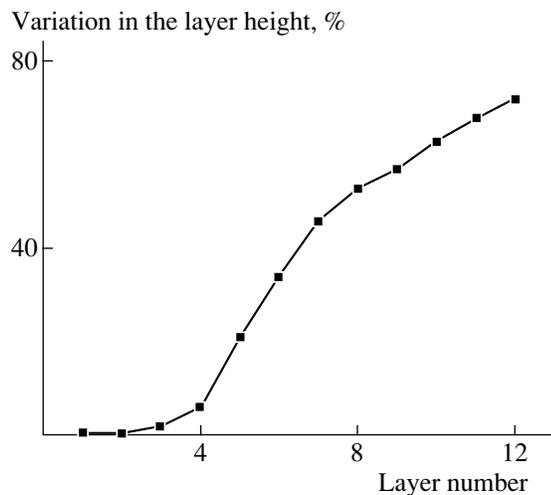


Fig. 5. Uniaxial compression strain of individual layers of PMMA (the initial thickness of each layer is 1 mm) vs. their location with respect to the compressing surface. The total uniaxial compression strain of the multilayered sample is equal to 30%.

ature component of the temperature-induced strain recovery. This component comes into play at an annealing temperature of $\sim 50\text{--}55^\circ\text{C}$. Just at this temperature, the strain recovery of all the other fragments of the multilayered sample commences. Furthermore, for all the test samples, their high-temperature component of the temperature-induced strain recovery (in the glass transition region of PMMA) arises and becomes better pronounced. With increasing the distance from the “barrel” bottom, this contribution to the temperature-induced shrinkage gradually increases, and, finally, its absolute value exceeds the low-temperature component.

Hence, the deformation of a cylindrical polymer sample, which is commonly used in uniaxial compression experiments, appears to be rather inhomogeneous. After its uniaxial compression, the deformed sample contains regions with different strains. As follows from Fig. 6, these layers are characterized not only by different strains but their behavior upon further annealing also appears to be different.

The advantages of the tomographic approach are not limited by gaining new information concerning the mechanical and thermomechanical response of the systems under study. The combination of the tomographic approach and the earlier procedure for visualization of structural rearrangements [1–3] provides a deeper insight into the bulk of the deformed polymer. Actually, after the deformation of the multilayered sample, it could be disassembled into the component layers. The surface of each layer may be decorated by deposition of the rigid coating and studied by direct microscopic observations after annealing and the related temperature-induced shrinkage.

Such experiments were conducted, and their results are summarized in Fig. 7. As is well seen (curve 3 in

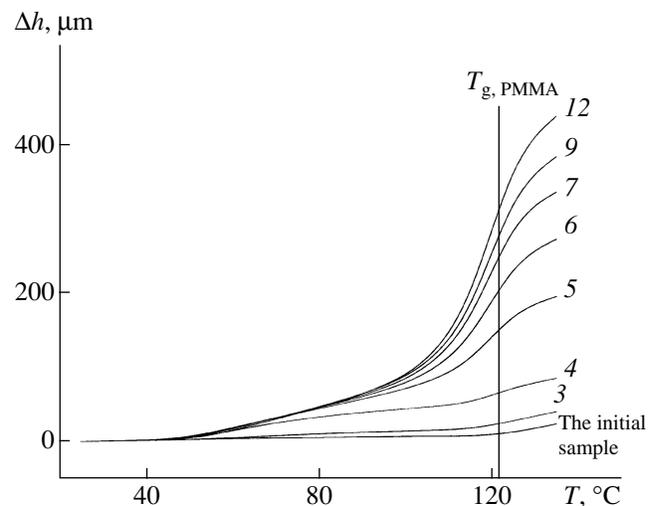


Fig. 6. Absolute changes in the height of individual PMMA layers after deformation of the multilayered sample by 30% at room temperature. Numbers at curves correspond to the position of each layer with respect to the compressing surface.

Fig. 6), layer 3, which is relatively close to the compressing surface, is characterized by a low strain and, correspondingly, by a low degree of shrinkage (1.7%). The shrinkage of this sample proceeds via retraction of the polymer material from the surface into bulk in well-pronounced shear bands. With increasing the strain and, correspondingly, shrinkage to 20.8% (layer 5), the material between shear bands also appears to be involved in the temperature-induced strain recovery (Fig. 7b). Figure 7 shows the initial stage of this involvement; as a result, the as-formed relief turns out to be rather imperfect and irregular. As the degree of compression in the coating increases to 45% (layer 7), a highly regular and perfect relief is developed; one may hardly distinguish its difference from the microrelief formed upon the shrinkage of the polymer sample deformed above its glass transition temperature (cf. Figs. 2 and 7c). A striking similarity between these two patterns suggests an ultimate closeness or even identity of the mechanisms behind the microrelief development. At high strains, the shrinkage of a glassy polymer proceeds in the same way as the shrinkage of the polymer sample deformed above its glass transition temperature. The key feature of this deformation concerns its homogeneity (affinity). Hence, it is not surprising that most of the polymer material is involved in the temperature-induced shrinkage in the temperature region of its glass transition (Fig. 6). Its bulk rather than surface character is related to the fact that, at this stage of polymer deformation, no new surfaces (shear bands) are formed. This evidence also supports earlier conclusions concerning the mechanism of inelastic deformation of polymer glasses derived for other polymers [1–3].

The above experimental evidence leads us to outline the deformation mechanism of a glassy polymer under uniaxial compression as follows.

At the early stages of deformation (below the yield point and in the yield region), nucleation and propagation (percolation) of narrow regions (shear bands) of a plastically deformed polymer through the entire polymer cross section take place. Shear bands in polymers are appreciably different from those in low-molecular-mass solids. As was found [17–19], shear bands in polymers are filled with a highly dispersed oriented fibrillar material which is identical to that in the volume of crazes.

This important similarity is proved by direct microscopic observations. When the material containing shear bands is subjected to a minor stretching, the shear bands open and expose their crazelike structure. In this case, this similarity with the craze structure is so evident that such shear bands are referred to as shear band crazes [18]. A certain morphological difference between a shear band craze and a classical craze concerns the fact that fibrils in such shear bands are inclined with respect to the craze plane.

The key difference between the craze structure and shear bands is that shear bands have no any marked porosity, which is typical of the craze structure. Never-

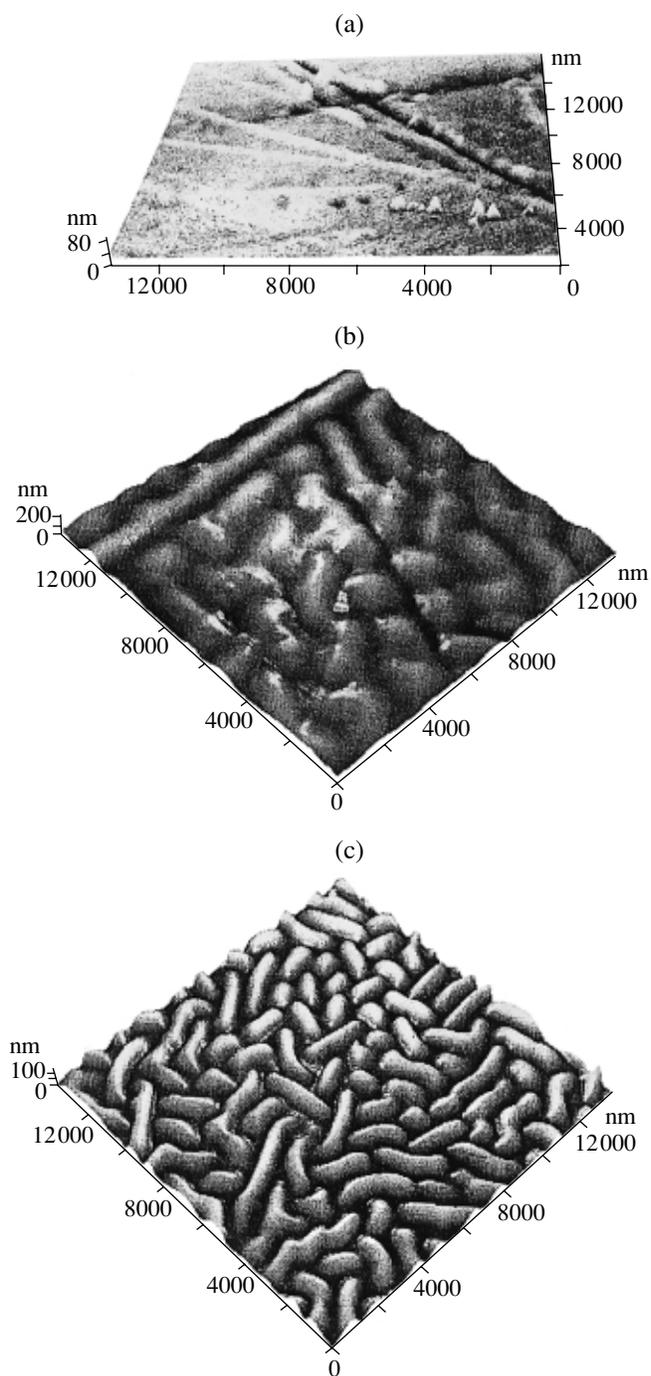


Fig. 7. AFM images of individual layers after deformation of the multilayered PMMA sample by 30%. The individual layers were coated with a thin (15 nm) platinum coating and annealed at 130°C. Shrinkage: (a) 1.7, (b) 20.8, and (c) 45%.

theless, shear bands are characterized by a much lower density than that of the initial bulk polymer. This conclusion is supported, in particular, by a higher rate of penetration of low-molecular-mass compounds into shear bands as compared with the surrounding bulk polymer [2, 20, 21].

The above speculations give us grounds to conclude that deformation of a glassy polymer, which is accompanied by the nucleation of shear bands, actually presents its loading with interfacial surfaces. As the diameters of fibrils in the craze structure and shear bands equal hundreds of angstroms, the polymer material in these regions is actually dispersed into a certain surface layer. In a fibrillar structure, the polymer is not only dispersed down to fine aggregates but also acquires a well-pronounced molecular orientation [22]. Naturally, the oriented glassy polymer in the above local regions is capable of shrinkage during annealing when its glass transition temperature is achieved. It should be noted that the glass transition temperature in thin surface layers is markedly depressed compared to the glass transition temperature of the initial bulk polymer [4]. This is the key reason behind polymer relaxation in shear bands by tens degrees below the glass transition temperature of the bulk polymer [23]. As shear bands cross (percolate) the whole cross section of the polymer sample, the shrinkage of the material in shear bands upon annealing leads to the low-temperature shrinkage of the entire deformed sample.

Hence, shear bands show a well-pronounced oriented fibrillar structure and they are separated from the bulk polymer by interfacial boundaries. Due to the presence of a highly dispersed "matter" in the shear bands of the deformed polymer, the surface component of the entire polymer structure is induced.

A further deformation (the plateau region) proceeds via a total orientation of the polymer material localized between the grown shear bands. This process is not accompanied by the formation of new interfacial surfaces and, by its essence, is similar to the polymer orientation above its glass transition temperature. At this stage, the bulk (volume) component of the entire polymer structure is developed.

Therefore, the deformation of a glassy polymer leads to the formation of a complex structure composed of two interconnected components: a certain part of the oriented polymer localized in shear bands (the surface component) and the oriented polymer localized in regions between shear bands (the volume or bulk component). It is important that the shear bands nucleated at the early stages of deformation are involved in the polymer structure even after its complete transition into an oriented state and preserve their own features and properties. The surface component of the polymer structure is characterized by a depressed glass transition temperature within a wide temperature interval.

The annealing of this bicomponent system formed under inelastic deformation of the glassy polymer is accompanied by the following structural rearrangements. When the deformed polymer sample is heated in the temperature interval below its glass transition temperature, one may observe its shrinkage in shear bands (the surface component), where the polymer has a decreased glass transition temperature in a wide tem-

perature range (low-temperature contribution to the temperature-induced strain recovery).

A further heating leads to the relaxation of the basic part of the oriented polymer (the volume component) which, in fact, is similar to the shrinkage of the bulk rubbery polymer and, therefore, takes place in its glass transition region (the high-temperature contribution to the temperature-induced strain recovery).

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