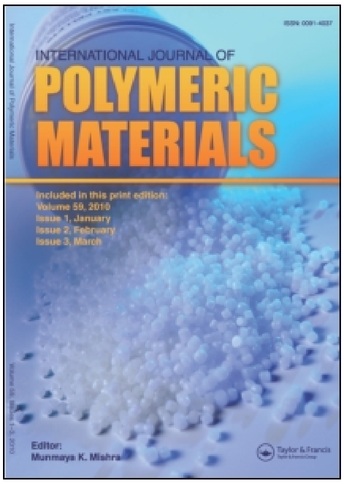

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Physical and Mechanical Behavior of Polymer Glasses II. Poly(Methyl Methacrylate)

M. S. Arzhakov[a]; S. A. Arzhakov[a]
[a] Polymer Department, Faculty of Chemistry, Lomonosov Moscow State University, Moscow, Russia

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Physical and Mechanical Behavior of Polymer Glasses
II. Poly(Methyl Methacrylate)

M. S. ARZHAKOV and S. A. ARZHAKOV

Polymer Department, Faculty of Chemistry, Lomonosov Moscow State University, Vorob'evy Gory, Moscow, 119899 Russia

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Physical and mechanical behavior of PMMA samples compressed in the press mold was characterized. The development of plastic deformation and accumulation of residual deformation were shown to take place even at temperatures far below glass transition temperature. The pressure dependence of glass transition temperature as well as the compression stress-strain diagram of PMMA samples showed well-pronounced inflection points at pressures of 0.09–0.1 and 0.38–0.4 GPa. Physical and mechanical behavior of PMMA was discussed in terms of structural pattern of plastic deformation concerning the gradual involvement of structural sublevels with different packing densities in deformation and relaxation.

Keywords: PMMA; plastic deformation; relaxation; structure

INTRODUCTION

Temperature-induced relaxation of plastic deformation in polymer glasses is known [1–4] to involve low-temperature component within glassy state and high-temperature component at temperatures close to glass transition temperature T_g. The high-temperature component is associated with the transition of excited chain conformations to their initial equilibrium state via segmental mobility of polymer chains. The origin of the low-temperature component of relaxation of residual plastic deformation ε_{res} is not so clear. At the present time, the appearance of this mode of relaxation is treated in terms of two approaches: recovery of small-scale plastic shear transformations [3, 4] (i) and structural inhomogeneity of glassy polymers [2, 5, 6] (ii). Within the framework of the latter approach, structure of glassy polymer involves a set of structural sublevels with different packing densities and degrees of ordering.

Each of these structural sublevels is characterized by its own relaxation time and activation energy of segmental mobility. Hence, at each temperature below T_g, local segmental mobility in certain structural sublevels is allowed. With increasing temperature, structural sublevels with higher packing densities acquire segmental mobility, and finally at T_g, all polymer sample is involved in segmental mobility. Hence, a wide spectrum of segmental mobility in glassy polymer is provided by the existence of a set of structural sublevels with different packing densities.

As shown earlier [5, 6], there is a good correlation between the contribution of low-temperature component to the temperature-induced relaxation of ε_{res} and mechanical parameters of uniaxial compression of glassy polymer. This experimental evidence allowed one to suggest that the deformation of polymer at strains below yield strain ε_y is developed via deformation of structural sublevels with lower packing densities. In the case of uniaxial compression, these speculations were supported by structural studies of deformation of PMMA samples using the method of positron annihilation lifetime spectroscopy [7–9].

The results obtained allowed us to advance the following structural pattern of the development of plastic deformation in glassy polymers. At strains below ε_y, deformation is controlled by the stress-induced segmental mobility within the structural sublevels with lower packing densities. At temperatures well below T_g, temperature-induced relaxation of this portion of plastic deformation is controlled by low-temperature portion of the spectrum of segmental mobility, which is provided by gradual appearance of segmental mobility in the above structural sublevels. At strains above ε_y, plastic deformation is controlled by the stress-induced segmental mobility within the densely packed structural sublevels. This portion of plastic deformation is able to relax at temperatures close to T_g when all polymer sample is involved in segmental mobility.

Obviously, structural inhomogeneity of polymer glasses, that is, inhomogeneity of packing densities within different structural sublevels, seems to be even more pronounced under the triaxial compression of polymers. Uniaxial compression is accompanied by increase in lateral sizes of the polymer sample, and plastic deformation shows rather complicated character. To gain a detailed information concerning the effect of structural inhomogeneity on the development of plastic deformation, one should invoke such mode of deformation when compression-induced decrease in the height of the sample is accompanied by no changes in lateral direction. This particular mode of loading may be realized by compression of polymer samples in cylindrical press mold. Earlier [10], this mode of compression was applied to investigate the monolithization of powderlike polymer thermoplastics.

Note that, the studies concerning the deformation of powderlike glassy thermoplastics in the press mold under the parallel action of pressure and temperature evidenced that temperature-induced relaxation of plastic deformation of powderlike polymer also involves low-temperature component and high-temperature component. Both components are associated with the appearance of segmental mobility in deformed polymer sample on heating. The mechanism of the low-temperature component of relaxation is supposed to be controlled by the activation of low-temperature segmental mobility induced by the stored inner stress in the deformed polymer sample. However, the complicated character of deformation of powderlike polymers under their compression in the press mold does not allow one to obtain a detailed information concerning the deformation behavior of glassy polymers at this particular mode of loading.

The aim of this work was to study the deformation of bulk PMMA in the press mold to reveal the effect of structural inhomogeneity of glassy polymers on their physical and mechanical behavior.

EXPERIMENTAL

In this work, PMMA prepared by bulk polymerization ($M_\eta = 3 \times 10^6$) was used. The test samples were cylinders with a height of 20 mm. Prior to testing, polymer samples were annealed at temperatures above T_g by 10–15 K, and then they were slowly cooled down to room temperature.

To study the temperature-induced relaxation of plastic deformation, polymer samples were compressed in the cylindrical press mold with a diameter of 10 mm up to pressures 0.3 and 0.5 GPa with a strain rate of 0.1 mm/min. Deformation temperatures T_{def} were varied from 173 to 463 K. The tests were performed using an UTS-100 tensile machine (Germany). To provide the close contact between sample and press mold, the following procedure was used. The difference between thermal expansion of the sample and the press mold was accounted for. When tests were performed at low temperatures, the sample with a certain diameter was placed in the press mold at temperatures by 10–20 K below T_{def}. As temperature increases to T_{def}, a close contact between the sample and the press mold was provided as a result of thermal expansion of polymer. When tests were performed at elevated temperatures, the sample with the certain diameter was placed in the press mold at room temperature. As temperature increases to T_{def} the close contact between sample and press mold was provided as a result of thermal expansion of polymer.

Note that, reference hydrostatic compression of bulk PMMA was carried out. These tests demonstrated a fair agreement between the changes in the volume of the samples compressed in the press mold and under hydrostatic loading in the studied range of pressures and temperatures. This experimental evidence allowed one to conclude that compression in the mold does not involve uniaxial deformation because of the clearance between mold and sample.

After loading of the samples up to a certain pressure they were kept at this pressure until their equilibrium height was attained. Then, the stressed samples were cooled down with liquid nitrogen and unloaded at this temperature. The free-standing samples were heated from 213 K at a heating rate of 1 K/min. The relaxation (recovery) of residual deformation was estimated by measuring the height of the samples with an accuracy of ±0.001 mm.

To obtain the pressure dependence of T_g, the isothermal compressibility of PMMA was studied at pressures varying from 0.03 to 0.66 GPa at temperatures from 370 to 490 K. To provide a close contact between the sample and the press mold, the samples in the press mold were heated up to 500 K. Then, the samples were loaded to a pressure of 0.015 GPa and kept at this pressure for 15 min. Then, the stressed samples were cooled down in the press mold to the test temperature with a rate of 0.2 K/min. At test temperature, the samples were kept at this pressure until the equilibrium height was attained. After this procedure the samples were unloaded and kept at test temperature until the equilibrium height h_o was attained. No changes in the weight of the sample, molecular mass of polymer, and concentration of residual monomer in PMMA evidenced that during this training physical and chemical changes in polymer did not take place.

At the test temperature, the sample were compressed up to a certain pressure with a loading rate of 0.1 mm/min. The stressed samples were kept at this pressure until the equilibrium height h_p was attained. Then the pressure was increased. This experimental evidence allowed one to estimate the specific equilibrium volume of polymer at a given pressure and temperature. Thermal expansion and compressibility of working parts of tensile machine were taken into account. Specific volume was estimated with an accuracy of ± 0.25%.

The pressure dependence of specific volume of polymer at a given temperature allowed one to estimate the isothermal compressibility factor β, that is, the relative change in volume with increasing pressure by ΔP:

$$\beta = \Delta V / V_o \Delta P,$$

where

$$\Delta V = V_o - V_P,$$

V_o is the specific volume of the polymer before loading, V_P is the specific volume of the polymer at pressure P. Temperature dependences of β at different pressures are shown in Figure 1.

The deformation behavior of PMMA under the compression in the press mold was studied at 293 K. Before tests, the samples were treated according to the procedure similar to that used for the studies of isothermal compressibility of PMMA samples. The equilibrium height of the as-prepared sample was h_o. The samples were loaded in the press mold up to a certain pressure with a loading rate of 0.1 mm/min. At this pressure, the samples were kept until the equilibrium height h_p was attained. Then, the pressure was again increased up to a certain value. Deformation of polymer was estimated as $\varepsilon = (h_o - h_P)/h_o$.

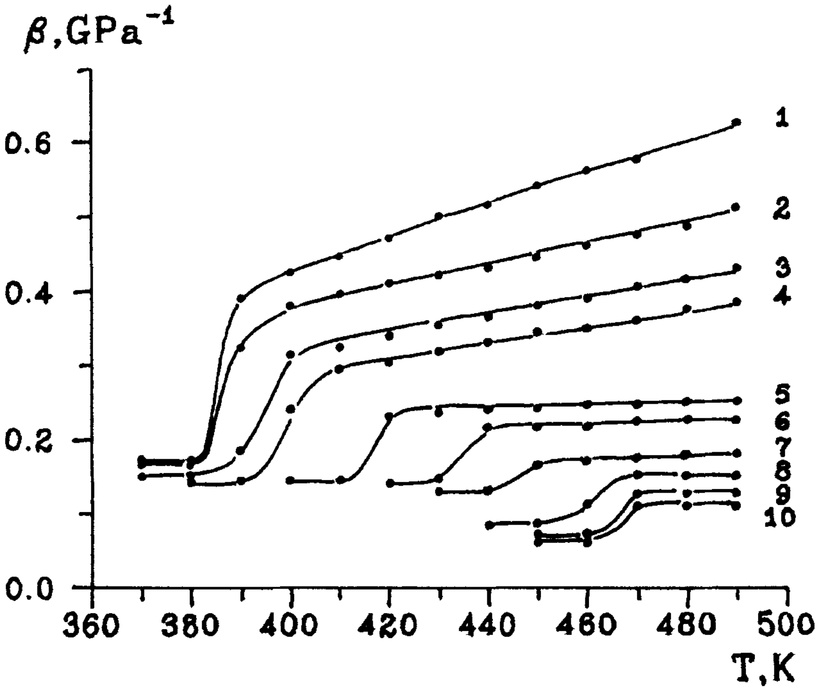

FIGURE 1 Temperature dependences of compressibility factor β for PMMA at pressures: 0.03 (1), 0.06 (2), 0.09 (3), 0.12 (4), 0.21 (5), 0.3 (6), 0.39 (7), 0.48 (8), 0.6 (9) and 0.66 GPa (10).

RESULTS AND DISCUSSION

Figure 2 shows the temperature dependences of residual deformation ε_{res} for PMMA samples compressed in the press mold in the wide range of temperatures. For the samples compressed at temperatures below glass transition temperature T_g, the recovery of ε_{res} takes place within the glassy state via low-temperature component of relaxation (Fig. 2a, curves 1–5; Fig. 2b, curve 1). A complete relaxation of ε_{res} is observed at temperatures close to deformation temperature T_{def}. Hence, at temperatures far below T_g (the lowest T_{def} was 173 K), compression of PMMA samples in the press mold is accompanied by development of plastic deformation and accumulation of ε_{res}.

Note that, for the samples compressed at the temperature of liquid nitrogen (78 K), the complete relaxation takes place during unloading at this temperature. This experimental evidence allows one to conclude that, in this case, only elastic Hookean deformation occurs. Critical temperature corresponding to the transition from elastic Hookean deformation to plastic deformation lies in the temperature range from 78 to 173 K.

According to the structural pattern of plastic deformation of polymer glasses [5, 6], the development of plastic deformation of polymer under compression in the press mold is likely to be associated with the stress-induced segmental mobility within the structural sublevels with lower packing densities. On heating unloaded samples, temperature-induced segmental mobility within above structural sublevels results in relaxation of ε_{res} within glassy state.

For PMMA samples compressed at temperature much above T_g, relaxation of ε_{res} is observed in the vicinity of T_g (Fig. 2a, curve 6). This implies that, at this temperature deformation of PMMA samples is

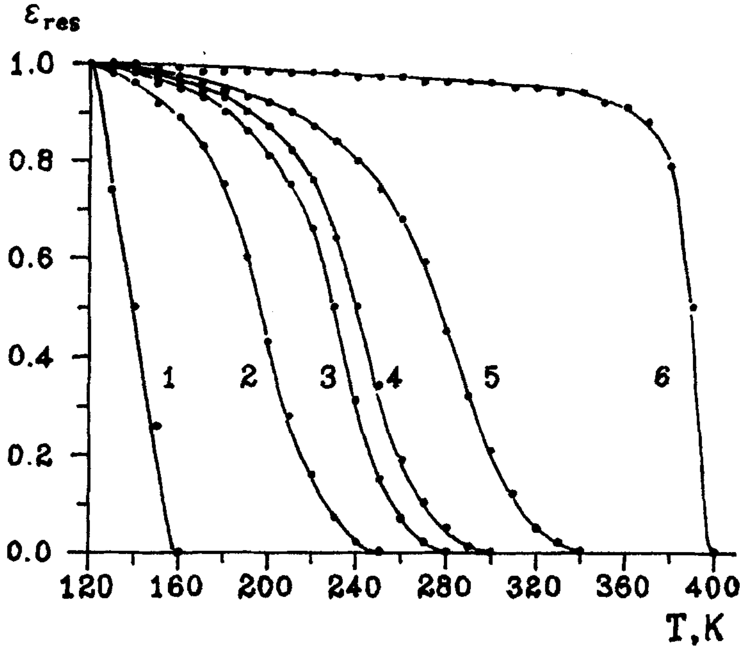

FIGURE 2a Temperature dependences of residual deformation ε_{res} for PMMA samples compressed to 0.3 GPa at temperatures 173 (1), 233 (2), 273 (3), 293 (4), 353 (5) and 463 K (6) (A); and to 0.5 GPa at temperatures 353 (1) and 393 K (2) (B).

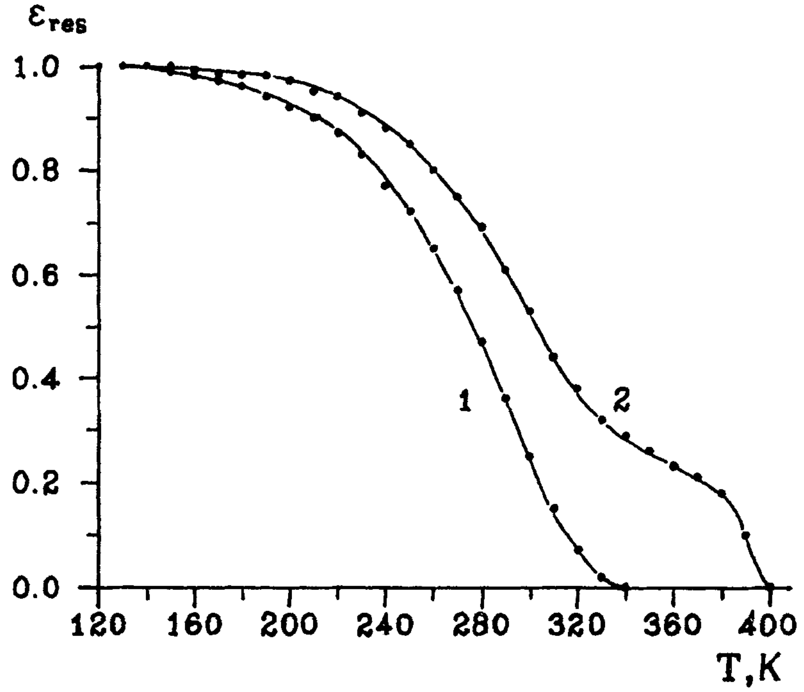

FIGURE 2b (Contd.).

accompanied by relaxation of low-temperature mode of the spectrum of segmental mobility during compression as a result of the appearance of segmental mobility within structural sublevels with lower packing densities. Hence, relaxation of ε_{res} takes place at temperatures close to T_g because of temperature-induced segmental mobility in the whole polymer sample.

For PMMA samples compressed at T_g, relaxation of ε_{res} involves two components: low-temperature component within glassy state and high-temperature component in the vicinity of T_g (Fig. 2b, curve 2). The results discussed above allow one to conclude that the appearance of two-stage recovery of ε_{res} is likely to be related to an increase in T_g during compression. At the initial stage, deformation takes place at T_g (393 K). In this case, during compression relaxation of low-temperature mode of the spectrum of segmental mobility is observed, and accumulation of high-temperature component of relaxation takes place. As a result of loading, T_g of PMMA increases over 393 K, and, hence, further deformation proceeds at temperatures below T_g. Accumulation of low-temperature component of relaxation in plastically deformed samples therewith takes place.

The effect of pressure on glass transition temperature of polymers is widely discussed in literature (for example, in [11–14]). In most cases, with increasing pressure, a linear growth in T_g was observed.

To obtain a detailed information concerning the pressure dependence of T_g of PMMA, we studied the temperature dependence of compressibility factor β in the wide range of pressures (Fig. 1). Let us emphasize that, under compression in the press mold or under hydrostatic compression, physical and mechanical behavior is primarily controlled by the ratio between the loading time and relaxation time. Relaxation time is a function both of temperature and pressure. With increasing hydrostatic pressure, a significant increase in relaxation time is observed. From this standpoint, the experimental procedures for studying physical and mechanical behavior of polymers under the parallel action of pressure and temperature on loading or heating with a constant rate are not quite correct. In this case, the ratio between the loading time and relaxation time is different at each stage of test. To overcome these difficulties, in this work a step-by-step increase in pressure at fixed temperature was used. At each pressure, the samples were allowed to relax until the equilibrium state was attained.

Temperature interval corresponding to the jumplike change in compressibility factor β (Fig. 1) is associated with the glass transition of polymer at this pressure. Pressure dependence of T_g is shown in Figure 3. This dependence is characterized by three well-pronounced regions. At pressures below 0.09–0.1 GPa, T_g is almost independent of the applied pressure. Within the pressure range from 0.09–0.1 to 0.38–0.4 GPa, with increasing temperature, the linear growth of T_g is observed. At pressures about 0.38–0.4 GPa, the pressure dependence of T_g shows an inflection point. The further increase in pressure leads to a slight increase in T_g.

Earlier [10], the dependence of T_g on the applied pressure was discussed when monolithization of powderlike PMMA was studied under the parallel action of pressure and temperature. In Figure 4, curve 1 bounds the region of pressures and temperatures where monolithic

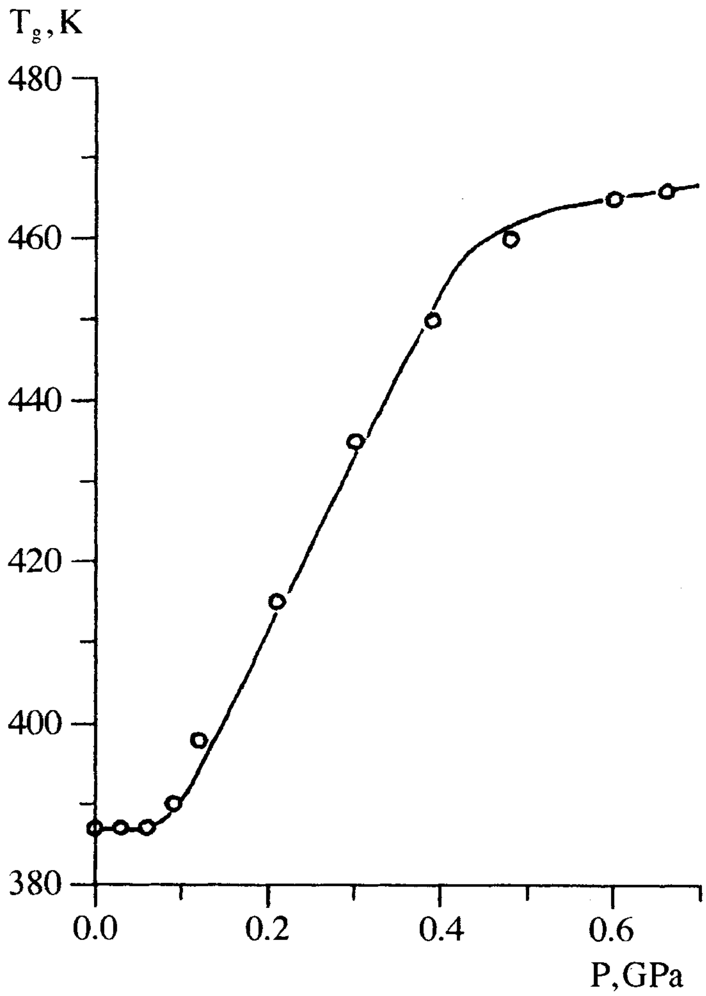

FIGURE 3 Pressure dependence of glass transition temperature T_g of PMMA.

PMMA samples are produced. These samples are monolithic up to temperatures corresponding to glass transition of PMMA. This reasoning allows one to conclude that the upper branch of curve 1 (Fig. 4) is the pressure dependence of T_g. Note that, in the case of monolithization of powderlike PMMA the pressure dependence of T_g (upper branch of the curve 1, Fig. 4) is well correlated with the pressure dependence of T_g obtained in this work for bulk polymer (curve 2).

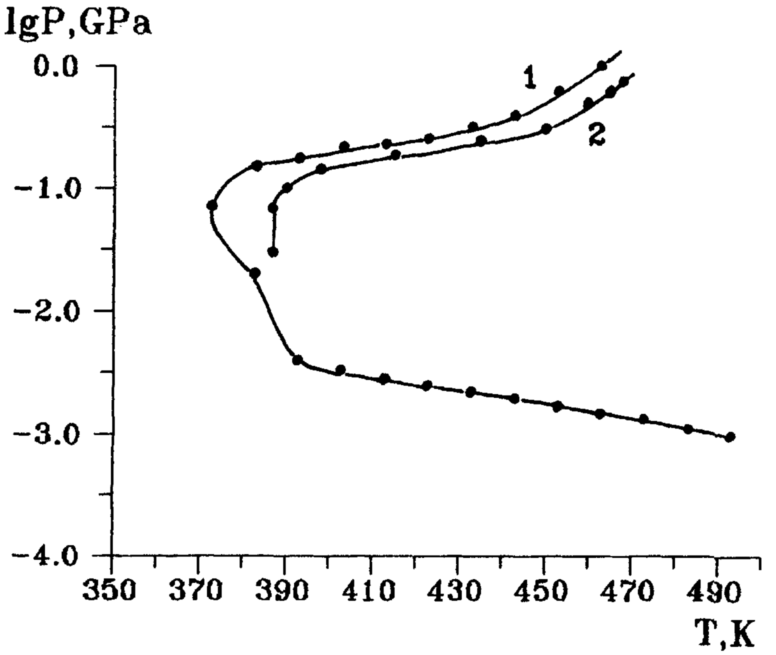

FIGURE 4 "Pressure-temperature" diagram for preparation of monolithic PMMA samples from powderlike polymer (curve 1) and pressure dependence of glass transition temperature of bulk PMMA (curve 2).

Hence, for PMMA samples the pressure dependence of T_g is characterized by two inflection points at pressures 0.09–0.1 GPa and 0.38–0.4 GPa. Let us emphasize that for the compression of PMMA samples in the press mold at 293 K (Fig. 5a, curve 1), the stress-strain diagram shows the inflection points at the same pressures. Such behavior of T_g with respect to the applied pressure and compression stress-strain diagram may be explained in terms of the structural inhomogeneity of polymer glasses.

Note that, at pressures below 0.1 GPa stress-strain diagrams describing compression of PMMA samples in the mold (Fig. 5a, curve 1) and uniaxial compression of PMMA samples (Fig. 5a, curve 2) agree very closely. Let us emphasize that, the pressure about 0.1 GPa corresponds to yield point σ_y in the case of uniaxial compression of polymer. On the other hand, as it was shown in [10], at the pressure about 0.1

GPa, the plastic deformation in powderlike PMMA comes to a play (inflection in $\sigma - \Delta h$ diagram, Fig. 5b). It leads to monolithization of powderlike polymer due to diffusion of segments through the boundaries of particles of powder.

Similar profiles of the stress-strain diagrams corresponding to uniaxial compression of PMMA samples and compression in the press mold are likely to be associated with the fact that, in this range of pressures, the compression is controlled by the deformation of structural regions with lower packing densities. In the case of uniaxial compression, this assumption is supported by the direct structural studies of deformation of PMMA using positron annihilation lifetime spectroscopy [7–9]. This method allows one to identify structural

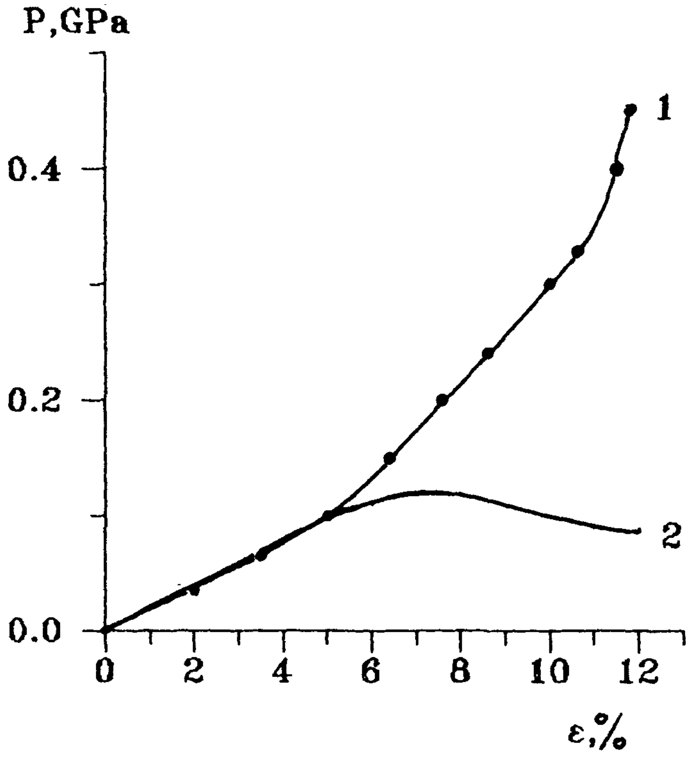

FIGURE 5 Stress-strain diagrams for the compression of bulk PMMA samples in the press mold (1) and for the uniaxial compression of PMMA samples (2) (A), and for the compression of powderlike PMMA in the press mold (B).

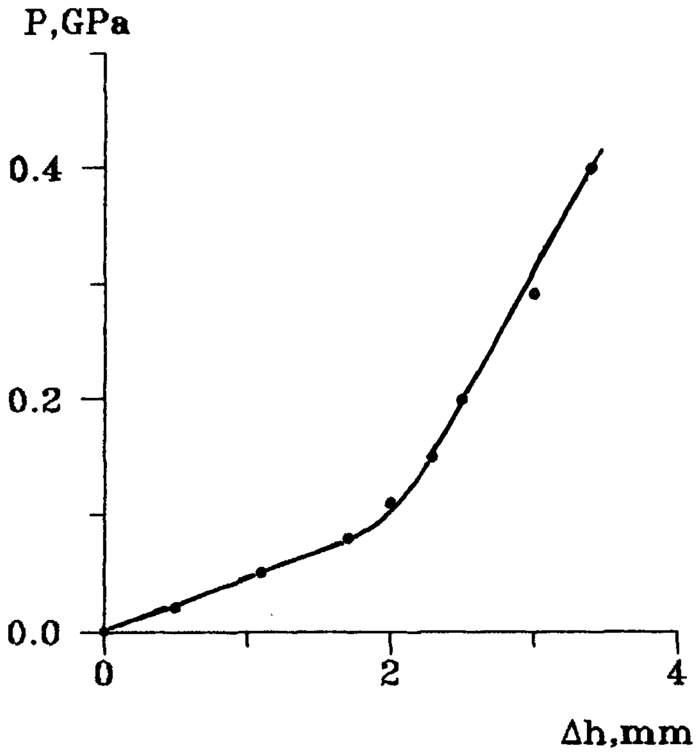

FIGURE 5b (Contd.).

sublevels with different packing densities in polymer glasses and to estimate concentration and sizes of free volume microregions within the above sublevels. As was shown, at initial portion of stress-strain diagram, the uniaxial compression of polymer samples is accompanied by the deformation of structural sublevels with lower packing densities via the decrease in the concentration of the microregions of free volume. Concentration of microregions of free volume in the more densely packed structural sublevels remains unchanged. This experimental evidence allows one to conclude that, at these pressures these structural regions are not involved in the deformation.

In this range of pressures the constant values of T_g correlates well with the results reported in [15–18], in which specific dual transitions were observed in the temperature region of glass transition. This fact was treated in terms of the existence of structural regions with different packing densities. Low-temperature transition is attributed to the appearance of segmental mobility in the loosely packed regions, whereas the high-temperature transition is provided by the segmental mobility in the densely packed domains. This high-temperature transition is associated with the macroscopic glass transition, when segmental mobility is realized in the whole polymer sample. When the densely packed structural regions are not involved in the deformation at pressures below 0.1 GPa, segmental mobility within these structural sublevels remains unchanged, and macroscopic T_g is constant.

When pressure increases above 0.1 GPa, the deformation behavior of polymer under compression in the press mold is quite different as compared with that under uniaxial compression (Fig. 5a). The development of plastic deformation under uniaxial compression is accompanied by an increase in lateral sizes of the polymer samples at pressures about 0.1 GPa, that is, when σ_y is attained. In the case of compression in the press mold, lateral sizes of the sample remain unchanged. Plastic deformation of polymer is controlled by relatively uniform deformation of the densely packed structural sublevels. With increasing pressure, this process leads to densification of these structural regions, restriction of segmental mobility within these regions, and, finally, to the growth in T_g (Fig. 3).

As pressure increases to 0.4 GPa, the deformability of the densely packed structural regions is likely to be exhausted. Further increase in pressure is accompanied by a slight growth in strain (Fig. 5a, curve 1) and T_g (Fig. 3).

CONCLUSION

Let us summarize the experimental evidence obtained.

1. At temperatures far below T_g, compression of bulk PMMA in the press mold is accompanied by the development of plastic deformation and accumulation of residual deformation. Relaxation of the residual deformation takes place at temperatures below T_g within glassy state polymer;
2. The pressure dependence of T_g as well as the compression stress-strain diagram of PMMA show two well-pronounced inflection points at pressures of 0.09–0.1 and 0.38–0.4 GPa;

3. At pressures below 0.1 GPa, the stress-strain diagrams corresponding to uniaxial compression and compression in the press mold coincide.

These experimental evidence proves earlier speculations concerning the structural pattern for plastic deformation of polymer glasses under uniaxial compression. These speculations are based on the ideas concerning the gradual involvement of various structural sublevels with different packing densities in deformation.

At pressures below 0.09–0.1 GPa plastic deformation is controlled by stress-induced segmental mobility within structural sublevels with lower packing densities. In this case, the stress-strain diagrams for uniaxial compression and compression in the press mold are quite similar, and T_g remains unchanged independently on applied pressure.

At pressures close to σ_y, that is, about 0.1 GPa, the densely packed structural sublevels are involved in plastic deformation. In the case of uniaxial compression, the development of plastic deformation is accompanied by the increase in lateral sizes of polymer samples. Under compression in the press mold the lateral sizes remain unchanged, and plastic deformation is controlled by a relatively uniform deformation of the densely packed structural regions. This leads to an increase in T_g because of the restriction of segmental mobility within these structural sublevels.

At pressures about 0.38–0.4 GPa, deformability of the densely packed structural sublevels is exhausted, and further increase in the applied pressure leads to a slight growth in strain and T_g.

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