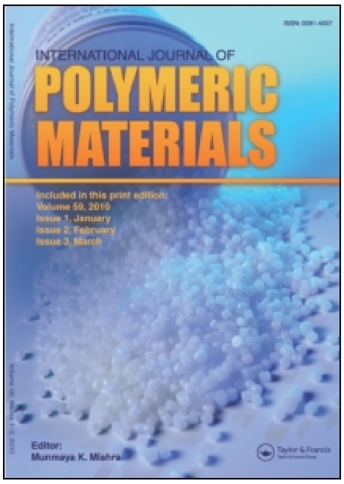

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Physical and Mechanical Behavior of Polymer Glasses. IV. Cross-Linked Poly(Methyl Methacrylate)

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Temperature-induced relaxation of plastic deformation in cross-linked PMMA samples was studied. For cross-linked PMMA with low concentration of cross-linking agent (less, than 5.2 mol.%), relaxation curves involve low-temperature component at temperatures well below glass transition temperature and high-temperature component at temperatures close to glass transition. Increasing concentration of cross-linked agents in polymer samples to 11.2 mol.% is accompanied with degeneration of high-temperature component of relaxation, and complete relaxation of plastic deformation proceeds via low-temperature component. The effect of cross-linking on temperature-induced relaxation of plastic deformation was discussed in terms of restriction of segmental mobility within certain structural regions in polymer sample.

Keywords: PMMA; cross-linking; plastic deformation; relaxation

INTRODUCTION

Temperature-induced relaxation of plastic deformation of polymer glasses is known to involve low-temperature component at temperatures well below glass transition temperature and high-temperature component in the vicinity of glass transition [1–4]. Earlier [5,6], two-stage character of relaxation was discussed in terms of structural inhomogeneity of glassy polymers, that is, the existence of structural sublevels with different packing densities and degrees of ordering. The existence of a set of the above structural sublevels is responsible for the gradual involvement of segmental mobility in temperature-induced relaxation of plastically deformed polymer sample.

Decreasing contribution from low-temperature component to total relaxation of residual deformation was observed as a result of increasing deformation temperature of PMMA, plasticization of PMMA, and copolymerization of methyl methacrylate with methacrylic monomers [5, 7]. This experimental evidence was attributed to enhancement of local segmental mobility in certain structural sublevels. From this standpoint, the ratio between low-temperature and high-temperature components of temperature-induced relaxation of plastic deformation provides an important information concerning structural pattern of development of segmental mobility in glassy polymer. Generally speaking, this ratio may be treated as a physical parameter describing plastic deformation of polymer glasses, and their physical and mechanical behavior [5, 6].

In the present work, temperature-induced relaxation of plastic deformation of cross-linked PMMA was studied to gain a deeper insight in physical and mechanical behavior of glassy polymers.

EXPERIMENTAL

The copolymers of methyl methacrylate (MMA) with bifunctional monomers ethylene glycol dimethacrylate (EGDM) and triethylene glycol dimethacrylate (TGDM) were used as cross-linked PMMA. The content of bifunctional monomer in polymerization system was 2.5, 5.2 and 11.2 mol%. The development of network took place immediately during bulk polymerization.

Glass transition temperatures of copolymers studied were estimated by differential scanning calorimetry using a "Mettler TA-4000". Heating rate was 20 K/min.

The test samples were cylinders with a height of 30 mm and a diameter of 15 mm. Prior to testing, polymer samples were annealed at temperatures, which exceeded glass transition temperature by 10–15 K. Then, they were cooled down to room temperature. The height of as-prepared samples was denoted as h_0.

The samples of initial PMMA and PMMA, cross-linked with EGDM and TGDM, were uniaxially compressed at 293 K with strain rate of 0.1 mm/min using an UTS-100 tensile machine (Germany). After that, they were unloaded at this temperature with the same rate. The height of deformed samples was denoted as h_{def}.

In the deformed polymer samples, temperature-induced relaxation of residual deformation was studied by measuring the changes in their height on the heating from 293 K at a heating rate of 1 K/min. The height of the samples at a given temperature was denoted as h_T. Residual deformation at a given temperature was estimated as $\varepsilon_{\mathrm{res}} = (h_o - h_T)/(h_o - h_{\mathrm{def}})$ with an accuracy of $\pm 2\%$.

RESULTS AND DISCUSSION

For initial PMMA and PMMA, cross-linked with EGDM and TGDM, Figure 1 shows stress-strain diagrams, corresponding to uniaxial compression of polymer samples. Note, that all samples show well-pronounced plastic deformation and storing residual deformation after their unloading. Let us emphasize, that for cross-linked samples their elastic modulus and yield stress seem to be independent of the concentration of cross-linking agent (EGDM and TGDM), and are equal to those for initial PMMA.

For initial PMMA and cross-linked PMMA, Figures 2 and 3 show temperature dependences of residual deformation $\varepsilon_{\mathrm{res}}$. For the lack of space, relaxation curves are presented only for polymer samples with 20 and 30% strains. As follows from Figures 2 and 3, for PMMA samples (curves 1), temperature-induced relaxation of plastic deformation takes place in two well-defined temperature regions below glass transition temperature T_g and close to T_g via low-temperature component ε_1 and high-temperature component ε_2, respectively. These components of relaxation are shown in Figure 2a.

Earlier [5,6], two-stage character of temperature-induced relaxation of residual deformation of polymer glasses was interpreted in terms of their structural inhomogeneity, that is, coexistence of structural sublevels with different packing densities and degrees of ordering. Each of these sublevels is characterized by its own relaxation time and activation energy of segmental mobility. Hence, at each temperature below glass transition temperature local segmental mobility in certain structural sublevels is allowed. With increasing temperature, structural

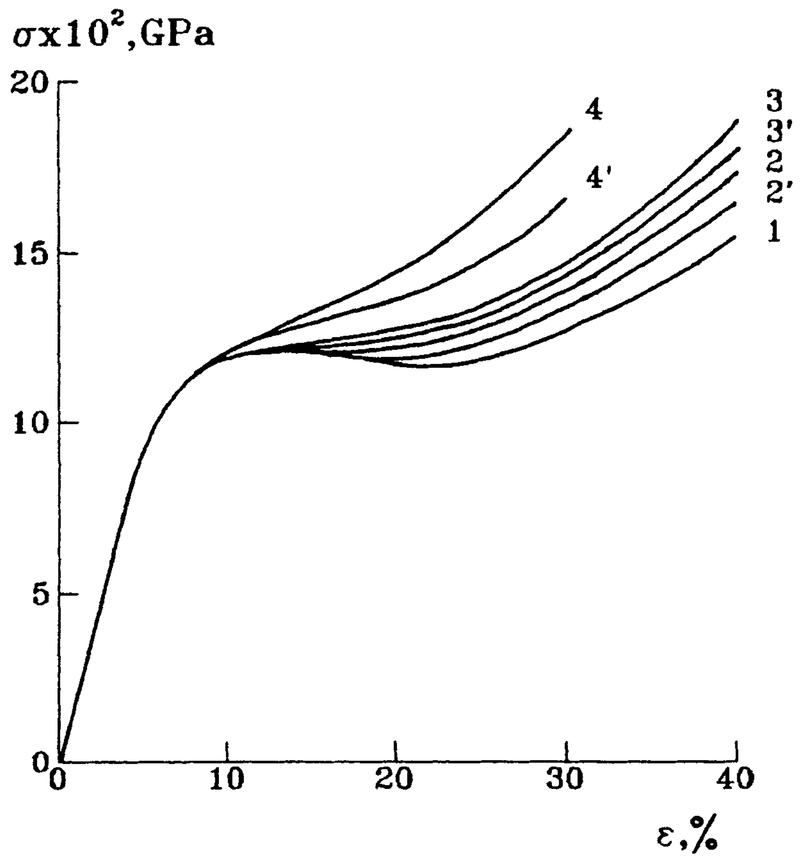

FIGURE 1 Stress-strain diagrams of PMMA (1) and PMMA, cross-linked with EGDM (2 – 4) and TGDM (2' – 4'). Concentration of cross-linking agents: 2.5 (2, 2'), 5.2 (3, 3') and 11.2 mol.% (4, 4'). Uniaxial compression at 293 K.

sublevels with higher packing densities become involved in segmental mobility, and, finally, at glass transition temperature segmental mobility is observed in the whole polymer sample. In other words, the existence of a set of structural sublevels with different packing densities is responsible for the spectrum of segmental mobility in polymer glasses.

Low-temperature relaxation of residual deformation is controlled by low-temperature fraction of the spectrum of segmental mobility because of temperature-induced segmental mobility within structural sublevels with lower packing densities at temperatures well below T_g. Evidently, a certain part of low-temperature fraction of the spectrum

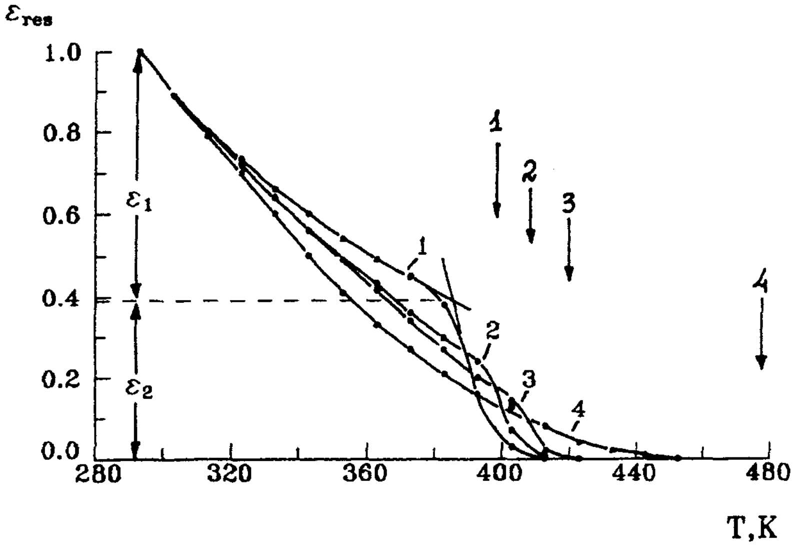

FIGURE 2 Temperature dependences of residual deformation ε_{res} of PMMA (1) and PMMA, cross-linked with 2.5 (2), 5.2 (3) and 11.2 mol.% EGDM (4). Strain: 20 (A) and 30% (B). The arrows show T_g of the corresponding polymer samples.

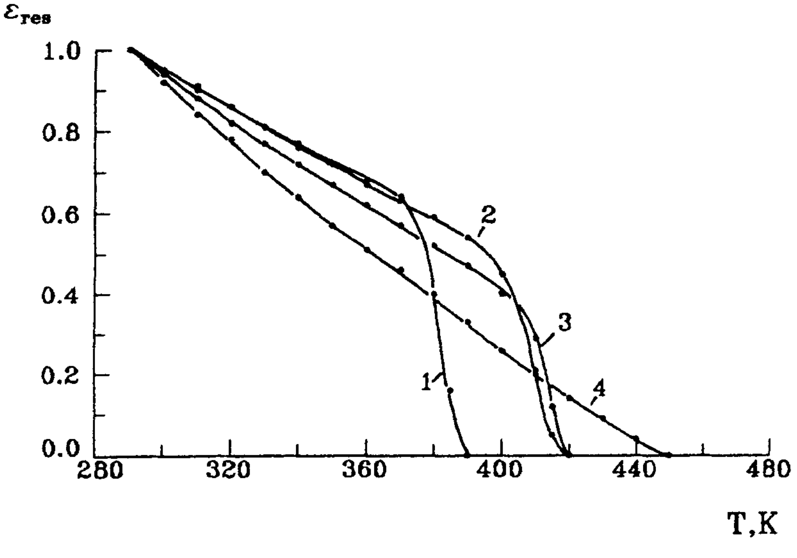

FIGURE 2b (Contd.)

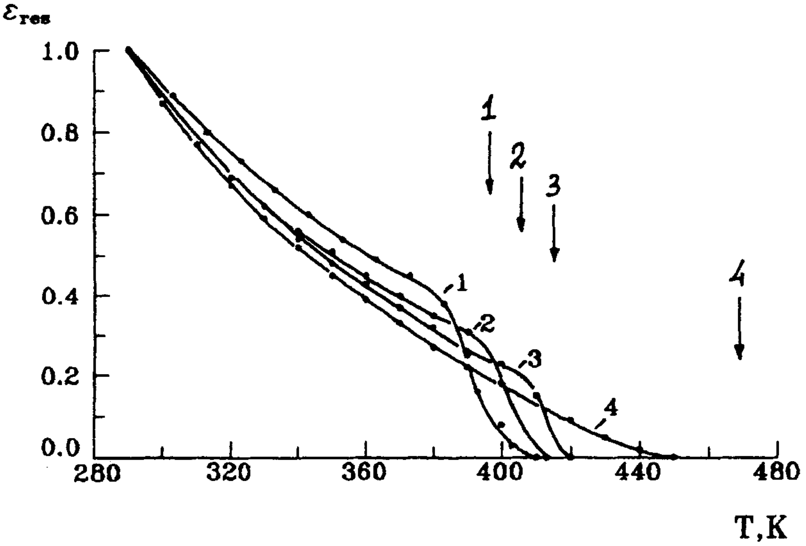

FIGURE 3 Temperature dependences of residual deformation ε_{res} of PMMA (1) and PMMA, cross-linked with 2.5 (2), 5.2 (3) and 11.2 mol.% TGDM (4). Strain: 20 (A) and 30% (B). The arrows show T_g of the corresponding polymer samples.

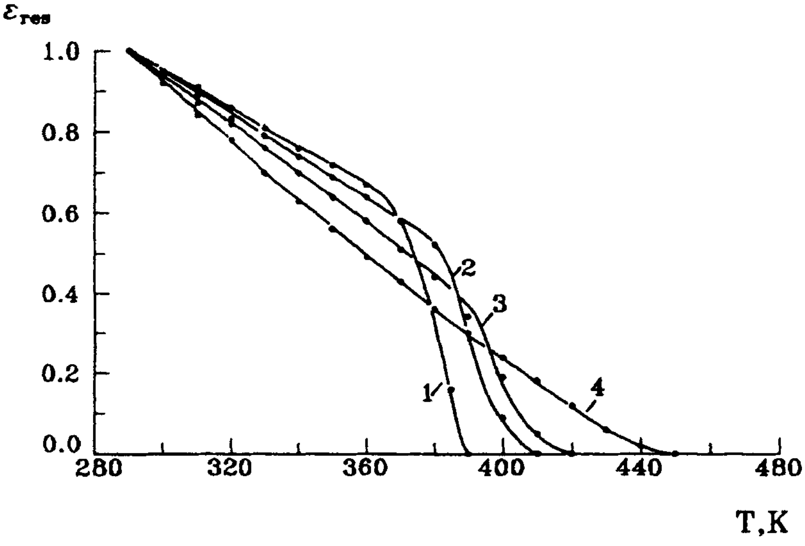

FIGURE 3b (Contd.)

of segmental mobility is able to relax during polymer loading. From this standpoint, low-temperature component ε_1 of relaxation is likely to be associated with stored plastic deformation, which remained unrelaxed during loading.

High-temperature fraction of the spectrum of segmental mobility is responsible for high-temperature component ε_2 of relaxation. This component is accumulated in polymer during loading, and is able to relax only at temperatures close to T_g via temperature-induced segmental mobility within structural sublevels with higher packing densities.

Hence, the ratio between low-temperature and high-temperature components of relaxation provides an important information concerning structural pattern of the development of temperature-induced segmental mobility in plastically deformed glassy polymer.

The effect of strain on the ratio between low-temperature and high-temperature components of relaxation [5, 6] in combination with direct structural studies in deformation using positron annihilation lifetime spectroscopy [8, 9] allowed us to advance the structural pattern of plastic deformation. Polymer deformation to strains below or equal to yield strain is associated with stress-induced local segmental mobility within structural sublevels with lower packing densities. With increasing strain above yield point, segmental mobility within structural sublevels with higher packing densities comes to a play. In other words, for polymer glasses plastic deformation is controlled by gradual involvement of segmental mobility within structural sublevels characterized by different packing densities in deformation and relaxation processes.

Earlier [5, 7], increasing deformation temperature, plasticization of PMMA, or copolymerization of methyl methacrylate with methacrylic monomers was shown to be accompanied with decrease in contribution from low-temperature component ε_1 to total temperature-induced relaxation of residual deformation. This fact is likely to be associated with enhancement in local segmental mobility in certain structural sublevels. As a result, the higher fraction of low-temperature mode of the whole spectrum of segmental mobility is able to relax during deformation, and decrease in low-temperature component ε_1 is observed.

This experimental evidence allows one to suggest that restriction of segmental mobility in polymer should result in the growth in contribution from low-temperature component ε_1 to relaxation. Restriction of segmental mobility in polymer sample may be achieved by cross-linking of polymers [10]. For PMMA samples, cross-linked with EGDM and TGDM, restriction of segmental mobility is evidenced by increasing T_g with increase in concentration of cross-linking agents in polymer samples. To verify the effect of cross-linking on the ratio between low-temperature and high-temperature components of relaxation, temperature-induced relaxation of cross-linked PMMA samples was studied.

For PMMA samples, cross-linked with 2.5 and 5.2 mol.% of cross-linking agents (Figs. 2 and 3, curves 2 and 3), temperature dependences of residual deformation also are characterized by low-temperature and high-temperature components. A well-pronounced two-stage character of temperature-induced relaxation of residual deformation allows one to suggest that, for cross-linked samples, relaxation is controlled by temperature-induced segmental mobility within structural sublevels with different packing densities as for the initial PMMA. In other words, cross-linked PMMA samples are likely to be characterized by structural inhomogeneity. Note, that, at low concentration of cross-linking agents, morphology of cross-linked polymer is known to be similar to that for linear polymer [10]. This experimental evidence allows one to suggests, that, in these cases, cross-links are localized in both loosely and densely packed structural sublevels.

Cross-linking of structural sublevels with lower packing densities is responsible for the increase in low-temperature component ε_1 of relaxation because of restriction of segmental mobility within these structural regions.

Cross-linking of structural sublevels with higher packing densities is evidenced by stress-strain diagrams of cross-linked polymer samples (Fig. 1). As was mentioned above, post-yield behavior of polymer glasses is controlled by stress-induced segmental mobility in structural sublevels with higher packing densities. As follows from Figure 1, for cross-linked PMMA samples, post-yield deformation proceeds at higher stress as compared with initial polymer. This fact may be attributed to the restriction of segmental mobility within these structural regions because of cross-linking.

With increasing concentration of EGDM and TGDM to 11.2 mol.% (Figs. 2 and 3, curves 4), high-temperature component ε_2 is degenerated, and temperature-induced relaxation of residual deformation proceeds via low-temperature component ε_1. Complete relaxation is observed at temperatures well below T_g within glassy state.

Such relaxation behavior may be explained from two standpoints. At first, increasing concentration of cross-linking agent in PMMA is likely to be responsible for the further cross-linking of structural sublevels with lower packing densities. As a result, a noticeable restriction of segmental mobility within these structural sublevels is observed, and total temperature-induced relaxation of residual deformation is primarily controlled by low-temperature component ε_1. Secondly, increasing concentration of cross-linking agent in polymerization system is known [10] to present a severe difficulties for formation of morphological structures with high degree of ordering. Finally, the degeneration of these structures is observed. In this case, one could expect one-stage recovery of residual deformation.

Hence, cross-linking of PMMA is accompanied by restriction of segmental mobility within certain structural sublevels in polymer samples. As a result, the lower fraction of low-temperature mode of the whole spectrum of segmental mobility is able to relax during deformation, and increase in contribution from low-temperature component ε_1 to total temperature-induced relaxation of residual deformation is observed. Qbviously, restriction of segmental mobility should be controlled by the length of the molecule of cross-linking agent.

Figure 4 shows the temperature dependences of residual deformation ε_{res} for cross-linked PMMA samples with the similar concentration of EGDM and TGDM. When passing from EGDM to TGDM (curves 2 and 3, respectively), increasing the length of cross-links results in decrease in low-temperature component ε_1. Note, that, for the samples cross-linked with EGDM, post-yield deformation proceeds at higher stress as compared with the samples cross-linked with TGDM (Fig. 1). This behavior may be attributed to the fact, that the higher restriction of segmental mobility is observed for the samples cross-linked with the shorter cross-linking agent.

CONCLUSION

The effect of cross-linking on temperature-induced relaxation of plastic deformation of PMMA was studied. Increasing concentration of

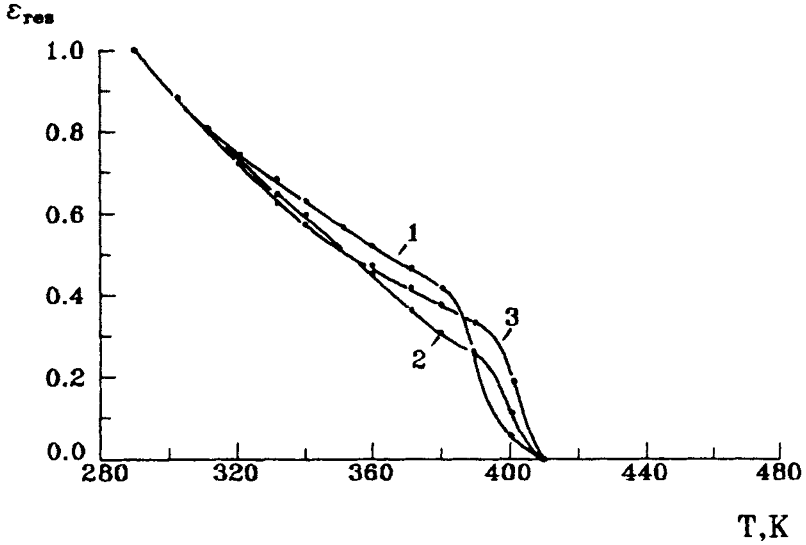

FIGURE 4 Temperature dependences of residual deformation ε_{res} of PMMA (1) and PMMA, cross-linked with EGDM (2) and TGDM (3). Concentration of cross-linking agents: 2.5 (A) and 5.2 mol.% (B). Strain: 20%.

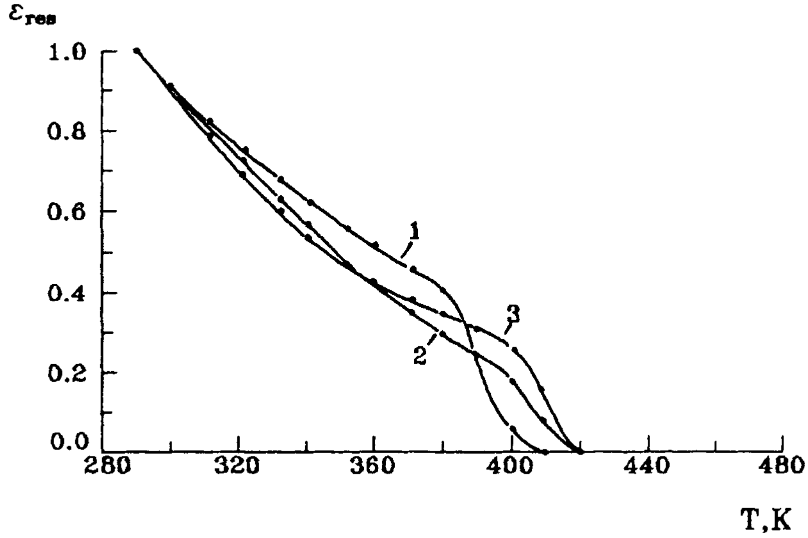

FIGURE 4b (Contd.)

cross-linking agent in polymerization system to 5.2 mol.% is responsible for increase in low-temperature component of relaxation. For polymer samples with 11.2 mol.% of cross-linking agent, complete relaxation is observed at temperatures well below glass transition temperature via only low-temperature component. Increasing contribution from low-temperature component to total relaxation of plastic deformation, and, finally, degeneration of high-temperature component is likely to be controlled by restriction of segmental mobility within certain structural sublevels.

Increasing the length of cross-links results in decrease in low-temperature component of relaxation. This behavior may be explained by the fact, that the higher restriction of segmental mobility is observed for the samples cross-linked with the shorter cross-linking agent.

This experimental evidence suggests the possibilities to control low-temperature reversibility of strain in polymer glasses at temperatures well below glass transition temperature via their cross-linking.

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