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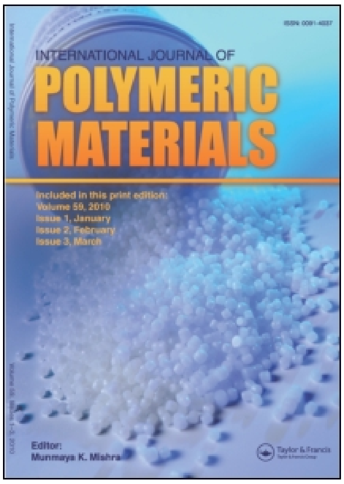

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Physical and Mechanical Behavior of Polymer Glasses. III. Copolymers of Methyl Methacrylate

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Physical and mechanical behavior of copolymers of methyl methacrylate and PMMA was studied. The contribution from low-temperature component to total temperature-induced relaxation of plastic deformation was shown to correlate well with the mechanical characteristics of polymer samples. This correlation was discussed in terms of the structural inhomogeneity of polymer glasses: coexistence of structural sublevels with characteristic values of relaxation time and energy of activation of segmental mobility. From this standpoint, plastic deformation and, in general, physical and mechanical behavior of polymer glasses is likely to be controlled by a gradual involvement of segmental mobility within above structural sublevels in deformation and relaxation processes.

Keywords: Glassy polymers; copolymers of methyl methacrylate; plastic deformation; relaxation

INTRODUCTION

A two-stage character of temperature-induced relaxation of plastic deformation of polymer glasses, that is, existence of low-temperature and high-temperature components of relaxation, is considered as a manifestation of structural rearrangements which are responsible for and accompany plastic deformation [1–4]. In this case, physical and mechanical properties of glassy polymers are likely to be controlled by the coexistence of the above two components of temperature-induced relaxation.

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The earlier studies concerning physical and mechanical behavior of PMMA samples [3,4] allowed us to reveal a certain correlation between the mechanical properties of polymer and the contributions from low-temperature and high-temperature components to total temperature-induced relaxation of plastic deformation. From this standpoint, the ratio between these components of relaxation is treated as a new physical parameter, which was advanced to describe plastic deformation in glassy polymers. This reasoning is based on the speculations concerning the structural pattern of plastic deformation of polymer glasses, that is, a gradual involvement of segmental mobility within various structural sublevels in deformation and relaxation processes.

To gain a deeper insight into the nature of low-temperature and high-temperature components of relaxation and their role in development of polymer deformation, we studied physical and mechanical behavior of copolymers of methyl methacrylate with methacrylic monomers.

EXPERIMENTAL

In this work, random copolymers of methyl methacrylate (MMA) with butyl methacrylate (BMA), octyl methacrylate (OMA), and lauryl methacrylate (LMA) were used.

Prior to copolymerization, the monomers were distilled under vacuum in a nitrogen flow. The initiator of copolymerization (lauroyl peroxide) was purified by recrystallization from ethanol.

The monomer feed composition was the following: for MMA/BMA-95/5, 90/10, 80/20, 70/30 and 50/50; for MMA/OMA-95/5, 90/10 and 80/20; for MMA/LMA-95/5, 90/10 and 85/15. The monomer mixtures with initiator were deoxygenated by repeated freezing-defreezing at a pressure of 10^{-2} mmHg. For all mixtures, the content of lauroyl peroxide was 5×10^{-3} mol/l.

Copolymerization was carried out in the sealed glass tubes with a diameter of 10 mm and a height of 100 mm at 333 K under vacuum. To achieve the complete conversion, at the final stage of copolymerization reactions temperature was increased up to temperatures, which exceeded glass transition temperatures of the corresponding copolymers by 10–15 K.

Glass transition temperatures of the copolymers studied were estimated by differential scanning calorimetry using "Mettler TA-4000". Heating rate was 20 K/min. Glass transition temperatures of copolymer samples are summarized in Table I.

For mechanical tests, the cylindrical copolymer samples with a height of 5 mm and a diameter of 5 mm were used. Prior to testing, the samples were annealed at temperatures above glass transition temperature by 10–15 K. Then the samples were slowly cooled down to room temperature. The height of the as-prepared samples was denoted as h_0.

The test samples were uniaxially compressed at 293 K with strain rates 0.1, 1, 10 and 100%/min using an UTS-10 tensile machine (Germany). Strain was 20%. Yield stress σ_y was estimated with an accuracy of ± 5%. The height of stressed sample was denoted as h_{def}. Then, the samples were unloaded at 293 K with the same rates.

TABLE 1 Physical and mechanical parameters of PMMA and various copolymers of methyl methacrylate

Sample	T_g,K	T_{def},K	σ_y,GPA	$\varepsilon_1/(\varepsilon_1+\varepsilon_2)$	ΔT_{def},K
PMMA	393	293	0.124	0.88	100
		320	0.082	0.78	73
		333	0.070	0.72	60
		353	0.060	0.61	40
		383	0.050	0.50	10
PMMA + 5 wt% of DBPh	383	293	0.102	0.85	90
PMMA + 10 wt% of DBPh	373	–	0.086	0.78	80
PMMA + 20 wt% of DBPh	343	–	0.065	0.68	50
MMA/BMA					
95/5	383	–	0.115	0.88	90
90/10	373	–	0.110	0.88	80
80/20	363	–	0.094	0.85	70
70/30	353	–	0.083	0.82	60
50/50	333	–	0.060	0.70	40
MMA/OMA					
95/5	378	–	0.096	0.83	85
90/10	363	–	0.075	0.75	70
80/20	343	–	0.055	0.63	50
MMA/LMA					
95/5	368	–	0.090	0.78	75
90/10	353	–	0.060	0.68	60
85/15	338	–	0.050	0.57	45

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In the deformed polymer samples, temperature-induced relaxation of residual deformation was studied by measuring the changes in the height of the test samples on their heating in the temperature range from 293 K to T_g. The free-standing samples were allowed to relax at certain temperatures within the above temperature interval until the equilibrium height was attained. The equilibrium height of samples at a given temperature was denoted as h_T. Residual deformation at a given temperature was estimated as $\varepsilon_{\mathrm{res}} = (h_0 - h_T)/(h_0 - h_{\mathrm{def}})$ with an accuracy of $\pm 2\%$.

RESULTS AND DISCUSSION

Figure 1 shows stress-strain diagrams describing uniaxial compression of the copolymer samples. As follows from Figure 1, with increasing the concentration of BMA, OMA and LMA in their copolymers with MMA, a well-pronounced decrease in mechanical characteristics of polymer, in particular, yield stress σ_y, is observed. The values of σ_y are summarized in Table I.

For plastically deformed copolymer samples, the temperature dependences of residual deformation $\varepsilon_{\mathrm{res}}$ are shown in Figure 2. Note, that temperature-induced relaxation of residual deformation takes place in two temperature regions and involves two components: low-temperature component ε_1 and high-temperature component ε_2. These components of relaxation are shown in Figure 1A for the temperature dependence of $\varepsilon_{\mathrm{res}}$ of plastically deformed PMMA (curve 1).

A complete relaxation is observed in a narrow temperature range in the vicinity of glass transition temperature T_g of copolymers via high-temperature component ε_2. However, relaxation of a marked fraction of plastic deformation is observed in the wide temperature range at temperatures well below T_g via low-temperature component ε_1.

Earlier [3–5], two-stage character of temperature-induced relaxation of plastic deformation of polymer glasses was explained by structural inhomogeneity of polymer glasses, 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

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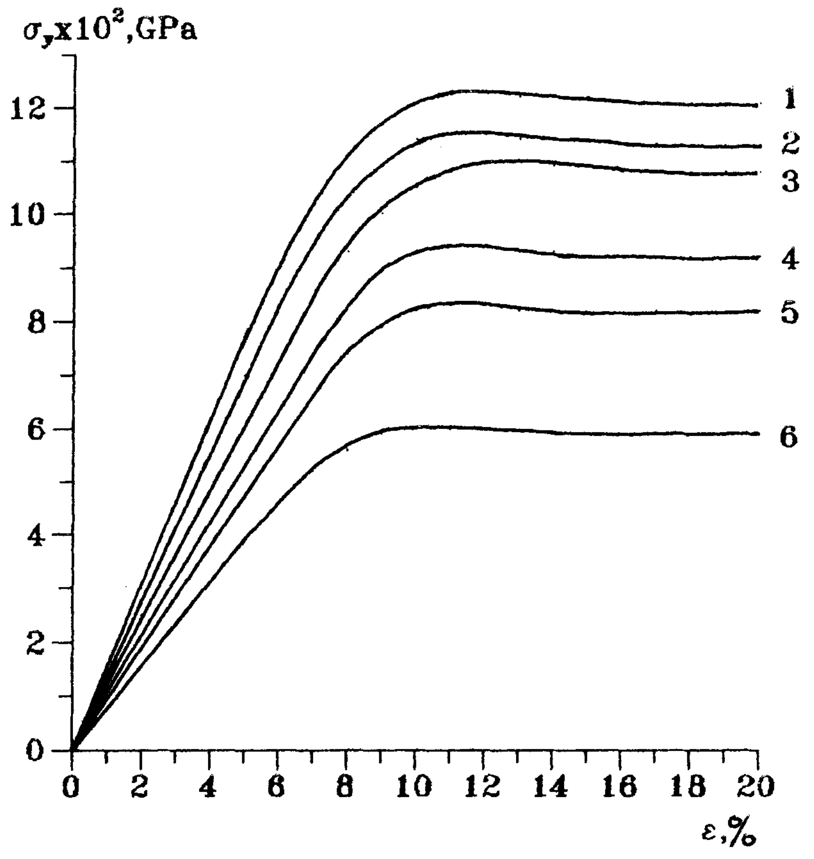

FIGURE 1 Stress-strain diagrams of PMMA (curves 1) and various copolymers of MMA. Monomer feed composition: MMA/BMA-95/5(2), 90/10(3), 80/20(4), 70/30(5) and 50/50(6) (A); MMA/OMA-95/5(2), 90/10(3) and 80/20(4) (B); MMA/LMA-95/5(2), 90/10(3) and 85/15(4) (C). Uniaxial compression at 293 K. Strain rate 1%/min.

mobility in certain structural sublevels is allowed. With increasing temperature, structural sublevels with higher packing densities become involved in segmental mobility, and finally, at T_g, 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 glassy polymer.

Let us emphasize, that a possible segmental mobility in the local structural sublevels at temperatures below T_g is widely discussed in literature (for example, in [6–10]).

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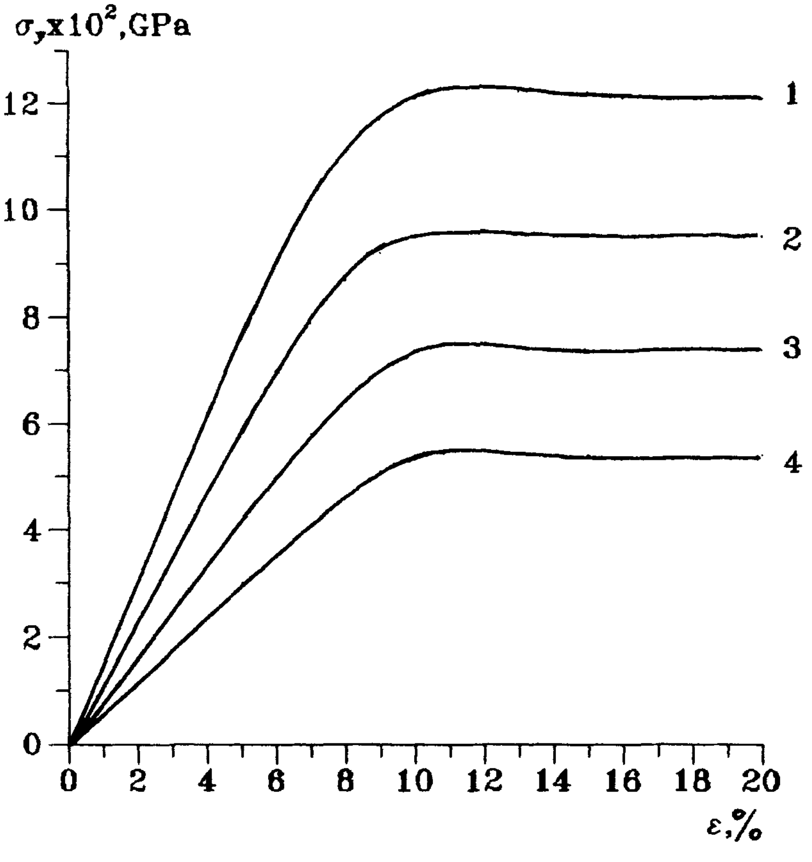

FIGURE 1b (Contd.)

The low-temperature component ε_1 of relaxation of residual deformation is associated with the low-temperature mode of the spectrum of segmental mobility due to the temperature-induced local segmental mobility, which is observed within structural sublevels with lower packing densities at temperatures well below glass transition temperature. A complete relaxation of plastic deformation is accomplished at glass transition and is provided by high-temperature component ε_2, when segmental mobility is observed in a whole polymer sample. Hence, molecular mechanism of low-temperature component of relaxation of residual deformation seems to be similar to that of high-temperature component and involves the transition of the excited chain conformations to initial equilibrium state via segmental mobility.

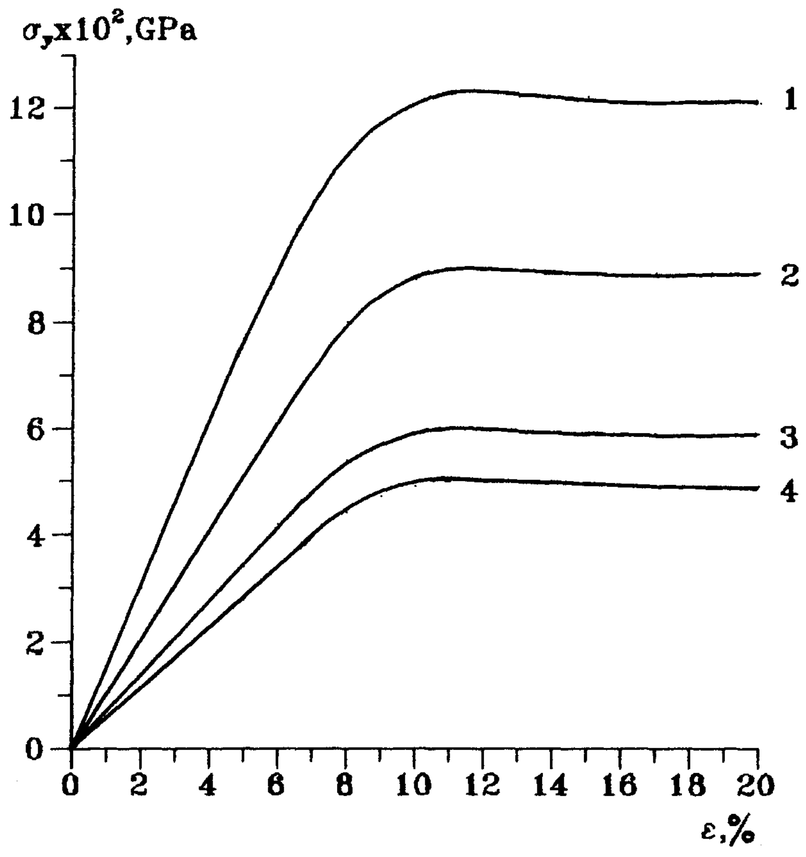

FIGURE 1c (Contd.)

The effect of strain on the ratio between ε_1 and ε_2 was studied in [3]. As shown in [3], in the case of glassy polymers with strains below or equal to yield strain ε_y, relaxation of residual deformation is controlled only by low-temperature component ε_1, that is, by temperature-induced segmental mobility within the structural sublevels with lower packing densities. This evidence implies, that polymer deformation to strains below yield strain is associated with stress-induced local segmental mobility within these structural sublevels. With increasing strain above yield point, at constant ε_1 appearance and growth of high-temperature component of relaxation ε_2 is observed. Relaxation of high-temperature component ε_2 is controlled by

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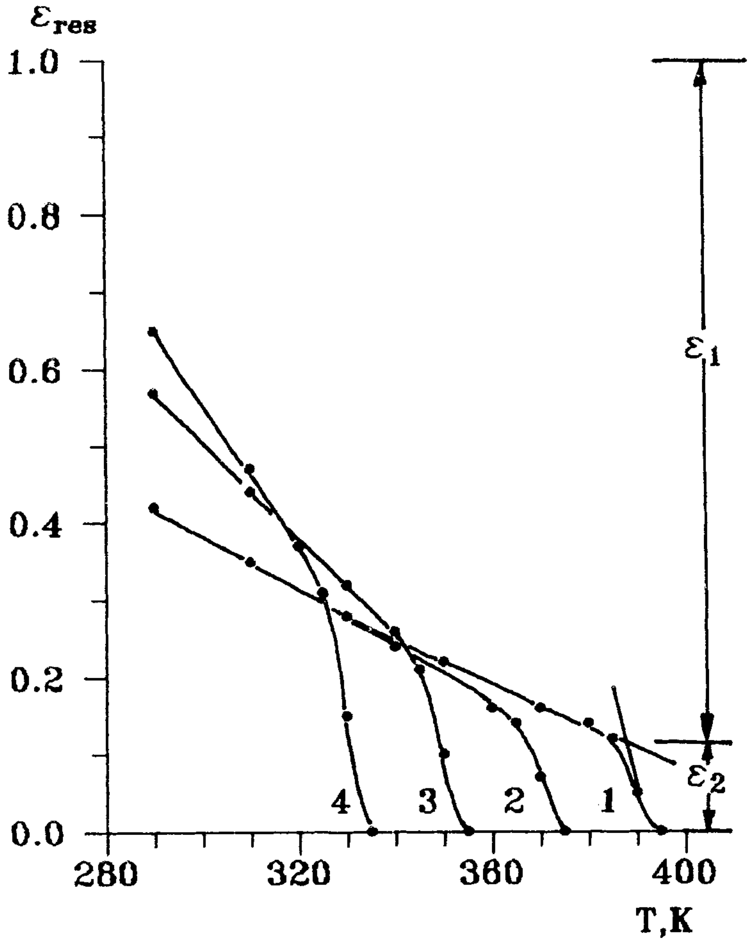

FIGURE 2 Temperature dependences of residual deformation ε_{res} of various copolymers of MMA. Monomer feed composition: MMA/BMA-100/0(1), 90/10(2), 70/30(3) and 50/50(4) (A); MMA/OMA-95/5(1), 90/10(2) and 80/20(3) (B); MMA/LMA-95/5(1), 90/10(2) and 85/15(3) (C).

temperature-induced segmental mobility in the whole polymer sample. This reasoning suggests that, at strains above yield strain, all segments in polymer sample are involved in plastic deformation. Hence, two components of relaxation of residual deformation allow one to advance some speculations concerning the structural pattern of plastic deformation. According to these speculations, for polymer glasses plastic deformation is controlled by a gradual involvement of the

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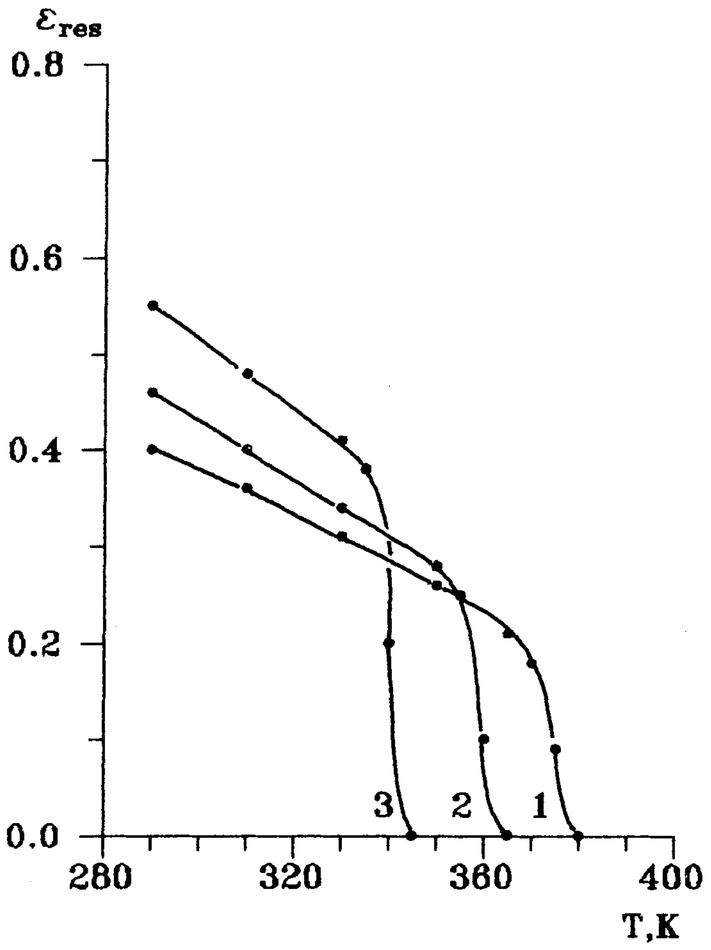

FIGURE 2b (Contd.)

structural sublevels with different packing densities in deformation and relaxation processes. In other words, plastic deformation of polymer glasses may be described by the contributions from low-temperature and high-temperature components to relaxation of residual deformation. From this standpoint, finding correlation between the contributions from these components to relaxation of residual deformation and polymer strength properties is necessary to describe physical and mechanical behavior of polymer glasses.

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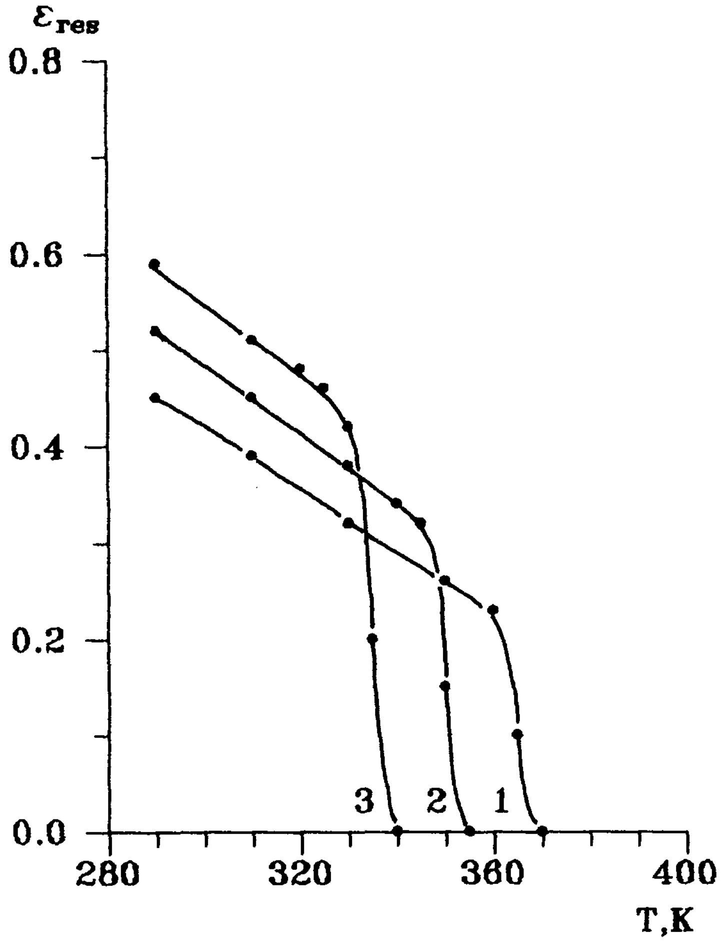

FIGURE 2c (Contd.)

With respect to polymer strength properties, consideration of the contribution from low-temperature component to total relaxation of residual deformation $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ seems to be of most interest. This parameter concerns the development of polymer deformation at initial portion of stress-strain diagram at strains below or equal to ε_y, which is associated with such strength properties as elastic modulus E_0 and σ_y. Earlier [3], the parallel decrease in E_0, σ_y and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ was observed as a result of increasing deformation temperature T_{def} of PMMA as well as plasticization of PMMA with dibutyl phtalate

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(DBPh). For PMMA samples deformed at different T_{def} and PMMA plasticized with DBPh, the values of σ_y and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ are summarized in Table I.

As evidenced by Table I, with increasing concentration of BMA, OMA and LMA in copolymers with MMA, decrease in both σ_y and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ is observed. Let us consider the correlation between the above parameters for all polymer samples studied.

For copolymers of MMA as well as for PMMA deformed at different T_{def} and plasticized PMMA, Figure 3 shows the dependence of σ_y on $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$. As follows from Figure 3, all experimental data fit one

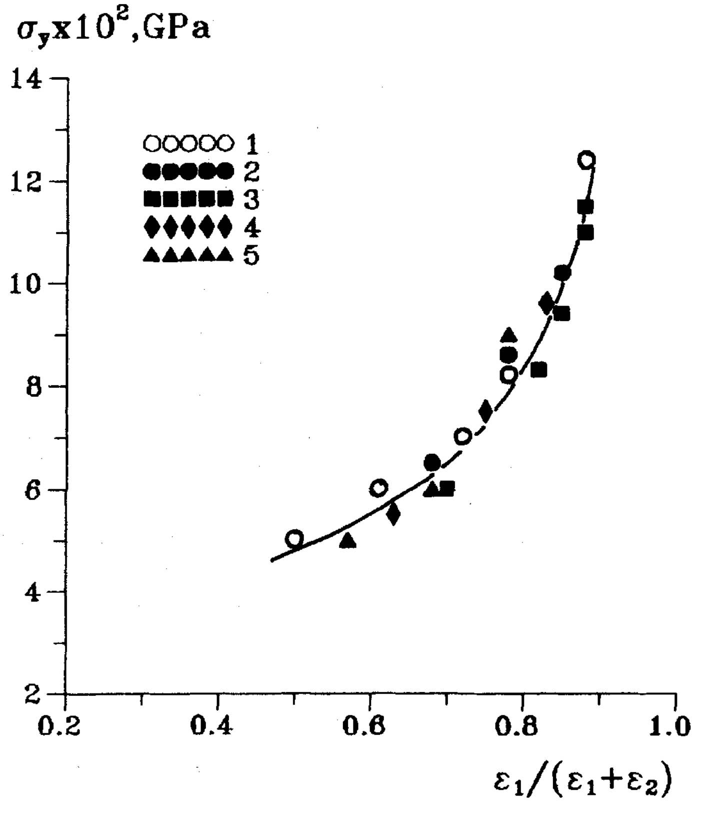

FIGURE 3 Yield stress σ_y versus contribution from low-temperature component to relaxation of residual deformation $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ for PMMA compressed at different temperatures (1), plasticized PMMA (2), and copolymers of MMA with BMA (3), OMA (4), and LMA (5).

curve. Hence, there is a good correlation between σ_y and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ and this correlation is independent of any variations in these parameters: either by varying $T_{\rm def}$ of PMMA, or plasticization of PMMA, or copolymerization of MMA with BMA, OMA and LMA. This fact is likely to be associated with the difference between T_g and $T_{\rm def}$, which is defined as $\Delta T_{\rm def}=T_g-T_{\rm def}$.

Experimental evidence allows one to estimate both σ_y and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ at a certain $\Delta T_{\rm def}$ (Tab. II). At a given $\Delta T_{\rm def}$, σ_y and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ remain unchanged and are independent of any variations in $\Delta T_{\rm def}$: by increasing $T_{\rm def}$ at a fixed T_g or by decreasing T_g at a fixed $T_{\rm def}$. Depression in T_g was attained by either plasticization of PMMA or by copolymerization of MMA with BMA, OMA and LMA. Note, that such behavior is likely to be associated with the dynamics of segmental mobility in polymer glasses.

As was mentioned earlier, low-temperature relaxation of residual deformation at temperatures well below T_g proceeds via low-temperature mode of the spectrum of segmental mobility within structural sublevels with lower packing densities. Obviously, a certain fraction of low-temperature mode of segmental mobility is able to relax during polymer loading. From this viewpoint, low-temperature component ε_1 is likely to be associated with stored plastic deformation, which remained unrelaxed during deformation. With decreasing $\Delta T_{\rm def}$, local segmental mobility in certain structural regions is enhanced. 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 both $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ and σ_y is observed.

The dynamics of segmental mobility seems to be controlled not only by $\Delta T_{\rm def}$ but also by strain rate [11, 12]. One could expect, that with increasing strain rate, the fraction of low-temperature mode of

TABLE II Yield stress σ_y and contribution from low-temperature component to relaxation of residual deformation $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ of PMMA and various copolymers of methyl methacrylate at a given $\Delta T_{\rm def}$

$\Delta T_{def}, K$	σ_y, GPA	$\varepsilon_1/(\varepsilon_1+\varepsilon_2)$
80–90	0.105 ± 0.010	0.86 ± 0.02
70–80	0.090 ± 0.005	0.81 ± 0.04
60–70	0.065 ± 0.005	0.70 ± 0.02
40–50	0.055 ± 0.005	0.60 ± 0.03

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segmental mobility, which is able to relax during deformation, decreases. As a result, both σ_y and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ should increase. To verify this idea, copolymers of MMA with BMA, OMA and LMA were tested under the compression with different strain rates.

For copolymer samples, with increasing strain rate from 0.1 to 100%/min, increase in both σ_y and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ is observed. Figure 4 shows the dependence of σ_y on $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$, when these parameters were varied by changing strain rate. In this case, a well-pronounced correlation between σ_y and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ is also observed.

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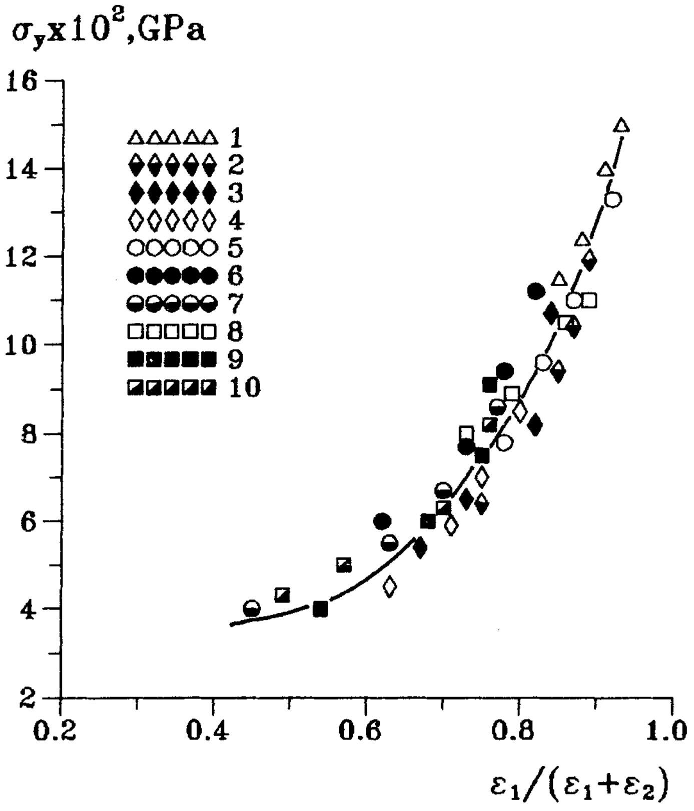

FIGURE 4 Yield stress σ_y versus contribution from low-temperature component of relaxation of residual deformation $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ for PMMA (1) and various copolymers of MMA. Monomer feed composition: MMA/BMA-80/20(2), 70/30(3) and 50/50(4); MMA/OMA-95/5(5), 90/10(6) and 80/20(7); MMA/LMA-95/5(8), 90/10(9) and 85/15(10). Comments are given in text.

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CONCLUSION

Low-temperature and high-temperature components of temperature-induced relaxation of residual plastic deformation are related to structural inhomogeneity of polymer glasses: coexistence of structural sublevels with characteristic relaxation time and energy of activation of segmental mobility. In other words, the spectrum of segmental mobility in glassy polymer is controlled by structural inhomogeneity in polymer glasses.

The ratio between low-temperature and high-temperature components of relaxation of residual deformation provides an information concerning the dynamics of segmental mobility within certain structural sublevels during loading. For copolymers of MMA with BMA, OMA and LMA and for PMMA samples, there is an evident correlation between the above ratio and yield stress, and this correlation is independent of any variations in these parameters: either by varying $\Delta T_{\mathrm{def}} = T_g - T_{\mathrm{def}}$ or by varying strain rate. This experimental evidence allows one to conclude that plastic deformation and, in general, physical and mechanical behavior of polymer glasses is likely to be controlled by segmental mobility within different structural sublevels and their contributions to deformation and relaxation.

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