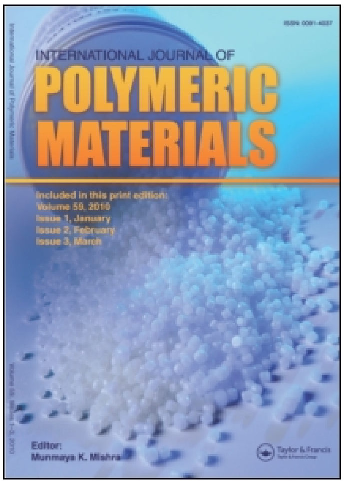

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Physical and Mechanical Behavior of Polymer Glasses in Terms of Temperature-Induced Relaxation of Plastic Deformation

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Temperature-induced relaxation of residual plastic deformation of polymer glasses was discussed in terms of structural inhomogeneity of glassy polymers. Mechanical properties of glassy polymers were shown to be controlled by the ratio between low-temperature and high-temperature components of temperature-induced relaxation of residual deformation. This ratio was treated as a new physical parameter describing physical and mechanical behavior of polymer glasses. The applied aspects of studying temperature-induced relaxation of residual deformation concerning the prepartion of modern polymer materials were discussed.

Keywords: Polymer glasses; plastic deformation; relaxation; mechanical properties

INTRODUCTION

Polymer glasses are widely used as modern materials (for example, engineering plastics) because of their unique properties, in particular, lowered brittleness and well-pronounced ductility as compared with low-molecular-mass glassy materials. For further development of advanced polymeric materials based on glassy polymers one should understand and origin of the specific properties of polymer glasses and, in general, the origin of their physical and mechanical behavior.

To solve this problem, studying temperature-induced relaxation of residual plastic deformation in polymer glasses was shown [1 – 6] to provide an important information. Temperature-induced relaxation of plastic deformation in polymer glasses is known [7 – 10] to involve low-temperature component at temperatures well below glass transition temperature T_g and high-temperature component at temperatures close to T_g. Obviously, such complicated character of relaxation of plastic deformation is a manifestation of physical processes, which are responsible for an accompany plastic deformation. In this case, development of plastic deformation and physical and mechanical behavior of glassy polymers are likely to be controlled by the coexistence of the above components of relaxation.

Earlier [4, 5, 11], mechanical characteristics and the ratio between low-temperature and high-temperature components of temperature-induced relaxation of plastic deformation of polymer glasses were shown to be well correlated. The origin of this correlation was discussed in terms of structural inhomogeneity of polymer glasses.

In the present paper, we summarized our previous speculations concerning the description of physical and mechanical behaviour of polymer glasses from the standpoint of temperature-induced relaxation of plastic deformation. These speculations are based on the studying temperature-induced relaxation of plastic deformation in virgin PMMA [4, 5, 10], PMMA plasticized with dibutyl phtalate (DBPh) [4, 5], PMMA containing diethyl siloxane oligomer (DES) [12, 13], PMMA cross-linked with ethylene glycol dimethacrylate (EGDM) and triethylene glycol dimethacrylate (TGDM) [14], and copolymers of methyl methacrylate (MMA) with butyl methacrylate (BMA), octyl methacrylate (OMA), and lauryl methacrylate (LMA) [11].

1. Some Comments Concerning the Experimental Methods to Study the Temperature-Induced Relaxation of Residual Plastic Deformation of Polymer Glasses

To study temperature-induced relaxation of residual deformation of polymer glasses we used the following porcedures:

A. For initial PMMA, PMMA plasticized with DBPh, and PMMA containing DES, cylindrical test samples with a height h_0 were uniaxially compressed at different temperatures to a given strain. After that, they were cooled with liquid nitrogen in a stressed state. Then, the free-standing samples were heated to 213 K. The height of the samples at this temperature was denoted as h_{213}. The relaxation of residual deformation was estimated by measuring the height of the samples on heating from 213 K at a heating rate of 1 K/min. The height of the samples at a given temperature was denoted as h_T. The relative residual deformation at a given temperature was estimated as $\varepsilon_{res} = (h_0 - h_T)/(h_0 - h_{213})$. For PMMA sample, typical temperature dependence of ε_{res} is shown in Figure 1. Low-temperature component ε_1 and high-temperature component ε_2 of residual deformation was estimated as follows from Figure 1. Note, that, in this case, a certain fraction of residual deformation is lost on heating free-standing polymer sample to initial test temperature (213 K).

B. For copolymers of MMA with BMA, OMA, and LMA, cylindrical test samples with a height h_0 were uniaxially compressed at 293 K to a given strain. The height of stressed samples was denoted as h_{def}. After that, they were unloaded at this temperature. The free-

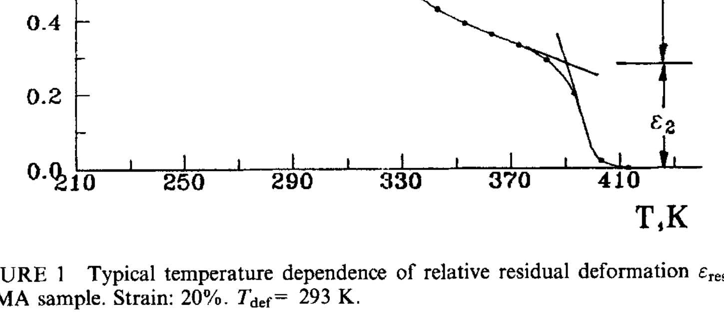


FIGURE 1 Typical temperature dependence of relative residual deformation ε_{res} in PMMA sample. Strain: 20%. T_{def} = 293 K.

standing samples were heated to a given temperature and allowed to relax at this temperature until the equilibrium height h_T was attained. Relative residual deformation at a given temperature was estimated as $\varepsilon_{res} = (h_0 - h_T)/(h_0 - h_{def})$. Note, that, in this case, residual deformation estiamted involves Hookean component of relaxation.

Reference tests demostrated that results obtained by methods A and B are in a fair agreement and may be compared with each other.

C. For cross-linked PMMA samples, cylindrical test samples with a height h_0 were uniaxially compressed at 293 K to a given strain. After that, they were unloaded at this temperature and allowed to relax at this temperature until the equilibrium height h_{293} was attained. Then, the free-standing samples were heated 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. Relative residual deformation at a given temperature was estimated as $\varepsilon_{res} = (h_0 - h_T)/(h_0 - h_{293})$. In this case, the fraction of residual deformation, which is able to relax at temperatures below 293 K, is lost. So, the results obtained by this method can not be quantitatively compared with those obtained methods A and B.

2. Structural Intepretation of Temperature-Induced Relaxation of Plastic Deformation of Polymer Glasses

A typical temperature dependence of relative residual deformation ε_{res} in PMMA samples (Fig. 1) shows that residual deformation ε_{res} involves low-temperature (ε_1) and high-temperature (ε_2) components and may be represented as follows

$$\varepsilon_{res} = \varepsilon_1 + \varepsilon_2 \tag{1}$$

Note, that temperature-induced relaxation of residual deformation via high-temperature component ε_2 is observed in rather narrow temperature region close to glass transition. Relaxation of plastic deformation via low-temperature component ε_1 takes place in a wide temperature region well below glass transition temperature, and each temperature is associated with a certain portion of relaxation of residual deformation.

High-temperature component of relaxation is associated with the transition of excited chain conformations to their initial equilirbrium state via segmental mobility in polymer sample. The origin of low-temperature component of relaxation 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 [1, 2] (i) and structural inhomogeneity of glassy polymers [4, 5, 10] (ii). Within the framework of the later approach, glassy polymer is characterized by a set of structural sublevels with different packing densities and ordering.

Each of these sublevels is associated with its own relaxation time and activation energy of segmental mobility. As a result, at each temperature below glass transition temperature, 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 and local ordering.

In the case of the deformed polymer samples, as temperature increases, the appearance of segmental mobility in strucutural levels with higher packing density is accompanied by a gradual recovery of local plastic deformation within the above structural sublevels. In other words, 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. A complete relaxation of plastic deformation at T_g via high-temperature component is controlled by high-temperature fraction of the spectrum of segmental mobility. Hence, molecular mechanism of low-temperature relaxation is similar to that of high-temperature mode and involves transition of excited chain conformations to initial equilibrium state via segmental motion within certain structural sublevels.

In [4, 5], ratio between the components associated with low-temperature and high-temperature relaxation was studied as a function of strain. For the compressed samples with rather low strains (Fig. 2, curves 1, 2), complete relaxation takes place at temperatures well below T_g. On the contrary, a complete relaxation of the compressed samples with high strains is observed on heating to T_g (Fig. 2, curves 3–5). Note, that in this case, low-temperature component of relaxation is also involved.

Figure 3 presents low-temperature (ε_1) and high-temperature (ε_2) components of temperature-induced relaxation of plastic deformation as a function of strain and the corresponding stress-strain curve of uniaxial compression of PMMA samples. As follows from Figure 3, in the case of the samples with strains below yield strain ε_y, temperature-induced relaxation of plastic deformation proceeds via low-temperature component ε_1. At the strain corresponding to ε_y, component ε_1 is maximal, and further increase in compression strain is associated with the appearance and growth in the high-temperature component ε_2 at constant ε_1.

The results obtained allowed us to advance the following structural pattern of the development of plastic deformation in glassy polymers. At strains below yield strain, deformation is controlled by the stress-

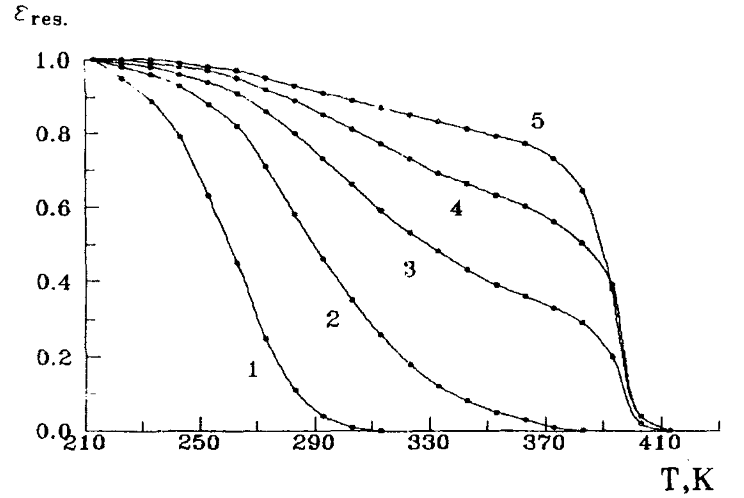


FIGURE 2 Temperature dependences of relative residual deformation ε_{res} in PMMA samples with strains 10 (1), 14 (2), 20 (3), 30 (4), and 50% (5). T_{def} = 293 K.

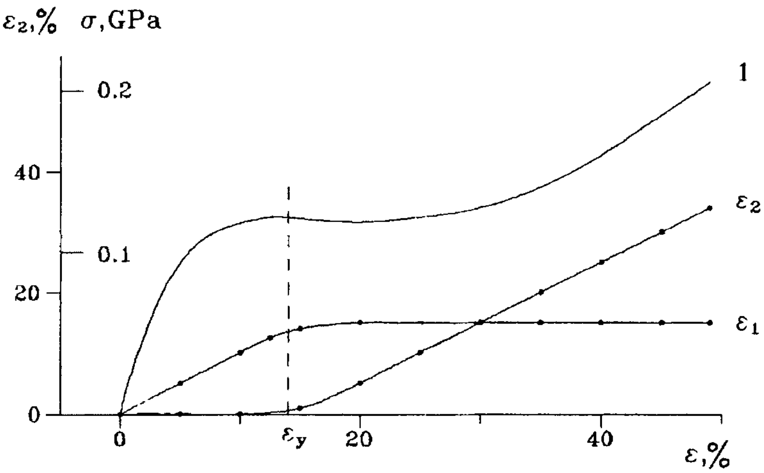


FIGURE 3 Stress-strain curve corresponding to uniaxial compression of PMMA samples at 293 K (1) and low-temperature ε_1 and high-temperature components ε_2 of temperature-induced relaxation of residual deformation versus strain ε.

induced segmental mobility within 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 mode of the spectrum of segmental mobility. At strains above yield strain, plastic deformation is controlled by the stress-induced segmental mobility within 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.

Let us descuss the validity of the mechanism proposed, namely, the validity of the following assumptions: structural inhomogeneity of polymer glasses (i), and realization of low-temperature segmental mobility at temperatures well below T_g within certain structural sublevels (ii).

2.1. On Structural Inhomogeneity of Polymer Glasses

Note, that during recent decades, structural inhomogeneity in glassy polymers is widely discussed in literature. Review of existing experimental evidences is is beyond the scope of the present paper. Let us mention only some of them.

As demonstrated by electron microscopy [15–22], electron diffraction [21, 23], positron annihilation lifetime spectroscopy [12, 24], light scattering measurements [25], small-angle X-ray scattering [19], and wide-angle X-ray scattering [23], polymer glasses are characterized by structural inhomogeneity related to the existence of heterogeneous ordered regions with higher packing density (domains, clusters) with dimensions up to several nanometers. These domains are joined with each other by numerous tie chains, which constitute the regions with lower packing densities and degrees of ordering.

Experimental evidence obtained provided a fundamental basis for the development of various structural models of glassy polymers. The difference between the models advanced is related to the type of principal morphological structural unit: fibril [9, 10], domain [26, 27], globule [28–30], and cluster [31, 32]. However, at the present time a certain lack of convincing experimental evidence does not allow one to decide in favor of this or that particular model. Hence, in this work, our speculations will be based only on unequivocal conclusion concerning structural inhomogeneity of glassy polymer, which is associated with the existence of, at least, two local strucutral sublevels with different packing densities and degrees of ordering of macromolecules or their fragments. Note, that these speculations allow a plausible description of specific effect of plasticizing agents on molecular mobility in polymers [33, 34], dual-mode sorption of gases by glassy polymers [35–37], and development of the irreversibly bound form of low-molecular-mass compounds in polymers [38–40].

In our opinion, the speculations concerning structural inhomogeneity in polymer glasses should have loical development. Structural sublevels with higher and lower packing densities as recognized by modern structural studies are limiting cases in structural organization of glassy polymer. We believe, that there is a continuous spectrum of intermediate states (structural sublevels) with different packing densities and degrees of ordering. As was mentioned above, this structural spectrum is likely to be responsible for the spectrum of segmental mobility in glassy polymers.

2.2. On Low-Temperature Segmental Mobility in Polymer Glasses

A possible realization of segmental mobility in local structural sublevels at temperatures well below glass transition temperature is widely discussed in literature. Let us mention some works [34, 41–43], in which specific dual transitions observed in temperature region of glass transition were treated in terms of existence of structural regions with different packing densities. In this case, low-temperature transition is attributed to the appearance of segmental mobility in loosely packed regions, whereas high-temperature transition is related to segmental mobility in densely packed domains.

Speculations concerning the mechanism of the β-relaxation in glassy polymers [44] based on DSC measurements of activation parameters of the β-transition [45–47] allowed one to conclude that β-transition involves quasi-independent and localized motion of statistic segments within structural regions with lower packing densities.

As was shown in [12, 24] using positron annihilation lifetime spectroscopy, the dimensions of free volume microregions in loosely packed structural regions in PMMA at 293 K are equal to 0.3–0.4 nm^3. By order of magnitude, this value coincides with activation volume of relaxation segmental transition (0.8–1.0 nm^3) and with the volume of statistic segment of PMMA (0.9 nm^3) [44]. This fact may serve as a supporting evidence concerning realization of segmental mobility within structural sublevels with lower packing densities at temperatures well below T_g.

Additional factors assisting segmental mobility in local structural regions in glassy polymer are the following. First, asymmetry of the field of intermolecular interaction provided by free volume microregions is associated with a decrease in activation energy of segmental mobility [48]. Secondly, a certain decrease in activation energy of segmental mobility may be also related to the existence of inner stresses stored in polymer during deformation [9, 10]. From this standpoint, low-temperature segmental mobility is controlled by mechanical activation under inner stresses stored in deformed polymer sample.

Hence, literature data evidence the validity of our speculations concerning the structural pattern of plastic deformation and its temperature-induced relaxation in polymer glasses.

To provide experimental support of the mechanism proposed, the structural changes during plastic deformation were studied using positron annihilation lifetime spectroscopy [12, 24]. Application of this technique allows one to estimate the effective radius R_+ and concentration of free volume microregions N_+ in structural sublevels with higher packing densities as well as the corresponding values of R_{Ps} and N_{Ps} in structural sublevels with lower packing densities. As was shown, for initial PMMA samples at 293 K, $R_+ \approx 0.34$ nm, $N_+ \approx 0.7 \times 10^{16}$ cm^{-3}, $R_{Ps} \approx 0.42$ nm, and $N_{Ps} \approx 1.46 \times 10^{19}$ cm^{-3}. For plastically deformed PMMA samples (residual deformation stored in unloaded samples was 16.5%), the corresponding values were the following; $R_+ \approx 0.34$ nm, $N_+ \approx 1.0 \times 10^{16}$ cm^{-3}, $R_{Ps} \approx 0.45$ nm, and $N_{Ps} \approx 0.66 \times 10^{-3}$. As follows from these data, deformation of PMMA is accompanied by slight change in N_+ from 0.7×10^{16} to 1.0×10^{16} cm^{-3}. Note, that this change in N_+ lies within anticipated experimental error (20%). At the same time, a two-fold decrease in N_{Ps} is observed: from 1.46×10^{19} to 0.66×10^{19} cm^{-3}. Dimensions of free volume microregions (R_+ and R_{Ps}) remains unchanged. This experimental evidence allows one to conclude, that, for PMMA samples with strains close to yield strain, deformation is likely to be controlled by densification of structural regions with low packing densities whereas densely packed structural sublevels remain intact.

Obviously, any changes in initial polymer structure and concomitant changes in packing density within the above structural sublevels should have a certain effect on both mechanical and relaxation properties of glassy polymers. Structural changes in polymer may be accomplished by introduction of incompatible low-molecular-mass compounds, which are unable to produce a uniform distribution in polymer volume. This approach was formalized in terms of structural plasticization of polymers [49, 50]. Structural plasticization may be rationalized as follows: a low-molecular-mass compound with a low thermodynamic affinity to polymer is localized within local structural regions at boundaries between supramolecular or suprasegmental structures of glassy polymer. In this case, within these regions, changes in mobility of macromolecules or their fragments is observed, and this has a certain effect on mechanical behavior of polymer material. In [13], for PMMA, diethyl siloxane oligomer (DES) was used as such low-molecular-mass modifying agent.

Figure 4 shows the concentration dependences of yield stress σ_Y for uniaxial compression of PMMA samples containing DES (curve 1) as well as contribution from low-temperature component to total temperature-induced relaxation of residual deformation $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ (curve 2). As follows from Figure 4, at 0.1 wt.% of DES in PMMA, an increase in both σ_y and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ is observed. With increasing concentration of DES in polymer, these parameters decrease. The effect of DES in PMMA on σ_y and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ is likely to be related to changes in segmental mobility in certain structural sublevels because of changes in packing density and fractional content of free volume. To verify this assumption, the positron annihilation lifetime spectroscopy was used to follow changes on elementary free volume induced by introduction of DES in PMMA samples.

For all samples studied at 293 K, $R_+ \approx 0.34$ nm and $R_{Ps} \approx 0.42$ nm. For initial PMMA and PMMA containing 0.1 wt.% of DES, $N_+ \approx 0.9\times10^{16}\,\text{cm}^{-3}$ and $N_{Ps} \approx 1.0\times10^{19}\,\text{cm}^{-3}$. As content of DES in PMMA increases, increasing both N_+ and N_{Ps} is observed. For PMMA

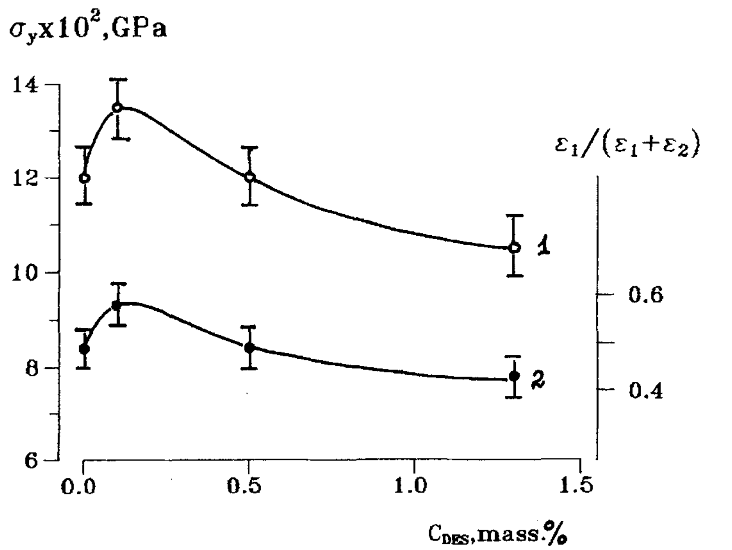


FIGURE 4 Dependences of yield stress σ_y (1) and contribution from low-temperature component to relaxation of residual deformation $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ (2) on the content of DES in PMMA.

samples containing 0.5 and 1.3 wt. % of Des, $N_+ \approx 1.15 \times 10^{16}$ cm^{-3} and $N_{Ps} \approx 2.2 \times 10^{19}$ cm^{-3}.

Hence, introduction of DES into PMMA is not accompanied with the changes in the dimensions of free volume microregions both in structural regions with increased and decreased packing density in polymer. The content of free volume microregions in more densely packed structural regions N_+ changes with increasing DES content in PMMA but still lies within expected error (20%). Concentration of free volume microregions in loosely packed structural regions N_{Ps} increases by two times, and this evidence suggests that introduction of DES into polymer is associated with loosening of these structural regions. Constancy of annihilation characteristics for PMMA samples containing 0.1 wt % of DES as compared with virgin PMMA may be reationalized by the fact that low-molecular-mass additive occupies rather large free volume microregions. These regions are located far away from each other, and distances between them are much higher than diffusion paths of positron and positronium. As a results, they appear to be beyond the detection limit of this method.

This structural interpretation of experimental evidence obtained by the method of positron annihilation correlates well with earlier structural studies in polymer glasses (for example, [15–17]). Structure of glassy polymer was shown to be characterized by a set of densely packed regions (domains) separated by structural regions with lower packing density. (Let us note that the term "domains" is used only to specify structural elements with increased packing density and carries no information concerning the structure of these regions). Domains are able to aggregate with each other and produce more complicated supradomain structures. The boundary regions between supradomain structures are more loosely packed as compared with interdomain regions. Hence, experimental evidence obtained allowed identification of three structural sublevels in glassy polymers listed in order of increase in free volume: domains, interdomain regions, and boundary regions between supradomain structures. Three-component treatment of lifetime distributions of annihilation radiation allows one obtain information concerning free volume fraction for domains and interdomain regions.

According to this approach, the effect of introduction of DES on mechanical properties of PMMA containing DES may be presented as follows. At low content of DES (0.1 wt %), DES molecules occupy rather large free volume microregions located at boundaries between supradomain structures. As a result, segmental mobility in the vicinity of these microregions is hindered, and mechanical properties of polymer material increase (Fig. 4). With increasing the content of DES in PMMA to 0.5 and 1.3 wt %, low-molecular-mass additive is able to enter interdomain structural regions. This penetration is accompanied by loosening of these regions and additional free volume microregions appear. As a result, within these structural regions, segmental mobility of macromolecules is enhanced, and σ_y and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ decrease (Fig. 4). During introduction of DES into PMMA, densely packed domains remain intact and do not contribute to changes in mechanical properties of the system.

The effect of DES on segmental mobility of PMMA is supported by DSC data (Fig. 5). At 0.1 % of DES in PMMA, endothermic jump in glass transition region increases as compared with initial PMMA (transition from curve 1 to curve 2). This evidence suggests a suppressed segmental mobility of polymer chains from polymer samples containing low-molecular-mass additive. As concentration

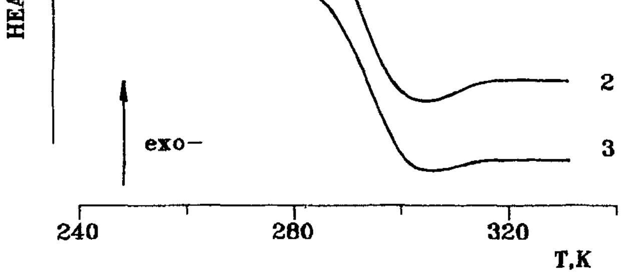


FIGURE 5 DSC curves of PMMA (1) and PMMA with 0.1 (2) and 1,3 wt % of DES (3).

of DES in PMMA increases (curve 3), endothermic jump decreases, and this behavior is related to an enhanced segmental mobility of polymer chains.

Hence, structural interpretation of temperature-induced relaxation of plastic deformation allowed us to advance structural pattern of plastic deformation of polymer glasses based on gradual involvement of segmental mobility within structural sublevels with different packing densities in deformation and relaxation. The validity of this structural pattern is supported by literature data as well as by direct structural studies using positron annihilation lifetime spectroscopy.

3. A New Approach to Description of Physical and Mechanical Behaviour of Polymer Glasses

As was mentioned above, 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 of segmental mobiliy is able to relax during polymer loading. Let us define this component as ε_1^*. 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.

From this standpoint, plastic deformation of glassy polymer may be presented as

$$\varepsilon = \varepsilon_1^* + \varepsilon_{\text{res}} = (\varepsilon_1^* + \varepsilon_1) + \varepsilon_2 \qquad (2)$$

According to equation (2), plastic deformation of glassy polymer may be described by the contributions from components ε_1 and ε_2 to temperature-induced relaxation of residual deformation. At $\varepsilon \leq \varepsilon_y$, deformation is primarily controlled by $(\varepsilon_1^* + \varepsilon_1)$, whereas at $\varepsilon \geq \varepsilon_y$ component ε_2 comes into play.

With respect to polymer strength properties, consideration of component $(\varepsilon_1^* + \varepsilon_1)$ is of most interest. This parameter is responsible for the development of polymer deformation at initial portion of $\sigma-\varepsilon$ curve, i.e., at $\varepsilon \leq \varepsilon_y$, which is associated with such mechanical properties as elastic modulus E_0 and yield stress σ_y. This allows one to suggest the correlation between relaxation $(\varepsilon_1^* + \varepsilon_1)$ and mechanical characteristics E_0 and σ_y.

To verify this correlation, PMMA samples were compressed to different strains at different temperatures. Then, temperature-induced relaxation of residual deformation ε_{res} was studied (Fig. 6). For the lack of space, recovery curves are presented only for the samples with 14 and 20% strains. As deformation temperature T_{def} increases, the contribution from low-temperature component ε_1 to relaxation of residual deformation is seen to decrease. At test temperatures close to glass transition temperature, the relaxation of ε_{res} is controlled only by

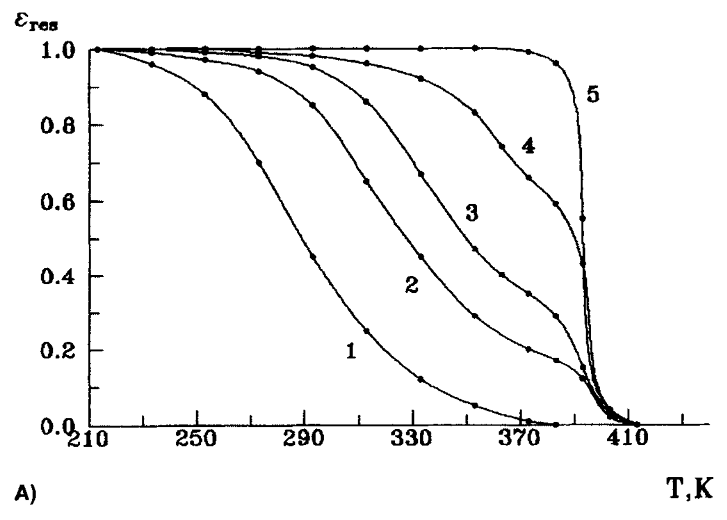
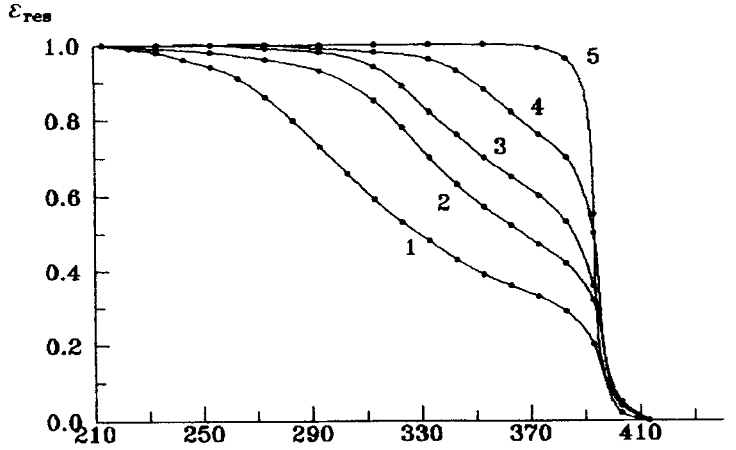


FIGURE 6 Temperature dependence of relative residual deformation ε_{res} in PMMA samples at $T_{def}=293$ (1), 320 (2), 333 (3), 353 (4), and 383 K(5). Strain: 14 (A) and 20% (B).



B)

FIGURE 6 (Continued).

high-temperature component ε_2 (Fig. 6, curves 5). On the other hand, as T_{def} increases, elastic modulus and yield point go down.

This experimental evidence suggests an intimate correlation of elastic modulus and yield stress with the contribution from low-temperature component to total relaxation of plastic deformation $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ (Fig. 7). At any strains, similar tendency is observed: as contribution from component ε_1 to relaxation of ε_{res} decreases, both elastic modulus and yield stress tend to decrease.

With increasing T_{def}, the parallel decrease in both $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ and E_0 and σ_y is likely to be controlled by the fact, that, in this case, local segmental mobility in certain structural sublevels 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. In terms of equation (2), this implies an concrease in component ε_1^* via decreasing component ε_1. In turn, as contribution from component ε_1 to relaxation of ε_{res} decreases, component ε_2 increases.

Obviously, the enhancement of segmental mobility in polymer sample is controlled not only by increasing T_{def}, but also by decreasing T_g. Depression in T_g may be attained by either plasticization of PMMA or by copolymerization of MMA with methacrylic monomers.

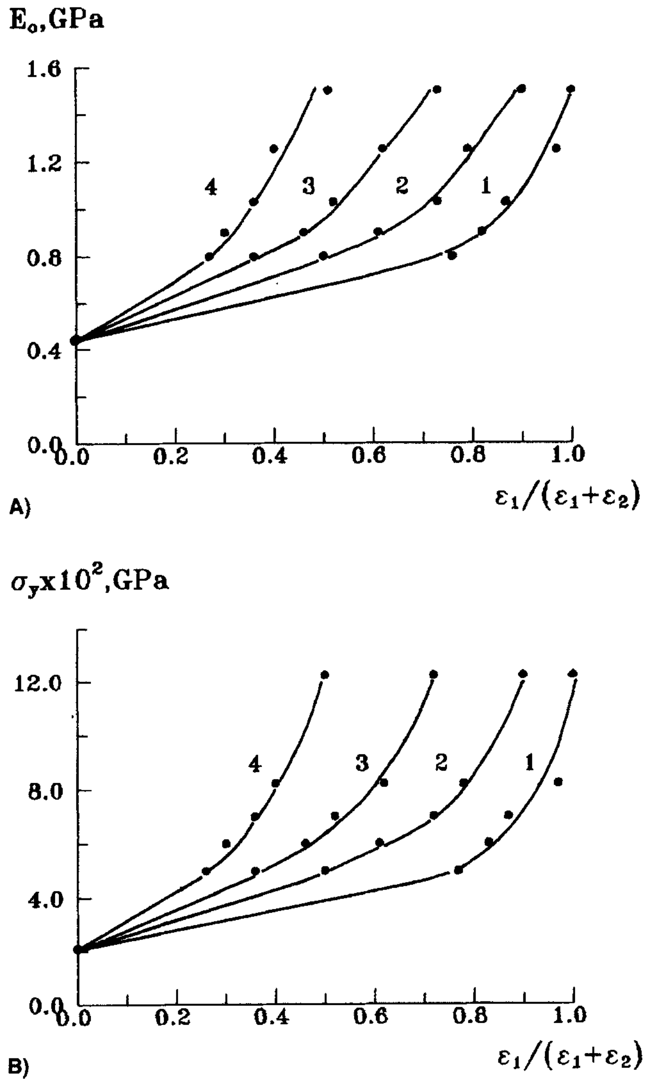


FIGURE 7 The dependence of elastic modulus E_0(A) and yield stress σ_y(B) of PMMA samples on the contribution from low-temperature component to relaxation of residual deformation $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$. Strain: 10 (1), 14 (2), 20 (3), and 30% (4).

To verify this idea, for PMMA samples plasticized with DBPh as well as for copolymers of MMA with BMA, OMA, and LMA, mechanical behavior and temperature-induced relaxation of residual deformation were studied [4, 5, 11]. As was shown, with increasing concentration of DBPh in PMMA and 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 (Tab. I).

For copolymers of MMA as well as for PMMA deformed at different $T_{\rm def}$ and plasticized PMMA, Figure 8 shows the dependence of σ_y on $\varepsilon_1(\varepsilon_1+\varepsilon_2)$. As follows from Figure 8, all experimental data fit one 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 presented in Table I 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

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

Sample	T_g	$T_{\rm def}$, *K*	σ_y,*GPa*	$\varepsilon_1/(\varepsilon_1+\varepsilon_2)$	$\Delta T_{\rm def}$, *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	–	0.90	0.78	75
90/10	353	–	0.060	0.68	60
85/15	338	–	0.050	0.57	45

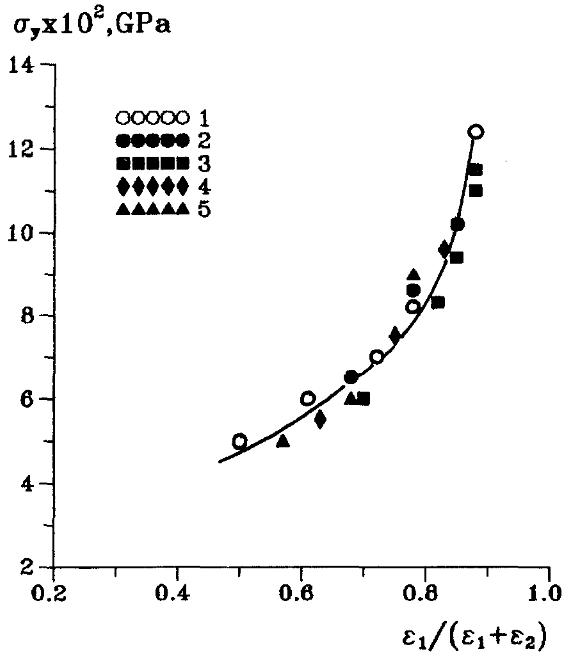


FIGURE 8 Yield stress σ_y versus contribution from low-temperature component to relaxation of residual deformation $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ for PMMA compressed at different temperautres (1), plasticized PMMA (2), and copolymers of MMA with BMA (3), OMA (4), and LMA (5).

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 $\Delta T_{\rm def}$

$\Delta T_{\rm def}$, *K*	σ_y, *GPa*	$\varepsilon_1/(\varepsilon_1+\varepsilon_2)$
80–90	0.105 ± 0.010	0.86 ± 0.04
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

variations in $\Delta T_{\rm def}$: by increasing $T_{\rm def}$ at a fixed T_g or by decreasing T_g at a fixed $T_{\rm def}$. Note, that such behavior is likely to be associated with the dynamics of segmental mobility in polymer glasses.

The dynamics of segmental mobility seems to be controlled not only by $\Delta T_{\rm def}$ but also by strain rate [51, 52]. One could expect, that with increasing strain rate, the fraction of low-temperature mode of 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, wtih increasing strain rate from 0.1 to 100 % min, increase in both σ_y and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ is observed. Figure 9 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.

The above 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. Note, that such restriction of segmental mobility in

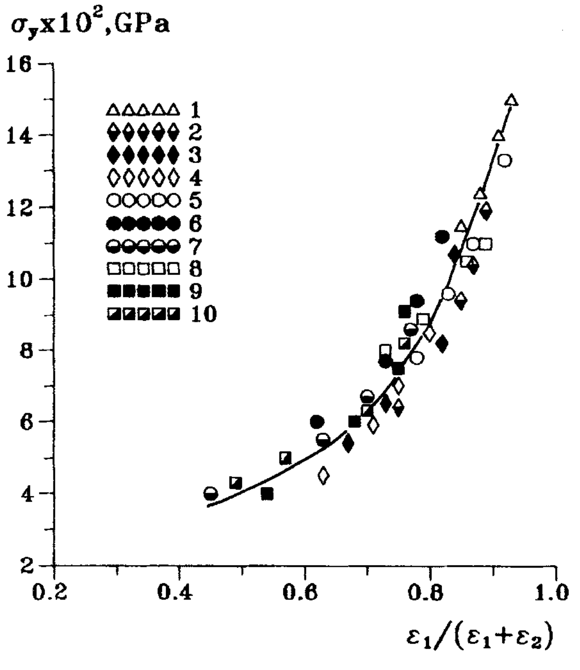


FIGURE 9 Yield stress σ_y versus conctribution from low-temperature component to relaxation of residual deformation $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ for PMMA (1) and various copolymers of MMA. Monomer feed composition: MMA/BMA - 80/20 (2), 70/30 (3), and 50/50 (4); MMA/OMA - 95/5 (5), 90/10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

polymer sample may be achieved by cross-linking of polymers [53]. To verify this idea, for PMMA samples cross-linked with bifunctional monomers ethylene glycol dimethacrylate (EGDM) and triethylene glycol dimethacrylate (TGDM), temperature-induced relaxation of residual deformation was studied.

For PMMA samples, cross-linked with EGDM, temperature dependences of residual deformation are shown in Figure 10. Note, that, with increasing concentration of cross-linking agent in PMMA samples to 2.5 and 5.2 mol% (curves 2 and 3), contribution from low-temperature component ε_1 to total relaxation of residual deformation increases as compared with initial PMMA (curve 1). With increasing concentration of EGDM to 11.2 mol% (curve 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.

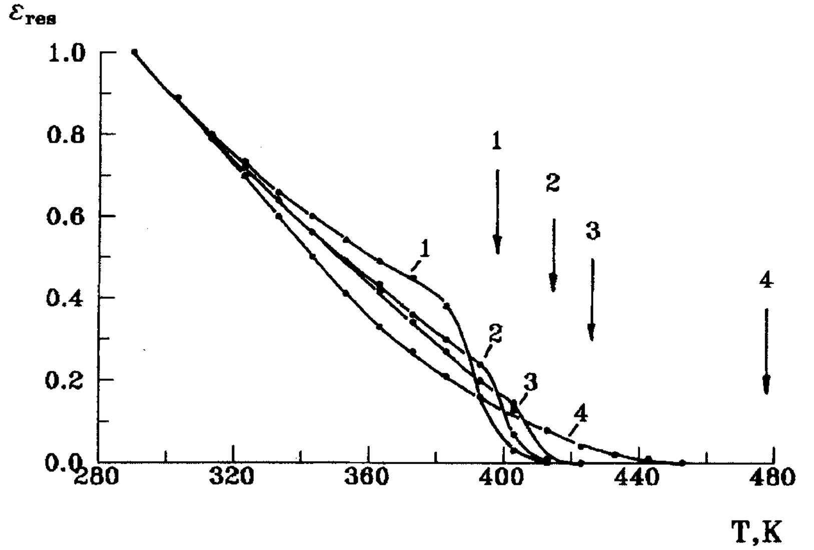


FIGURE 10 Temperature dependences of relative residual deformation ε_{res} of PMMA (1) and PMMA, cross-linked with 2.5 (2), 5.3 (3), and 11.2 mol.% EGDM (4). Strain: 20% $T_{def}=293$ K. The arrows show T_g of the corresponding polymer samples.

Hence, for cross-linked PMMA samples, restriction of segmental mobility within certain structural sublevels is accompanied by increasing contribution from low-temperature component ε_1 to total temperature-induced relaxation of residual deformation. This experimental evidence may be attributed to the fact, that, in this case, low-temperature mode of the whole spectrum of segmental mobility is not able to relax during deformation. Obvioulsy, restriction segmental mobility should be controlled by the length of the molecule of cross-linking agent.

Figure 11 shows the temperature dependences of residual deformation ε_{res} for cross-linked PMMA samples with the similar concentration of EGDM and TGDM. At transition from EGDM to TGDM (curves 2 and 3, respectively), increasing the length of cross-links results in decrease in low-temperature component ε_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.

Hence, the ratio between components ε_1 and ε_2 to recovery of plastic deformation provides an important information concerning specific features of polymer deformation and relaxation and is

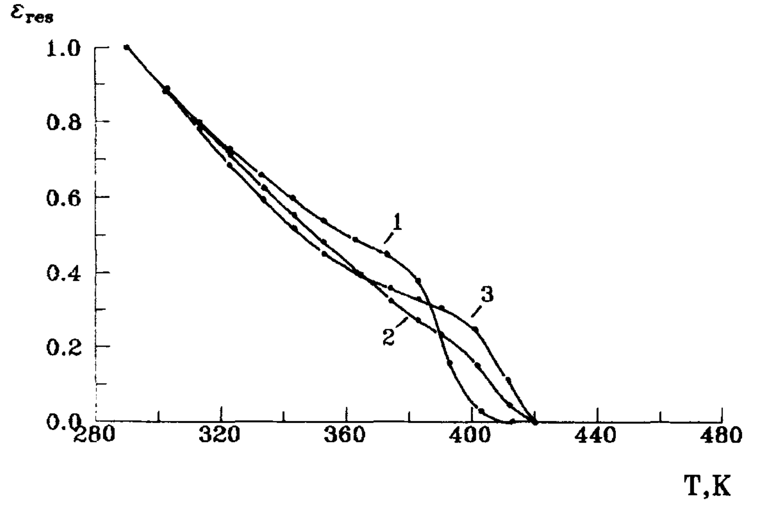


FIGURE 11 Temperature dependences of relative residual deformation ε_{res} of PMMA (1) and PMMA, cross-linked with EGDM (2) and TGDM (3). Concentration of cross-linking agents: 5.2 mol.%. Strain: 20%. $T_{def} = 293$ K.

responsible for polymer mechanical behavior. This ratio may be treated as new physical parameter describing physical and mechanical behavior of polymer glasses.

Correlation between the above components of temperature-induced relaxation of residual deformation and polymer brittleness is quite evident. As was shown earlier, as T_{def} decreases, component ε_2 tends to vanish (Fig. 6). Brittle fracture of polymer material is likely to take place at temperatures, where component ε_1 is not able to store during deformation. Degeneration of component ε_1 implies that segmental mobility in polymer samples is ceased at all levels of structural inhomogeneity. Hence, temperature region from T_{br} to T_g may be treated as temperature interval, where higher limit is associated with manifestation of segmental mobility in whole polymer sample, and lower limit corresponds to frozen-in segmental mobility in whole polymer sample.

4. Applied Aspects of Studying Temperature-Induced Relaxation of Plastic Deformation of Polymer Glasses

Well pronounced plastic deformation of polymer glasses allows the processability of these materials into final articles by rolling, stamping, pressing, etc. And a substantial improvement in their mechanical properties. One of the approaches to improve the mechanical properties of commercial glassy polymers, in particular, toughness, is provided by the method of orientation strengthening.

However, such plastically deformed or oriented materials have one main disadvantage: as operating temperature increases, they appear to lose their shape and orientation and, as a result, their mechanical properties deteriorate dramatically and approach those characteristic of undeformed and unoriented materials. As was shown above, these processes may be rationalized as temperature-induced relaxation of plastic deformation or temperature-induced shrinkage of oriented polymers via low-temperature component ε_1 and high-temperature component ε_2. In connection with this, lowering or suppression of both components of relaxation presents a challenging task for many scientists and engineers.

A satisfactory solution of this problem offers numerous advantages. If we manage to prevent the low-temperature relaxation, this implies a substantial broadening of the temperature range of operating conditions up to T_g. However, if both components of relaxation are prevented, this will allow much progress in the development of new generation of orientation-strengthened shrinkproof polymer materials based on well-known commercial glassy polymers.

Experimental evidence concerning the relaxation of residual deformation in PMMA samples compressed at different temperatures suggests that preventing low-temperature component ε_1 of relaxation is provided by increasing deformation temperature T_{def} (Fig. 6). When polymer compression is carried out at temperatures in the vicinity of T_g, the total relaxation is primarlity controlled only by high-temperature component ε_2. This approach may serve as a serve as a scientific basis for traditional technology of preparation of orientation-strengthened polymer glasses. This technology involves orientation (tensile drawing) of a polymer above its glass transition temperature and its further cooling in a stressed state. Materials and articles prepared via this method are characterized by a stability of their both shape and orientation and, hence, resulting mechanical properties up to temperatures not exceeding T_g.

The fundamentals concerning the structural pattern of plastic deformation and its further temperature-induced relaxation in polymer glasses allowed us to solve the second part of the above problem: to suppress high-temperature component of relaxation of plastic deformation via a new approach to orientation strengthening of polymers [6]. Technological application of this approach makes it possible to prepare orientation-strengthened shrinkproof polymer materials based on PMMa. Mechanical characteristics of these materials appear to be comparable to those of a conventional oriented glass produced by a traditional technological method. However, the main advantage of such materials is associated with their high thermal stability, i.e., retention of shape, orientation and, finally, mechanical characteristics in a wide temperature range and even after heating the samples up to temperatures above the softening temperature of PMMA.

CONCLUSION

Studying temperature-induced relaxation of residual plastic deformation of polymer glasses was shown to provide an important information concerning development of plastic deformation and, in general, physical and mechanical behaviour of glassy polymers. Interpretation of temperature-induced relaxation of residual deformation in terms of structural inhomogeneity of glassy polymers allowed us to advance structural pattern of their plastic deformation based on gradual involvement of segmental mobility within different structural sublevels in deformation and relaxation.

Mechanical characteristics of glassy polymers and the ratio between low-temperature and high-temperature components of relaxation were shown to be well correlated. This correlation is independent of any variations in the above parameters: either by varying deformation temperature and strain rate, or by physicochemical modification of polymer – plasticization, cross-linking, and copolymerization. Such behavior is likely to be associated with the dynamics of segmental mobility within certain structural sublevels in glassy polymers. These speculations allowed us to treat the ratio between low-temperature and high-temperature components of temperature-induced relaxation of residual deformation as a new physical parameter describing physical and mechanical properties of polymer glasses.

From this standpoint, the problems concerning modification of polymer materials based on polymer glasses should be treated as controlled variation in the ratio between the above components of relaxation. This approach allowed us to advance a new principle of preparation of orientation-strengthened polymer glasses, which are characterized by no shrinkage in a wide range of operating temperatures even at temperatures above glass transition temperature.

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