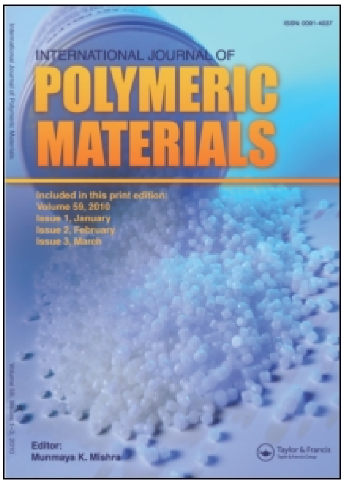

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A New Approach to the Description of Mechanical Behavior of Polymer Glasses

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

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A New Approach to the Description of Mechanical Behavior of Polymer Glasses

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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Temperature-induced relaxation of plastic deformation of polymer glasses based on PMMA was studied. Plastic deformation of polymers and their mechanical properties were described in terms of contributions from low-temperature and high-temperature components to the recovery of residual deformation. The above components of relaxation were treated as physical parameters of deformation and relaxation in polymer glasses. The ratio between low-temperature and high-temperature components was shown to be controlled by physicochemical modification of polymer materials.

KEY WORDS PMMA, polymer glasses, plastic deformation, relaxation.

INTRODUCTION

Temperature-induced relaxation of plastic deformation of polymer glasses is known to take place in two well-defined temperature regions.[1-5] A complete recovery of geometrical sizes of plastically deformed polymers is observed in glass transition region. However, a marked fraction of plastic deformation is shown to relax at temperatures much below glass transition point. In other words, relaxation of plastic deformation involves two modes: low-temperature and high-temperature modes. The studies on mechanical behavior of glassy polymers under various modes of deformation (uniaxial compression and drawing, hydrostatic compression, and creep) show[3-5] that two-stage character of relaxation of plastic deformation is a universal feature of all polymer bodies.

Complicated character of relaxation of plastic deformation of glassy polymers is a manifestation of physical processes, which are responsible for and accompany plastic deformation. In this case, mechanical properties of polymer bodies seem to be controlled by coexistence of the above modes of relaxation.

The aim of this work is to describe mechanical behavior of polymer glasses in terms of low-temperature and high-temperature components of relaxation of plastic deformation in glassy polymers.

EXPERIMENTAL

Commercial PMMA samples were used. Dibutyl phthalate (DBPh) was used as plasticizing agent. The content of plasticizing agent was varied from 1 to 10 mass%. The copolymers of MMA with bifunctional monomer ethylene glycol dimethacrylate (EGDM) were used as cross-linked PMMA. The development of network took place immediately during bulk copolymerization. The content of EGDM in polymerization system was 1.0, 5.2, and 11.2 mol%.

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 above T_g by 10–15° and then they were slowly cooled down to room temperature.

The samples of initial and plasticized PMMA were uniaxially compressed at temperatures 293, 320, 333, 343, 353, and 383 K with a strain rate of 0.1 mm/min using an UTS-100 tensile machine (Germany). After that, they were cooled with liquid nitrogen in a stressed state. Then, the free-standing samples were heated from 213 K at a heating rate of 1 K/min. The relaxation (recovery) of residual plastic deformation was estimated by measuring the height of the samples with an accuracy of ±0.001 mm.

The samples of the cross-linked PMMA were uniaxially compressed at 293 K and then they were unloaded with the same rate at this temperature. The relaxation of residual deformation was studied starting with 293 K.

Elastic modulus was estimated from the initial slope of the $\sigma - \varepsilon$ curve at strains below 3%.

RESULTS AND DISCUSSION

A typical temperature dependence of recovery (relaxation) of residual deformation ε_{res} in PMMA samples is presented in Figure 1. This curve shows that ε_{res} involves

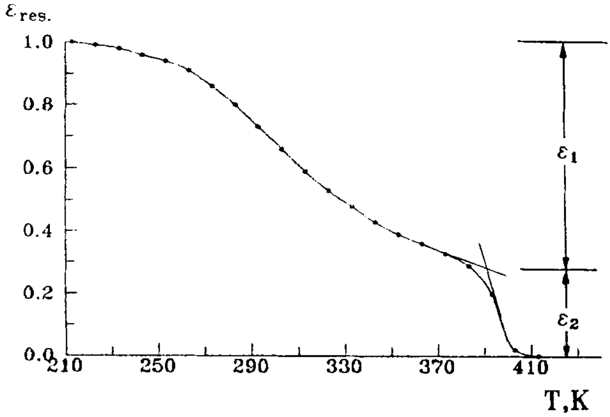

FIGURE 1 Typical curve of recovery of residual deformation ε_{res} in PMMA sample. Strain: 20%. T_{def} = 293 K.

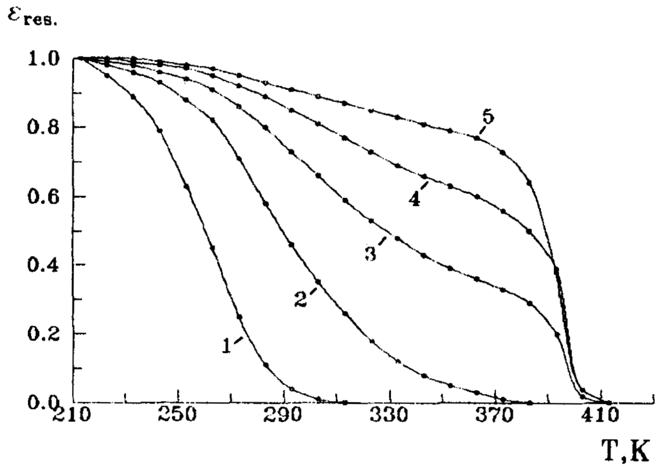

FIGURE 2 Recovery of residual deformation ε_{res} in PMMA samples with strains 10 (1), 14 (2), 20 (3), 30 (4), and 50% (5). T_{def} = 293 K.

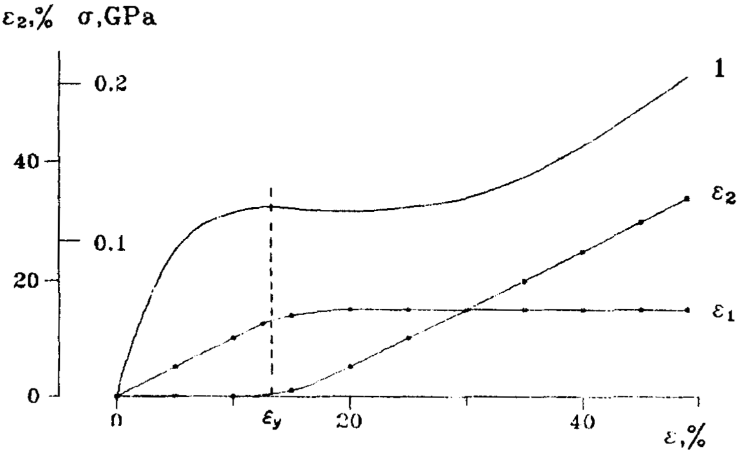

FIGURE 3 Stress-strain curve corresponding to uniaxial compression of PMMA samples at 293 K (curve 1) and low-temperature ε_1 and high-temperature components ε_2 of strain recovery versus strain ε.

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 relaxation of ε_{res} via high-temperature mode ε_2 is observed in rather narrow temperature region of glass transition. Relaxation of plastic deformation via low-temperature component ε_1 takes place in a wide temperature region below glass transition point, and each temperature is associated with a certain portion of recovery of ε_{res}.

The 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 (Figure 2, curves 1, 2), complete strain recovery takes place at temperatures below T_g. On the contrary, a complete strain recovery of the compressed samples with high strains is observed on heating to T_g (Figure 2, curves 3–5). Note that in this case low-temperature relaxation is also involved.

Figure 3 presents low-temperature (ε_1) and high-temperature (ε_2) components of 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, relaxation of plastic deformation proceeds via low-temperature mode 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 component ε_2 at constant ε_1.

At the present time, the two-stage character of recovery of polymer plastic deformation is treated in terms of two models: step-by-step recovery of small-scale plastic shear transformations and excited chain conformations[4,5] (i) and structural heterogeneity of glassy polymers[3] (ii).

Within the framework of the latter approach, glassy polymer is characterized by a set of structural sublevels with different packing densities and ordering. Let us note that structural heterogeneity in glassy polymers is widely discussed in literature.[6–9]

In our opinion, each of these sublevels is associated with its own relaxation time and activation energy of segmental motion. Hence, at each temperature below glass transition point local segmental mobility in certain structural sublevels is allowed. As temperature increases, segmental mobility in structural levels with higher packing density appears, and finally at T_g all polymer sample is involved in segmental mobility.

In the case of the deformed polymer samples, as temperature increases, the appearance of segmental mobility in structural levels with higher packing density is accompanied by a gradual recovery of local plastic deformation within the above structural sublevels. (In addition, the appearance of local segmental mobility at temperatures below T_g is likely to be controlled by stored inner stresses. As a result, effective energy of activation of segmental motion decreases, and segmental relaxation at local structural sublevels is allowed.) Gradual appearance of segmental mobility in structural levels with higher packing density allows one to explain monotonous temperature dependence of recovery of ε_{res} (Figure 1, component ε_1) as well as the fact that each temperature is associated with a certain value of strain recovery. A complete recovery of plastic deformation is accomplished at T_g, when all segments are involved in segmental motion (Figure 1, component ε_2). 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.

So, in the case of glassy polymers with low strains below or equal to ε_y, residual deformation is controlled by low-temperature relaxation via local segmental mobility at structural levels with lower packing density (component ε_1). This implies that polymer deformation to low strains below ε_y is associated with local segmental mobility within certain structural levels.

As strain increases above ε_y, component ε_2 increases. This mode of relaxation is observed in glass transition region and realized via segmental mobility of polymer sample in whole. This suggests that at such strains segments of all polymer sample are involved in plastic deformation.

Relaxation of plastic deformation at temperatures below T_g (component ε_1) allows one to conclude that relaxation of this portion of plastic deformation is allowed even during polymer loading. Let us define this component as ε_1^*. From this viewpoint, component ε_1 stands for stored plastic deformation, which did not relax during polymer loading. Furthermore, a certain fraction of component ε_1 is lost on heating polymer sample unloaded in liquid nitrogen to initial test temperature (213 K). Nevertheless, with an accuracy to this value plastic deformation of glassy polymer may be presented as

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

(In this case, Hookean components of deformation and relaxation are ignored.)

According to equation (2), plastic deformation of glassy polymer may be described by the contributions from ε_1 and ε_2 to 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 advance the correlation between relaxation $(\varepsilon_1^* + \varepsilon_1)$ and mechanical characteristics E_0 II σ_y.

To verify this correlation, PMMA samples were compressed to different strains at different temperatures. Then, relaxation of ε_{res} was studied (Figure 4). For the lack of space, recovery curves are presented only for the samples with 14 and 20% strains. As T_{def} increases, the contribution from component ε_1 to strain recovery is seen to decrease. At test temperatures close to glass transition point, the value of ε_{res} is controlled only by component ε_2 (Figure 4, curves 5). Furthermore, as T_{def} increases, elastic modulus and yield point go down.

The similar results were observed for deformation and relaxation of PMMA samples plasticized with DBPh (Figure 5). The effect of plasticizing agent on the ratio between ε_1 and ε_2 is similar to increasing deformation temperature T_{def}. Moreover, experiments revealed that at deformation temperatures equidistant from glass transition point both initial and plasticized samples showed the same ratio between ε_1 and ε_2.

This experimental evidence suggests an intimate correlation of elastic modulus and yield stress with low-temperature component of relaxation of plastic deformation (Figure 6). At any strains, similar tendency is observed: as contribution from component ε_1 to recovery of ε_{res} decreases, both elastic modulus and yield stress tend to decrease. In this case, the way of varying the above parameters [by

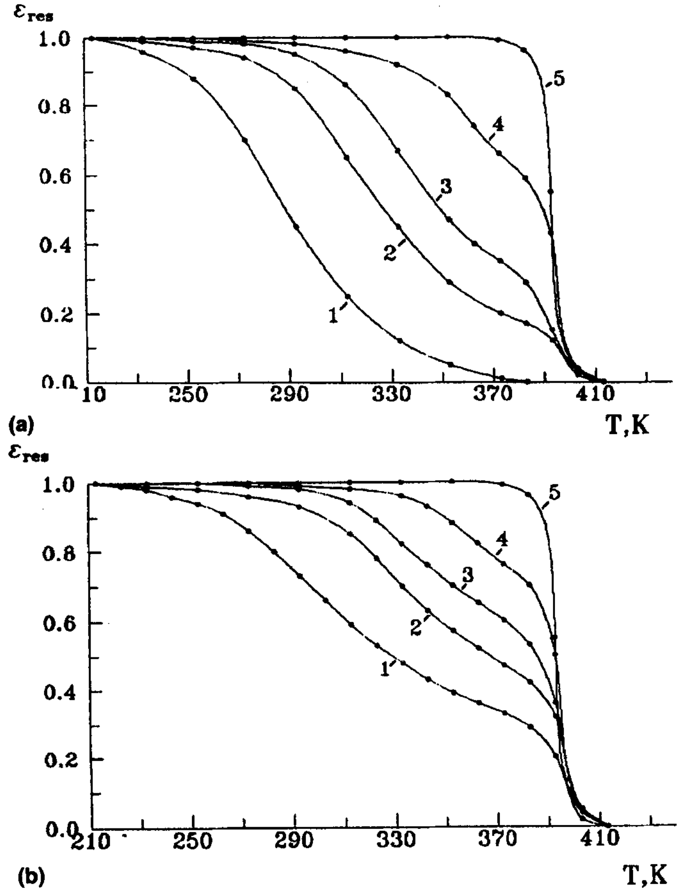

FIGURE 4 Recovery of residual deformation ε_{res} in PMMA samples at T_{def} = 293 (1), 320 (2), 333 (3), 353 (4), and 383 K (5). Strain: 14 (A) and 20% (B).

increasing T_{def} (circles in Figure 6) or content of plasticizing agent (squares in Figure 6B)] has no importance.

Let us note that the dependences of E_0 and σ_y on contribution from component ε_1 to recovery of ε_{res} show a well-pronounced inflection at temperatures from 343 to 353 K. The dependence of abscissa of this inflection point $[\varepsilon_1/(\varepsilon_1 + \varepsilon_2)]^*$ on strain ε is linear (Figure 7). The origin of such behavior is beyond the scope of this work and will be discussed in the following paper.

A noticeable decrease in E_0 and σ_y with decreasing component ε_1 is rationalized by the fact that as T_{def} or content of plasticizing agent in polymer increases, the fraction of plastic deformation that relaxes during polymer deformation increases. In terms of equation (2), this implies an increase in component ε_1^* via decreasing component ε_1. In turn, as contribution from component ε_1 to recovery of ε_{res} decreases, component ε_2 increases. The increase in component ε_1^* associated with relaxation during loading is accompanied by a concomitant decrease in E_0 and σ_y of glassy polymer, for these parameters are controlled by molecular dynamics of polymer macrochains.

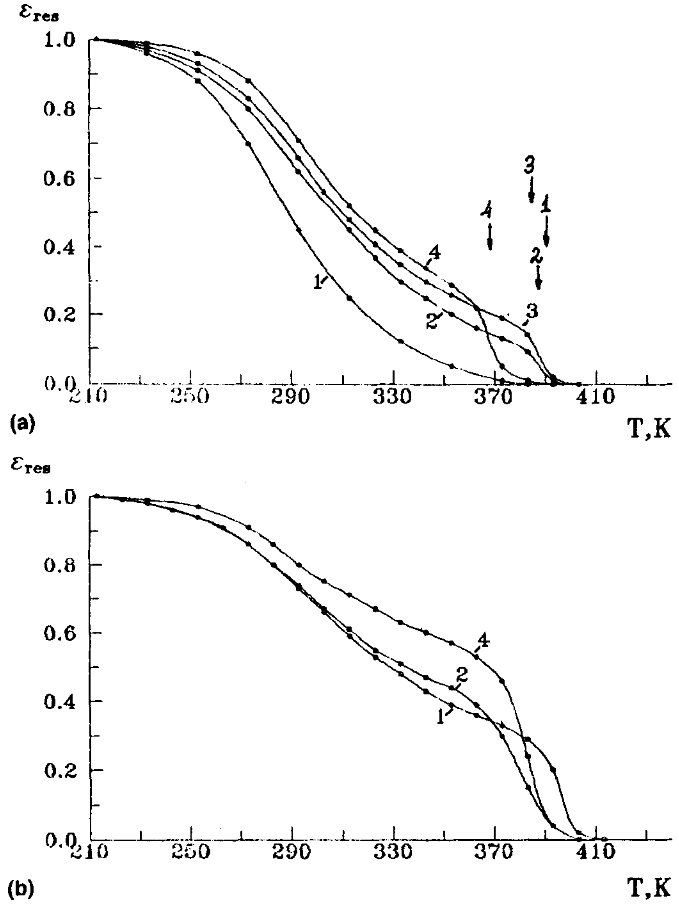

FIGURE 5 Recovery of residual deformation ε_{res} of plasticized PMMA samples. Content of plasticizing agent DBPh: 0 (1), 1 (2), 5 (3), and 10 mass % (4). Strain: 14 (A) and 20% (B). T_{def} = 293 K. The arrows show T_g of the corresponding polymers.

As T_{def} approaches T_g, ε_1 tends to zero, and residual deformation is controlled only by component ε_2 (Figure 4, curves 5). In this case, elastic modulus and yield stress of PMMA samples approach the values, which are characteristic of rubbery state.

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 responsible for polymer mechanical behavior. The above values may be treated as new physical parameters of deformation of polymer glasses.

Correlation between the above parameters and polymer brittleness is quite evident. As was shown earlier, as T_{def} decreases, component ε_2 tends to vanish (Figure 4). Brittle fracture of polymer material is likely to take place at temperatures, where component ε_1 is zero. Degeneration of component ε_1 implies that segmental mobility in polymer samples is ceased at all levels of structural inhomogeneity.

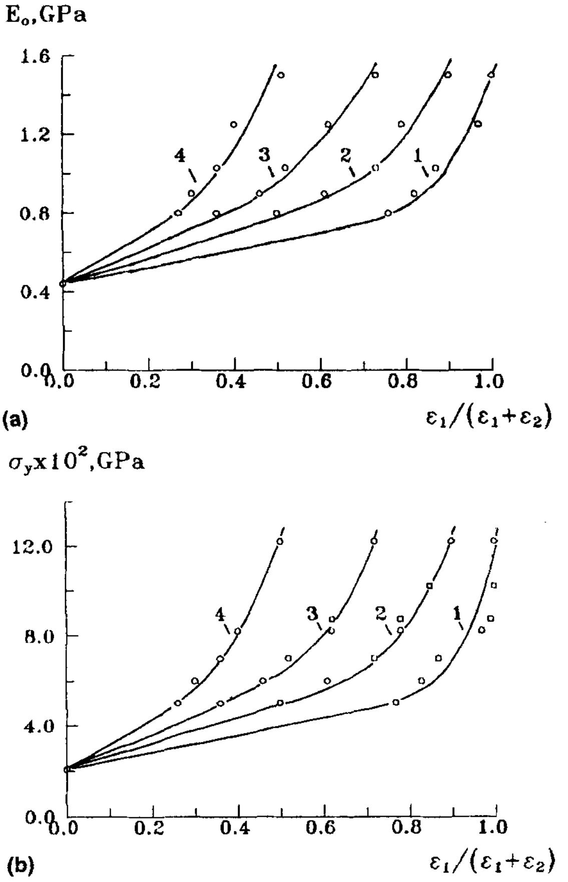

FIGURE 6 The dependence of elastic modulus E_0 (A) and yield stress σ_y (B) of PMMA samples on the contribution of low-temperature component ε_l to total recovery of residual deformation ε_{res}. Strain: 10 (1), 14 (2), 20 (3), and 30% (4).

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.

Furthermore, studying the contributions of components ε_l and ε_2 to recovery of plastic deformation of polymer glasses is of primary importance from the viewpoint of polymer processing into final articles. Component ε_l is the main reason of such common phenomenon as low shape stability of deformed or oriented polymer samples at temperatures much below polymer glass point. In turn, this low-temperature shrinkage is associated with dramatic deterioration in mechanical properties of polymer articles. In connection with this, preventing this mode of polymer relaxation is of primary importance.

The data presented in Figure 4 suggests that preventing relaxation component ε_l is provided by increasing deformation temperature T_{def}. This approach is used as a basis for traditional technology of preparation of orientation-strengthened

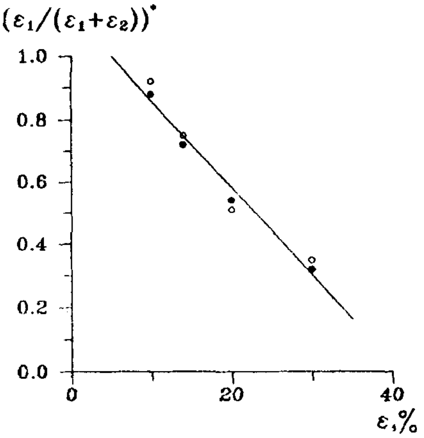

FIGURE 7 The dependence of abscissa of inflection point $[\varepsilon_1/(\varepsilon_1 + \varepsilon_2)]^*$ in curves $E_0 = f[\varepsilon_1/(\varepsilon_1 + \varepsilon_2)]$ and $\sigma_y = f[\varepsilon_1/(\varepsilon_1 + \varepsilon_2)]$ on strain ε as obtained from curves $E_0 = f[\varepsilon_1/(\varepsilon_1 + \varepsilon_2)]$ (closed circles) and $\sigma_y = f[\varepsilon_1/(\varepsilon_1 + \varepsilon_2)]$ (open circles).

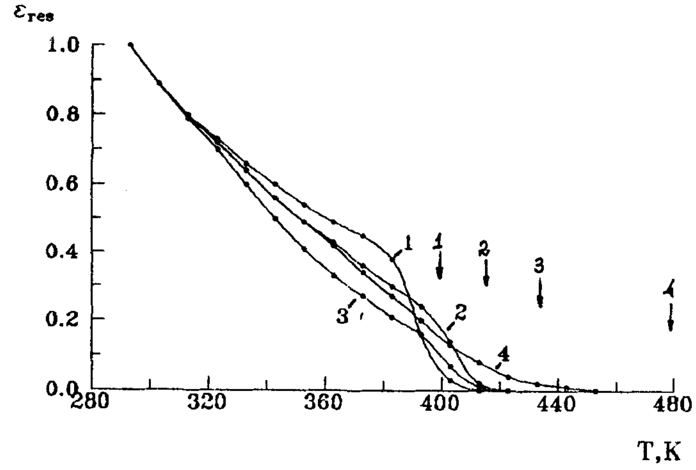

FIGURE 8 Recovery of residual deformation ε_{res} of cross-linked PMMA samples. Content of cross-linking agent (EGDM): 0 (1), 1 (2), 5.2 (3), and 11.2 mol. % (4). Strain: 20%. T_{def} = 293 K. The arrows show T_g of the corresponding polymers.

polymer glasses. This technology involves polymer orientation (tensile drawing) at temperatures above glass transition point and further cooling in a stressed state. Materials and articles prepared via this method are characterized by rather high shape and orientation stability and, hence, by high mechanical properties at temperatures below T_g.

On the other hand, component ε_1 is responsible for low-temperature plasticity of polymer bodies and high reversible strains, which are known to be valuable properties of polymer plastics. This important feature of deformation and relaxation behavior of polymer glasses seems to be intimately related to their unique properties, in particular, lowered brittleness as compared with low-molecular-mass glasses.

Hence, mechanical behavior of polymer glasses is mainly controlled by low-temperature component of relaxation of polymer glasses, that is, by the contribution from component ε_l to recovery of ε_{res}. In connection with this, the problems concerning modification of polymer materials should be treated, in general, as controlled variation in the contribution of component ε_l in polymer relaxation. In our opinion this approach offers many advantages in controlled modification of polymer materials.

As was shown earlier, increasing T_{def} as well as polymer plasticization is accompanied by a decrease in contribution from component ε_l to recovery of plastic deformation of PMMA samples. In contrast, cross-linking of PMMA samples with EGDM is associated with increasing contribution from component ε_l (Figure 8), and at relatively high content of EGDM (5–11 mol%), relaxation of plastic deformation is completed at temperatures below T_g only via component ε_l.

So, the above experimental evidence suggests possibilities, which allow one to control variations in the contribution of ε_l in relaxation of plastic deformation of polymer glasses via physicochemical modification.

CONCLUSION

Plastic deformation of glassy polymers may be described by the contributions from low-temperature and high-temperature components temperature-induced relaxation of residual deformation.

Below yield point, polymer deformation is primarily associated with low-temperature component ε_l. In this case, elastic modulus and yield stress are controlled by contribution from component ε_l to relaxation of plastic deformation.

In more general sense, the ratio between low-temperature and high-temperature components is responsible for mechanical behavior of polymer glasses: brittleness, elasticity, and plasticity as well as shape stability and shrinkage of oriented polymer glasses. In connection with this, the above ratio between low-temperature and high-temperature components may be treated as a new physical parameter of deformation and relaxation of polymer glasses.

This ratio may be varied by physicochemical modification of polymer materials, i.e., by plasticization and cross-linking. This approach, in our opinion, offers many advantages in controlled modification of the mechanical behavior of polymer materials.

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