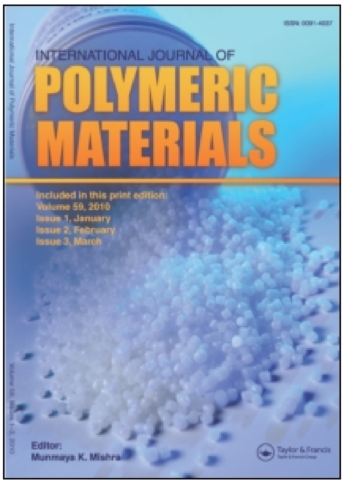

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M. S. Arzhakov[a]; S. A. Arzhakov[a]; V. A. Chernavin[b]
[a] Polymer Department, Faculty of Chemistry, Lomonosov Moscow State University, Moscow, Russia [b] Technological and Scientific Center of Organic Glasses, Dzerzhinsk, Russia

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A New Approach For Preparation of Modern Polymeric Materials Based on Polymer Glasses

M. S. ARZHAKOV[a], S. A. ARZHAKOV and V. A. CHERNAVIN[b]

[a]*Polymer Department, Faculty of Chemistry, Lomonosov Moscow State University, Vorob'evy Gory, Moscow, 119899 Russia;*
[b]*Technological and Scientific Center of Organic Glasses, Dzerzhinsk, 606006 Russia*

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Temperature-induced relaxation of plastic deformation of bulk PMMA was studied. The coexistence of low-temperature and high-temperature components of relaxation was discussed in terms of structural inhomogeneity of polymer glasses. The problems concerning mechanical behavior of polymer materials and their modification were treated, in general, as the problems concerning controlled variations in the contributions from low-temperature and high-temperature components to temperature-induced relaxation of plastic deformation. The speculations on the role of structural inhomogeneity in the development of mechanical properties of polymer glasses allowed development of scientific and technological approach to prepare orientation-strengthened and shrinkproof polymeric materials.

Keywords: Polymer glasses; plastic deformation; relaxation; structure; shrinkproof materials

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 preparation of advanced polymeric materials and controlled modification of their physical and mechanical behavior one should understand the origin of these properties.

Studying temperature-induced relaxation of residual plastic deformation of polymer glasses provides an important information concerning physical and mechanical behavior of these materials. Temperature-induced relaxation of plastic deformation of polymer glasses shows a well-pronounced two-stage character, and involves low-temperature component at temperatures well below glass transition temperature T_g and high-temperature component at temperatures close to T_g [1–4]. Two-stage character of temperature-induced relaxation of plastic deformation allowed us to advance some speculations concerning the structural pattern of plastic deformation [5–7]. From this standpoint, plastic deformation and, in general, physical and mechanical behavior of polymer glasses is likely to be controlled by gradual involvement of segmental mobility within structural sublevels with different packing densities in deformation and relaxation processes.

On the other hand, temperature-induced relaxation of plastic deformation should be taken into account to predict behavior of polymeric materials under operating conditions.

A well-pronounced plastic deformation of polymer glasses allows processability of polymer materials (rolling, stamping, etc.) and substantial improvement in their mechanical properties. One of the approaches to improve mechanical properties of commercial glassy polymers, in particular, toughness, is provided by the method of orientation strengthening.

However, such plastically deformed or oriented polymer materials and articles have one main disadvantage: as temperature exceeds polymer softening temperature, they appear to lose their shape and orientation, and, as a result, their mechanical properties dramatically deteriorate and approach those characteristic of undeformed and unoriented material. These processes are associated with high-temperature component of temperature-induced relaxation of plastic deformation or temperature-induced shrinkage of oriented glassy polymer. Moreover, the shrinkage of oriented polymer glasses takes place also in glassy state at temperatures well below glass transition temperature T_g via low-temperature component of relaxation.

In this work, we outlined the origin of low-temperature and high-temperature components of temperature-induced relaxation of plastic deformation and their contributions to deformation and relaxation processes in polymer glasses. The aim of the present paper was the development of scientific approach to control physical and mechanical behavior of materials based on glassy polymers and to prepare polymeric materials with specified properties.

EXPERIMENTAL

In this work, PMMA prepared by bulk polymerization ($M_\eta = 3\times10^6$) was 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 samples. The development of network took place immediately during bulk polymerization. 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, which exceeded glass transition temperature by 10 – 15 K. Then, they were slowly cooled down to room temperature.

The samples of initial and plasticized PMMA were uniaxially compressed at temperatures 293, 320, 333, 353, and 383K 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. To study temperature-induced relaxation of residual deformation, the free-standing samples were heated from 213K with the rate of heating 1 K/min. Temperature-induced relaxation of residual 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 with a strain rate of 0.1 mm/min. Then, they were unloaded with the same rate at this temperature. Temperature-induced relaxation of residual deformation was studied starting with 293 K.

Orientation-strengthened samples were prepared by multiaxial plane drawing of PMMA sheets to strains of 60 and 120% at temperatures, which exceeded glass transition temperature by 30 K. Then, the stressed samples were slowly cooled down to room temperature.

To determine ultimate strain of initial and orientation-strengthened PMMA samples, the dumbbell samples were tested under uniaxial drawing at a strain rate of 10 %/ min at 293 K. Polymer toughness was determined according to Izod [8] at 293 K. Shrinkage of orientation-strengthened PMMA samples was estimated by changes in their linear dimensions on heating to temperature, which exceeded softening temperature by 20 K.

RESULTS AND DISCUSSION

Figure 1 shows a typical temperature dependence of relaxation of residual deformation ε_{res} in PMMA samples. Temperature-induced relaxation of residual deformation takes place within two well-defined temperature regions and involves low-temperature ε_1 and high-temperature ε_2 components. This experimental evidence suggests that on heating the relaxation of plastically deformed samples is related to restructuring of, at least, two different structural elements.

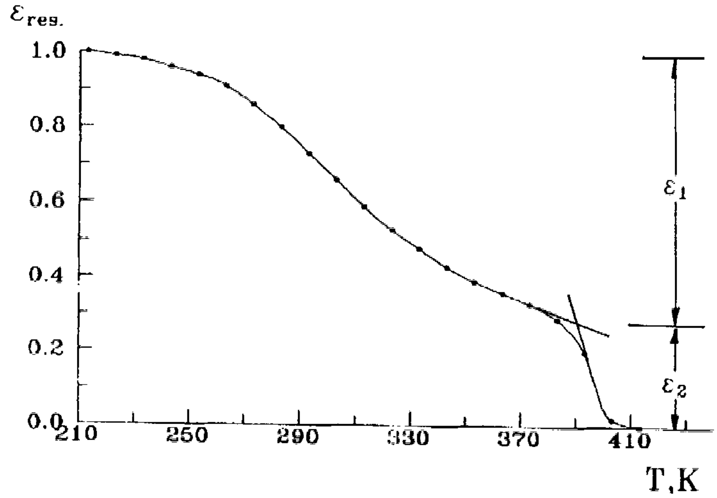

FIGURE 1 Typical temperature dependence of relative residual deformation ε_{res} of PMMA. Strain: 20%. $T_{def} = 293$ K.

The ratio between the components associated with low-temperature and high-temperature relaxation was studied as a function of strain. For the samples compressed to rather low strain, the complete temperature-induced relaxation of residual deformation takes place at temperatures well below glass transition temperature T_g (Fig. 2). On the contrary, for the samples compressed to rather high strains, a complete relaxation is observed on heating up to temperatures close to T_g. Note that, in this case, the low-temperature relaxation is also involved.

Figure 3 presents low-temperature ε_1 and high-temperature ε_2 components of temperature-induced relaxation of residual deformation as a function of strain and the stress-strain diagram corresponding to uniaxial compression of PMMA samples. This figure shows that, for the samples with strains below yield strain ε_y, relaxation of residual deformation proceeds via low-temperature mode ε_1. With increasing strain above ε_y, the appearance and growth in high-temperature component ε_2 at constant ε_1 is observed.

Two-stage character of temperature-induced relaxation of residual deformation allows a convincing conclusion that plastic deformation

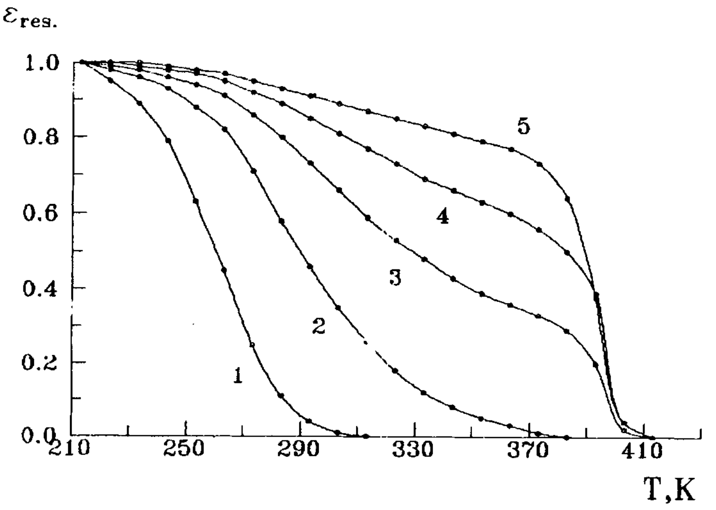

FIGURE 2 Temperature dependences of relative residual deformation ε_{res} of PMMA samples. Strain: 6 (1), 14 (2), 21 (3), 30 (4), and 49% (5). $T_{def}=293$ K.

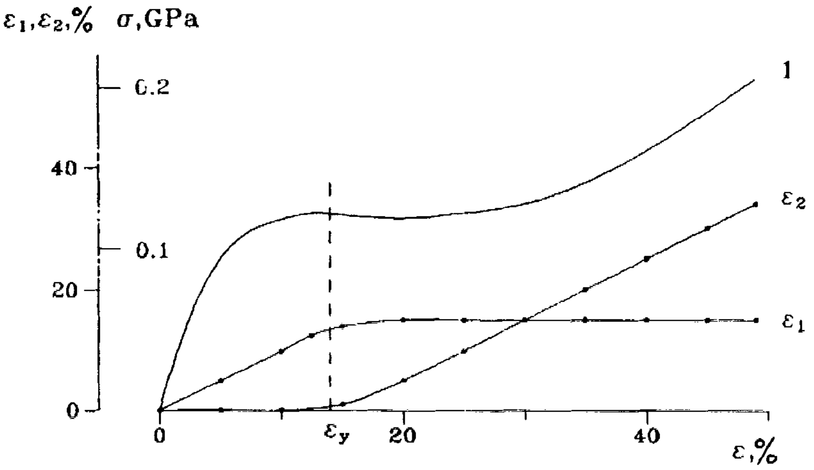

FIGURE 3 Stress-strain curve corresponding to uniaxial compression of PMMA samples at 293 K (1) and low-temperature ε_1 and high-temperature component ε_2 of relaxation of residual deformation versus total strain ε.

of polymers involves two modes which relax via low-temperature and high-temperature components. In other words, this implies realization of two modes of molecular mechanism of both plastic deformation and its relaxation in polymers.

As this takes place, elastic relaxation of plastic deformation via high-temperature component ε_2 is observed in a narrow temperature region in the vicinity of T_g. This relaxation is associated with transition of excited chain conformations to initial equilibrium state via segmental motion within the polymer bulk.

Alternatively, elastic relaxation of plastic deformation via low-temperature component ε_1 is observed at temperatures well below T_g in a wide temperature range within polymer glassy state. Note, that each temperature is associated with a certain value of relaxation of this fraction of plastic deformation. In other words, we deal with a temperature-dependent mode of elastic recovery of plastic deformation.

At the present time, the two-stage character of temperature-induced relaxation of polymer plastic deformation is treated in terms of two standpoints: step by step recovery of small-scale plastic shear transformations and excited chain conformations [3,4] (i) and structural inhomogeneity of glassy polymers [5, 7] (ii).

Within the framework of the latter approach, glassy polymer is characterized by a set of structural sublevels with different packing densities and degrees of ordering.

During recent decades, the problems related to structure of glassy polymers are being widely discussed in literature. Let us mention some of them.

As demonstrated by electron microscopy (for example, [9, 11]), positron annihilation [7, 12], light scattering measurements [13], small-angle X-ray scattering [14], and wide-angle X-ray scattering [15], polymer glasses are characterized by structural inhomogeneity related to the existence of heterogeneous ordered regions with higher packing densities (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 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 [16], domain [17, 18], globule [19–21], and cluster [22, 23]. 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 these work, our speculations will be based on only unequivocal conclusion concerning structural inhomogeneity of glassy polymer, which is associated with the existence of local structural regions with different packing of macromolecules or their fragments.

Each of these sublevels is associated with its own relaxation time and activation energy of segmental mobility. Molecular mechanism of the low-temperature relaxation is similar to that of high-temperature mode. According to this mechanism, each temperature is related to the appearance of segmental mobility within a certain structural sublevel. Let us emphasize that a possible realization of segmental mobility in local structural sublevels at temperatures below T_g is discussed in [24–27]. In addition, the appearance of local segmental mobility at temperatures below T_g is likely to be controlled by accumulation of inner stresses [28] as well as by asymmetry of the field of intermolecular interaction provided by free volume microregions [29]. As a result, a decrease in effective energy of activation of segmental mobility is observed, and relaxation of segments in local structural sublevels is allowed within glassy state.

Appearance of low-temperature and high-temperature components of relaxation of plastic deformation allowed us [5 – 7] to advance the structural pattern of plastic deformation of glassy polymers concerning a gradual involvement of various structural elements with different packing densities into deformation and relaxation. From this standpoint, the ratio between low-temperature component ε_1 and high-temperature component ε_2 (or contributions of ε_1 and ε_2 to temperature-induced relaxation of residual deformation) describes the development of plastic deformation of polymer glasses. Let us consider in detail the role of the above components of relaxation in the development of physical and mechanical behavior of polymer glasses.

Low-temperature component is likely to be responsible for low-temperature plasticity of glassy polymers 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. Let us emphasize that the strength properties of polymer, such as elastic modulus and yield stress, and the contribution from low-temperature component to relaxation of residual deformation are well correlated [5].

On the other hand, with increasing operating temperature, low-temperature and high-temperature components of temperature-induced relaxation of plastic deformation are the main reason of poor shape stability of deformed polymer articles and shrinkage of oriented materials. As a result, a dramatic deterioration in mechanical properties of materials is observed.

In connection with this, the problems concerning preparation of polymeric materials with specified properties and controlled mechanical behavior under operating conditions should be discussed in two aspects.

At first, for oriented and unoriented polymeric materials at a given operating temperature, the problems concerning modification of their physical and mechanical behavior should be treated, in general, as the problems concerning controlled variation in the ratio between low-temperature and high-temperature components of temperature-induced relaxation of residual deformation.

Secondly, for oriented polymeric materials in a wide range of operating temperatures, lowering or suppression of both low-temperature and high-temperature components of relaxation presents a challenging task for many scientists and engineers. A happy solution of this problem offers numerous advantages. If we manage to prevent low-temperature relaxation mode, this implies a substantial broadening of temperature interval of operating conditions up to T_g. But if both modes of relaxation are prevented, this will allow much progress in development of a new generation of orientation-strengthened and shrinkproof polymer materials based on well-known commercial polymers.

To outline scientific approaches to control the ratio between low-temperature and high-temperature components of relaxation, let us consider the temperature-induced relaxation of plastic deformation for various PMMA samples.

Figure 4 shows temperature dependences of residual deformation for PMMA samples plasticized with DBPh. For the lack of space,

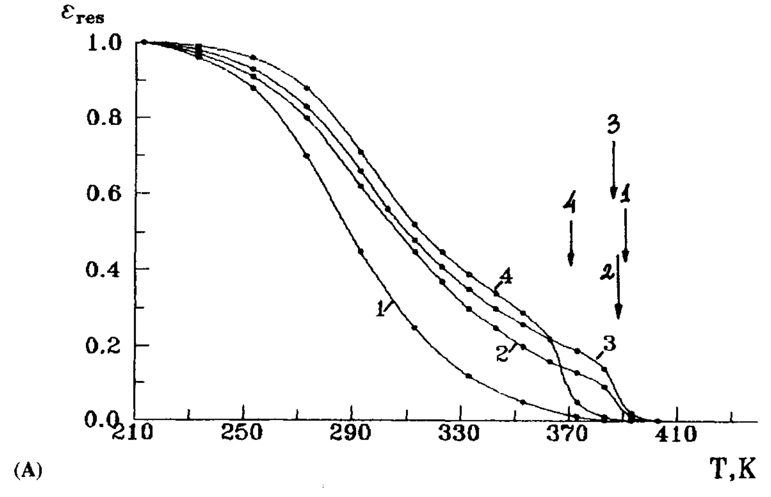

FIGURE 4 Temperature dependences of relative residual deformation ε_{res} of plasticized PMMA samples. Content of plasticizing agent DBPh: 0 (1), 1 (2), 5 (3), and 10 mass % (4). Strain: 14 (A) and 20% (B). $T_{ref} = 293$ K. The arrows show T_g of the corresponding polymer samples.

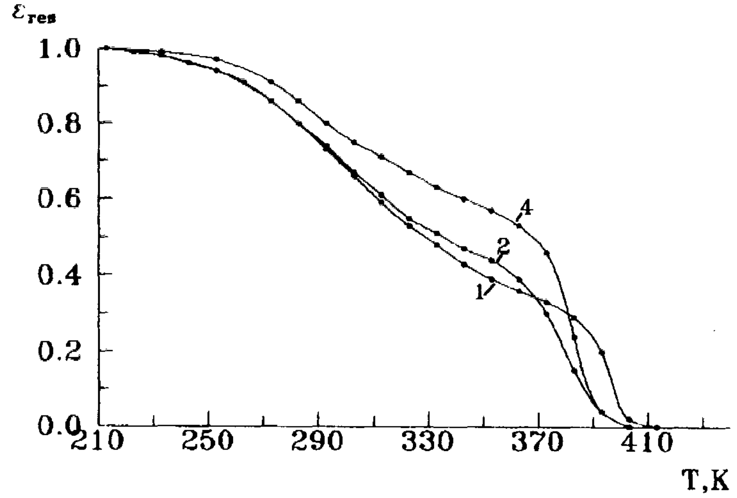

FIGURE 4 (Continued).

relaxation curves are presented only for the samples compressed to strains of 14 and 20 %. Plasticization of PMMA leads to appearance and growth in high-temperature component of relaxation and decrease in low-temperature component. In contrast, the cross-linking of PMMA samples with EGDM is associated with increasing low-temperature component of relaxation and degeneration of high-temperature component (Fig. 5). As a result, at relatively high content of EGDM ([5 – 11] mol %), relaxation of plastic deformation proceeds via low-temperature component at temperatures well below T_g. These experimental evidence suggests possibilities, which allow one to control contributions from low-temperature and high-temperature components to relaxation of residual deformation via physicochemical modification.

For PMMA samples compressed at different temperatures, experimental evidence suggests that preventing low-temperature component ε_l is provided by increasing deformation temperature T_{def} (Fig. 6). As the temperature of deformation increases, a contribution from the low-temperature component ε_l to temperature-induced relaxation of residual deformation decreases. When compression of polymer samples is carried out at temperatures in the vicinity of T_g, relaxation of component ε_l is likely to take place during the deformation. In this

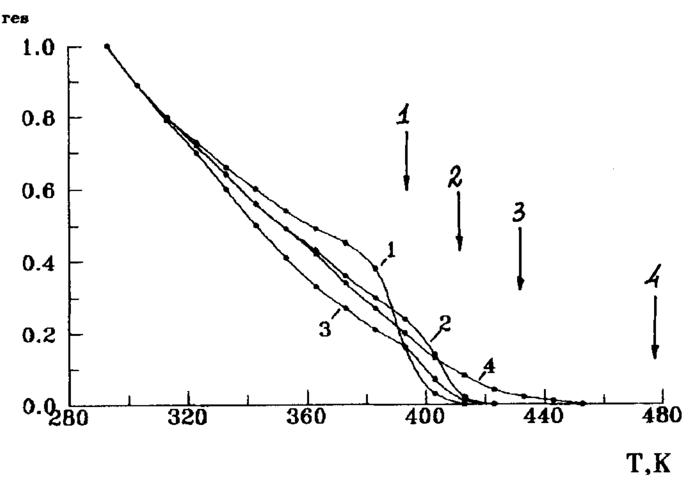

FIGURE 5 Temperature dependences of relative residual deformation $\varepsilon_{\mathrm{ref}}$ of cross-linked PMMA samples. Content of cross-linking agent EGDM: 0 (1), 1 (2), 5.2 (3), and 11.2 mol. % (4). Strain: 20% T_{ref}= 293 K. The arrows show T_g of the corresponding polymer samples.

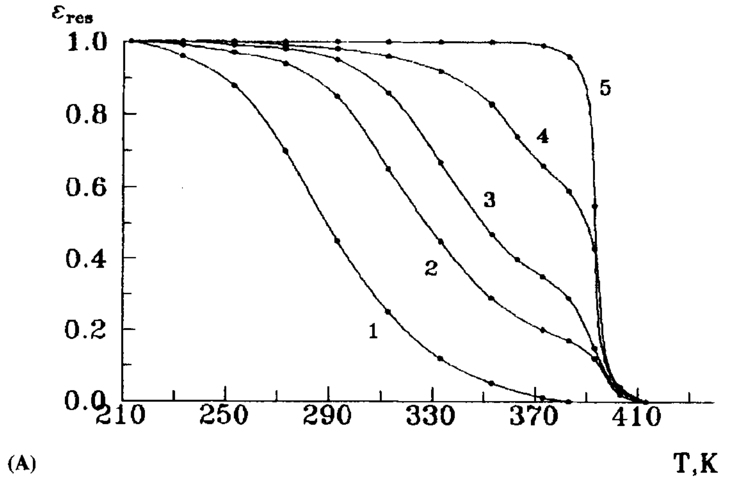

FIGURE 6 Temperature dependences of relative residual deformation $\varepsilon_{\mathrm{res}}$ of PMMA samples. T_{ref}=293 (1), 320 (2), 333 (3), 353 (4), and 383 K (5). Strain: 14 (A) and 20% (B).

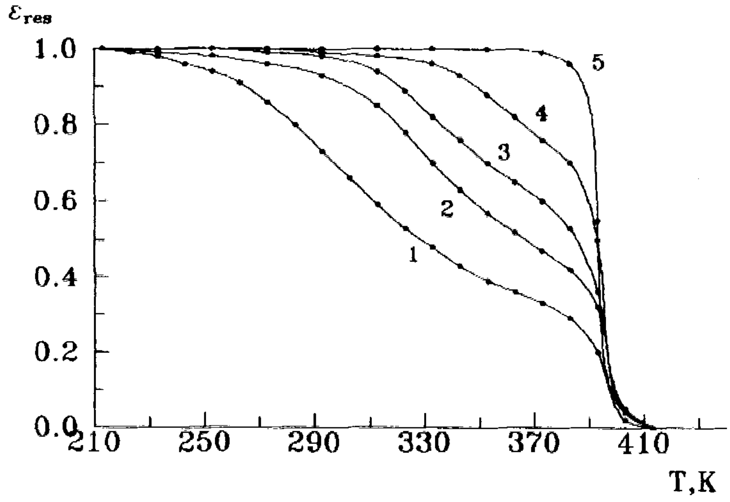

FIGURE 6 (Continued).

case, the total relaxation is primarily controlled by high-temperature component ε_2 Figure 6, curves 5.

This approach may be served as a basis for traditional technology of preparation of orientation-strengthened polymer glasses. This technology involves orientation (tensile drawing) of a polymer samples above glass transition temperature and their 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 consideration of the plastic deformation and its further relaxation in polymer glasses from the standpoint of the structural inhomgeneity of these materials allowed us to solve the problem concerning suppression of high-temperature component of relaxation of plastic deformation via a new approach to orientation strengthening of polymers. 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

TABLE I Mechanical Characteristics of PMMA Glasses as Obtained by New Technology

Material	*Strain* %	*Ultimate Strain,* %	*Toughness,* KJ/m^2	*Shrinkage on heating above softening temperature, %*
Unoriented PMMA	0	6	12	0
PMMA Orientational	60	26	25	100
Strengthening by Traditional Technology	120	6	55	100
PMMA Orientational Strengthening by New Technology				
PMMA-I	60	16	22	52
	120	23	50	40
PMMA-II	60	6	20	0
	120	6	26	0

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 (393 K). The comparison of the properties of PMMA samples prepared via the new technology (PMMA-I and PMMA-II) with those of unoriented PMMA and PMMA prepared via traditional technology is presented in Table I.

This new approach of orientation strengthening of polymer materials can be effectively used in many areas of technological production of the finished articles based on various polymers in the course of extrusion or fiber spinning from melts and solutions. Furthermore, this new method allows polymer processing just in the course of polymerization.

CONCLUSION

The coexistence of low-temperature and high-temperature components of temperature-induced relaxation of residual plastic deformation is considered in terms of structural inhomogeneity of polymer glasses.

From this standpoint, the development of physical and mechanical behavior of glassy polymers can be presented as gradual involvement of structural sublevels with different packing densities to deformation and relaxation. At macroscopic level, this process manifests itself as a temperature-dependent mode of elastic recovery, which is specific feature of glassy polymers.

Low-temperature component is likely to be responsible for low-temperature plasticity of glassy polymers 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 is intimately related to a number of their unique properties, in particular, lowered brittleness as compared with low-molecular-mass glasses. On the other hand, this relaxation mode was shown to be responsible for low-temperature shrinkage (loss in orientation) of oriented polymer materials on heating the samples at temperatures below T_g.

Hence, for polymer materials based on glassy polymers mechanical behavior is mainly controlled by low-temperature component of temperature-induced relaxation of plastic deformation of polymer glasses. In connection with this, the problems concerning preparation of modern polymeric materials based on glassy polymers should be treated, in general, as the problems concerning controlled variations in the ratio between low-temperature and high-temperature components of relaxation. The experimental evidence obtained suggests possibilities, which allow one to control variations in the contribution from low-temperature component to relaxation via physicochemical modification.

The speculations concerning the role of structural inhomogeneity in the development of both mechanical and relaxation properties of polymer glasses make it possible to put forth new technology of preparation of orientation-strengthened and shrinkproof polymer materials.

References

[1] Arzhakov, S. A. and Kabanov, V. A. (1971). *Vysokomol. Soedin. B*, **13**, 318 (in Russian)

[2] Skorobogatova, A. E. Arzhakov, S. A. Bakeev, N. F. and Kabanov, V. A. (1973). *Dokl. Akad. Nauk SSSR*, **211**, 151 (in Russian).

[3] Oleynik, E. (1989). *Colloid and Polym. Sci.*, **80**, 140.

[4] Oleinik, E. F. Salamatina, O. B. Rundev, S. N. and Shenogin, S. V. (1993). *Polymer Science*, **35**, 1532.

[5] Arzhakov, M. S. and Arzhakov, S. A. (1995). *Intern. J. Polymeric Mater.*, **29**, 249.

[6] Arzhakov, M. S. and Arzhakov, S. A. (1996). in: Fizikokhimiya polimerov (*Physics and Chemistry of Polymers*), Tver', **2**, 64, (in Russian).

[7] Arzhakov, M. S. Arzhakov, S. A., Kevdina, I. B. and Shantarovich, V. P. (1996). in: Fiziokokhimiya polimerov (*Physics and Chemistry of Polymers*), Tver', **2**, 59, (in Russian).

[8] Tuner, S. (1973). Mechanical Testing of Plastics, Lindon: Iliffe Books.

[9] Atsuta, M. and Turner, D. T. (1982). *J. Mater. Sci., Lett.*, **1**, 167.

[10] Kelley, F. N. and Trainor, D. R. (1982). *Polym. Bull.*, **7**, 369.

[11] Topchiev, D. A. (1990). *Vysokomol. Soedin. A*, **32**, 2243 (in Russian).

[12] Shantarovich, V. P. Arzhakov, M. S. and Kevdina, I. B. (1995). *Polymer Science B*, **37**, 171.

[13] Tanio, N. Koike, Y. and Ohntsuka, Y. (1989). *Polym. J*, **21**, 259.

[14] Yah, G. S. J. (1979). IUPAC *Macro 26th Symp., Mainz, Prepr. Short Commun.*, **2**, 1176.

[15] Wendorff, J. (1982). *Polymer*, **53**, 543.

[16] Arzhakov, S. A. Bakeev, N. F. and Kabanov, V. A. (1973). *Vysokomol. Soedin. A*, **15**, 1154 (in Russian).

[17] Yeh, G. S. J. (1972). *J. Macromol. Sci.* B, **6**, 465.

[18] Klement, I. J. and Geil, P. H. (1971). *J. Macromol. Sci. B*, **5**, 505.

[19] Mikheev, Yu. A. and Guseva, L. N. (1991). *Khim. Fiz.*, **10**, 724 (in Russian).

[20] Mikheev, Yu. A. (1992). *Intern. J. Polymeric Mater.*, **16**, 221.

[21] Mikheev, Yu. I. A. and Askadskii, A. A. (1986). *Vysokomol. Soedin. A*, **28**, 1365 (in Russian).

[22] Belousov, V. N., Kozlov, G. V., Mikitaev, A. K. and Lipatov, Yu. S. (1990). *Dokl. Akad. Nauk SSSR*, **313**, 630 (in Russian).

[23] Kozlov, G. V., Sanditov, D. S. and Serdyuk, V. D. (1993). *Polymer Science A*, **35**, 1742.

[24] Bershtein, V. A. and Egorov V. M. (1990). Differentsial'naya skaniruyushchaya kalorimetriya v fizikokhimii polimerov (Differential Scanning Caloimetry in Physicl Chemistry of Polymers), Leningrad: Khimiya (in Russian).

[25] Surovtsev, V. I., Pelishenko, S. S., Zelenskaya-Surovtseva, N. M., Savitskaya, A. A. and Degtyarev, V. A. (1989). *Vysokomol. Soedin. A*, **31**, 339 (in Russian).

[26] Belousov, V. N., Kotsev, B. Kh. and Mikitaev, A. K. (1985). *Dokl. Akad. Nauk SSSR*, **280**, 1140 (in Russian).

[27] Perepechko, I. I. (1973). Akusticheskie metody issledovaniya polimerov (Acoustic Studies in Polymers), Moscow: Khimiya (in Russian).

[28] Arzhakov, M. S. and Arzhakov, S. A. (1996). *Intern. J. Polymeric Mater.* (in press).

[29] Kozlov, G. V., Shogenov, V. N. and Mikitaev, A. K. (1988). *Dokl. Akad. Nauk SSSR*, **298**, 142 (in Russian).