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Physical and Mechanical Behavior of Polymer Glasses. V. Structural Plasticization

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For poly(methyl methacrylate) (PMMA) containing incompatible diethyl siloxane oligomer (DES), the effect of DES on the mechanical behavior of polymer was discussed in terms of the structural plasticization. Using positron annihilation lifetime spectroscopy (PALS), the introduction of DES to polymer was shown to change the free volume content primarily within structural sublevels with lowered packing densities. Examination of polymer samples using the studies in the temperature-induced recovery of residual deformation, dynamic mechanical analysis, differential scanning calorimetry, and thermostimulated luminescence evidenced that the changes in the polymer microstructure control the variations in the molecular and segmental mobility in PMMA. Enhancement of the molecular and segmental mobility decreases the mechanical parameters such as elastic modulus and yield stress whereas the restriction of molecular and segmental mobility increases the above mechanical characteristics. Mechanism of structural plasticization of glassy polymers involves the effect of a plasticizing agent on the local free volume in the certain structural sublevels, the resultant changes in the microscopic molecular and segmental mobility, and the corresponding modification of the macroscopic mechanical behavior of polymer materials.

Keywords: Glassy polymers; plasticization; mechanics; relaxation; structure; PALS

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INTRODUCTION

Plasticization of glassy polymers is associated with the introduction of low-molecular-mass diluents to polymer materials. As a result of plasticization, glass transition temperature of polymer decreases. Changes in the bulk mechanical properties depend strongly on the amount of the introduced plasticizing agent. At low concentrations, the addition of the plasticizing agent increases the mechanical parameters of polymer such as elastic modulus and yield stress. This phenomenon is referred to as antiplasticization. With increasing the content of plasticizing agent, these mechanical characteristics decrease below those of the initial polymer, and plasticization of polymer takes place. The mechanism of antiplasticization and plasticization of polymer glasses with compatible low-molecular-mass diluents is related to the effect of the plasticizing agent on the free volume content and molecular mobility in polymer materials [1–4].

However, in some cases, the low-molecular-mass substances with a poor compatibility with polymer have the noticeable effect on the mechanical behavior of polymer. Introduction of the minor amounts (fractions of percent) of these low-molecular-mass substances in glassy polymers decreases markedly their mechanical properties such as elastic modulus, yield stress, strength, *etc.*, and the temperatures of relaxation transitions. This phenomenon was referred to as structural plasticization of polymers [1, 5, 6]. To explain the effect of the minor amounts of incompatible agents on the bulk mechanical properties, a heterogeneous structural model of glassy polymers was invoked.

According to this model, the structure of glassy polymer is characterized by the densely packed supramolecular (or suprasegmental) structural domains [7–11]. These domains are interconnected with each other by tie-chains. These tie-chains constitute the interdomain structural regions with lowered packing densities. As compared with the compatible plasticizing agents, in the case of structural plasticization, the low-molecular-mass additive is not homogeneously distributed in the polymer matrix. Plasticizing agent seems to occupy the interdomain structural regions and to enhance the mutual rearrangements of the supramolecular domains during deformation or processing. As a result, mechanical characteristics of glassy polymer tend to decrease.

Note that the problem of structural plasticization is of interest to both scientists and engineers. From the fundamental viewpoint, this problem is related to the correlation between microscopic structure and macroscopic mechanical behavior of glassy polymers. As for the applied aspects of this problem, the structural plasticization provides the wide possibilities for an effective physical modification of polymer materials with negligible amounts of modifying agents.

To get a deeper insight into the problem, in this work, the model polymer systems based on poly(methyl methacrylate) (PMMA) containing incompatible diethyl siloxane oligomer (DES) were studied. The studies in the effect of DES on the mechanical behavior of polymer were combined with the characterization of the microstructural changes in PMMA caused by DES.

EXPERIMENTAL

We studied poly(methyl methacrylate) (PMMA) samples ($M_w = 1,500,000$) containing diethyl siloxane oligomer (DES) with five repeat units. The test samples were prepared by bulk polymerization. The monomer feed compositions contained 0.1, 0.5, and 1.3 wt% of DES. Benzoyl peroxide was used as an initiator of polymerization.

For the mechanical tests, the test samples were cut as cylinders with a height of 5 mm and a diameter of 5 mm. Prior to tests, the samples were annealed at a temperature by 15 K above glass transition temperature for 2 hours. Then, the samples were slowly cooled down to room temperature. The height of the as-prepared samples was denoted as h_0 .

The test samples were uniaxially compressed at 293 K to a strain of 20%. Strain rate was $1.7 \times 10^{-4} \text{ s}^{-1}$. The tests were performed using an UTS-10 tensile machine (Germany). Elastic modulus was estimated from the slope of the initial portion of the $\sigma - \varepsilon$ curve at strains below 3%. The accuracy of estimation of elastic modulus E_0 and yield stress σ_y was equal to $\pm 5\%$.

To study the temperature-induced recovery of residual deformation ε_{res} , the stressed samples were cooled down with a liquid nitrogen and released at this temperature. After that, the free-standing samples

were heated from 213 K with a heating rate 1 K/min. At 213 K, the height of the samples was denoted as h_{213} .

The temperature-induced recovery of residual deformation was studied by measuring the changes in the height of the test samples on their heating. At a given temperature, the height of the as-relaxed sample was denoted as h_T . Residual deformation was estimated as $\epsilon_{\text{res}} = (h_0 - h_T)/(h_0 - h_{213})$ with an accuracy of $\pm 2\%$.

Dynamic mechanical analysis (DMA) of the polymer samples was performed using a Rheometrics Solid Analyzer RSA-II (USA). Frequency of the uniaxial compression was 3.14 rad/s (0.5 Hz). Strain was 0.1%. Heating rate was 1 K/min.

Differential scanning calorimetry (DSC) studies were carried out using a Mettler TA-4000 thermal analyzer (Switzerland). Heating rate was 20 K/min.

Thermostimulated luminescence analysis (TSL) was performed using TGL-68 [12]. The polymer samples were exposed to radiation using γ -ray source ^{60}Co up to 10 kGy at the temperature of liquid nitrogen. The measurements were carried out at the temperatures from 80 to 375 K. Heating rate was 10 K/min.

The initial structure of polymer samples was studied by positron annihilation lifetime spectroscopy (PALS). PAL measurements were carried out at 293 K using a conventional ORTEC spectrometer with a time-resolution (full width on a half maximum of the prompt coincidence curve) of 230 ps. ^{22}Na sandwiched between the two sheets of nickel foil was used as a positron source. For both three-component and four-component analysis, PATFIT computing program [13] was used to calculate the annihilation characteristics (lifetimes τ_i and intensities I_i) from the corresponding lifetime distributions of annihilation radiation.

RESULTS

For the samples of PMMA containing DES, Figure 1 shows the corresponding stress-strain curves. Introduction of 0.1 wt% of DES to PMMA results in the hardening of polymer (transition from curve 1 to curve 2). As the concentration of DES in polymer (C_{DES}) is increased up to 1.3 wt%, weakening of PMMA is observed (curve 4).

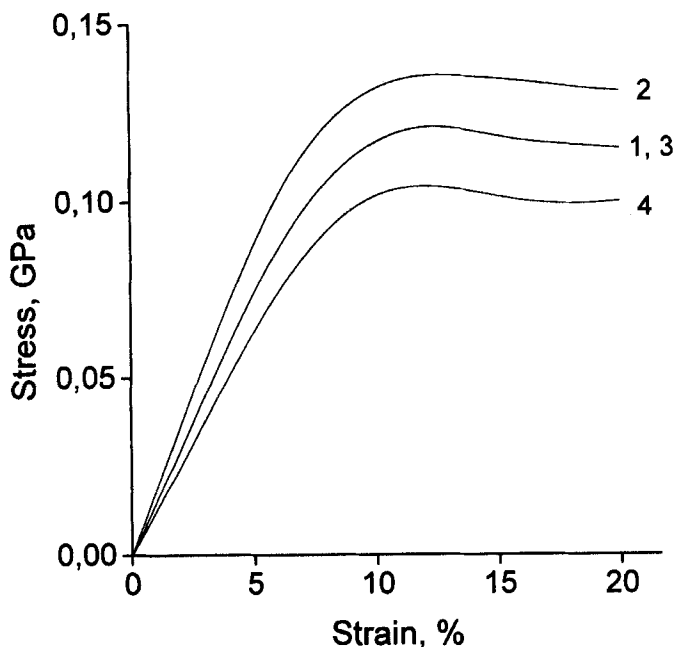


FIGURE 1 Stress-strain curves for PMMA (1) and PMMA containing 0.1 (2), 0.5 (3), and 1.3 wt% of DES (4).

For the deformed PMMA/DES samples, Figure 2 presents the temperature dependences of the relative residual deformation ε_{res} . The temperature-induced recovery of residual deformation proceeds in the two well-defined temperature intervals: at temperatures below glass transition temperature T_g (component ε_1) and at temperatures close to T_g (component ε_2). These two components of recovery are shown for the PMMA sample containing 1.3 wt% of DES. Note that the introduction of 0.1 wt% of DES increases the low-temperature component ε_1 of the recovery of residual deformation. Further increase in C_{DES} decreases component ε_1 .

For PMMA/DES samples, Figure 3 shows the temperature dependences of loss tangent $\tan \delta$ at glass transition. When C_{DES} is equal to 0.1 wt%, the low-temperature branch of the loss tangent peak shows a slight decrease in mechanical losses. As C_{DES} is increased up to 1.3 wt%, the values of $\tan \delta$ increase. Note that the introduction of

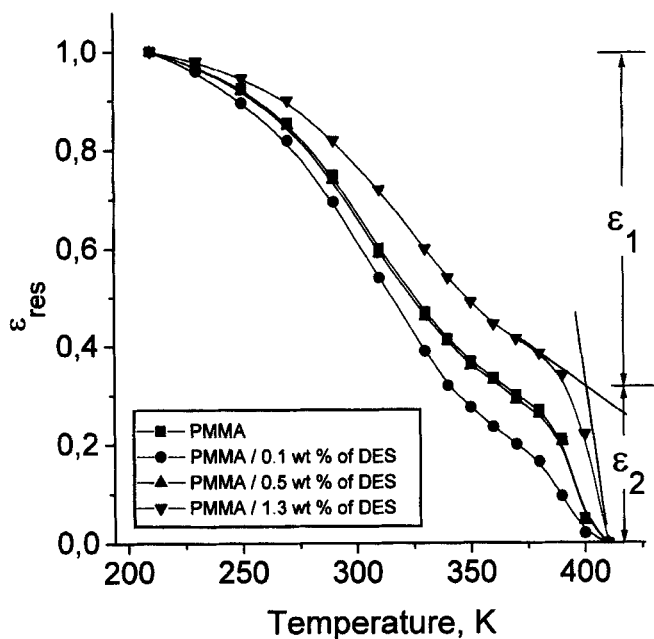


FIGURE 2 Temperature dependences of the residual deformation ϵ_{res} for PMMA and PMMA containing DES.

DES to PMMA does not change the temperature position of the $\tan \delta$ peaks, and all PMMA/DES samples are characterized by the same T_g .

For PMMA samples containing DES, the frequency dependences of $\tan \delta$ at different temperatures were studied. For the lack of space, these dependences are presented only for the PMMA samples containing 0.1 wt% of DES (Fig. 4A). Master curves of frequency dependences of these samples (Fig. 4B) were obtained by shifting each curve horizontally onto the curve corresponding to the reference temperature of 403 K. As a result of introduction of 0.1 wt% of DES to PMMA, the high-frequency branch of the master curves shows the decrease in mechanical losses. When C_{DES} is increased up to 1.3 wt%, the values of $\tan \delta$ increase. Hence, DES has an effect on the mechanical losses of polymer, and this effect is pronounced either at low temperatures or high frequencies.

At temperatures corresponding to glass transition region, Figure 5 shows the DSC curves of the PMMA samples containing DES. At

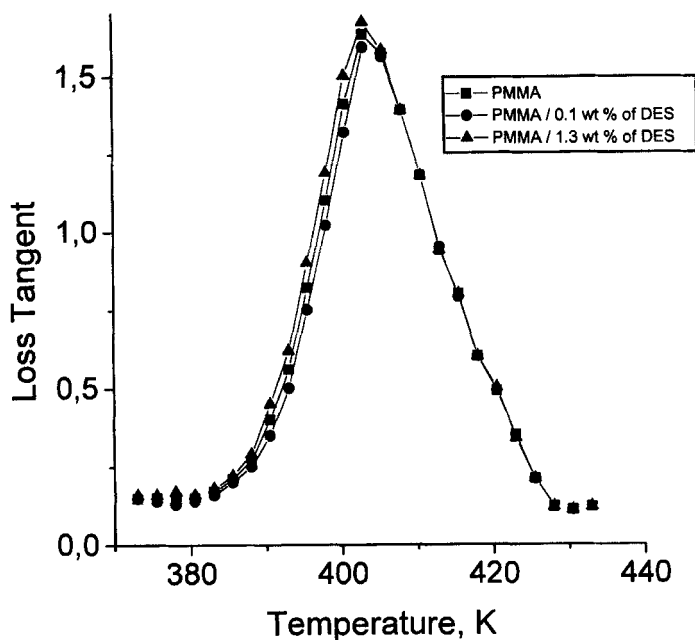


FIGURE 3 Temperature dependences of loss tangent for PMMA and PMMA containing DES.

$C_{DES} = 0.1$ wt%, endothermic heat flow jump abruptly increases (curve 2) as compared with that for initial polymer (curve 1). As C_{DES} is increased up to 1.3 wt%, heat flow jump decreases (curve 3). Note that, DES does not influence the temperature position of this endothermic jump, that is, T_g of polymer.

Figure 6 shows the thermostimulated luminescence spectra of PMMA/DES samples. As follows from Figure 6, DES manifests itself as a narrow peak at 135–140 K (curves 2–4). This peak corresponds to the glass transition of this additive in polymer matrix. Note that, as C_{DES} is increased, intensity of this peak increases in a linear fashion. On the other hand, initial PMMA shows a broad peak in this temperature region (curve 1), and this peak may be attributed to the relaxation processes with the participation of side atomic groups [14]. Introduction of 0.1 wt% of DES decreases markedly the intensity of this peak. With increasing C_{DES} up to 0.5 and 1.3 wt%, the intensity of this peak increases.

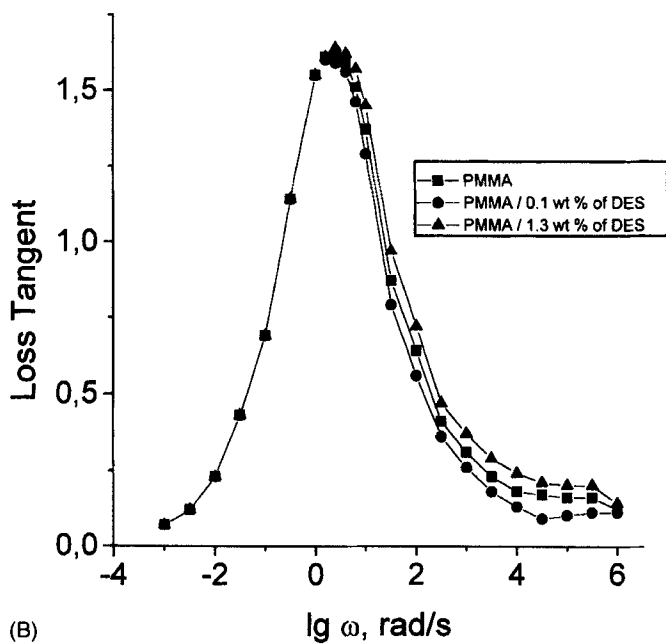
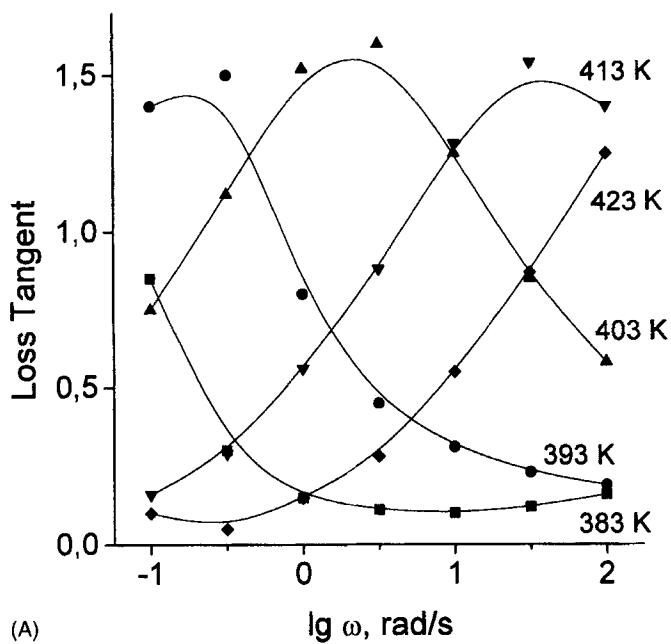


FIGURE 4 Frequency dependences of loss tangent for PMMA containing 0.1 wt% of DES at different temperatures (A) and master curves for PMMA containing DES (B).

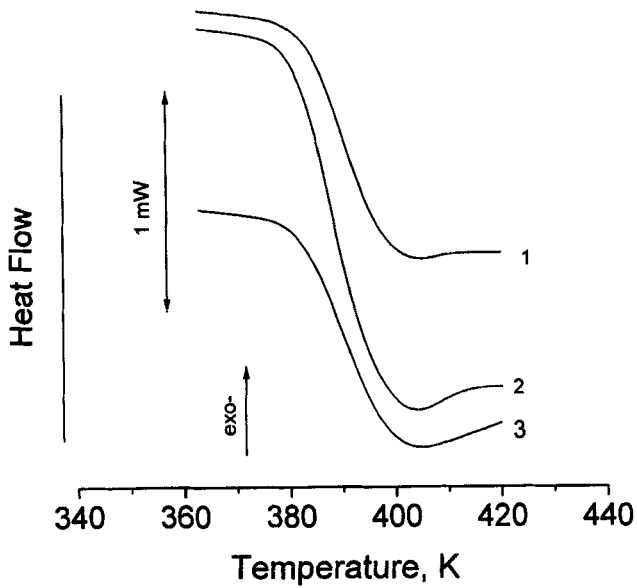


FIGURE 5 DSC curves for PMMA (1) and PMMA containing 0.1 (2) and 1.3 wt% of DES (3).

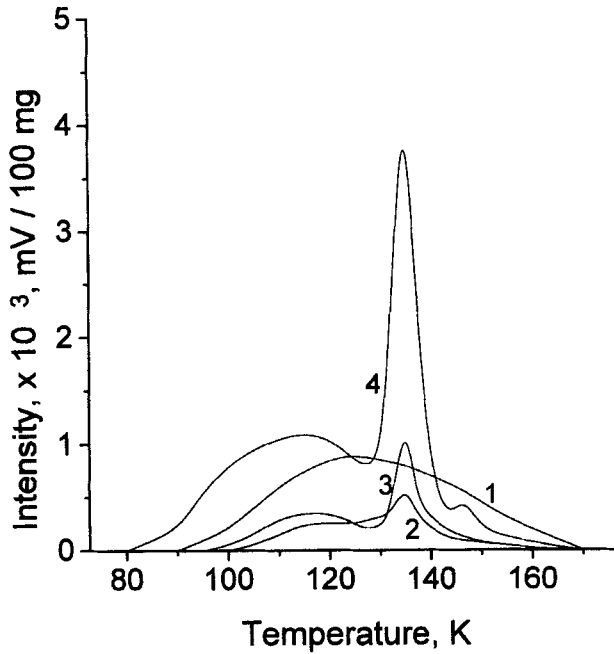


FIGURE 6 Thermostimulated luminescence curves for PMMA (1) and PMMA containing 0.1 (2), 0.5 (3), and 1.3 wt% of DES (4).

The PAL data (lifetimes τ_i and intensities I_i) for PMMA/DES samples are summarized in Tables I (for three-component analysis) and II (for four-component analysis). Recently, PALS was widely used to study the microstructure of polymers [15–25]. According to the theoretical speculations based on numerous model experiments [26–28], in the heterogeneous polymer structures, positrons tend to localize and annihilate in free volume holes within ordered (densely packed) structural regions, whereas positronium occupies and annihilates in the free volume holes within disordered (loosely packed) structural regions [16]. This theoretical model was supported by the PAL studies for heterogeneous polymer materials such as semicrystalline polymers [19], polymers containing rigid inorganic fillers [16, 19], and cured epoxy polymers [25].

According to the heterogeneous structural model of glassy polymers [7–11], positrons are expected to occupy and annihilate in the structural sublevels with increased packing densities, whereas positronium – in the structural sublevels with lowered packing densities.

For both three-component and four-component analyses, the shortest-lived component with lifetime τ_1 and intensity I_1 is associated with the annihilation of singlet positronium (^1Ps) and non-localized positrons. The second component with lifetime τ_2 and intensity I_2 is partially associated with non-localized positrons and is primarily related to a preferential localization of positrons in the free volume microregions within the structural sublevels with increased packing densities. Ortho-positronium occupies and annihilates in the free volume microregions within the structural sublevels with lowered packing densities. This factor contributes to the longest-lived components of the PAL spectra: the third component with the lifetime τ_3 and intensity I_3 (three-component analysis), and the third and fourth components with lifetimes τ_3 and τ_4 and intensities I_3 and I_4 (four-component analysis).

As follows from Tables I and II, introduction of 0.1 wt% of DES has no marked effect on the annihilation characteristics of polymer samples. As C_{DES} is increased up to 0.5 and 1.3 wt%, the three-component analysis (Tab. I) shows an increase in lifetime τ_3 and intensity I_3 of the third component, whereas the corresponding annihilation parameters of the second component with τ_2 and I_2 remain unchanged. For the four-component analysis (Tab. II), when

TABLE I Annihilation parameters of PMMA and PMMA containing DES for the three-component analysis of positron lifetime spectra from the PATFIT

Sample	τ_1, ns	$I_1, \%$	τ_2, ns	$I_2, \%$	τ_3, ns	$I_3, \%$
PMMA	0.240 ± 0.003	44.23 ± 1.29	0.482 ± 0.008	31.48 ± 1.21	1.962 ± 0.005	24.29 ± 0.11
PMMA with 0.1 wt%	0.240 ± 0.003	44.24 ± 1.29	0.480 ± 0.008	31.40 ± 0.005	1.960 ± 0.005	24.32 ± 0.11
0.5 wt%	0.242 ± 0.003	44.11 ± 1.11	0.478 ± 0.008	31.24 ± 1.05	1.970 ± 0.005	24.78 ± 0.1
1.3 wt%	0.234 ± 0.003	44.09 ± 1.08	0.484 ± 0.007	31.09 ± 1.01	1.981 ± 0.004	24.83 ± 0.1
of DES						

TABLE II Annihilation parameters of PMMA and PMMA containing DES for the four-component analysis of positron lifetime spectra from the PATFIT

Sample	τ_1, ns	$I_1, \%$	τ_2, ns	$I_2, \%$	τ_3, ns	$I_3, \%$	τ_4, ns	$I_4, \%$
PMMA	0.220 ± 0.003	35.38 ± 1.32	0.420 ± 0.007	38.77 ± 1.19	1.730 ± 0.005	19.72 ± 0.12	2.460 fixed	6.14 ± 0.32
PMMA with 0.1 wt%	0.210 ± 0.005	31.37 ± 1.89	0.410 ± 0.008	41.95 ± 1.740	1.710 ± 0.020	20.57 ± 0.244	2.490 fixed	6.11 ± 0.38
0.5 wt%	0.210 ± 0.004	30.47 ± 1.09	0.400 ± 0.010	42.45 ± 1.09	1.660 ± 0.006	19.43 ± 0.12	2.450 fixed	7.65 ± 0.29
1.3 wt%	0.202 ± 0.005	28.75 ± 1.84	0.394 ± 0.007	43.93 ± 1.70	1.660 ± 0.018	19.54 ± 0.18	2.490 fixed	7.77 ± 0.29
of DES								

C_{DES} is increased from 0.1 to 1.3 wt%, the intensity of the fourth component I_4 increases, whereas no noticeable changes in the characteristics of the shorter-lived components are observed. The increase in the values of lifetimes and intensities of positron annihilation is associated with an increase in the free volume content in polymer samples. The increase in the parameters of the longest-lived components of the PAL spectra and unchanged parameters of the shorter-lived components suggest that free volume increases primarily in the structural sublevels with lowered packing densities.

DISCUSSION

As follows from the DMA data (Fig. 3) and DSC data (Fig. 5), introduction of DES to PMMA has no effect on glass transition

temperature of polymer. The TSL data (Fig. 6) show that DES in PMMA is characterized by its own glass transition peak. This experimental evidence suggests the poor compatibility between DES and polymer. However, DES has a pronounced effect on the mechanical behavior of PMMA.

Figure 7A shows the concentration dependences of the mechanical characteristics such as elastic modulus E_0 (curve 1) and yield stress σ_y (curve 2). Both curves pass maximum at $C_{DES} = 0.1$ wt%. At $C_{DES} > 0.5$ wt%, the mechanical parameters are lower than those of the initial polymer. In other words, depending on concentration, DES has an antiplasticizing (reinforcing) action and a plasticizing (weakening) action on PMMA. Note that antiplasticization and plasticization are observed within rather narrow concentration interval (0.1 – 1.3 wt%) of DES in PMMA.

The concentration dependence of the contribution from the low-temperature component to the temperature-induced recovery of residual deformation $\varepsilon_1/(\varepsilon_1 + \varepsilon_2)$ (Fig. 7A, curve 3) is similar to concentration dependences of both E_0 and σ_y (curves 1 and 2, respectively). For polymer glasses, the correlation between $\varepsilon_1/(\varepsilon_1 + \varepsilon_2)$ and mechanical characteristics was discussed in [29–31] within the framework of the heterogeneous structural model of glassy polymers. According to this approach, structure of a glassy polymer is characterized by a set of structural sublevels with different packing densities. Shear deformation of glassy polymer involves a gradual stress activation of the local segmental mobility within the above structural sublevels. For the deformed polymer glasses, the temperature-induced recovery of residual deformation is a macroscopic manifestation of these microscopic segmental rearrangements, which are responsible for the deformation localized in the shear bands. As segmental mobility is enhanced by increasing the temperature of deformation and by physicochemical modification, $\varepsilon_1/(\varepsilon_1 + \varepsilon_2)$ decreases. As a result, E_0 and σ_y decrease [30]. Restriction of the segmental mobility *via* cross-linking increases $\varepsilon_1/(\varepsilon_1 + \varepsilon_2)$ [32]. From this standpoint, parameter $\varepsilon_1/(\varepsilon_1 + \varepsilon_2)$ describes the dynamics of the microscopic local segmental mobility, which controls deformation and the resultant macroscopic mechanical behavior.

When $C_{DES} = 0.1$ wt%, the increase in $\varepsilon_1/(\varepsilon_1 + \varepsilon_2)$ (Fig. 7A, curve 3) suggests that local segmental mobility in polymer is inhibited. As a

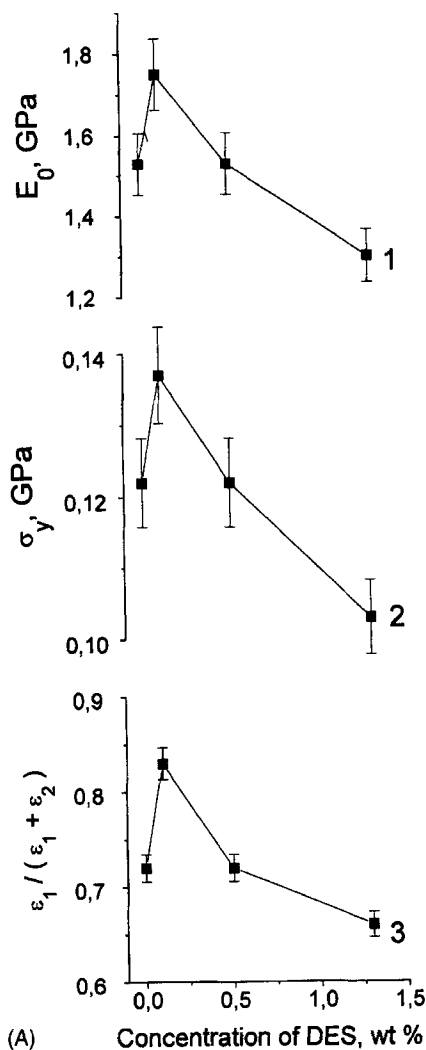


FIGURE 7 Elastic modulus E_0' (1), yield stress σ_y (2), and contribution from the low-temperature component to the temperature-induced recovery of residual deformation $\epsilon_1 / (\epsilon_1 + \epsilon_2)$ (3) (A); the areas under the loss tangent peaks estimated from the temperature dependences of loss tangent $S_{\tan\delta}(T)$ (1) and from the master frequency dependences of loss tangent $S_{\tan\delta}(\omega)$ (2), heat flow jumps (3) estimated from the DSC data, and the areas under the PMMA relaxation peaks estimated from TSL data S_{TSL} (4) (B); lifetimes τ_3 (1) and the products of τ_3 and intensity I_3 (2) of the third components of PAL spectra for three-component analysis, intensities I_4 (3) and the products of I_4 and lifetime τ_3 (4) of the fourth component of PAL spectra for four-component analysis (C) versus concentration of DES in PMMA.

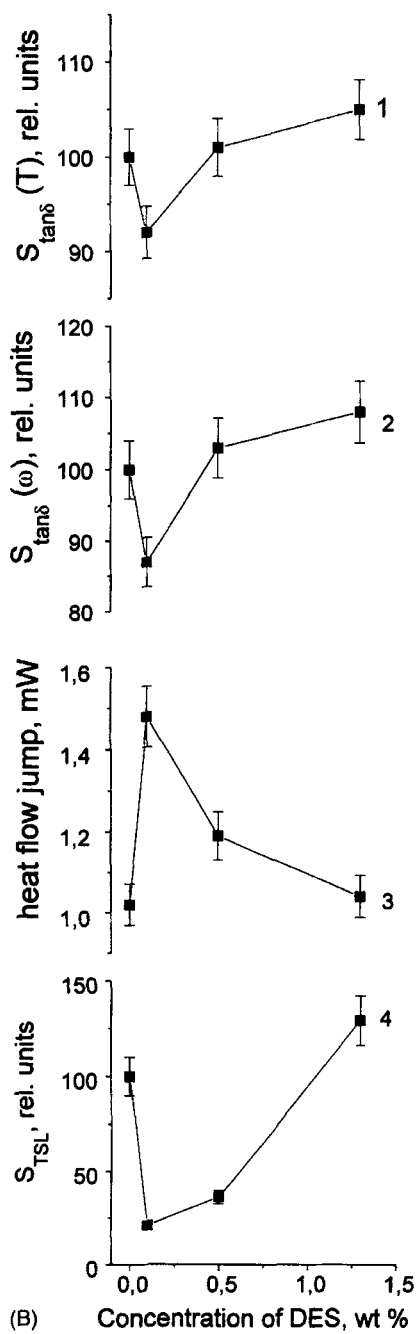


FIGURE 7 (Continued).

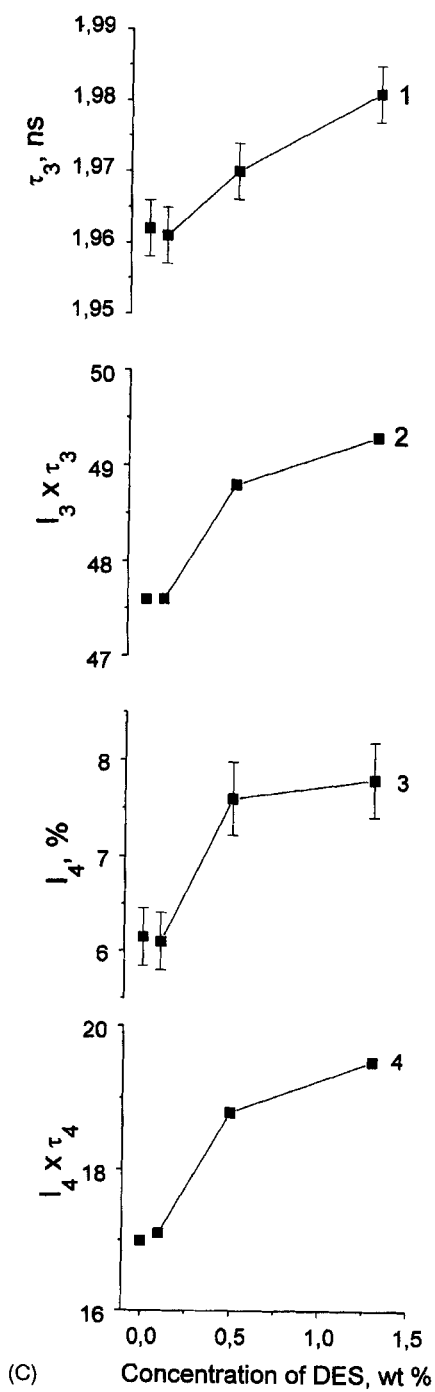


FIGURE 7 (Continued).

result, E_0 and σ_y increase (curves 1 and 2, respectively). As C_{DES} is increased up to 0.5 and 1.3 wt%, the decrease in $\varepsilon_1/(\varepsilon_1 + \varepsilon_2)$ implies that microscopic local segmental rearrangements are enhanced, and macroscopic mechanical parameters decrease.

Hence, antiplasticizing and plasticizing actions of DES on PMMA are associated with the effect of DES on the local segmental mobility which controls the development of deformation. To verify this effect of DES on the molecular mobility in PMMA, let us consider the following experimental data.

Figure 7B (curves 1 and 2) shows the concentration dependences of the areas under the loss tangent α -relaxation peaks $S_{\tan\delta}$ estimated from the temperature dependences of $\tan\delta$ (Fig. 3) and from the master frequency dependences of $\tan\delta$ (Fig. 4B). For PMMA samples containing 0.1 wt% of DES, the decrease in $S_{\tan\delta}$ suggests the decreasing segmental mobility responsible for α -relaxation. As C_{DES} is increased up to 1.3 wt%, these areas increase. This behavior may be explained by an enhanced segmental mobility in the polymer sample.

The effect of DES on the segmental mobility in PMMA is supported by the DSC data (Fig. 5). For PMMA containing 0.1 wt% of DES, endothermic heat flow jump at glass transition increases as compared with that for initial polymer (Fig. 7B, curve 3). This behavior suggests an inhibited segmental mobility as a result of the introduction of DES to PMMA. As C_{DES} is increased up to 0.5 and 1.3 wt%, heat flow jump decreases. This effect evidences that, at these concentrations of DES, segmental mobility is enhanced. Hence, DES molecules have a pronounced effect not only on the local segmental mobility, which controls the development of shear deformation, but also on the total segmental mobility responsible for glass transition in polymer.

Thermostimulated luminescence spectra (Fig. 6) suggest that DES molecules have an effect not only on the large-scale segmental mobility but also on the small-scale molecular mobility of the PMMA macrochains. As compared with initial polymer, introduction of 0.1 wt% of DES in PMMA decreases the area under the broad peak in the temperature interval from 110 to 160 K (Fig. 7B, curve 4). This effect suggests the inhibited mobility of small-scale kinetic units responsible for this relaxation transition. When C_{DES} is increased up to 0.5 and 1.3 wt%, the mobility of these kinetic units is enhanced, and the areas under the above peaks increase.

Hence, at low concentration of DES in PMMA (0.1 wt%), introduction of DES to PMMA restricts the microscopic molecular (segmental) mobility of polymer. This trend provides an increase in the macroscopic mechanical parameters of PMMA. When C_{DES} is increased up to 0.5 and 1.3 wt%, DES enhances molecular mobility of PMMA, and mechanical characteristics of polymer tend to decrease. Taking into account a poor compatibility of DES and PMMA, this behavior is not controlled by a homogeneous distribution of DES in polymer. The effect of DES on both microscopic molecular mobility and macroscopic mechanical response of PMMA is expected to be localized in the certain structural regions of polymer.

To follow the structural changes induced by the introduction of DES to PMMA, let us consider the results of the PAL measurements. Figure 7C shows the concentration dependences of the parameters of the longest-lived components of the PAL spectra: for three-component analysis, lifetime τ_3 and the product of τ_3 and intensity I_3 (curves 1 and 2, respectively), and, for four-component analysis, intensity I_4 and the product of I_4 and lifetime τ_3 (curves 3 and 4, respectively). Introduction of 0.5 and 1.3 wt% of DES to PMMA increases the above PAL parameters, whereas, at $C_{DES} = 0.1$ wt%, no changes in the PAL characteristics is observed.

At low concentration of DES (0.1 wt%) in the feed mixture with MMA, during polymerization, DES molecules are likely to be pushed out to the large free volume microholes within the structural sublevels with lowered packing densities. In this case, the annihilation parameters of the PMMA/DES samples are comparable to those of initial PMMA. The constancy of the annihilation characteristics may be rationalized by the fact that these microholes are located far away from each other. The distances between these microholes exceed the diffusion paths of both positron and positronium. As a result, they appear to be beyond the detection limit of this technique. However, within these structural sublevels, DES molecules are able to inhibit the molecular mobility (Fig. 7B), and a well-pronounced antiplasticizing action of DES on PMMA takes place (Fig. 7A).

As the concentration of DES in the feed mixture with MMA is increased up to 0.5 and 1.3 wt%, during polymerization, DES molecules prevent a dense packaging of the growing PMMA macrochains. This trend is responsible for an increase in the longest-lived

annihilation parameters of PAL spectra (Fig. 7C), that is, for an increase in the free volume content primarily within the structural sublevels with lowered packing densities. As a result, the molecular mobility in the polymer samples is enhanced (Fig. 7B), and plasticization of PMMA with DES is observed (Fig. 7A).

CONCLUSION

The above experimental evidence allows one to describe the effect of DES on the mechanical behavior of PMMA according to the following structural and molecular approach.

When the content of DES in PMMA is equal to 0.1 wt%, DES has no noticeable effect on the free volume content of polymer. DES molecules are likely to occupy the large free volume microholes, which are beyond the detection limit of the PALS technique. However, DES restricts the microscopic molecular mobility in these microstructural sublevels. As the molecular mobility in the local structural sublevels is inhibited, the macroscopic mechanical characteristics of polymer (E_0 and σ_y) increase.

When C_{DES} is increased up to 0.5 and 1.3wt%, free volume content in PMMA increases primarily in the structural sublevels with lowered packing densities. Loosening of these structural sublevels provides the enhancement of the microscopic molecular mobility and a decrease in macroscopic mechanical properties.

From this standpoint, the mechanism of the structural plasticization of polymer with incompatible low-molecular-mass plasticizing agents involves the effect of molecules of plasticizing agent on the microstructure of polymer, resultant changes in the microscopic molecular mobility, and the corresponding variations in the macroscopic mechanical behavior.

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