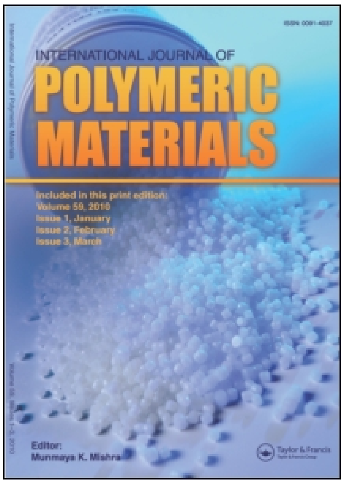

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Glass transition of undrawn and drawn copolyetherester thermoplastic elastomers

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GLASS TRANSITION OF UNDRAWN AND DRAWN COPOLYETHERESTER THERMOPLASTIC ELASTOMERS

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The phase and deformation behaviour of two types of copolyetheresters (the block copolymers E and P) were studied by means of DSC, dynamic mechanical spectroscopy and X-ray diffraction. The block copolymers E and P based on poly(-butylene therephtalate) (PBT) as a hard block have poly(tetramethylene oxide) (PTMO) and triblock copolymer (PEO-PPO-PEO) with a middle poly(propylene oxide) (PPO) block and two end poly(ethylene oxide) (PEO) as a soft block, respectively. The complex investigation shows that the studied copolyetheresters are microphase separated polymer systems in the amorphous matrix of which the PBT crystallites are embedded. The volume fraction of PBT crystallites depends on the block copolymer composition and changes from 5 to 20%. In the amorphous matrix that is the mixed PBT/ the soft block phase the soft block acts as a PBT plasticizer reducing the glass transition temperature of the amorphous mixed phase. The most interesting aspect of the phase behaviour of the copolyetheresters consists in the fact that, in comparison with PTMO, the triblock is characterized by a more pronounced PBT plasticization effect. A special emphasis was placed in this work on the investigation of an increased glass transition temperature of drawn copolyetheresters. It was found that this process depends on the volume fraction of PBT crystallites and chemical structure of the soft blocks. The first factor characterizes the interaction between the amorphous mixed phase and PBT crystallites and, therefore, the higher value of the volume fraction of PBT crystallites the higher is the glass transition temperature of drawn copolyetheresters. The second factor determines the PBT plasticization effect of the soft blocks and a level of the interaction of chains in the amorphous mixed phase. Because of a weaker PBT plasticization effect of PTMO in comparison with that of the triblock, the deformation of the block copolymer E is accompanied by a more pronounced

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elevation of the glass transition temperature in comparison with the block copolymer P.

Keywords: dynamic mechanical properties, glass transition, molecular mobility, copolyetherester thermoplastic elastomers

1. INTRODUCTION

The glass transition temperature (T_g) determines an activation of the cooperative molecular motions in the amorphous phase of flexible semicrystalline polymers and is important for understanding changes in their mechanical properties with temperature. The influences of the crystallites on the mechanical properties of these polymers are twofold. On the one hand, the crystallites stiffen the polymeric materials and, on the other hand, their constraining effect on the amorphous chains leads to an increase in T_g [1, 2].

Upon drawing, the crystallites prefer to orient and the amorphous chain tend to become more aligned in the draw direction. As a result of it, a fraction of domains in the amorphous phase of oriented polymers is preferentially oriented [3]. The chain segments in these domains are more densely packed and there are some changes in their conformation. According to the recent modeling [2] of the behaviour of chains in the amorphous phase of oriented semicrystalline polymers, these transformations in the structure of the oriented amorphous phase should be accompanied by a drastic increase in T_g.

This theoretical predication is supported by the experimental observations of T_g of the oriented polymers such as nylons and polyesters [4–6]. However, there is some controversy in the literature concerning T_g of stretched rubbers [7–9]. One can find the mentions about both increased [7, 8] and decreased [9] T_g of stretched rubbers.

Thermoplastic elastomers (TEPs) of this study are two types of copolyetheresters manufactured by DSM under the trade name Arnitel E and Arnitel P. Macromolecules of these block copolymers consist of alternating soft (usually amorphous) blocks of polyether and hard (able to crystallization) blocks of poly(butylene therephtalate) (PBT) [10]. Poly(tetramethylene oxide) (PTMO) and triblock copolymer (PEO-PPO-PEO) with a middle poly(propylene oxide) (PPO) block and two end poly(ethylene oxide) (PEO) blocks are used as a soft block for the block copolymers E and P, respectively.

The complex investigation of the phase and deformation behaviour of the block copolymers E has shown [11–14] that the rubbery regions in these TEP's are, as a rule, the mixed amorphous phase of PBT and PTMO blocks while PBT crystallites act as physical network junctions connecting the rubbery regions. The deformation properties of the block copolymers E are determined by T_g of the mixed amorphous phase and the volume fraction (χ) of PBT crystallites. The sample E with a high content of PTMO (60% wt.) are characterized by low values of T_g (−50°C) and χ (5%) and are slightly stiffer than rubbers [15, 16]. A decrease in the PTMO content to 35% wt. leads to an increase in T_g to −17°C and χ to 20%. Furthermore, the width of the glass transition increases and, as a result, a part of the mixed amorphous phase of the sample E with 35% wt. of PTMO is glassy at the room temperature. Therefore, the deformation properties of this sample are close to that of the pure PBT [15, 17].

In this work we extend the investigation of the deformation behaviour of the block copolymers E by the study of changes in the cooperative molecular mobility in the rubber regions of these TEP's during stretching.

Keeping in mind the above-stated reasons, we do not expect considerable changes in T_g of the mixed amorphous phase of the samples E with a high content of PTMO during stretching. However, T_g of the mixed amorphous phase of the samples E with a low content of PTMO will drastically increase during stretching. This process is important for understanding the mechanism of deformation of these TEP's. It is also interesting to study the phase and deformation behaviour of the block copolymers P and clarify effects of the chemical structure of the soft blocks on the cooperative molecular mobility in the mixed amorphous phase of the copolyetheresters.

2. EXPERIMENTAL PART

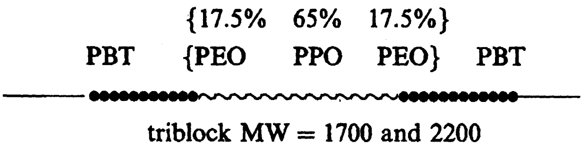
2.1. Characteristics of Samples

The investigation was carried out on two types of copolyetheresters (E and P) consisting of:

(1) PBT as a hard block and PTMO as a soft block (block copolymer E):

PTMO MW = 1000, 1500 and 2000

(2) PBT as a hard block and triblock copolymer (PEO-PPO-PEO) as a soft block (block copolymer P):



The sample designation and composition (MW and content of the soft block) of the block copolymers E and P are presented in Table 1.

2.2. Methods

The dynamic mechanical properties of the polymers were studied using a version of the resonance method related to longitudinal oscillations of a vertically positioned polymer film ($0.5 \times 0.5\,\text{mm}^2$) in cross-sectional area and 30 mm in length in the temperature range from -160 to 200°C. The resonance oscillation frequency (f_r) was varied from 400 to 40 Hz. Young's modulus was calculated according to the formula:

$$E' = 4\pi^2 lmf_r/S$$

where l and S are the length and cross-sectional area of the polymer film, and m is the weight of the load.

The mechanical loss tangent ($\tan\delta$) was calculated from the width of the resonance curve Δf at the $1/\sqrt{2}$ of the maximum

$$\tan\delta = \Delta f/f_r$$

TABLE 1 Composition and DSC and X-ray Data for the Copolyetheresters E and P

Sample	MW of the soft block, g/mol	Content of the soft block %wt.	T_g, °C	T_{mPBT}, °C	α_{PBT}, %	χ_{PBT}, %	T_{mPTMO}, °C
E-1	1000	35	−65	210	40	20	−16
E-2	1000	50	−71	190	33	13	−20
E-3	1000	60	−71	150	20	5	−20
E-4	1500	50	−68	200	35	15	−20
E-5	1500	60	−72	173	30	8	−20
E-6	2000	10	50	225	35	–	–
E-7	2000	60	−65	194	40	12	−8
P-1	1700	25	−48	217	34	20	–
P-2	1700	40	−52	211	39	16	–
P-3	2200	55	−60	207	35	11	–

The temperature dependence of E' and $\tan\delta$ were obtained for as prepared and drawn to various degrees of stretching block copolymer samples. The preparation of drawn samples for the experiment was the following. Firstly, an as prepared polymer sample was drawn to a preselected degree of stretching. Then the drawn sample in constrained conditions was frozen in liquid N_2 and, finely, a part of the frozen sample about 30 mm in length was cut and transported quickly into the DMA apparatus cooled to about −160°C. From this temperature the study of the dynamic mechanical behavior of the drawn sample was begun. During experiment the shrinkage of the drawn sample was observed at a temperature which depended on the block copolymer composition. The experiment finished when the length of the sample decreased to about a half of its initial length. Therefore, the temperature at which the experiment was stopped depended on the block copolymer composition: it was close to room temperature for samples with a high content of the soft block while for samples with a low content of the soft block it was about 100°C.

Calorimetric characterizations of the polymers were carried out with use a Perkin-Elmer DSC-7 analyzer in an atmosphere of helium at the temperature range from −150 to +250°C at a scanning rate of 20°C/min. The polymer sample weights were 10−15 mg.

The volume fraction of PBT crystallites (χ) was estimated from the wide angle X-ray data of as-prepared polymer samples as the ratio of the crystalline scattering to the total scattering, after correction for instrumental background scattering and Lorentz and polarisation effects.

3. RESULTS AND DISCUSSION

3.1. Phase Behavior of Copolyetheresters E and P

Figure 1 shows the DSC heating traces of the samples E-7 and P-3 that are typical for the DSC traces of the other samples E [6] and P, respectively. There are three transitions for all samples E: the glass transition (T_g) and the endo-peak of melting of PTMO block (T_{mPTMO}) in a low temperature region and the endo-peak of melting of PBT block (T_{mPBT}) at the temperature about 200°C. The only difference of the DSC-traces of the samples P is an absence of the endo-peak of melting of the triblock. The data obtained from analysis of the two transitions for the samples P are given in comparison with the data for three transitions of the samples E in Table 1.

Based on the data of Table 1, we can reach two conclusions. At first, in contrast with E, the cooling of the block copolymers P below room

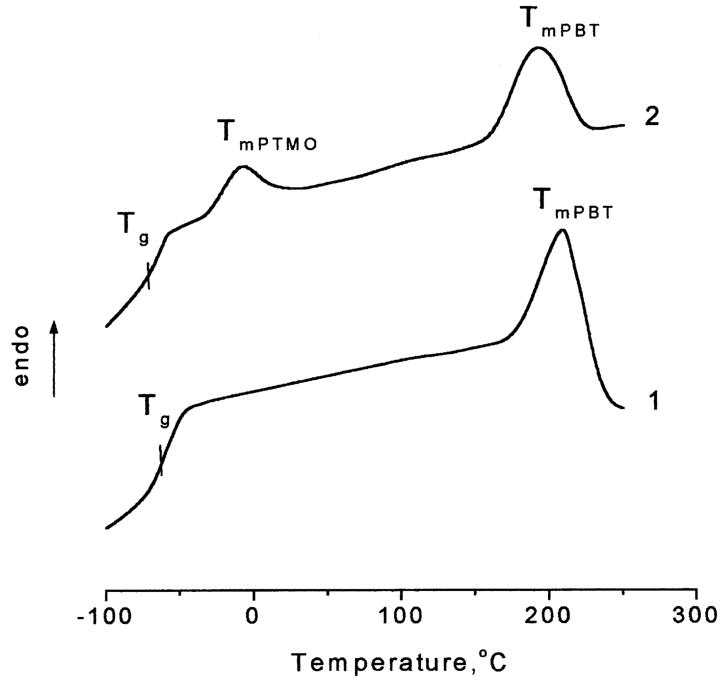


FIGURE 1 DSC heating traces of as-prepared samples of (1) P-3 and (2) E-7.

temperature is not accompanied by the crystallization of the soft block. At second, as expected, the ability of PBT block to crystallize in the block copolymers P practically does not differ from that in E. For both E and P, increasing the soft block MW and decreasing its content increase the degree of crystallinity of PBT block (α_{PBT}). α_{PBT} calculated from heat of fusion of PBT block was normalized on its content (heat of fusion of 100% crystalline PBT is equal to 144,5 J/g [18]). WAXS data about the volume fraction of PBT crystallites (χ_{PBT}) for all samples are also listed in Table 1. As well as α_{PBT}, χ_{PBT} depends on the block copolymer composition.

To clarify a degree of the microphase separation in the amorphous phase of the block copolymers, we analyzed their relaxation spectra.

Figure 2 shows the temperature dependence of $\tan\delta$ for P-1, P-2 and P-3 in comparison with E-4 and E-7. There are four transitions in the relaxation spectra for all samples P designated by T_1, T_2, T_3 and $T_{g\,mix}$ in contrast with the samples E that are characterized by the existence of three transitions (T_1, T_3 and $T_{g\,mix}$). The temperatures of the transitions T_1 (-120), T_2 (-80) and T_3 (-60°C) are independent

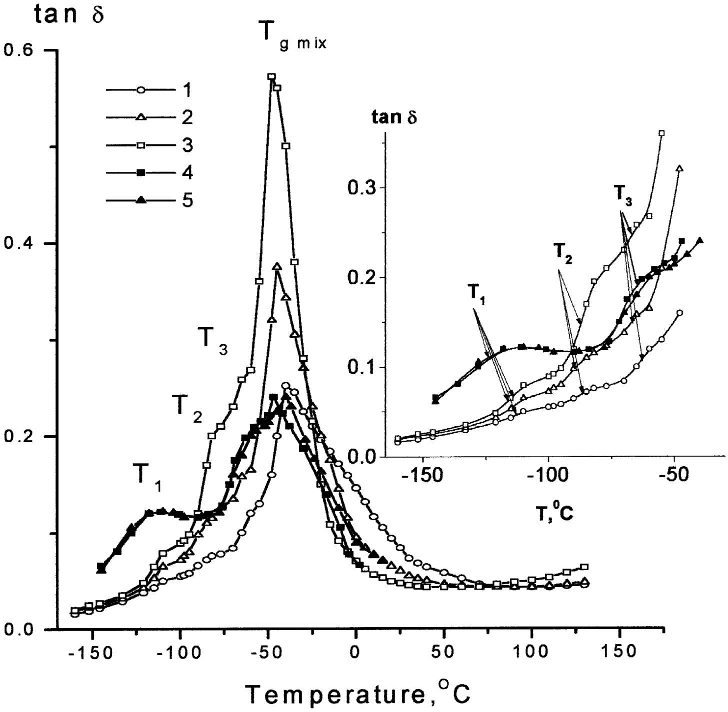


FIGURE 2 Temperature dependence of tan δ for (1) P-1, (2) P-2, (3) P-3, (4) E-6 and (5) E-4.

of the block copolymer composition while the temperature interval of $T_{g\,mix}$ depends drastically on the soft block content.

Figure 3 summarizes the position of all transitions as a function of the soft block content for the samples P and E. The following identification of the transitions can be suggested:

(i) T_1, T_2 and T_3 correspond to an activation of local motions of main chain structural units of the block copolymers P and E;

(ii) $T_{g\,mix}$ corresponds to the glass transition of the amorphous mixed PBT/soft block phase.

An absence of the transition T_2 at −80°C in the relaxation spectra of the samples E may be explained by different chemical structures of the soft blocks of the block copolymers P (triblock PEO-PPO-PEO) and E (PTMO). All three polymers (PTMO, PEO and PPO) are related to the group of oxide polymers, however, PTMO and PEO have two structural units involved in their main chain (CH_2-and the ether bond O) while PPO contains additionally the carbon atom with the side

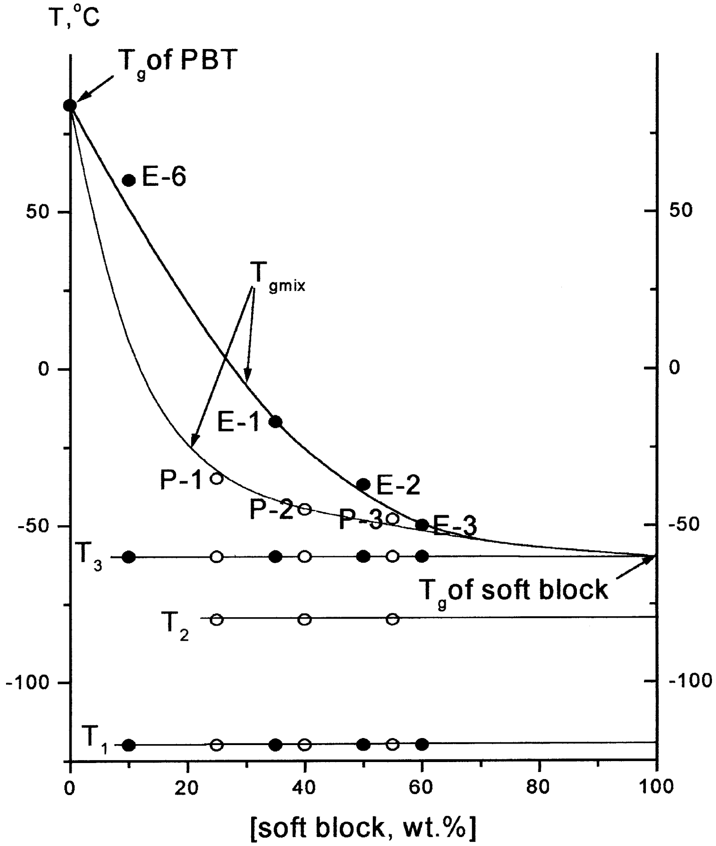


FIGURE 3 Composition dependence of the local transitions T_1, T_2 and T_3 and $T_{g\,mix}$ for copolyetheresters E (•) and P (o).

methyl group, $CH(CH_3)$-group. According to our investigation of the dynamic mechanical characterization of the molecular mobility in oxide polymers [19,20], an activation of local motions of CH_2-group, $CH(CH_3)$-group and the ether bond O involved in a main chain of these polymers take place at -120, -80 and -70°C, respectively. It is important that an appearance of local motions of the most rigid structural unit (the ether bond) of the oxide polymers determines their glass transition . Therefore, we have suggested that all oxide polymers are characterized by T_g about -70°C.

We believe that the transitions T_1 and T_2 at -120 and -80°C in the relaxation spectra of the samples P are associated with local motions of CH_2- and $CH(CH_3)$-groups. The block copolymers E do not contain

$CH(CH_3)$-groups in their main chain and, therefore, T_2 at $-80°C$ is not observed in the relaxation spectra of the samples E.

Analyzing the transition T_3 observed at $-60°C$ in the relaxation spectra of the samples P and E, we have to take into account local motions of the structural units involved in a main chain of PBT block, CH_2-group and the ester carboxyl group (CO)O. Figure 4 shows the temperature dependence of tan δ for the pure PBT and E-6. One can see that there is no considerable difference in these relaxation spectra. CH_2-groups show their local mobility at $-120°C$ and on further heating an activation of (CO)O groups occurs at $-50°C$ for both polymers. The only difference is decreasing of T_g for E-6 (60°C) in comparison with T_g for the pure PBT (84°C) because of the plasticizing effect of PTMO block.

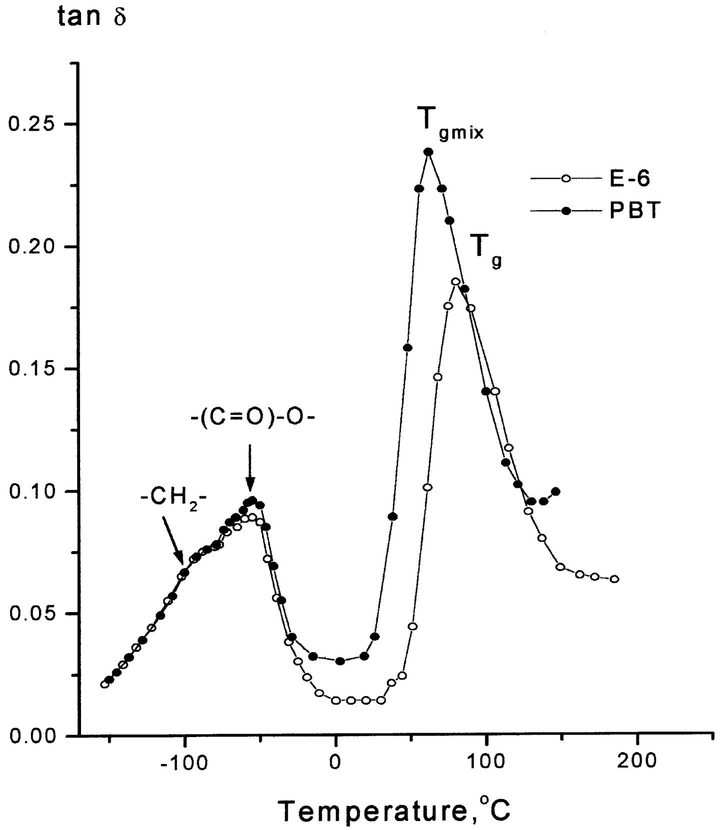


FIGURE 4 Temperature dependence of tan δ for pure PBT and E-6.

Therefore, the transition T_3 observed at $-60°C$ in the relaxation spectra of the block copolymers P and E is related to a simultaneous appearance of the local motions of two structural units. These include the ether bond O involved in a main chain of the soft blocks and the ester carboxyl group (CO)O involved in a main chain of the PBT block. Furthermore, in this temperature range T_g of the pure amorphous PTMO phase also can appear in a case of the separation of the amorphous mixed phase of the block copolymers E with the highest content of PTMO [4].

Hence, above $-50°C$ all the main chain structural units of both block copolymers are mobile and on further heating, cooperative motion in the amorphous mixed PBT/soft block phase can take place. As a result of the plasticizing effect of the soft block, $T_{g\,mix}$ for all samples are observed at a lower temperature than T_g of pure PBT (Fig. 3). Figure 3 shows also that the plasticizing effect of the PEO-PPO-PEO triblock is more pronounced than that of the PTMO block. This may be associated with the existence of the side methyl groups in the soft block of the block copolymers P. Due to these side methyl groups, in comparison with E, the block copolymers P are characterized by lower density and intermolecular interaction in the amorphous mixed phase.

In summary, the investigation of the phase behaviour of the block copolymers P shows that they, as well as the block copolymers E [6], are microphase separated polymer systems in the amorphous matrix in which the PBT crystallites are embedded. The volume fraction of PBT crystallites depends on the sample composition and changes from 11 to 20%. In the amorphous matrix that is the mixed PBT/triblock phase the triblock acts as a PBT plasticizer reducing its glass transition temperature. The most interesting aspect of the phase behaviour of the studied copolyetheresters consists of the fact that, in comparison with PTMO, the triblock is characterized by a more pronounced PBT plasticization effect.

3.2. Glass Transition of Drawn Copolyetheresters E and P

To clarify the changes in the cooperative molecular mobility in the rubber regions of the studied TEP's during stretching, we analyzed the temperature dependencies of tan δ of the samples E and P drawn to various degrees of stretching (λ). Figures 5a and 6a show the relaxation spectra of the drawn samples P-3 and E-1 for various λ. As can be seen from these Figures, the temperatures of the local transitions $T_1 - T_3$ are independent of λ while $T_{g\,mix}$ increases with λ (Figs. 5b and 6b). The stretching of P-3 with 55% wt. of the triblock is typical for

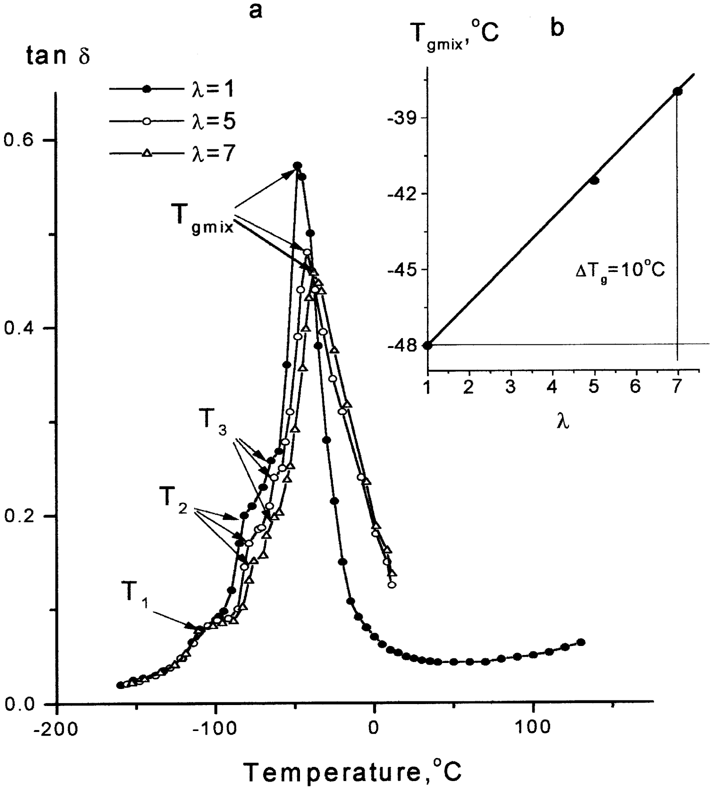


FIGURE 5 (a) Temperature dependence of tan δ for sample P-3 at different degrees of stretching (λ). (b) Dependence of $T_{g\,mix}$ as a function λ for P-3.

rubbers and characterized by slightly considerable changes in $T_{g\,mix}$ while $T_{g\,mix}$ of E-1 with 35% wt. of PTMO increases drastically with deformation. Attention is drawn to the fact that E-3 deforms plastically with a slightly notable neck like semicrystalline polymers. The formation of the neck finishes up to about $\lambda = 4$, therefore, the relaxation spectra of this sample were obtained for λ which is not less 4. The remaining samples are intermediate between P-1 and E-3 and their $T_{g\ mix}$ as a function of λ are listed in Table 2.

Figure 7 shows the temperature dependences of tan δ of the pure PBT for undrawn sample ($\lambda = 1$) and for the sample plastically deformed with necking up to about $\lambda = 6$. There is no difference between these dependencies in the temperature range of the local transitions (below the room temperature) while T_g of the PBT sample

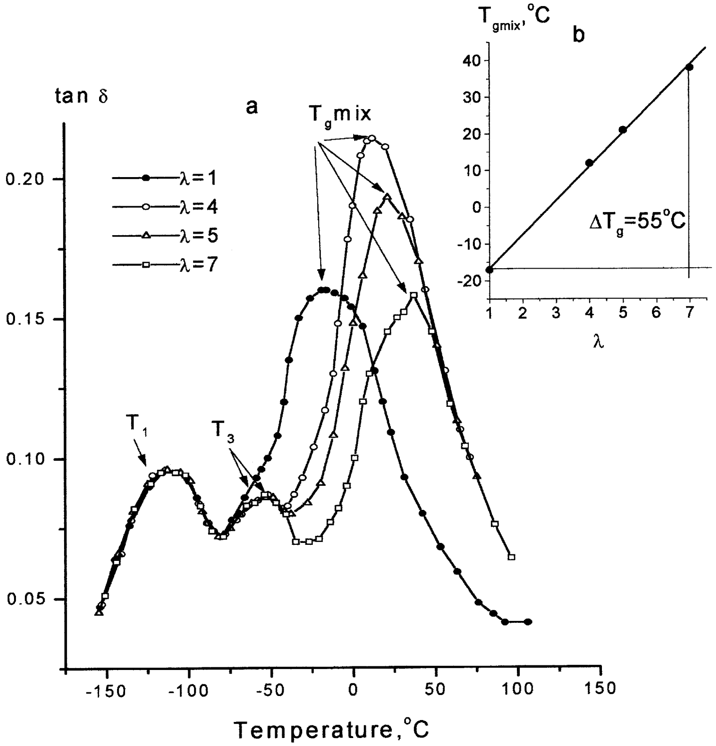


FIGURE 6 (a) Temperature dependence of tan δ for sample E-1 at different degree of stretching (λ). (b) Dependence of $T_{g\,mix}$ as a function λ for E-1.

TABLE 2 $T_{g\,mix}$ of the Copolyetherester Samples Drawn to Various λ and ΔT_g for $\lambda = 7$

$T_{g\,mix}$, °C Sample	$\lambda=1$	$\lambda=3$	$\lambda=4$	$\lambda=5$	$\lambda=6$	$\lambda=7$	ΔT_g, °C ($\lambda=7$)
E-1	−17	–	12	21	–	37	55
E-2	−37	−21	−15	−6	−1	5	42
E-3	−51	−42	−37	−33	−27	−22	29
E-4	−40	−24	−15	−9	−2	5	45
E-5	−49	−38	−33	−26	−20	−15	34
E-7	−47	−35	−28	−22	−15	−9	38
P-1	−35	–	–	−18	–	−9	26
P-2	−45	–	–	−34	–	−28	17
P-3	−48	–	–	−42	–	−38	10
PBT	84	–	–	–	113	–	36

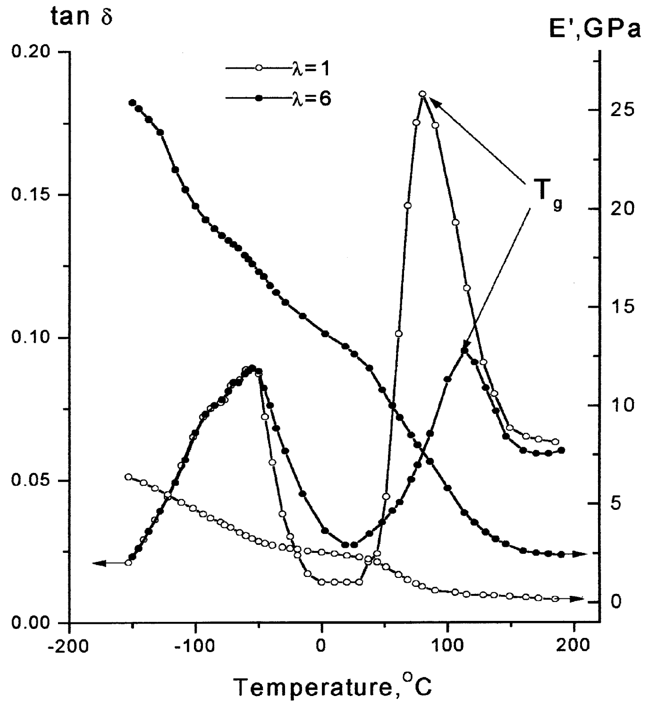


FIGURE 7 Temperature dependence of dynamic modulus (E′) and tan δ for virgin sample ($\lambda = 1$) and sample of pure PBT plastic deformed through the neck up to the degree of elongation $\lambda = 6$.

after the plastic deformation shifts to a higher temperature as well as for the block copolymers E and P.

To compare an increase in $T_{g\,mix}$ with deformation for different samples we used the ΔT_g values calculated by the equation:

$$\Delta T_g = T^*_{g\,mix} - T_{g\,mix}$$

where $T^*_{g\,mix}$ is $T_{g\,mix}$ of a polymer sample at $\lambda = 7$. The ΔT_g values for all samples are listed in Table 2.

Figure 8 shows the dependencies of the ΔT_g values as a function of the soft block content for all samples. We divided these dependencies in five groups (curves 1–5). Each of the curves is characterized by a constant MW of the soft block but its different content. The families of the curves 1–3 and 4,5 are related to the block copolymers E and P, respectively.

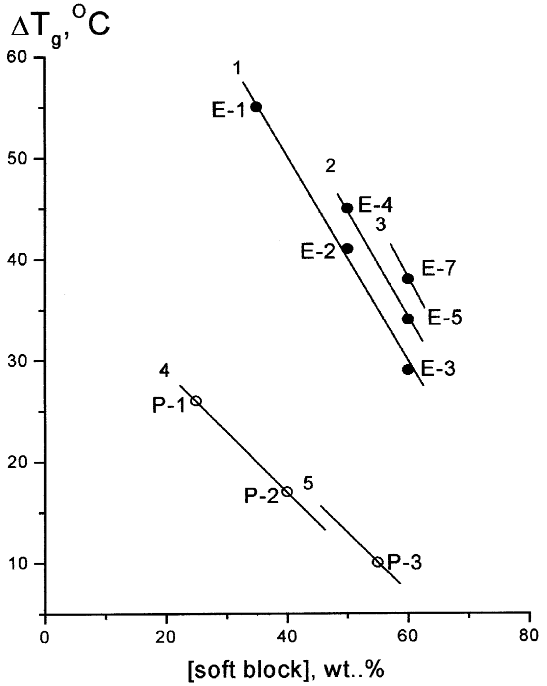


FIGURE 8 Dependence of ΔT_g as a function of the soft block content.

It is interesting to analyze the dependencies of the ΔT_g values as a function of the volume fraction of PBT crystallites (χ) (Fig. 9). As can be seen from Figure 9, for each of two families of block copolymers an elevation of $T_{g\,mix}$ with deformation is affected only by the volume fraction of PBT crystallites.

However, the polymer family E is characterized by considerably larger values of ΔT_g than the family P at the same values of χ_{PBT}. As was stated above, due to the side methyl groups, the PEO-PPO-PEO triblock is characterized by a stronger plasticizing effect in comparison with PTMO. Because of a lower density and a lower level of the intermolecular interaction in the amorphous mixed phase of the block copolymers P, their stretching is accompanied by a smaller elevation of $T_{g\,mix}$.

CONCLUSIONS

The investigation of the phase behaviour of the copolyetheresters E and P shows that they are microphase separated polymer systems in

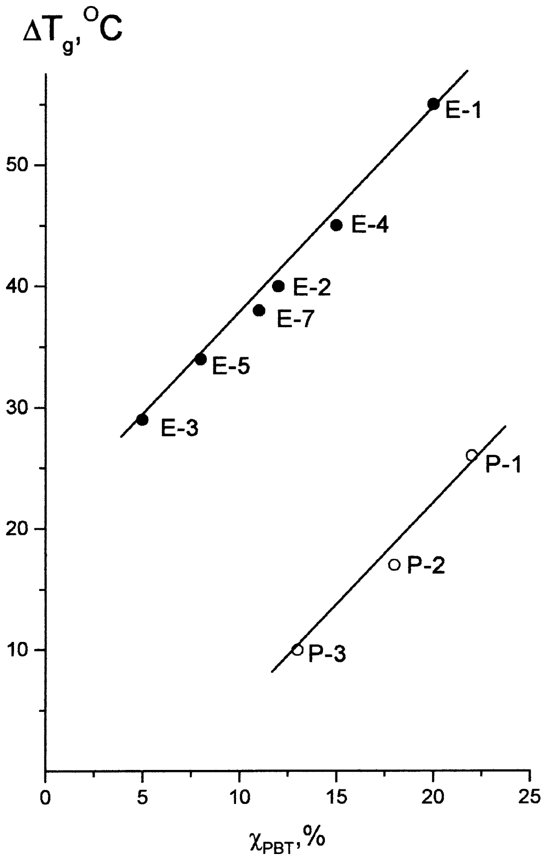


FIGURE 9 Dependence of ΔT_g as a function of the volume fraction of PBT crystallites (χ_{PBT}).

the amorphous matrix of which the PBT crystallites are embedded. The volume fraction of PBT crystallites depends on the sample composition and changes from 5 to 20%. In the amorphous matrix that is the mixed PBT/soft block phase, the soft block acts as a PBT plasticizer reducing its glass transition temperature. The most interesting aspect of the phase behaviour of the studied copolyetheresters consist of the fact that, in comparison with PTMO, the triblock is characterized by a more pronounced PBT plasticization effect.

Analysis of the relaxation spectra of the copolyetheresters samples drawn to various degrees of stretching allows us to suggest that the deformation of these TEP's is accompanied by an increase in the glass transition temperature of the amorphous mixed phase. Two factors play a key role in this process: the volume fraction of PBT crystallites and PBT plastisizing effect of the soft block. The first factor characterizes the interaction between the amorphous mixed phase and PBT crystallites. The second factor determines a level of the interaction of chains in the amorphous mixed phase of the studied copolyetheresters.

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