Volume Relaxation Rate in *a*-PMMA and *a*-PMMA/PEO Amorphous Blends

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ABSTRACT: Volume relaxation in *a*-PMMA and *a*-PMMA/PEO amorphous blends was investigated by employing a mercury-in-glass dilatometer after a temperature down-jump from equilibrium above glass transition temperature, T_g, to an aging temperature below T_g. From volume contraction isotherms, volume relaxation rate, $\beta_v = -1/V(dV/d\log t)$, was determined as a parameter quantifying the rate of volume changes, where V is the volume and t the aging time. The addition of PEO into blends has been found to considerably increase β_v.
     KEY WORDS   Volume Relaxation / Amorphous Blend / PMMA / PEO /

Polymer melt transforms to glassy state by cooling below glass transition temperature, T_g. Due to the kinetic disability of the macromolecules to achieve appropriate conformations immediately, material is in a thermodynamically non-equilibrium state. This causes a process of structural relaxation to attain a closer packing and thus to achieve thermodynamically equilibrium conformations, when the polymer is cooled below T_g. This aging process occurring on the level of microstructure is reflected in time dependent changes of macroscopic properties such as density, modulus, refractive index, dielectric constant and others.[1–3]

The macrostructural response of a material to the non-equilibrium state is usually studied by monitoring time-dependence of volume after temperature down-jump or up-jump. In the former method a material is cooled from an equilibrium state above T_g to an isothermal aging temperature, T_a (below T_g), which is followed by monitoring isothermal volume relaxation, *i.e.* material contraction.[4] The latter method is based on heating of the sample in the glassy state, which causes its expansion.[5]

The volume relaxation process can be quantitatively analyzed by the volume relaxation rate, β_v, *i.e.* the slope of the contraction isotherms in the region where the volume, V, varies linearly with the logarithm of aging time, t:

$$\beta_v = \left(\frac{d\delta}{d\log t} \right)_{\inf} \cong -\frac{1}{V}\left(\frac{dV}{d\log t} \right)_{\inf} \qquad (1)$$

where δ is the relative departure of actual volume, $V_{(t)}$, from equilibrium volume, V_∞, defined as:[6]

$$\delta = \frac{V_{(t)} - V_\infty}{V_\infty} \qquad (2)$$

The initial departure from equilibrium, δ_i immediately

after the temperature jump is related to the magnitude of temperature jump, ΔT:

$$\delta_i = \Delta\alpha\Delta T \qquad (3)$$

where $\Delta\alpha$ is the difference between the volume expansion coefficient of equilibrium liquid and glassy states. Thus, increasing ΔT and $\Delta\alpha$ leads to higher initial departure from equilibrium and subsequently faster volume relaxation rate. However, experimentally measured dependencies of β_v for many glassy polymers show a discrepancy between this expectation. β_v follows the relationship for lower magnitudes of ΔT, but for higher temperature jumps β_v becomes smaller than the predicted value. This is usually attributed to underestimation of β_v for bigger ΔT.[4,6] Another possible explanation is that for higher ΔT the process of volume relaxation becomes thermorheologically complex.[6,7]

Among various blends a special kind of miscible blends, composed of one amorphous component and the other crystallizable, atactic poly(methyl methacrylate)/poly(ethylene oxide), (*a*-PMMA/PEO), has been lately extensively investigated.[8–21] The presence of PMMA in blend restricts PEO crystallization, and hence the degree of crystallinity decreases with rising amount of PMMA.[8–10] When the content of *a*-PMMA is higher than 70–80%, the blend becomes completely amorphous and shows a single T_g dependent on the blend composition.[9,11–14] Such blends are considered to be completely miscible in melt.[15,16] In the glassy state, however, phase separation occurs creating amorphous nanoheterogenous structure with an approximate domain size of 20–70 nm.[11,12]

The glass transition temperature of PEO was predicted to be in the range of -42 to $-72\,°C$,[13,14] which is much lower than T_g of PMMA, about $105\,°C$. It means that at room temperature the amorphous phase

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of pure PEO is well above the glass transition temperature and its mobility remains liquid-like.[11] This idea is also supported by the difference IR spectra of 70/30 and 90/10 PMMA/PEO blends, which resemble very closely the spectrum of non-crystalline PEO as found in the melt.[17] A recent free-volume study[18] shows that in these blends free volume is lager than what can be expected from a linear relationship between the pure polymers; in other words, free volume tends to increase when the chain mobility increases. Surprisingly, an opposite effect indicating contraction of free volume by blending PMMA with PEO was reported.[19] These conflicting results can be explained by different preparation techniques of the blends; in the first case it was mixed in melt, in the other in chloroform solution. Also NMR studies indicate changes in the mobility of polymer segments with blending.[11,12,20] It can be generalized, together with Schantz,[11] that while the mobility of PEO in the blends is lowered, *a*-PMMA segments move faster and/or with larger amplitudes. Nevertheless, it seems to be very difficult to interpret these results from component dynamics in glassy PMMA/PEO blends.[11]

A few papers dealing with physical aging in *a*-PMMA/PEO blends have been published.[14,19,21] Vernel *et al.*[21] investigate enthalpy and volume relaxations. They also investigated the effects of aging on dynamic mechanical moduli in the T_g region, just above the dilatometric and below enthalpic T_g. With increasing PEO content the physical aging rates decreased. Chang,[19] on the other hand, made stress relaxation measurements of quenched samples concluding that time scales increased with added PEO and stress relaxation rate slowed down compared to PMMA homopolymer. Both papers gave contrary results on the relaxation rate of mechanical properties, which was attributed in Ref 21 to different methods of preparation (melt, solution). Both papers, however, led to the common conclusion that blending PEO into PMMA causes a reduction in the segmental mobility and the relaxation process is hindered by coupling of molecular motions with their surrounding matrix. Shimada and Isogai[14] reported the behavior of isotactic PMMA with PEO blended at the ratio of 10:1 by weight. The specific volume was measured at 27 °C after aging of the blend in a broad range of temperatures. The authors found that the volume changes cannot be attributed to crystallization of PEO chains or melting of the crystals, but they are a result of free-volume relaxation in an amorphous region of the blend.

The present paper reports the effect of blending PEO in *a*-PMMA on the dynamics of structural relaxation by monitoring the volume relaxation. The technique of temperature down-jump is used. Volume relaxation isotherms are discussed in terms of volume relaxation rate, β_v. The work is expected to contribute in filling the gap in the description of the kinetics of structural relaxation of *a*-PMMA/PEO amorphous blends.

EXPERIMENTAL

Materials

For the experiments two basic materials were used: the first was a random copolymer of methyl metacrylate and methyl acrylate denoted *a*-PMMA (Plexiglas 6N, Röhm GmbH), content of methyl acrylate was determined 6 mol% by ^{13}C NMR,[11] molar mass averages $M_n = 47$ kg/mol and $M_w = 90$ kg/mol, density 1.19 g/cm^3, glass transition temperature measured on DSC = 95 °C and the second one was semicrystalline poly(ethylene oxide) denoted PEO (Scientific Polymer Products, Inc.), molar mass average $M_w = 200$ kg/mol, density 1.21 g/cm^3, melting point $T_m = 65$ °C.

Preparation of Blends

Before blending, both polymers were vacuum dried for 12 h. Five *a*-PMMA/PEO blends with different compositions (0, 3, 6, 10 and 14 vol% PEO) were mixed in a Brabender kneader at 180 °C for 15 min at 30 rev/min.

DSC Measurements

DSC measurements were carried out using a Perkin-Elmer differential scanning calorimeter, DSC 1 Pyris. The samples were first annealed in molten state to erase previous thermal histories, then they were undercooled to the solid state, and finally DSC up-scan was performed. The cooling/heating rate was 10 °C/min.

Dilatometry

Mercury-in-glass dilatometry according to ASTM Standard D864-52 was employed for dilatometric measurements. From neat *a*-PMMA and *a*-PMMA/PEO blends the specimens were prepared by compression molding. Finally, the shape of specimens was finished by milling to rectangular shape of bars with rounded edges (cross-section approximately 6 × 6 mm and volume about 3 cm^3). The specimens were annealed at T_g for 10 h in an oven to erase internal stresses built in the material by the preparation process. Then the samples were inserted into dilatometers, the dilatometers were sealed and filled with pure filtered mercury (purity 99.995%) under vacuum.

The dilatometers were used for the determination of glass transition temperatures through volume–temperature dependencies recorded at cooling the dilatometers at the rate of −0.8 °C/min. T_g is determined here

as the intersection of the equilibrium liquid line with the asymptotic glassy line. Further, the technique of temperature down-jumps was used to initiate the process of relaxation, which is based on prompt transfer of the dilatometer from the annealing to the relaxation thermostatic bath. The annealing temperatures were chosen to be 20 °C above the corresponding glass transition temperatures of pure *a*-PMMA or *a*-PMMA/PEO blends. After annealing for 20 min, no more change of the capillary meniscus was observed. Then the dilatometer was transferred into isothermal precision thermostatic bath (Grant Instrument (Cambridge) Ltd, UK). The temperature fluctuations of the bath reported by the manufacturer are ±0.004 °C. Time needed for temperature equilibrium after *T*-jump is about 4 min. The materials were allowed to relax for up to 44 h. For *a*-PMMA one long-term test was performed at the relaxation temperature of 80 °C, where the dilatometer was maintained for 1396 h. A zero time for collecting volume change data was taken the moment of immersing the dilatometer into the relaxation bath.

RESULTS

DSC

First of all, we tested by DSC whether the blend samples were amorphous. The results depicted in Figure 1 clearly show that while for crystalline PEO exhibits a sharp melting peak, PMMA/PEO blend and pure PMMA do not. The enthalpy of fusion of PEO was measured to be around $146.5\,\mathrm{J/g^{-1}}$ and
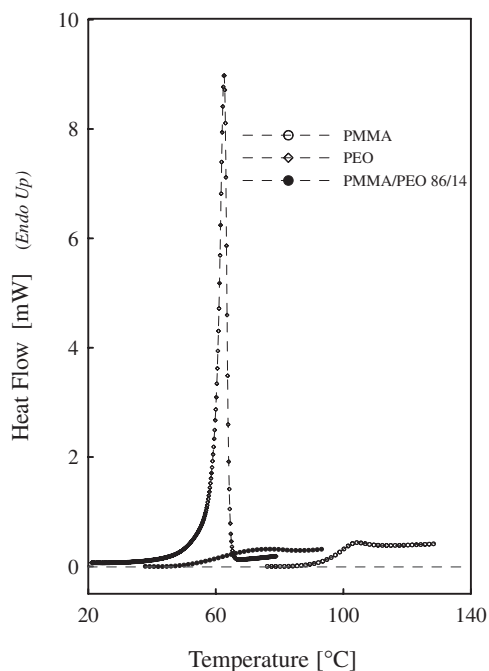
the melting point was determined to be 64.4 °C as a peak maximum. In Ref 18 the authors calculated enthalpy of fusion of 100% crystalline PEO to be $203\,\mathrm{J/g^{-1}}$. In the case of DCS trace for PMMA/PEO 86/14 blend the specimen for test contained quantitatively the same amount of PEO as for testing pure PEO (*ca.* 1.5 mg). But the enthalpy of the endothermic peak was determined to be only $0.92\,\mathrm{J/g^{-1}}$, which is close to the value found for pure PMMA under similar test conditions, $0.77\,\mathrm{J/g^{-1}}$, representing glass-rubber transformation. This small difference is not due to crystallization, but due to faster relaxation of blend molecules during cooling/heating procedure in T_g determination. Thus, blends used here are amorphous. Figure 1 also clearly demonstrates the decrease in glass transition temperature of PMMA on the addition of PEO, together with broadening of the transition zone. In the case of pure *a*-PMMA the temperature interval was 18 °C while for PMMA/PEO 86/14 blend it was more than 35 °C.

Dilatometry

As a reference point the glass transition temperatures were measured by the dilatometry mentioned in experimental section and are listed in Table I. Figure 2a and 2b represents the volume changes under cooling and heating for pure PMMA and PMMA/PEO 86/14 blend, respectively, measured at ±0.8 °C/min. They have originally been used for the determination of dilatometric glass transition temperature, T_g evaluated as the temperature at which the equilibrium liquid line and the glassy line intersect. The filled symbols indicate cooling measurements. After T_g determination the dilatometers were stored at ambient temperature for approximately four months. Then heating scan at the same rate as for cooling was performed. In the first stage the expansion of the material is caused by its heating following the direction of glassy line. But the volume is lower than cooling which is a consequence of structural relaxation occurred during storage at ambient temperature. By further heating the slope of the curve increases and finally the material achieves again the thermal equilibrium. It results in the peak in thermal expan-

Figure 1. DSC traces of PMMA, PEO and PMMA/PEO 86/14 blend.

Table I. Glass transition temperatures and thermal expansion coefficients for pure *a*-PMMA and different *a*-PMMA/PEO blends

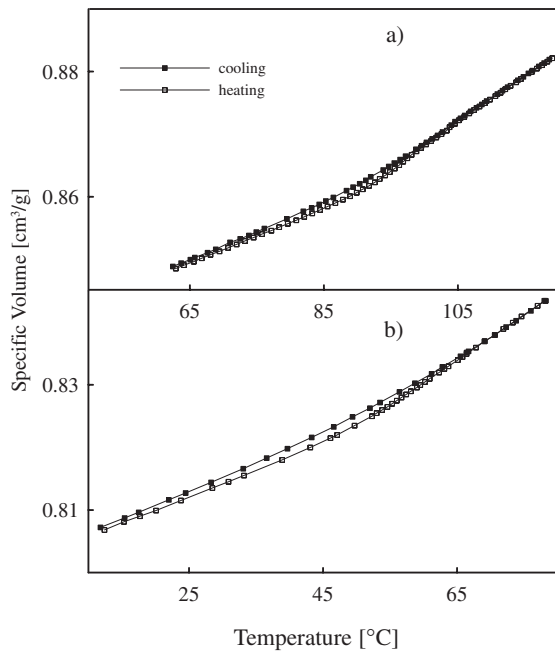| Composition	T_g [°C]	$\alpha_l \times 10^4$ [K^{-1}]	$\alpha_g \times 10^4$ [K^{-1}]	$\Delta\alpha \times 10^4$ [K^{-1}]
a-PMMA	88.9	6.13	2.12	4.01
a-PMMA/PEO 97/3	80.8	5.99	2.15	3.84
a-PMMA/PEO 94/6	74.6	6.02	2.20	3.82
a-PMMA/PEO 90/10	64.0	5.81	2.51	3.30
a-PMMA/PEO 86/14	55.2	5.78	2.80	2.98

Figure 2. Dependence of specific volume on temperature during cooling and heating of *a*-PMMA (a), and *a*-PMMA/PEO 86/14 blend (b).

sion coefficient as is well know for the enthalpy. As Figure 2 shows, even after four months of aging at room temperature there is no visible sign of crystals melting and only change seen on the curve is broadening of the transition area.

The glass transition temperatures measured by dilatometry and DSC, differ because of different experimental procedures: while dilatometric T_g is determined by cooling scan, DSC T_g is from heating scan. Also different rates of heating/cooling causes different T_g. A lower value of T_g measured for

PMMA, compared to commonly presented *ca.* 105 °C, can be explained by these factors. However, an important role would be also played by the presence of methyl acrylate (6 mol%).

An increasing content of PEO causes a significant decrease of T_g, as can be seen in Table I. The thermal expansion coefficients show that $\Delta\alpha$ also decreases with PEO content. The values of $\Delta\alpha$ predict smaller initial departure from equilibrium, δ_i for the blend (defined by Eq 3) leading to slower relaxation rate, according to Eq 1.

Volume Relaxation

Figure 3a–3e shows volume contraction isotherms following temperature down-jumps to an aging temperature T_a below T_g. When T_a is close to T_g equilibration of volume can be measured in reasonable experimental time-scales. The time to reach equilibrium for *a*-PMMA increases from approximately 140 h at 88.1 °C, *i.e.* 0.8 °C below T_g, to more than 1400 h at 80.0 °C, which is 8.9 °C below T_g. For the blend containing 6 vol% PEO, approaching equilibrium can be seen after approximately 50 h at 74.2 °C, *i.e.* 0.4 °C below T_g.

The relationships between volume relaxation rate, β_v, for all compositions are presented in Figure 4. The values of β_v were calculated as the slope of the relaxation isotherms from the parts of the curves varying linearly with logarithm of aging time. Satisfactory linearity was achieved for each material and temperature up to the relaxation times of 6×10^3 s after the jump, when the R-squared values were better than 0.995 for the case of the largest scatter of the experimental points, but mostly they were even better than 0.998. The error bars in Figure 4 show lower and up-
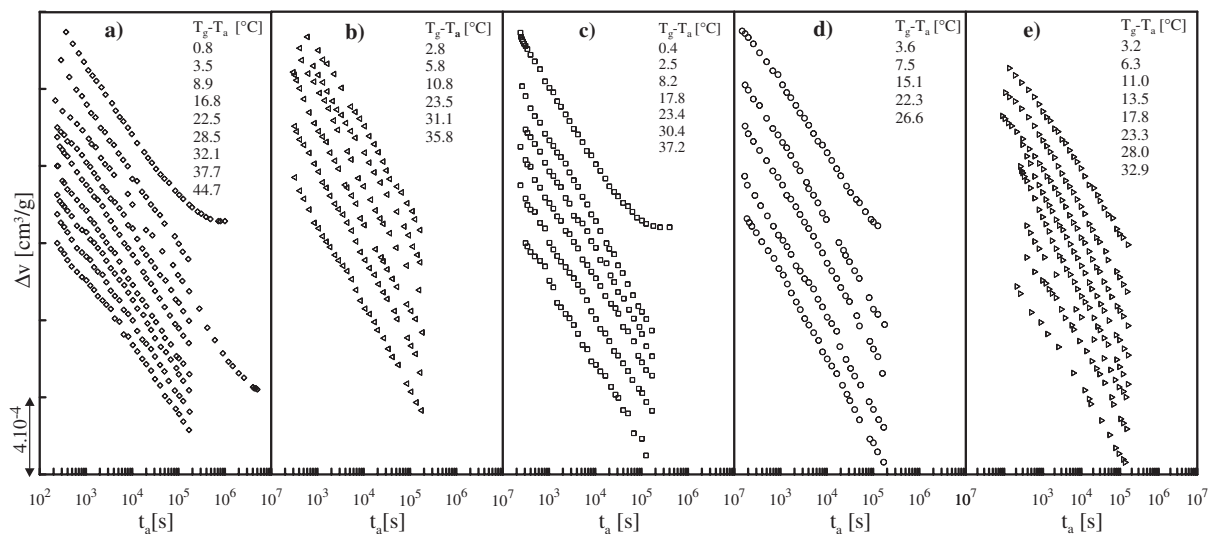

Figure 3. Volume relaxation curves after temperature jumps from equilibrium above T_g to aging temperatures for different blend compositions: (a) pure *a*-PMMA, (b) 3 vol% PEO, (c) 6 vol% PEO, (d) 10 vol% PEO, and (e) 14 vol% PEO in blend.
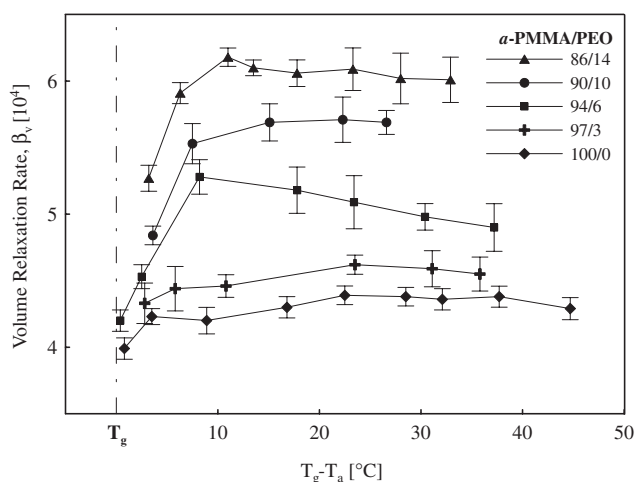
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Figure 4. Volume relaxation rates, β_v, as a function of $T_g - T_a$ for different blends compositions calculated from contraction isotherms after temperature jump.

per bounds on β_v.

The curves of β_v show a steep increase just below T_g and are flattened out with increasing $T_g - T_a$ temperature distance. Moreover, the graph demonstrates that with increasing PEO content the increase in β_v is more pronounced, *i.e.* the addition of PEO significantly increases the volume relaxation rate of the blends. For instance, at a relaxation temperature of 28 °C below T_g, for the blend containing 14 vol% of PEO the value of β_v is $6.02 \pm 0.19 \times 10^{-4}$, while for pure PMMA at 28.5 °C below T_g it is $4.38 \pm 0.07 \times 10^{-4}$. Comparing these values at nearly the same $T_g - T_a$ we can conclude that β_v for blend 86/14 is about 37% higher than for pure PMMA. The volume relaxation rate found for *a*-PMMA (β_v about 4.3×10^{-4}) is in a good agreement with the values published in literature: 4.2×10^{-4} Ref 4, 4.6×10^{-4} Ref 22 and 3.7×10^{-4} Ref 23. The values for *a*-PMMA/PEO amorphous blends are not available, so they cannot be compared.

DISCUSSION

In general, the relaxation response on the macroscopic level of a solid body has a direct link to changes in its microstructure. Therefore, the structural relaxation studies for systems with molecular arrangements modified by addition of an interaction component are interesting not only from the simple relaxation point of view but also from components' compatibility. This seems to be the case of *a*-PMMA/PEO. The present paper has shown that the volume changes depend on the amorphous structure. Despite the fact that according to Eq 3 the distance of PMMA sample from the equilibrium is higher, which should result in higher relaxation rate (Eq 1),

the values of β_v determined experimentally have an opposite trend. Therefore, PEO plays an important role here as it contributes to the interactions and mutual mobility of both types of molecules. However, PEO motion is restricted by the presence of PMMA molecules, *i.e.* PEO causes faster creation of equilibrium conformations of *a*-PMMA matrix or decreases the chains cooperativity of blend needed for molecular rearrangements.

It should be noted that our results are reverse to those reported in Refs 19 and 21, which present slowing down of the relaxation by addition of PEO molecules, *i.e.* molecular rearrangements are more restricted than in pure PMMA. These results, in fact, are not in conflict with our findings. In the first reference[19] a different type of relaxation tests was performed and a different property quantifying relaxation was measured. The authors followed stress relaxation of quenched samples, where one could expect that the relaxation process is different from volume relaxation due to molecular rearrangements. Therefore, relaxation responses determined by different techniques do not correspond with each other.[1,2,8] The authors[21] previously observed the relaxation responses above volumetric glass transition temperature, *i.e.* in a different temperature range than in this paper. They performed tests for materials in the transition zone close to the rubbery state. Thus, the results of our investigation supplement a piece of knowledge about relaxation of glassy *a*-PMMA/PEO blends, which has not been presented yet.

CONCLUSIONS

Addition of PEO into *a*-PMMA results in significant changes in its thermal properties, such as decrease in glass transition temperature, broadening of transition zone, and smaller $\Delta\alpha$. From the point of view of volume relaxation responses (expressed here as volume relaxation rate), PEO causes higher relaxation rate. The changes in thermal properties and relaxation responses caused by the addition of PEO into *a*-PMMA matrix are considered to be consequences of the modifications of molecular structure, *i.e.* mutual effect of molecular segmental motions of both materials in the blend.

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