

EVALUATION RELAXED VOLUME OF *a*-PMMA AND *a*-PMMA/CB FROM HEATING

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Abstract

Volume relaxation of *a*-PMMA and *a*-PMMA/carbon black composites during heating has been analyzed from the heating scans. It concerns two ways of physical aging initiation, temperature down-jump and cooling. Samples were heated and $v(T)$ dependency measured after annealing at various aging times bellow T_g . Relaxed volume was evaluated from peaks of $\alpha(T)$ dependencies, derivated from $v(T)$ curves. Good agreement between isothermal relaxation measurements and relaxed volume from heating has been found out. Presence of filler particles in composite lead to reduction of relaxation response and rate of relaxation changes in PMMA.

Introduction

The phenomenon of physical aging is connected with the glassy materials and can be observed as a time-dependence of the material properties at constant temperature at ambient pressure. Microstructural or molecular arrangement results, during the physical aging process, in changes of macrostructural properties as volume, V , enthalpy, H , mechanical and dielectric properties. The term of physical aging can be also named as a structural relaxation^{1,2}.

Mostly used method of physical aging initiation is cooling of the material bellow the glass transition temperature, T_g . This temperature is defined on particular volume dependence on temperature during cooling as a disruption, when the slope of the decrease changes from liquid to glass value. Initiated physical aging in the material is followed by the contraction of the volume or enthalpy in the time. This decrease is preceded until the

new equilibrium state is established^{1–3}. Glass transition is usually considered a second-order thermodynamic transition, but there are some thoughts that it is a kinetic effect only^{2,3}. The second-order transition concept is supported by the fact that decrease of the temperature will cause a disruption change in the temperature dependence of basic thermodynamic functions (volume and enthalpy) at the transition temperature. This also includes a step change of their first derivative – the coefficient of thermal expansion, α , and specific heat, c_p . The theory, which introduces glass transition as a kinetic effect, is based on the fact that glass transition temperature T_g is not an independent material constant, but instead of it is a function of cooling conditions. Some authors^{4–6} present another hypothesis: they assume that glass transition is a first-order thermodynamic transition, their idea is based on the dilatometric and calorimetric observations. The characteristic effect appears when slowly-cooled or annealed glassy specimens are heated through the transition range, where showing an abrupt, almost discontinuous increase in volume and enthalpy temperature dependence before approaching the steady state regime above T_g . Consequently, $\alpha(T)$ and $c_p(T)$ dependencies show a peak in the transition area before reaching, at high temperature, values characteristic for the liquid state^{2–4}. These peaks can be characterized by their size, temperature of the peak maximum, T_{max} , and values c_p and α at the top of the peak, $c_{p,max}$ or α_{max} , respectively. These parameters, commonly used for characterization of the relaxation process, are affected by several factors: rate of heating scan and an initial state of the glass, i.e. its thermal history^{7–15}. The increase of the heating rate shifts the T_{max} to higher temperature in volume^{7,8} and enthalpy^{9–11}. The influence of thermal history is rather complex and it is necessary to separate individual effects – annealing temperature (distance from T_g), annealing time and initial departure from an equilibrium. Decrease of the annealing temperature below T_g leads the T_{max} first to small reduction ($T_g - 4 < T < T_g$) and then to grow up significantly^{7,8}. Longer annealing time and higher initial departure from equilibrium cause shift of the T_{max} to higher temperatures of volume^{7,8,12} and enthalpy^{10,11,13}. Values of α_{max} or $c_{p,max}$ are influenced in the similar way as T_{max} , higher heating rate increases values of α_{max} (ref.^{7,8}), $c_{p,max}$ (ref.^{10,11,14}), as well as longer annealing time in case of α_{max} (ref.^{7,8}) and $c_{p,max}$ (ref.^{2,3,13,15}).

Generally most observed characteristic of peaks is its size on temperature dependency of c_p . Usual literature reviews^{2–4} represent size of the peaks as energy need to be added to the sample to transfer it into a liquid state. This additional energy corresponds to the energy disappeared during the re-arrangement of molecules during the

relaxation process. Moreover, calculation of relaxed enthalpy is based on the changes of energy added to the sample after previous relaxation. Enthalpy, which relaxed at the time t from the beginning of relaxation process is usually calculated from:

$$\Delta H_t = \int_{T_1}^{T_2} c_{p,t}(T) dT - \int_{T_1}^{T_2} c_{p0}(T) dT \quad (1)$$

where $c_{p,t}(T)$ is temperature dependence of specific heat of relaxed sample at time t , and $c_{p0}(T)$ is temperature dependence of specific heat of sample without relaxation, representing only cooling/heating cycle of the sample and temperatures T_1 , T_2 representing the begin and at the end of the transition peak, respectively^{2,3}.

According to some literature sources^{7,8,12} the calculation of relaxed enthalpy from heating scans can be adapted also for evaluation of relaxed volume from the $\alpha(T)$ dependency. Hutchinson et al. find and defined area below peak in thermal expansion as relaxed volume. Based on this assumption relaxed volume, ΔV , can be calculated analogically to relaxed enthalpy, ΔH :

$$\Delta V_t = V_0 \int_{T_1}^{T_2} \alpha_t(T) dT - V_0 \int_{T_1}^{T_2} \alpha_0(T) dT \quad (2)$$

where V_0 presents sample volume, $\alpha_t(T)$ is thermal expansion coefficient of relaxed sample and $\alpha_0(T)$ stands for thermal expansion coefficient of sample without relaxation, representing only cooling/heating cycle, T_1 is temperature below T_g ($T_1 < T_g$), and T_2 is temperature above T_g ($T_2 > T_g$).

Physical aging process is usually studied on pure amorphous materials, but small number of works deals also with influence of a filler dispersed in an amorphous polymer matrix^{18,22–25}. Before the influence of filler on physical aging can be discussed, some basic remarks must be mentioned concerning arrangement of filler in composites and thermal properties of composites. It is well-known that an addition of solid particles to a polymer is accompanied by the formation of boundary polymer layer near the solid surface of the particle. The thickness of the boundary layer depends on the properties of solid surface, characteristics of polymer phase, and also on the filler-polymer interaction^{16–18}. It has been reported, that filler addition changes thermal properties of pure polymers^{18–23}. Solomko and Pas'ko reported decrease of the difference between the values of specific heat in glass, c_{pg} , and liquid, c_{pl} , and increase of the T_g of 15 °C for the nanofiller of specific surface of 175 m² g⁻¹ added in PMMA, while it had no effect on T_g when PS was used as polymer matrix¹⁹. Their findings were later confirmed by Privalko^{16,23} also for polyurethane, and polydimethylsiloxane. In another work Privalko²⁰ reports smaller increase of T_g by 5 °C in PMMA, for the filler of micrometers size. A filler effect on relaxation behavior of polymers arises from the slower molecular motion in the interface zone^{18–25}, and results in

longer relaxation time scale in filled systems at equal temperatures, but shorter time scale at corresponding temperatures equidistant from the T_g (ref.^{18,22–25}). Moreover, broadening of the relaxation time spectra^{22,24} and decrease of volume relaxation rate²³ have been reported in the literature.

The present paper presents the evaluation of relaxed volume from the heating, analogically to the calculation of the relaxed enthalpy, using a down-jump technique. Evaluated relaxed volumes are compared with the isothermal relaxation measurements. Moreover a filler effect on the thermal behavior of polymer/carbon black composites is investigated.

Experimental

Materials

Poly(methyl methacrylate), *a*-PMMA, Plexiglass 6N, Rohm GmbH, density 1.19 g cm⁻³, M_w 90 kg mol⁻¹, midpoint enthalpic $T_{g,enth}$ 94 °C which was blended with acetylene Carbon Black filler (density 1.8 g cm⁻³, mean diameter 35 nm, average surface area 63 m² g⁻¹) to prepare PMMA/CB composites. *a*-PMMA and CB were vacuum dried for 12 hours before mixing, compounds with 10 and 20 vol.% content of CB in PMMA matrix in a laboratory kneader (Plasticoder Plasticoder PL-2000-6) with W 50E mixer type at 30 min⁻¹ for 15 minutes at temperature 180 °C.

Experimental set-up

The volumetric measurements were carried out using a Mercury-in-Glass dilatometry (MIG) constructed according to ASTM Standard D 864-52 in our laboratory. The accuracy of this method fluctuated slightly with each specimen according to the appropriate amount of sample and mercury in each dilatometer and dilatometer capillary bore from 1.2×10⁻⁵ cm³/cm³ for pure PMMA, 2.0×10⁻⁵ cm³/cm³ for 10 % CB and 3.0×10⁻⁵ cm³/cm³ for 20 % CB content in PMMA, respectively. The appropriate specimens were prepared by compression molding and grinded to a bar with the cross-section approximately (6×6) mm, and whole volume of specimen in units of cm³. Before inserting of specimens into dilatometer, each of them was annealed in a furnace at temperature slightly above appropriate T_g in order to erase internal stress build up during preparation procedure. Then the samples were inserted into the dilatometers, dilatometers were sealed and filled with filtrated high purity (>99.999 %) mercury filled under vacuum. During filling procedure temperature of the specimens was kept close above their T_g . All temperature programs were performed with help of two precision thermostatic baths (GRAND W14, JULABO HP-4) filled with silicon oil were used by immersing of dilatometers into.

For enthalpic measurements differential scanning

calorimetry, DSC, was used. Samples for DSC analysis were prepared in the mass of about 6 mg. The temperature program was carried out by a technique similar to the dilatometric part. The samples were covered in aluminium foil and placed into thermostatic bath HUBER CC-130A Visco 3 in a strainer basket.

Procedures

Thermal analysis of PMMA and tested composites was done during uniform cooling of the dilatometers from equilibrium liquid state of the appropriate materials to glassy state by cooling with rate 0.5 °C/min. T_g 's were estimated from volume temperature dependences as intersection of equilibrium liquid line with asymptotic glassy line. Thermal expansion coefficients in liquid and glass were calculated as slopes from the portion of the curves, where volume varies linearly with temperature. Densities of the samples were measured by weighting at ambient temperature. Calorimetric analysis was performed after previous annealing.

Enthalpic T_g 's of PMMA and its composites with CB were evaluated from the heating scans at rate 10 °C/min after previous cooling at 10 °C/min from equilibrium liquid state using instrument software.

Structural relaxation was initiated by temperature change of the materials from their equilibrium state above T_g to temperatures below T_g , followed by isothermal relaxation at relaxation temperature, T_a . Annealing temperature, before temperature change, was chosen approximately $T_g + 20$ °C for 20 min. Two ways of solidification were used; first, temperature ramp of thermostatic bath of rate 0.33 °C/min, and second, manual transfer of the dilatometer from one to another bath (temperature down-jump technique). After an appropriate time of relaxation each dilatometer was heated to record volume temperature dependence. Conditions of announced procedures are summarized in Table I.

Temperature up-scans of annealed dilatometers were performed by their heating through the T_g region by constant rate of heating of 3 °C/min using temperature ramp of thermostatic bath.

Final calorimetric measurements of annealed enthalpic samples were carried out using Perkin-Elmer DSC 1 Pyris analyser. The temperature scans of samples relaxed for time t_a were performed on DSC at the heating rate of 3 °C/min from 60 °C to 120 °C. Temperature and

heat flows of DSC were calibrated on heating at 10 °C/min using indium standard.

Results and discussion

In the first part of this work, composites of *a*-PMMA with CB were prepared. In these composites PMMA creates continuous polymer matrix with distributed CB particles. The typical character of CB distribution in polymer matrix is shown in TEM micrographs, Figs. 1,2, demonstrating the view on particles distribution in *a*-PMMA/10%CB composition and *a*-PMMA/20%CB one

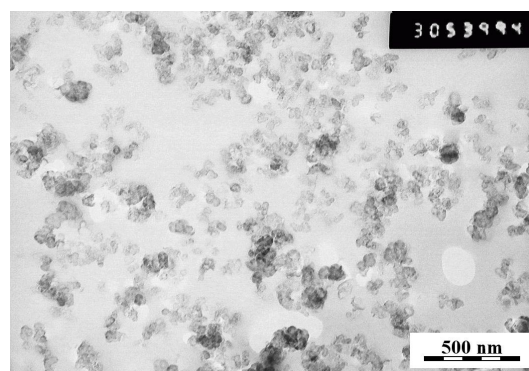


Fig. 1. TEM image of *a*-PMMA/CB 10

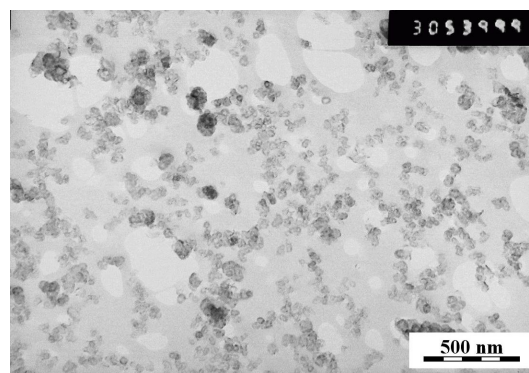


Fig. 2. TEM image of *a*-PMMA/CB 20

Table I
Experimental conditions of temperature down-jumps

| Material | T_a [°C] | Temperature change | Relaxation times [hours] |
|------------|------------|-----------------------|--|
| PMMA | 75;81 | cooling ; T down-jump | 0,14,192,520,1204; 0,22,47,97,282,812 |
| PMMA/10%CB | 75 | cooling | 0,14,192,520,1204 |
| PMMA/20%CB | 75 | cooling | 0,14,192,520,1204 |

Table II
Volumetric thermal properties of *a*-PMMA and its compositions with CB

| Materials composition | $T_{g,vol}$ [°C] | α_g [K ⁻¹] | α_l [K ⁻¹] | $\Delta\alpha_p$ [K ⁻¹] | Immobilized matrix x_v [%] |
|-----------------------|---------------------|----------------------------------|----------------------------------|--|---------------------------------|
| <i>a</i> -PMMA | 84.3 | 2.22 | 5.92 | 3.85 | 0 |
| <i>a</i> -PMMA/CB10 | 85.6 | 1.93 | 5.26 | 3.33 | 3.5 |
| <i>a</i> -PMMA/CB20 | 87.2 | 1.38 | 4.28 | 2.97 | 4.6 |

respectively. CB particles are fluently distributed through the composite in form of isolated carbon black particles, but also they create agglomerate or CB chains. There was not found any significant difference in particle distribution between both compositions.

The macroscopic thermal properties of *a*-PMMA matrix are changed by CB content, in more details presented in Table II. Glass transition temperature increase by presence of CB content from 84.3 °C for pure *a*-PMMA, 85.6 °C for composite with 10 vol.% of CB, and to 87.2 °C with 20 vol.% of CB composite, measured during cooling by 0.5 °C/min. The error of evaluated glass transition temperatures was calculated to be around ± 0.2 °C. This effect can be explained by different thermal properties of PMMA interface on CB particles. The same influence of CB particles on T_g of PMMA matrix was also detected by DSC measured by cooling/heating cycle 10 °C/min and evaluating appropriate values of T_g 's as the midpoint of heat flow-temperature records during sample heating presented also in Table II.

Thermal expansion coefficient above T_g , α_g , and also below T_g , α_l , are diminished by presence of CB. It leads to decrease the value of difference in thermal expansion coefficient in glass transition defined as $\Delta\alpha = \alpha_l - \alpha_g$. It is caused by smaller value of thermal expansion coefficient of CB comparing to PMMA, where measured macroscopic properties seem to result not only from simple addition of appropriate properties of the component, but also from an immobilization of PMMA molecules on CB surface. This effect is even more pronounced for higher CB content in composition. Further, densities of the samples are modified by the same additive principle. From such thermal data one can calculate amount of immobilized polymer by interface with CB particles using modified

equation, which was presented by ref.¹⁷ for specific heat measurements by analogy with thermal expansion coefficient:

$$x = \left(1 - \frac{\Delta c_p}{\Delta c_{p0}} - w_f \right) \approx \left(1 - \frac{\Delta\alpha}{\Delta\alpha_0} - v_f \right) \quad (3)$$

where w_f and v_f represent weight and volume proportion of filler in polymer matrix, respectively, Δc_p stands for difference in specific heat and $\Delta\alpha$ in thermal expansion coefficient between liquid and glass of pure polymer (denoted with subscript 0) and the same quantities representing data for filled polymer without a subscript. Applying a data in Table II one can obtain the amount of immobilized polymer matrix 3.5 and 4.6 vol.% for compositions containing 10 and 20 vol.% of CB, respectively. The corresponding values of Δc_p (Table III) give results 2.2 % and 3.3 wt.% of immobilized polymer for 10 and 20 vol.% of CB in PMMA matrix.

In the next experimental section the dependences of volume on temperature during sample heating was investigated. In this case the materials were heated from temperatures below T_g , where they are generally in non-equilibrium glassy state, through glass transition region, where they are melted and reach equilibrium liquid state. Typical heating and cooling curves are presented in Fig. 3a for PMMA measured by heating/cooling at rate 1 °C/min. The material was maintained to anneal at 60 °C for 140 hours before heating. Comparing both curves, during sample cooling and heating, one can clearly identify typical hysteresis arising in glass transition region. Here one can observe the typical behavior of glassy substances during heating through T_g , almost step change in $v(T)$ dependency^{10,12,26–28}. In the first step of heating, the

Table III
Enthalpic thermal properties of *a*-PMMA and its blends with CB

| Materials composition | $T_{g,ent}$ [°C] | Δc_p [J g ⁻¹ K ⁻¹] | Immobilized matrix x_w [%] |
|-----------------------|---------------------|--|---------------------------------|
| <i>a</i> -PMMA | 93.7 | 0.33 | 0 |
| <i>a</i> -PMMA/CB10 | 96 | 0.28 | 2.2 |
| <i>a</i> -PMMA/CB20 | 96.4 | 0.23 | 3.3 |

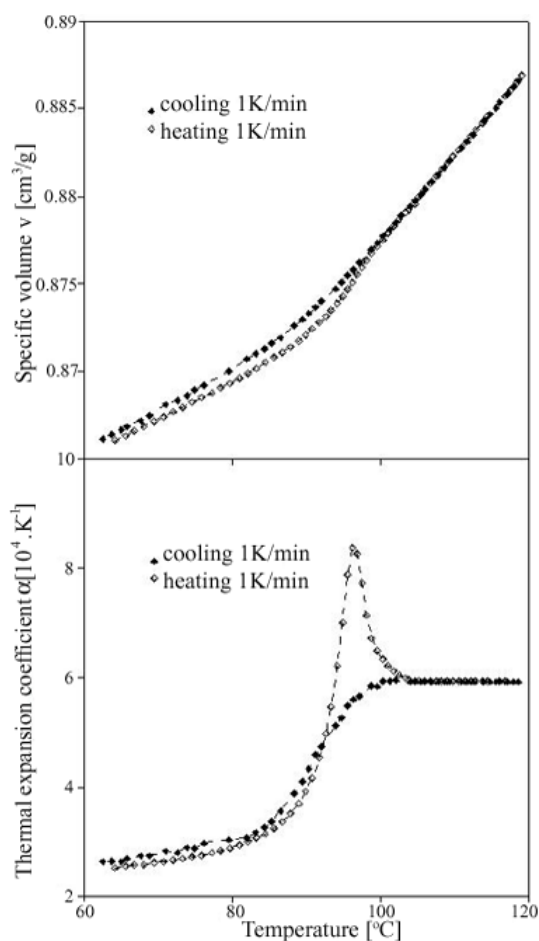


Fig. 3. Isobaric volume (a) and thermal expansion coefficient (b) cooling/heating curves of *a*-PMMA after isothermal annealing at 40 °C for 130 hours

material follows glassy line and continues indeed through T_g measured by cooling. Then, after sufficient overheating of the material through the extended liquid line, volume change abruptly finds its equilibrium liquid state.

Derivation of $v(T)$ dependency according to temperature gives course of thermal expansion coefficient on temperature during sample heating, Fig. 3b. One obtains peak in thermal expansion coefficient with significant overshoot through values of expansion coefficient in liquid state. In this case the maximum value of the thermal expansion coefficient, α_{\max} , which belongs to the inflexion point of volume temperature curve, is found to be $8.23 \times 10^{-4} \text{ K}^{-1}$ at temperature $T_{\max} = 97 \text{ °C}$ comparing to $\alpha_l = 5.90 \times 10^{-4} \text{ K}^{-1}$. Finally, there was found a significant shift of T_g values determined by cooling and heating. The T_g from cooling, usually evaluated as intersection of equilibrium liquid line with asymptotic glassy line, gives the value 84.3 °C for a cooling rate 1 °C/min while from heating at the same rate it reaches the

value 97 °C as an inflexion of volume abrupt, resulting in 13 °C difference. It is necessary note that such a difference between these two T_g 's results partly from shift of transition zone by sample annealed for 4 months at the room temperature.

Fig. 4 represents example of the DSC measurements. One can observe the results similar to those shown in Fig. 3b, which are typical for the methodology of calorimetric measurements with adequate dependence of a specific heat on temperature in glass transition region during heating^{2,13,25}. This experimental tool is usually used for classical DSC calculation of the position of material's T_g as well as for evaluation of relaxed enthalpy as a enthalpy lost during samples annealing in glassy state by integrating of the area below the peak according temperature, between points where peak overlaps an instrument baseline.

Figs. 5, 6, 7 and 8 (parts a) represent heating of *a*-PMMA and both composites after different time of annealing below T_g while parts b of the same figures show temperature dependences of thermal expansion coefficients. Figs. 5 and 6 stands for pure *a*-PMMA annealed at 81 and 75 °C, Fig. 7 for composition with 10 vol.% of CB annealed at 75 °C and in Fig. 8 the results obtained for composition with 20 vol.% of CB annealed at 75 °C are demonstrated. Overall, (parts a) characteristic abrupt on volume curves is shifted to higher temperatures together with its increasing by extending annealing time. This effect is manifested also in the case of thermal expansion coefficient with annealing time (parts b).

The tests of pure *a*-PMMA were performed after annealing at two different temperatures, in the first case at 81 °C = $T_{g,\text{vol}} - 3.3 \text{ °C}$, and in the second one at 75 °C = $T_{g,\text{vol}} - 9.3 \text{ °C}$, for annealing times up to 812 and 1204

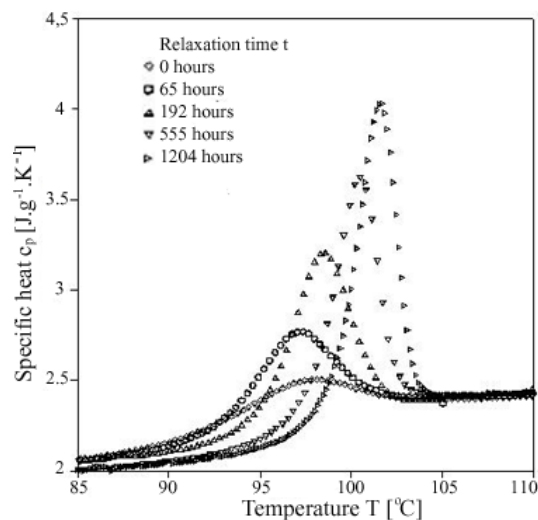


Fig. 4. DSC thermograms measured during heating after aging at 75 °C for various times t_a , as indicated

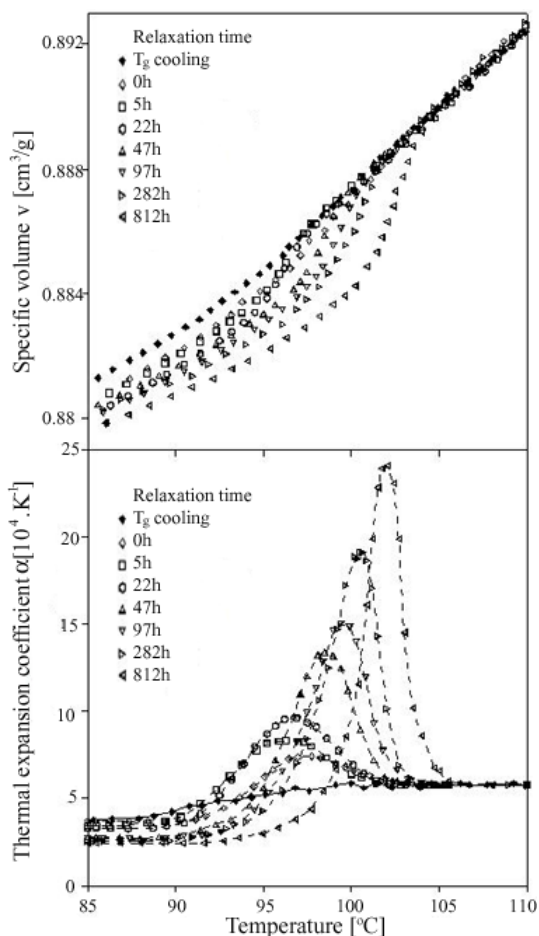


Fig. 5. Isobaric volume (a) and thermal expansion coefficient (b) heating curves of *a*-PMMA after isothermal annealing at 81 °C for various times t_a , as indicated. Cooling T_g curve is added for comparison

hours, respectively, see Fig. 5 and Fig. 6 and a slight influence of annealing temperature was observed. It was found that shift of transition zone, measured by characteristic points such as inflection point in v - T records or as a peak maximum, T_{max} , in α - T dependence, are linear in respect to logarithm of annealing time. Shift of the T_{max} with time of annealing can be quantified as a slope of $(dT_{max}/d\log t)$ dependency. This parameter gives value of (2.61 ± 0.43) °C/decade of annealing time for relaxation at 81 °C, slightly higher value for temperature 75 °C as (2.69 ± 0.28) °C/decade of annealing time. For compositions with CB it gives values of (2.47 ± 0.14) °C/decade of annealing time for 10 vol.% of CB annealed at 75 °C, and (2.02 ± 0.22) °C/decade of annealing time for composition with 20 vol.% of CB annealed at the same temperature. The effect of annealing on the maximum of the thermal expansion can be also quantified, $(d\alpha_{max}/d\log t)$, giving values for a PMMA $(5.97 \pm 0.97) \times 10^{-4}$ /K.decade for 81 °C and $(5.72 \pm 1.12) \times 10^{-4}$ /K.decade at 75 °C.

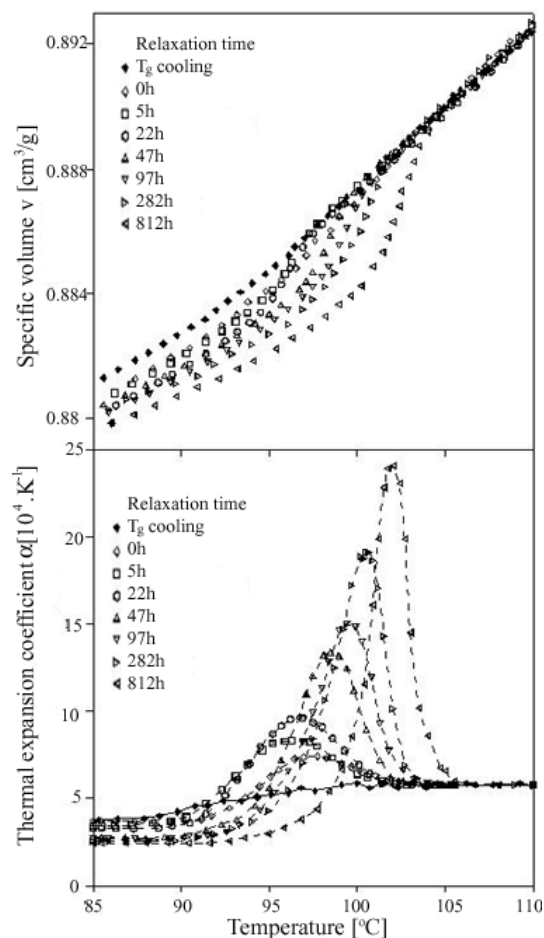


Fig. 6. Isobaric volume (a) and thermal expansion coefficient (b) heating curves of *a*-PMMA after isothermal annealing at 75 °C for various times t_a , as indicated. Cooling T_g curve is added for comparison

This calculation gives of $(3.96 \pm 0.67) \times 10^{-4}$ /K.decade for composition containing 10 vol.% of CB value and $(3.06 \pm 1.41) \times 10^{-4}$ /K.decade for 20 vol.% of CB based compound.

Analyzing parts b of Figs. 5 and 6 it was found that thermal expansion coefficient in liquid, α_l , gives value of $\alpha_l = 5.85 \times 10^{-4}$ for *a*-PMMA, close to the one from cooling experiment according ASTM standard, $\alpha_l = 5.92 \times 10^{-4}$ K $^{-1}$. Calculation of the thermal expansion coefficient in glass, α_g , gives slightly lower value from heating, approximately 2.05×10^{-4} K $^{-1}$, than value obtained from cooling experiment, 2.22×10^{-4} K $^{-1}$. This is caused by original course of volume, which in this region has a slope lower than the measured during cooling. This result in higher difference in α_l and α_g in heating scans, one can calculate value of $\Delta\alpha$ around 3.80×10^{-4} K $^{-1}$ in comparison to 3.70×10^{-4} K $^{-1}$ for cooling experiment. The thermal expansion coefficient was found to be nearly four times higher in the maximum of $\alpha(T)$ dependency than thermal

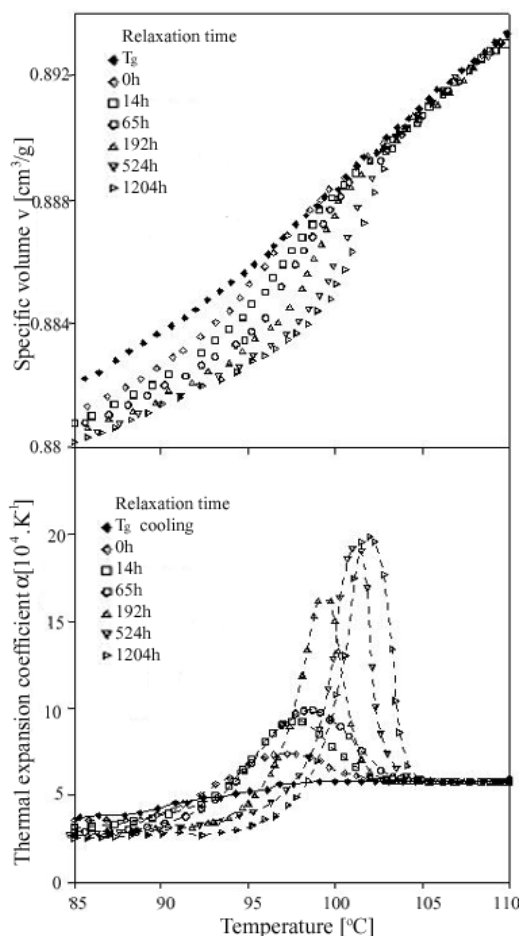


Fig. 7. Isobaric volume (a) and thermal expansion coefficient (b) heating curves of *a*-PMMA with 10 vol.% of CB after isothermal annealing at 75 °C for various times t_a , as indicated. Cooling T_g curve is added for comparison

expansion coefficient measured for liquid state; maximum value of $\alpha(T)$ achieve $23.29 \times 10^{-4} \text{ K}^{-1}$ at $T_{\max} = 105 \text{ }^\circ\text{C}$, calculation of α coefficient in liquid gives $\alpha_l = 5.85 \times 10^{-4} \text{ K}^{-1}$.

Figs. 7 and 8 present data for CB composites annealed at 75 °C, and subsequently reheated above T_g . The same phenomenological aspects were found also in this case, transition region is more pronounced and shifted to the higher temperature by relaxation. Values of α_l for both CB compositions are the same as those from cooling: $\alpha_l = 5.23 \times 10^{-4} \text{ K}^{-1}$ for 10 % and $\alpha_l = 4.3 \times 10^{-4} \text{ K}^{-1}$ for 20 % of CB in PMMA. The difference of thermal expansion coefficients in liquid and glass is also higher when calculated from heating $\Delta\alpha = 2.02 \times 10^{-4} \text{ K}^{-1}$ for 10 % and $\Delta\alpha = 1.73 \times 10^{-4} \text{ K}^{-1}$ for 20 vol.% of CB than from cooling $\Delta\alpha = 1.73 \times 10^{-4} \text{ K}^{-1}$ for 10 % and $\Delta\alpha = 1.58 \times 10^{-4} \text{ K}^{-1}$ for 20 vol.% of CB.

The peaks in $\alpha(T)$ dependencies in Figs. 5, 6, 7 and 8 were integrated according to Eq. (2) and calculated relaxed volumes are presented in Fig. 9. As can be seen, relaxed volume increases linearly with logarithm of time. The

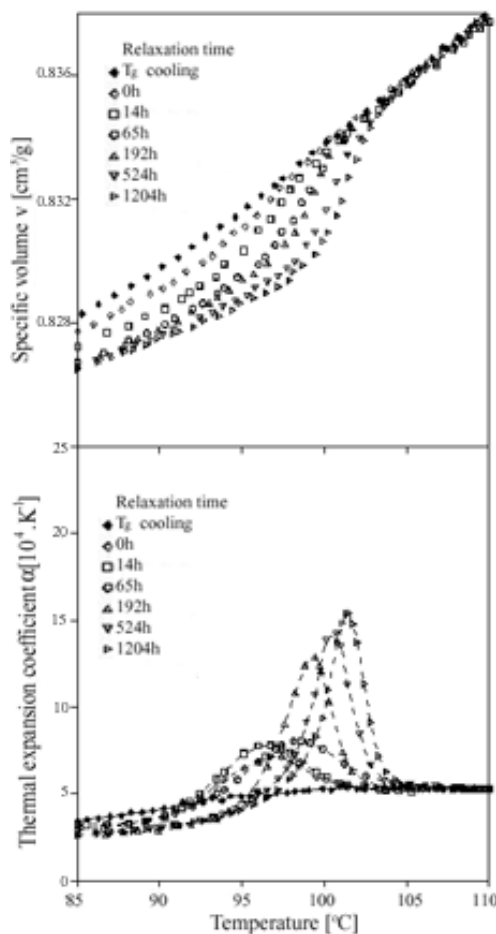


Fig. 8. Isobaric volume (a) and thermal expansion coefficient (b) heating curves of *a*-PMMA with 20 vol.% of CB after isothermal annealing at 75 °C for various times t_a , as indicated. Cooling T_g curve is added for comparison

isothermal relaxation curves at 81 °C and 75 °C are also shown in Fig. 9 for comparison, exhibiting very similar courses.

Another way of comparison measured and calculated relaxed volumes is volume relaxation rate, β_v , which is also capable to compare relaxation kinetics in various types of relaxed materials at temperatures well below T_g , following temperature down-jumps. This variable is defined as slope of the contraction isotherms in the region, where the specific volume varies linearly with the logarithm of aging time^{2,3,18}, expressed by the following equation:

$$\beta_v \cong -\frac{1}{v} \left(\frac{dv}{d \log t_a} \right)_{\text{inf}} \quad (4)$$

where t_a represents relaxation time.

The calculation of β_v using Eq. (4) gives value of $4.72 \pm 0.66 \times 10^{-4}$ for the volume relaxation curve calculated

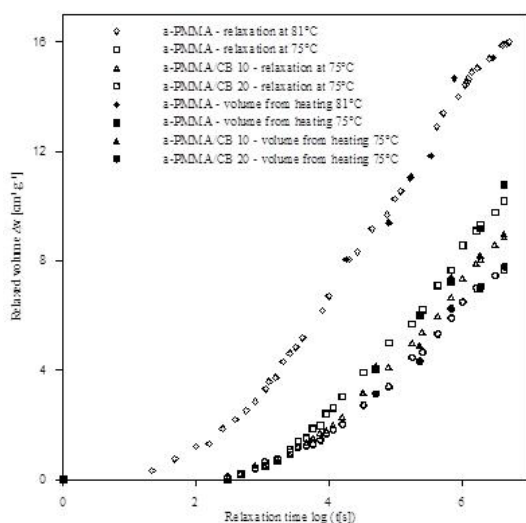


Fig. 9. Isothermal relaxation curves at 81 °C for *a*-PMMA and 75 °C for *a*-PMMA and its blends with CB and its comparison with calculated relaxed volume at appropriate temperatures

from heating experiment after relaxation at 81 °C, exhibiting a good agreement with the $4.44 \pm 0.10 \times 10^{-4}$ value evaluated from the isothermal measurement. Similar result can be obtained also for relaxation measurement in PMMA at 75 °C, where one can find $\beta_v = 4.10 \pm 0.42 \times 10^{-4}$ from relaxed volume calculated from heating experiment, and $4.27 \pm 0.25 \times 10^{-4}$ for isothermal relaxation. All these values are close to those reported for *a*-PMMA in literature: 4.3×10^{-4} (ref.²⁹), 4.2×10^{-4} (ref.³⁰), 4.6×10^{-4} (ref.³¹) and 3.7×10^{-4} (ref.³²).

Presence of CB in PMMA lowered volume relaxation rate; PMMA/CB system containing 10 vol.% of CB achieves value $3.37 \pm 0.71 \times 10^{-4}$ in case of relaxed volume calculated from heating experiment, and isothermal relaxation measurements for the same material shows $3.68 \pm 0.23 \times 10^{-4}$. Addition of 20 vol.% of CB to PMMA matrix results in higher decrease of both values of β_v , $3.30 \pm 0.42 \times 10^{-4}$ for heating experiment and $3.21 \pm 0.21 \times 10^{-4}$ for isothermal relaxation.

Analysis of isothermal volume relaxation curves (Fig. 9) and volume relaxation rate (Eq. 4) of PMMA/CB composites, and its comparison with results obtained for pure polymer, revealed the same effect; reduction of relaxed volume and relaxation rate, caused not only by the simple addition of appropriate properties of both components, but also by immobilization of PMMA molecules. This might be simply revealed by recalculation of relaxation response to the pure *a*-PMMA; by its increase by 10 and 20 % one may get the amount of immobilized layer 3.7 ± 1.1 % in blend with 10 vol.% of CB and 5.0 ± 1.2 in 20 vol.% of CB in PMMA.

Conclusion

The isobaric changes of volume and volume thermal expansion coefficient during heating, after previous annealing below T_g , have been investigated. It has been shown, that peaks in temperature dependence of thermal expansion coefficient are analogous to those of specific heat and integration of these peaks allows to evaluate relaxed volume. Volume relaxation curve evaluated from heating has been found to be equivalent to isothermal relaxation measurement, although it brings higher scatter of results.

Presence of carbon black particles in PMMA results in changes in thermal properties, such as increase in T_g , smaller Δc_p and $\Delta\alpha$. From the point of view of volume relaxation, filler particles cause reduction of relaxation response and relaxation rate. This finding points to the presence of amorphous phase with modified properties by proximity of filler as immobilized polymer layer on their interface.

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