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VOLUME AND ENTHALPY RELAXATION IN *a*-PMMA AFTER TEMPERATURE UP-JUMPS

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Abstract

The volume and enthalpy relaxation in *a*-PMMA subjected to temperature jumps in T_g region has been analysed. The measured H and V data were compared with respect to aging time and proportionality between them as a slope of $(\partial H/\partial V)_T$ dependencies has been found. According to previous works the slope was identified as an apparent bulk modulus, K_a. This method is applied to aging following temperature up-jumps after consolidation periods of varying lengths. The main finding is a marked increase of K_a with consolidation time, approaching a limiting value in an asymptotic fashion.

Keywords: *a*-PMMA, enthalpy relaxation, memory effect, physical aging, volume relaxation

Introduction

The physical aging phenomenon appears in the thermodynamic non-equilibrium of glassy state as a consequence of the transition from liquid to glass. It manifests itself as time-dependent changes in a number of material properties [1, 2].

Among others physical aging has been widely researched by monitoring enthalpy and volume relaxation [1–12]. The most used experimental technique for initiating physical aging is the method of temperature down- or up-jumps, when the temperature of the material is quickly changed, and this is followed by isothermal relaxation.

Both enthalpy and volume relaxation data cover the same general phenomenological features occurring during the process: non-exponentiality and non-linearity of responses, asymmetry of approaches when achieving the same state of material from different temperature change directions, hysteresis and memory effects [1–4]. However, in spite of intensive investigations there are still some unsolved questions regarded to correlation between enthalpy and volume relaxation data, which seems to relax in a similar but not identical way. It was, for example, noted that times required for equilibration are considerably longer in enthalpy relaxation than in relaxation of volume [1, 5, 6]. It leads to prediction that there are some motions, which appear in enthalpy relaxation, but involve

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no changes in volume [1]. Therefore, correlative enthalpy and volume relaxation of polymers is a topical problem of today's and its evaluation can play an important role in deeper understanding of the physical aging phenomenon.

Experimental works which compare enthalpy and volume relaxation data initiated by the same experimental conditions show that the ratio of enthalpy changes relative to those in volume, $(\partial H/\partial V)_T$, can be evaluated [3–9]. According to these authors the slope of the $(\partial H/\partial V)_T$ dependency constructed in respect to the aging time gives the value which expresses the energy of new free volume formation or disappearance in the case of sample expansion or contraction, respectively [3], with the physical unit of J m^{-3}, or a kind of internal pressure [3, 6] directed outwards (in the case of sample contraction) and inwards (at expansion) with the unit of GPa. Papers [7–9] suggest that the changes in enthalpy relative to those in volume can be recognized as apparent bulk modulus, K_a, also in GPa. Overall, such calculations give for amorphous polymers values of about 1–2 J m^{-3} or GPa after temperature down-jumps [3–6, 8]. The slope for the sample expansion (temperature up-jumps) was found to be higher by about 30% than for contraction, i.e., there is some asymmetry in the processes [6].

In the present work the idea of apparent bulk modulus as a quantity from simultaneous enthalpy and volume relaxation data was used. The calculation of K_a comes from simplifying the equation derived from standard equilibrium thermodynamics

$$\left(\frac{\partial H}{\partial V}\right)_T = K - p_i \tag{1}$$

where H and V denote enthalpy and volume, respectively, and represent the enthalpy and volume relaxation data in regard to aging time and aging temperature, and K means bulk modulus. The quantity of p_i is thermodynamic internal pressure defined by equation

$$p_i = K\alpha T - p \tag{2}$$

In this relationship, p is atmospheric pressure, α means thermal expansion coefficient and T is temperature. Because p is significantly smaller than p_i, and the quantity of p_i at ambient conditions is much smaller compared to K, we can neglect them both and take the slope of relaxed enthalpy to specific volume at isothermal aging as apparent bulk modulus, K_a, defined by equation

$$\left(\frac{\partial H}{\partial V}\right)_T = K_a \tag{3}$$

Experimental works [7, 8] confirmed such an assumption and apparent bulk modulus was calculated from the data measured after a single temperature down-jump.

In the present work the enthalpy and relaxations for *a*-PMMA after a temperature up-jumps were measured; the temperature history was modelled as a two-step jump. The samples were allowed to consolidate for a given time after an initial single temperature down-jump from the equilibrium above the glass transition temperature. This was followed by another temperature up-jump, after which relaxation changes were measured. The paper also deals with the effect of consolidation time on the relaxation process.

Experimental

Material

The material studied was atactic poly(methyl methacrylate) (*a*-PMMA), Plexiglas 6N by Röhm GmbH, with mass-average molecular mass of 90 kg mol^{-1}. The glass transition temperature was measured by differential scanning calorimetry at the heating rate of 10°C min^{-1} and was found to be 95°C.

Aging procedure

Both volume and enthalpy relaxation measurements were performed as double-step temperature jump experiments. First, the dilatometer or sample for calorimetry was kept at a temperature of T_i to erase any previous temperature or mechanical histories. Then a temperature down-jump to consolidation temperature, T_{a1}, was applied and the temperature was maintained constant for a prescribed time, t_{a1}. It was then up-jumped and kept at relaxation temperature, $T_{a2.}$ The temperatures were chosen as:

$$T_i > T_g > T_{a2} > T_{a1}$$

The measurement of volume or enthalpy relaxation was recorded as a function of elapsed time, t_{a2}, following the second temperature jump. Zero time for collecting the experimental data was the time at which the change in temperature was initiated.

The procedure can be briefly described as follows:

- Annealing at T_i=T_g +20°C for 20 min.
- Temperature down-jump to consolidation temperature T_{a1}=T_g–15°C and pre-annealing for time t_{a1} (from 2 to 1396 h).
- Temperature up-jump to relaxation temperature T_{a2}=T_g–5°C and relaxation for time t_{a2} (up to 140 h).

Volume relaxation measurements

Mercury-in-glass dilatometer according to ASTM, Standard D 864-52, was employed for volume relaxation measurements. The dilatometer capillary diameter was 0.720 mm. The sample was cut out from a compression-molded platelet in the form of bar with the cross-section of 6x6 mm and volume 3.2 cm^3. The isothermal stages of the dilatometer were performed by its immersing into precision thermostatic bath. The temperature fluctuations of the bath reported by the manufacturer (Grand Instrument, Shepreth, UK) are ±0.004°C.

The temperature jump technique is based on prompt transfer of the dilatometer from one to another thermostatic bath with different temperatures, T_a. In our case, the dilatometer was placed in a bath maintained at T_i until volume equilibrium was reached and then quickly transferred to the bath maintained at the consolidation temperature, T_{a1}. After the consolidation period the dilatometer was moved again to the bath with relaxation temperature, T_{a2}.

Enthalpy relaxation measurements

Calorimetric measurements were carried out using Perkin Elmer DSC 4 analyzer. A set of samples for DSC analysis was prepared, each sample of the mass of ca 6 mg. The temperature programme was carried out by a technique similar to the dilatometric part. The samples were placed into an aluminum cell immersed into thermostatic bath at temperature T_i to erase the previous history, and then manually moved to another bath with consolidation temperature, simultaneously with the dilatometer. After a given time the cell was moved to the bath with relaxation temperature. The temperature scans of samples relaxed for time t_{a2} following the second temperature jump was performed on DSC 4 at the heating rate of +10°C $\min^{-1}$ to T_g+30°C. Before the samples were moved into the measuring cell of DSC 4, each of the samples was rapidly quenched in a freezer to approximately –15°C.

Results and discussion

The volume relaxation is presented in Fig. 1 as time-dependent changes in specific volume for different aging modes. The figure illustrates a well-pronounced phenomenon: specific volume first increases, then passes thought a maximum, and finally decreases to an equilibrium value in the same way as after a single temperature down-jump. This phenomenon is usually called memory effect.

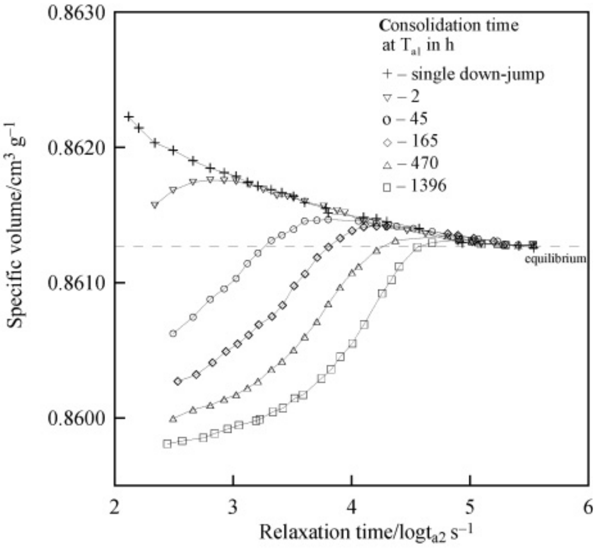

Fig. 1 Volume relaxation curves after a double temperature jump for different consolidation times. The dashed line represents equilibrium specific volume at $T_{a2}=T_g-5$°C

A very similar dependence was also found in enthalpy relaxation experiments presented in Fig. 2. In the initial stage of relaxation an endothermic change appears, but after some time of relaxation the process becomes exothermic. The only exception is for the shortest consolidation time, 2 h, which only shows exothermic changes. As the consolidation time increases, the memory effect is less pronounced. In the case of the thermodynamic equilibrium no residue of previous temperature down-jump and subsequently no memory effect can be observed; the situation is like for a single temperature up-jump. The described situation is close to relaxation after 1396 h consolidation, when the memory effect appears to be imperceptible and the sample practically only expands to the equilibrium value at T_{a2}.

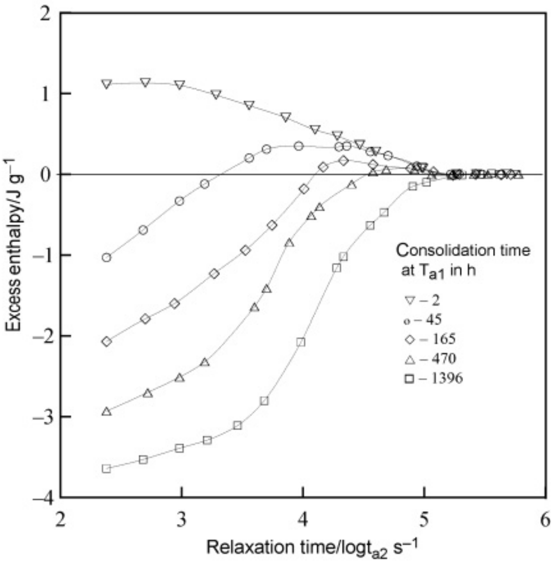

Fig. 2 Enthalpy relaxation curves after double temperature jump for different consolidation times

Volume and enthalpy relaxation data were combined, as can be seen in Fig. 3, for the longest consolidation time. The dependence between both quantities is linear with high accuracy. The graph served for the calculation of bulk modulus according to Eq. (3); K_a is the slope of the line. The data shows only the expansion part of the relaxation curves, which inverse to compression after reaching the maximum. The internal pressure becomes to be directed outwards and energy escapes from the sample instead of being sucked from the vicinity [3, 6]. Also $(\partial H/\partial V)_T$ dependencies change their directions and points represented by relaxed enthalpy and specific volume should return to equilibrium values at T_{a2} with a slope smaller by about 30% than in expansion [6]. Because the measured changes after the maximum are very small, with relatively high experimental errors based on resolution of experimental methods, $(\partial H/\partial V)_T$ calculations do not give satisfactory results and have inadmissible scatter. Hence such K_a rations were not presented. Also K_a for 2 h of consolidation was not

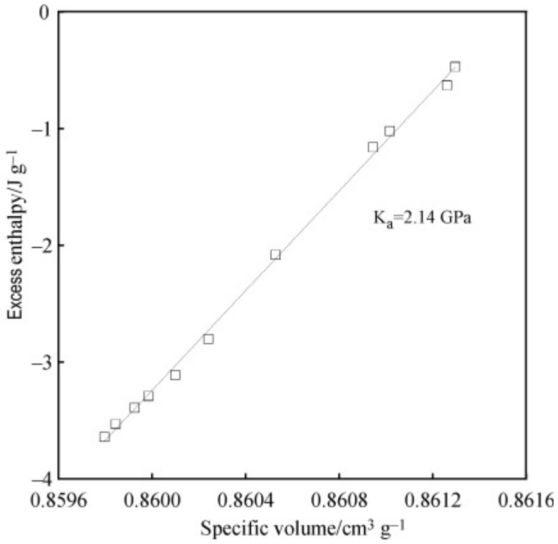

Fig. 3 Typical dependence of excess enthalpy *vs.* specific volume. Evaluation of apparent bulk modulus (consolidation for 1396 h)

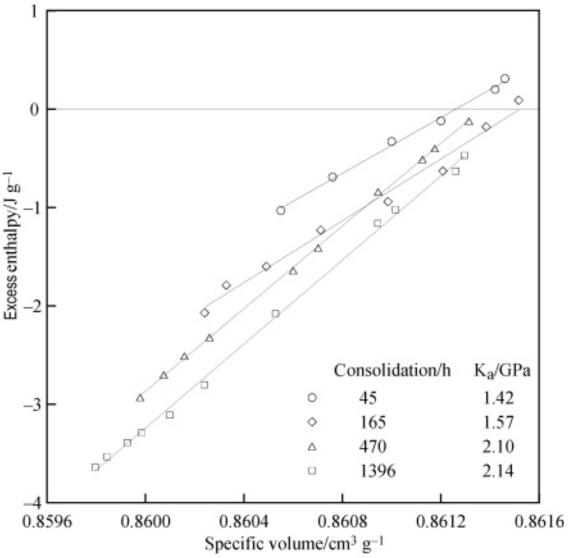

Fig. 4 Dependence of excess enthalpy *vs.* specific volume for different consolidation time. Evaluation of apparent bulk moduli

subsumed into Fig. 4 because the sample only expanded for a very short period of relaxation after a temperature up-jump.

The ratio of $\partial H/\partial V$ found in this work is close to the values published in literature [3–6, 8]. It ranges from 1.42 GPa for the consolidation time of 45 h to the value of 2.14 GPa for the up-jump carried out after consolidation for 1396 h, when the structure was close to thermodynamic equilibrium after temperature down-jump. Such a result shows that the ingredient of enthalpy relaxation becomes more significant than adequate volume changes when temperature up-jump is applied to better-equalized structure. Therefore, the values of K_a are strongly affected by consolidation time, which is illustrated in Fig. 4. On the one hand, the state of the structure does not affect the linear relationship between the quantities, but on the other hand, the residual part of relaxation initiated by the first temperature down-jump, which participates in the process as the memory effect, reduces K_a value of simultaneous enthalpy and volume relaxation response, i. e. the slope of the line increases with consolidation time, as can be clearly seen in the figure.

It can be predicted that the maximum value of K_a will be calculated from the data obtained in the test where the temperature up-jump is applied onto well-equalized structure after a temperature down-jump. In this case a single temperature up-jump is applied onto the material in thermodynamic equilibrium. In such measurements, K_a can be used as a measure of thermodynamic state of the matter before temperature up-jump is applied.

Conclusions

Volume and enthalpy relaxation measurements of *a*-PMMA have revealed the existence of memory effect, which diminishes with increasing consolidation time. The dependence of excess enthalpy and specific volume changes after a temperature up-jump is linear for each consolidation time tested. Apparent bulk modulus, K_a, calculated as a slope of excess enthalpy and specific volume dependency, increases with rising consolidation time, i.e. when the temperature up-jump is applied to a better-equalized structure. K_a can be considered a measure of thermodynamic equilibrium state and a potentially used for the assessment of physical aging of materials.

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