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Isobaric heating of polystyrene and evaluation of the Narayanaswamy parameter x from volume recovery data

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ABSTRACT

Structure parameter x, defining the relative contributions of temperature and structure to the relaxation times, which is applied in Tool–Narayanaswamy–Moynihan (TNM) equation, was evaluated from volume heating isobars for polystyrene (PS) applying the peak shift method. The peak shifted with changing structural state of PS prior heating, which was reached by different period of aging time at 89 °C < T_g up to 2544 h. In this novelized procedure for volume data, originally tested only for enthalpic measurements, high sensitivity of peak temperature (position of inflection point of the heating isobar) was shown, together with high linearity of data. This allows to directly and sensitively calculate the shift and consequently structure parameter x. The value found in the research, $x = 0.40 \pm 0.02$, is in good agreement with published results obtained by the peak-shift method from enthalpy data of PS.

1. Introduction

The fundamental features of amorphous solid materials, such as glass transition transformation and consecutive structural relaxation or the behavior of relaxed structures during their isobaric heating, can be better understood and approached through the analysis of glass-formation kinetics. One of the most powerful approaches is the concept of the fictive temperature, T_f, which is used to characterize the structural state of the glass. The concept is satisfactorily expressed in an empirical relationship called Tool–Narayanaswamy–Moynihan (TNM) equation [1,2]:

$$\ln \tau_i = \ln A + \frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f} \tag{1}$$

where τ_i is the ith relaxation time in the distribution of relaxation times, A means the pre-exponential factor reaching the value of τ_i at equilibrium and infinitely high temperature, Δh^* represents the apparent activation energy for structural relaxation, R is the gas constant, and x $(0 \leqslant x \leqslant 1)$ stands for a non-linearity or structure parameter defining the relative contributions of temperature and structure to the relaxation times.

With the help of well designed calorimetric or volumetric experiments it is possible to determine particular parameters of TNM equation. Hutchinson et al. developed so-called peak shift method, which is capable, among others, to evaluate structure parameter x from calorimetric measurements [3–7]. The applicability and validity is also supported by theoretical Hutchinson and Kovacs's work [8], where sensitivity of parameter x to volumetric peaks is clearly demonstrated. This method is based on quantification of the peak temperature, T_p, shift at $c_p(T)$ or $\alpha(T)$ dependences caused by variation of experimental variables. The relationship between T_p and one of the variables (while the others are held constant) is usually found to be linear. The shift factor used for the determination of parameter x is calculated by linear extrapolation of the data obtained from experiments based on three-step cycles. This procedure is schematically illustrated in Fig. 1. It involves cooling of the sample at a constant cooling rate, q_1, to aging or relaxation temperature $T_a < T_g$ from annealing temperature $T_{an} > T_g$, where the sample was left to anneal in order to erase any previous thermal or mechanical history. This is followed by isothermal relaxation for aging time t_a. Finally, the sample is reheated at a constant heating rate, q_2, to a temperature well above T_g.

This method can be also understood from the schematic illustration in Fig. 2. In the figure, part A demonstrates an abrupt change in volume, V, which is usually measured during isobaric heating of slowly-cooled and/or annealed specimens through the glass transition region (The same also applies to enthalpy.). This almost discontinuous increase in V with an inflection point is followed by steady state regime at a sufficiently high temperature. The derivation of $V(T)$ records produces rather sharp peaks in the thermal expansion coefficient, α, which is illustrated in part B and was theoretically or experimentally shown in [8–11], or even

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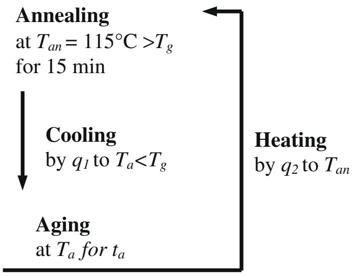

Fig. 1. Schematic illustration of the three-step cycle method.

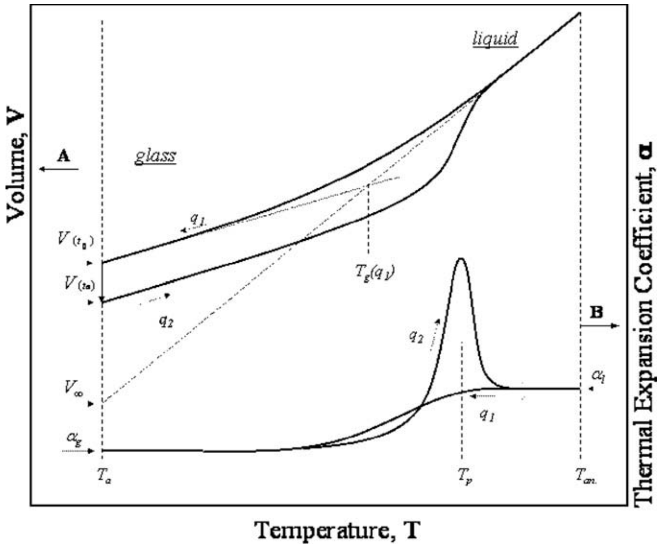

Fig. 2. Illustration of variation of volume, V, with temperature, T (Part A) and its derivative – thermal expansion coefficient, α, (Part B) during three-steep thermal cycles. Experimental variables: cooling and heating rates, q_1 and q_2, aging temperature, T_a, and aging time, t_a.

more commonly peaks in the specific heat capacity, c_p, [3–7] in the case of $H(T)$ dependences. The curve passes thought a maximum at the mentioned peak temperature, T_p, and then decreases to the values characteristic of the liquid state. In Fig. 2 subscripts t_0, t_a and symbol ∞ define the initial volume after achieving relaxation temperature, the volume after isothermal relaxation for annealing time t_a, and equilibrium volume at T_a, respectively. Thermal expansion coefficient is a characteristic value of glassy state, g, or liquid, l. On the temperature coordinate, $T_g(q_1)$ represents conventionally determined glass transition temperature from cooling scans, T_p stands for the peak temperature corresponding with the inflection point on $V(T)$ dependences, and T_{an} is initial annealing temperature before cooling.

An important role in the process is played by the used method. The value measured on conventional calorimeters represents directly the quantity, e.g. heat flow, which can be easily re-calculated, after appropriate calibration, to c_p. Thus most calorimetric experimental data is more suitable for conversion of $c_p(T)$ into $H(T)$ rather than the opposite way. On the other hand, the volumetric measurements represent usually directly measured $V(T)$ data, which can be converted into $\alpha(T)$.

As mentioned above, the character of the peak described by its shape, size and temperature position is a function of experimental variables, which can be defined as q_1, q_2, $\bar{\delta}_V$ or $\bar{\delta}_H$ and T_a. Here q_1 and q_2 mean cooling and heating rates, respectively, and quantities $\bar{\delta}_V$ or $\bar{\delta}_H$ represent the amount of volume or enthalpy isothermal relaxation at T_a. It must be kept in mind that the influence of thermal history is complex and it is necessary to separate individual effects (q_1, q_2, $\bar{\delta}_H$, $\bar{\delta}_V$, T_a) on T_p, so each of the effects must be followed individually.

The expansion of the peak area and peak shift to a higher temperature region is usually observed with increasing aging time, t_a [3,5–19]. Here, a linear relationship between T_p and $\bar{\delta}_H$ can be found. Hutchinson et al. [3–9] define the normalized (dimensionless) shift by $\bar{\delta}_H$ as:

$$\hat{s}(\bar{D}_H) = \Delta c_p \left(\frac{\partial T_p}{\partial \bar{\delta}_H}\right)_{q_1,T_\alpha,q_2} \tag{2}$$

where $\Delta c_p = c_{p,l} + c_{p,g}$ [J g^{-1} °C^{-1}]; $c_{p,l}$ and $c_{p,g}$ represent specific heat capacities of the liquid and glass, respectively. It has been shown [3–7] that this shift is interrelated and depends sensitively upon x throught function $F(x)$:

$$F(x) = \hat{s}(\bar{D}_H) \tag{3}$$

It has been theoretically found [3,4] that function $F(x)$ takes a simple hyperbolic form, Eq. (4), finally leading to the structure parameter x.

$$F(x) = x^{-1} - 1 \tag{4}$$

The reliability of this 'enthalpic' approach was tested for a number of glassy polymers, like PS [3], PC [6], PVAc [7], PMMA and its amorphous blends with PEO [13], poly[methyl(α-n-alkyl)acrylates] [12], for partially [14] or fully [15–17] cured epoxy resin with different curing agents, for organic-glass-forming substances, such as glucose, fructose and their mixtures [18], or for inorganic glasses based on AgI–AgPO$_3$–Ag$_2$Mo$_4$ composition [5] or recently for amorphous selenium [19].

Although the peak shift method was originally developed for both enthalpic and volumetric measurements, so far it has been entirely applied only onto the former; therefore dilatometric experimental data is missing in literature. For PS the value of 0.4 can be found for structure parameter x; this was, however, determined from enthalpic measurements [3]. Thus the main aim of this paper is to use volumetric heating data to determine the structure parameter x by the peak shift-method adapted for PS material in order to test the applicability of the method on volumetric data.

2. Experimental

2.1. Tested material

The material used for the measurements was polystyrene, PS (FMF, Freiburg, PS 140). Its weight average molecular weight $\bar{M}_w = 145 kg\ mol^{-1}$, and polydispersity ratio, $\bar{M}_w/\bar{M}_n = 1.03$ where $\bar{M}_n$ is number average molecular weight.

2.2. Method

Mercury-in-Glass Dilatometry (MIG) constructed according to ASTM Standard D 864-52 was used for experimental measurements. A PS specimen was prepared by compression molding and machined to form a bar with the cross-section approximately 6 × 6 mm. The volume of the specimen was 2.84 cm^3. Before the specimen was inserted into the dilatometer, it was annealed in a furnace at a temperature above T_g. Then the dilatometer was sealed and filled with high purity mercury (>99.999%) under vacuum of about 2 Pa. All temperature programs were realized by immersing the dilatometer into a precision thermostatic bath (JULABO HP-4) filled with silicon oil. The accuracy of volume changes measurement by this method is about 1.2×10^{-5} cm^3 cm^{-3} in respect to the amount of the sample, mercury, dilatometer capillary bore and temperature fluctuations of thermostatic bath. A 'blind' dilatometer, with a similar geometry as the dilatometer filled with mercury and sample, was produced to determine the lag between