Temperature gradient in sample and its effect on enthalpy relaxation model fitting of polystyrene

Guodong Liu *, Lixia Li, Yang Zheng, Yang Zuo

Institute of Polymer Science and Engineering, Hebei University of Technology, Tianjin 300130, PR China

ARTICLE INFO

ABSTRACT

A method to calculate the temperature profile in the polymer samples in differential scanning calorimetry (DSC) measurements by combining the Fourier's law of heat conduction and structural relaxation model is proposed. It is assumed that the temperature at the bottom of the sample is consistent with the program temperature but temperature lag exists between the top and bottom of the sample because that the thermal transfer paths to the two surfaces of the sample are different. The fitting quality of the apparent heat capacity data of polystyrene (PS) samples with different thicknesses using one set of Tool–Narayanaswamy–Moynihan (TNM) parameters are excellent, which conforms the method for temperature profile calculation. It was found that the temperature gradient has slight effect on the best fit TNM model parameters of PS samples with different thicknesses. The investigation on enthalpy relaxation of PS with different thermal histories showed that the temperature gradient existing in the sample only has slight effect on the thermal history dependence of TNM model parameters, which may originate mainly from the flaw of the model itself.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Structure relaxation and physical aging of the amorphous polymers near their T_g has been important topics in polymer science over many years because the direct relationship with polymer mechanical properties and the fundamental understanding of the nature of the glass transition [1–6]. Enthalpy and volume recovery measurements are the two methods mostly used [7]. Although being an area that is extensively studied, no universally accepted theory was achieved. It is well known, based on the experimental results, that the relaxation was characterized by nonexponentiality attributed to relaxation time distribution and nonlinearity attributed to the out-of-equilibrium nature of the glassy state.

The nonexponentiality was usually described by the empirical Kohlrausch–Williams–Watts (KWW) function which was first used by Williams in the study of the non-symmetrical dielectric relaxation [8,9]:

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{1}$$

where τ is some effective relaxation time and β is a positive parameter no greater than unity ($0 < \beta \leq 1$). Usually the Kohlrausch parameter β is considered as constant [1], whereas τ is considered to be structure and temperature dependent.

In the past years, researchers have proposed various expressions to describe the dependence of τ on material structure and temperature, such as Tool–Narayanaswamy–Moynihan (TNM) [10–12], Adam-Gibbs (AG) [13–17] and Gómez Ribelles (GR) [18–20] models. Among these, TNM model was most widely used in the study of structural relaxation of glassy polymer, which describes the dependence of τ on the degree of departure from equilibrium as:

$$\tau = A \exp\left[\frac{x\Delta h}{RT} + \frac{(1-x)\Delta h}{RT_f}\right] \tag{2}$$

where A, Δh and x ($0 < x \leq 1$) are constants, R is the ideal gas constant, T and T_f are actual and fictive temperature, respectively. The parameter x is a direct measure of nonlinearity, with $x = 1$ for a linear relaxation. T_f is defined as the temperature at which the measured value of a property would be the equilibrium one (the actual temperature at which the glass would be in equilibrium) if heated or cooled very rapidly [10].

$$\int_{T_1}^{T_f}\left(C_{pl} - C_{pg}\right)dT' = \int_{T_1}^{T}\left(C_p - C_{pg}\right)dT' \tag{3}$$

where T_1 is a temperature above T_g in the equilibrium liquid (rubber) state where the limit state coincides with the equilibrium state, C_p, C_{pl} and C_{pg} are isobaric heat capacity of the sample, liquid (rubber) and glass, respectively.

AG equation was introduced by Scherer as a theoretical basis for treating nonlinearity and referred to as Scherer-Hodge equation [16,17], but uncertainties in the best-fit values of T_2 are particularly large, although it is assumed to be an essential material parameter based on

* Corresponding author. Tel.: +86 22 60200453; fax: +86 22 60202421.
E-mail address: liugd@hebut.edu.cn (G. Liu).

the AG theory [21,22]. Gómez Ribelles introduced a concept of limit state to the structural relaxation process [18–20]. By adding a free parameter, standard deviation (sd) between the theoretical results and the experimental data decreased evidently compared with TNM and AG models. Whereas the uncertainty of T_2 still exists [1]. Meanwhile, the model of Gómez Ribelles and the concept of the limiting state entropy have been criticized and the evidence that the basis for the model is considered as invalid [23,24].

Differential scanning calorimetry (DSC) is the most widely used technique for studying the dynamics of enthalpy relaxation within and below the glass transition temperature range. But deviations were found between model calculations and experimental data determined by DSC and the fitting results were found to change regularly with the thermal treatment of the samples if only one set of model parameters were used [20,21,25]. When different sets of parameters were used, thermal history dependence of the model parameters has been reported [17,26–28], which was considered as deficiency of the models [28,29]. Unfortunately, no universally accepted theory has been achieved yet. Simon summarized the possible reasons for the problems as [30]: (1) the presence of thermal gradients in the sample, (2) an inconsistent equation for describing the effects of temperature and structure on the relaxation time, or (3) incorrect representation of structural recovery using the KWW function.

The model parameters are usually obtained from least-squares fitting of the isobaric heat capacity curves when enthalpy relaxation was investigated by using the DSC technique. Whereas the shapes of C_p curves are greatly affected by DSC instrumental response functions [31], the total thermal resistance between the DSC heater and the sample, as well as the temperature gradients existing in the sample [28]. Extraction of model parameters from DSC data is fought with technical intricacies that are almost certainly compromised by inadequate consideration of instrumental and sample response characteristics, although the dynamics is in need of a more precise description [32].

The measured heat-flow curves in DSC measurement are always with an intrinsic error due to the slow heat conduction phenomenon. Höhne studied the falsification (smearing) of the calorimetrically measured heat-flow curves and found that it was affected by the size, geometry and the heat conductivity of the sample [33]. Höhne also proposed complicated mathematical method by employing the Convolution-Integral equation to "desmear" the heat-flow curves. The method of desmearing was improved by Nicolaus [34], which is derived from an electrical analogy. The signal reconstruction is based on a second order differential equation and two different relaxation times are needed. Höhne, Schawe and coworkers [35–41] have given detailed analyses of the desmearing technique by applying linear response theory to DSC data in the case of badly heat conducting samples. They measured (instrumental + sample) Green functions and computed the true heat capacity of the sample using a deconvolution integral technique. The desmeared DSC curves of PVC with different masses were recognizable to be in good agreement. Whereas the Green's function was obtained under the assumption of only small changes in case of transitions without enthalpy step changes (e.g. glass transition, and second order transition) and temperature profile was assumed to be not change during a transition [36]. The Green's function (including sample and heat transfer) was found to be different from that necessary to desmear the sample heat flow and the qualities of the extracted Green's function are always different for different measuring conditions [37]. It was reported that every change of material properties during the thermal event causes an error in the desmearing procedure [38]. The Green's function estimated from the switch-on as well as from the switch-off behavior can be used to desmear the whole measured curve only if the material properties do not change markedly [39].

The instrumental thermal response time is assumed to be much less than the enthalpic retardation time in the transition region, and therefore assumed to be too small to produce significant changes in the best-fit parameters [28]. Hodge and Huvard postulated that the thermal

gradients in DSC measurements to be a factor in the discrepancies based on the fact that the magnitude of annealing peaks were overpredicted when the sample were annealed for high degrees (large overshoots) by using one set of TNM model parameters [25]. Nevertheless, the thermal resistance between the sample and DSC instrument will not be addressed here since it could be minimized by insuring that the sample pan is flat and the sample is in good contact with the pan, and by using proper temperature calibration procedures [30]. The effects of temperature gradients in the sample are of particular interest in this paper. Meanwhile, the temperature gradients may have effects on the ongoing relaxation phenomena to some extent as thermal stresses are inevitably induced which act as a mechanical stresses [42–45]. Then the paper is engaged in the model and algorithm of temperature gradient.

The temperature gradients exist across the samples of low thermal conductivity such as polymers and inorganic glasses have been discussed by Donoghue etal. and DeBolt tens years earlier [46,47]. O'Reilly and Hodge measured the temperature gradients across the samples by placing 3–4 mg indium above and below a disk of PS [28]. The differences between the melting peak temperatures were considered as the temperature gradient across the polymers. For a PS with 0.5 mm thickness, the gradient was obtained to be 1.3 K when it was heated at 20 K·min^{-1}, and 0.5 K at 5 K·min^{-1}. But the temperature profile in the polymer sample was not obtained. Mano and Gómez Ribelles determined the temperature profile along the sample thickness by calibration experiments with metallic standards positioned at different locations within layers of polymeric material [29]. Significant temperature gradients, amplitudes higher than 2.5 K, were found for samples with 0.6 mm thickness at a heating rate of 20 K·min^{-1}. The obtained temperature gradients by O'Reilly and Hodge [28], and Mano and Gómez Ribelles [29] are several times larger than that estimated from the typical thermal diffusivities of polymers $1 \pm 0.1 \times 10^{-7}$ m^2·s^{-1} for polymer [31]. Albright reported that the latent heat in the phase change process has great effect on the temperature gradients in the DSC samples [32] and temperature difference between the surface and the center of phase change materials increased due to the higher heat transfer caused by the large amounts of heat absorption during the phase change.

Hutchinson and co-workers [48] found that the DSC annealing peaks broadened and flattened when the cooling and heating rates increased at a constant ratio of them, which conflicts with TNM model and Kovacs–Aklonis–Hutchinson–Ramos (KAHR) model [49] that predict that the curves have same shape and could superposed each other by adjusting their temperature values. Hutchinson and co-workers attributed this result to thermal lag effects and then developed a correction for DSC data based on the assumption that TNM and KAHR models are correct. They also adopted a thermal network model to calculate the temperature lag. But their calculation does not involve the dynamic aspect of structure relaxation. Simon calculated the temperature gradients based on the thermal diffusivity of the material [30], which was assumed to be independent of temperature and decrease 50% through the glass transition. The thermal lag in the centre of a poly(ether imide) (PEI) sample above T_g was calculated to be twice of that in glassy state. Both the top and bottom of the sample were assumed to maintain at the program temperature (T_p), which conflicts with the experimental results of O'Reilly and Hodge [28], and Mano and Gómez Ribelles [29] that the temperature of the sample top was lower than the bottom in heating. Meanwhile, it is assumed that the rate of the temperature change within the sample is not a function of position, which also conflicts with the fact that the temperature in the centre of the sample differs from the bottom or top.

So in this paper we propose a new method to calculate the temperature profile in the sample which takes account of the asymmetric temperature distribution and the different enthalpy relaxation states at different positions in the sample. Although several inadequacies have been identified in the literature (including the underestimation of the activation energy parameter, uncertainty over actual meaning