

The effect of temperature gradients on the parameters of Adam–Gibbs model

Yang Zuo¹, Man Feng¹, Guodong Liu^{*}

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



ARTICLE INFO

Article history:

Received 22 October 2013

Received in revised form 14 December 2013

Available online 21 January 2014

Keywords:

Enthalpy relaxation;

DSC;

Temperature gradient;

AG model

ABSTRACT

The most commonly used method for studying relaxation processes in polymers is monitoring the enthalpy recovery by measuring differential scanning calorimetry (DSC) heat capacity data. Because of its great influence on heat capacity data, the effect of temperature gradients in the sample on relaxation dynamics study should be investigated. A model for calculating temperature profile in a DSC sample was proposed previously by combining Fourier's law of heat conduction with the Tool–Narayanaswamy–Moynihan (TNM) model. This model was examined using PS samples with different thicknesses. It was found that the temperature gradient influenced optimized values of the kinetic parameters. The thermal history dependence of model parameters is still prominent, however. Here the Scherer–Hodge (SH) equation (based on the Adam–Gibbs model) instead of the TNM equation, is used for describing the relaxation time–structure–temperature relationship in the temperature profile calculation. It is found that the influence of temperature gradients on the thermal history dependence of the Adam–Gibbs (AG) model parameters is greater than that of the TNM model parameters. But the thermal history dependence of the AG model parameters still exists when the thermal lag effect was incorporated.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Polymer in nonequilibrium will approach to the equilibrium state, but the process is very slow near T_g and shows obvious relaxation characteristics [1–3]. Structure relaxation and physical aging of polymer near T_g are important topics in polymer science, which have high values for the nature of the glass transition and the mechanical properties of polymer [4–10].

Large numbers of researches have been done in this topic. Relaxation processes in polymer were found to be characterized with nonexponentiality (showing memory effect) and nonlinearity. The nonexponentiality character is usually described using the Kohlrausch–Williams–Watts (KWW) stretch function [11,12]. Tool–Narayanaswamy–Moynihan (TNM) equation and Adam–Gibbs (AG) expression are the mostly used models to deal with the nonlinearity character [13–17]. But remarkable thermal history dependence of the model parameters, which were assumed to be fundamental quantities of polymer, was observed for these relaxation models. New constitutive equations for the relaxation time allow using a single set of parameters to capture the two principal features of the structural relaxation which have been proposed in recent years [18–21]. τ -Effective (τ_{eff}) paradox and the related expansion gap phenomena found by Kovacs [22] through analyzing the structural (volume) recovery data in asymmetry

of approach experiments that were reported could be captured, in the neighborhood of the equilibrium, when τ_{eff} is assumed to scale with δ^m , where δ is the (volume) departure from the equilibrium [23–25]. Nevertheless, neither TNM nor AG or even Kovacs–Aklonis–Hutchinson–Ramos (KAHR) constitutive equations for the relaxation times can accurately describe the τ -effective paradox and the related expansion gap phenomena even with different sets of model parameters.

Structural relaxation can be effectively studied using calorimetric techniques, one of the most common techniques being differential scanning calorimetry (DSC) [26–28]. Usually the kinetic parameters were obtained by fitting heat capacity data of samples. However, temperature at the inner part of the polymer sample lags behind the surface at fast heating (or cooling) rate due to polymer being a poor conductor of heat. The temperature distribution in the sample causes that the measured data of heat capacities (named apparent heat capacity) deviates from its intrinsic values. Then the acquired kinetic parameters may suffer flaws because they were obtained through fitting the apparent heat capacity data instead of the intrinsic ones. It was reported that usually significant deviation was obtained between theoretical values and experimental results of aging absorption peaks. The temperature gradients in the sample may be an important factor, which is firstly noted by Hodge [29]. Meanwhile, different thermal histories may induce frozen-in residual stresses that result in different glassy states at different locations within the sample [30–34], which will affect the ongoing relaxation process inevitably. Therefore, the model and algorithm of temperature

^{*} Corresponding author. Tel.: +86 22 60200453; fax: +86 22 60202421.

E-mail address: liugd@hebut.edu.cn (G. Liu).

¹ Tel.: +86 22 60200453; fax: +86 22 60202421.

Table 1
The masses and thicknesses of PS samples.

Mass (mg)	Thickness (mm)
3.07	0.11
5.95	0.19
8.96	0.29
12.04	0.42
15.01	0.49
17.89	0.62

profile in a DSC sample are the basic subjects in the investigation on enthalpy relaxation (or recovery) in polymer.

The temperature profile in a DSC sample was determined by measuring the differences of melting point of metal placed in, but it would be influenced by latent heat in phase transition of the metal [35,36]. The drawbacks could be overcome through the approach of model calculation. Schawe and coworkers [37–42] have given detailed analyses of desmearing technique by applying linear response theory to DSC data in the case of bad heat conducting samples. They measured (instrumental + sample) Green functions and calculated the true heat capacity of the sample using a deconvolution integral technique. Whereas, the Green function was obtained under the assumption of only small changes in heat capacity without enthalpy step changes (e.g. glass transition and second order transition) and the temperature profile was assumed to be not changed during a transition [37]. Simon [44] obtained temperature profile in a polymer sample by calculation using Fourier's law of heat conduction. Nevertheless, the achieved result showed a symmetrical curve for the temperature along the distance from the bottom of the sample, which was inconsistent with the reported results obtained experimentally [35]. Meanwhile, the effect of relaxation on heat capacity was not considered. In a previous work, a model with asymmetrical temperature profile was proposed by combining Fourier's law of heat conduction with the TNM model [45]. The model has been verified using PS samples with different thicknesses. It has been proved that the temperature gradients

surely have an effect on the TNM model parameters to some extent, but thermal history dependence of the TNM parameters was still pronounced.

The TNM equation is phenomenological and its parameters have no clear physical meanings [46,47]. The Adam–Gibbs (AG) expression is based on a thermodynamic theory of the glass transition [16,17,48] and yields the relationship of relaxation time with temperature and structure of materials as:

$$\tau = A \exp \left[\frac{\Delta\mu s_c}{kTS_c} \right] = A \exp \left[\frac{C}{TS_c} \right] \quad (1)$$

where τ is some effective relaxation time, $\Delta\mu$ is the free energy barrier hindering rearrangement, s_c is the conformational entropy of the smallest group able to rearrange and S_c is macroscopic configurational entropy. The fictive temperature is introduced into expression for S_c as:

$$S_c = \int_{T_2}^{T_f} \frac{\Delta C_p}{T} dT \quad (2)$$

where ΔC_p is the difference in specific heat between the equilibrium melt and the glass and T_2 is the second-order transition temperature in the Gibbs–DiMarzio thermodynamic theory of the glass transition. It was recognized that the empirical form $\Delta C_p = a + bT$ is generally more accurate [48]. Then τ is obtained to be:

$$\tau = A \exp \left[\frac{C/a}{T \left[\ln \frac{T_f}{T_2} + \frac{b}{a}(T_f - T_2) \right]} \right] \quad (3)$$

It is named Scherer–Hodge (SH) equation here because it was first used by Scherer and Hodge in studying structure relaxation [29,46].

In this paper, the temperature profile in a DSC sample is recalculated utilizing the method combined Fourier's law of heat conduction with the SH equation. The effect of temperature gradients on the optimization results and thermal history dependence of the AG model parameters is investigated.

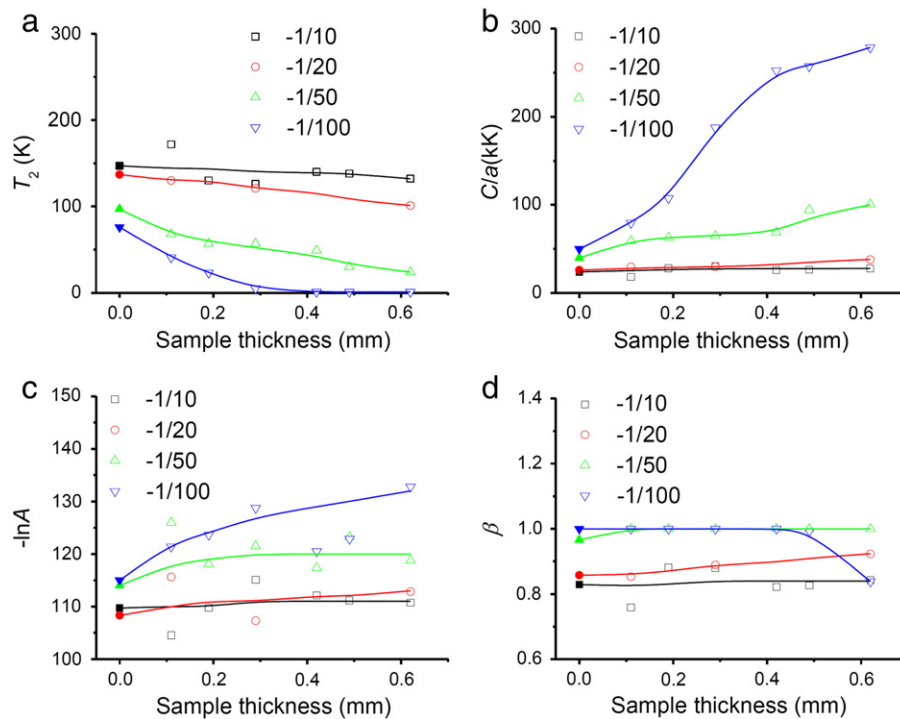


Fig. 1. The best fit AG model parameters T_2 (a), C/a (b), $-\ln A$ (c) and β (d) of PS samples with different thicknesses.

Download English Version:

<https://daneshyari.com/en/article/7902389>

Download Persian Version:

<https://daneshyari.com/article/7902389>

[Daneshyari.com](https://daneshyari.com)