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On the measurement of the width of the distribution of relaxation times in polymer glasses

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Abstract

A new method to determine the width of the distribution of relaxation times (DRT) based on calorimetric measurements by temperature modulated differential scanning calorimetry (TMDSC) is presented. The simulation of the glass transition by TMDSC, taking into account a DRT, shows that the inflectional slope of the complex heat capacity, C_p^* depends sensitively on the stretched exponential parameter β of the Kohlrausch–Williams–Watts equation, which is inversely related to the width of the DRT ($0 \leq \beta \leq 1$). Furthermore, it is shown that the normalised inflectional slope of C_p^*, defined as:

$$\bar{S} = \frac{1}{\Delta C_p^*}\frac{dC_p^*}{dT}$$

is independent of the nonlinearity parameter, but depends on the apparent activation energy, Δh^*, implying that it should be normalised also with respect to this. The procedure proposed here for the evaluation of β is to consider the dimensionless quantity $\bar{S}/\theta$, where $\theta = \Delta h^*/RT_g^2$ is the equivalent of an apparent activation energy in the KAHR model. For example, the value of $\bar{S}/\theta$ increases from 0.05 to 0.26 in the simulations as β increases from 0.2 to 0.8.

The method was applied to three epoxy resins obtained with different stoichiometric ratios ($r = 0.8$, 1 and 1.5), for which the values of the parameter β were previously estimated by conventional DSC, using the method of intrinsic cycles, being in the range $0.3 < \beta < 0.4$. The values of the normalised and dimensionless inflectional slope $\bar{S}/\theta$ were found experimentally by TMDSC to be 0.128 (for the resin $r = 1$), 0.132 (for $r = 1.5$) and 0.113 (for $r = 0.8$), all corresponding to β values close to 0.4, which agree very well with the earlier estimated values.

Keywords: Glass transition; Structural relaxation; Temperature modulated differential scanning calorimetry

1. Introduction

The kinetics of structural relaxation in glasses exhibits both nonlinear and nonexponential behaviour [1]. The nonlinearity is characterised by the dependence of the relaxation time (τ) on both temperature (T) and structure, the latter often being described by the so-called Tool–Narayanaswamy–Moynihan equations [2–4]:

$$\tau = \tau_g \exp\left[\frac{x\Delta h^*}{RT} - \frac{\Delta h^*}{RT_g} + \frac{(1-x)\Delta h^*}{RT_f}\right] \tag{1}$$

where τ_g is the relaxation time in equilibrium at the glass transition temperature T_g, T_f is the fictive temperature, characterising the structure of the glass, x is the nonlinearity parameter, which defines the relative contributions of temperature and structure to the relaxation time, and Δh^* is the apparent activation energy.

The nonexponentiality is a consequence of the distribution of relaxation times (DRT), which may be introduced by means of the Kohlrausch–Williams–Watts (KWW) response function $\phi(t)$ [5]:

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{2}$$

where β is the nonexponentiality parameter, inversely related to the width of the DRT. These three parameters (x, Δh^* and β) constitute the key to determine the behaviour of the glass during its structural relaxation. The procedures for the experimental evaluation of the parameters x and Δh^* have been reviewed elsewhere [6,7], and are not

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the objective of the present work; this is to describe a procedure for the evaluation of the nonexponentiality parameter.

The determination of β by enthalpy relaxation experiments has in the past usually been made either by curve-fitting (see Ref. [6]), in which the heat capacity data are fitted by simultaneously adjusting several parameters, including x and β, or by measuring the height of the endothermic peak, on heating immediately after cooling, as a function of the prior cooling rate [8]. The latter method gives an estimate of β, but requires the previous evaluation of x from the peak-shift method [9,10].

The technique of temperature modulated differential scanning calorimetry (TMDSC) was introduced by Reading and coworkers [11,12] in 1992, and allowed the determination of a 'dynamic' glass transition, which is frequency dependent. This should be contrasted with conventional DSC, which allows the determination of the 'conventional' glass transition (also called the 'thermal' glass transition), which is dependent on the cooling rate. In the present work, we demonstrate a new calorimetric method for the determination of β based upon TMDSC measurements. In the following sections, we describe the theoretical basis of this method, followed by its application to three epoxy resins, for which the necessary experimental results had already been obtained by TMDSC. The results for β obtained by this method agree very well with those obtained previously by conventional DSC.

2. Theoretical aspects of the method

The analysis of the method is based on the TNM formalism (Eq. (1)) and the KWW distribution function (Eq. (2)) applied to TMDSC by defining the temperature modulation as:

$$T = T_o + q_o t + A_T \sin(\omega t) \qquad (3)$$

where q_o is the underlying heating (or cooling) rate, A_T is the temperature amplitude and ω is the angular frequency related to the period of modulation $t_p = 2\pi/\omega$. From this expression, the heating rate modulation is given by the following equation:

$$q = \frac{dT}{dt} = q_o + A_T \omega \cos(\omega t). \qquad (4)$$

The application to a standard three-step thermal cycle (cooling, isothermal annealing and reheating) with a set of values of material constants gives the heat flow modulation in the glass transition region. The details of this analysis are described in an earlier work [13].

A sliding Fourier transformation of a single cycle of the heating rate and of the corresponding heat flow data allows the calculation of other quantities such as the total (or average) heat flow ($\langle \mathrm{HF} \rangle$), the average value of the heating rate (q_o), the amplitudes of the heating rate ($A_q = A_T \omega$) and heat flow (A_{HF}), and the phase angle (ϕ) of the heat flow with respect to the heating rate. From these quantities the evaluation of other thermal properties is possible, such as the average heat capacity ($C_{p,avg} = \langle \mathrm{HF} \rangle / q_o$), and the complex heat capacity (C_p^*), the modulus of which is given by the following equation: $|C_p^*| = A_{HF}/A_q$. A more detailed description of the evaluation and the use of these parameters in glass transition region has been shown in earlier works [14,15].

With respect to the effects of the key parameters on the complex heat capacity, the model predicts a rather small effect when the nonlinear parameter is varied over its full range, whereas a noticeable sharpening of the transition in C_p^* is observed when β changes between 0.2 and 1.0 (see Fig. 12b in Ref. [13]). A similar behaviour is observed in the phase angle. This means that C_p^*, which is an experimentally measurable quantity, is practically independent of x but is rather sensitive to β, thus suggesting a procedure to measure the width of the distribution of the relaxation times.

The change of the shape of C_p^* is measured as the inflectional slope of C_p^* as a function of temperature, normalised with respect to its variation ΔC_p^*, and hence can be expressed as:

$$\bar{S} = \frac{1}{\Delta C_p^*} \frac{dC_p^*}{dT} \qquad (5)$$

This normalised inflectional slope of C_p^* is a function of β. As the distribution of relaxation time becomes sharper, β increases, and $\bar{S}$ also increases. However, it transpires that $\bar{S}$ also depends linearly on the apparent activation energy, which implies the need for a normalisation also with respect to this parameter, which is made using the equivalent apparent activation energy θ, used in the KAHR model [16] ($\theta = \Delta h^*/RT_g^2$). The normalised and dimensionless quantity $\bar{S}/\theta$ is found to be a suitable and sensitive quantity for the evaluation of β. The theoretically calculated values of $\bar{S}/\theta$ for different values of the nonexponentiality parameter β are shown in Fig. 1 for a glassy polymer with the following material constants, which are typical for epoxy resins: $C_{p,l} = 1.6\ \mathrm{J\ g^{-1}\ K^{-1}}$, $C_{p,g} = 1.3\ \mathrm{J\ g^{-1}\ K^{-1}}$, $\Delta C_p = 0.3\ \mathrm{J\ g^{-1}\ K^{-1}}$, $T_g = 373\ \mathrm{K}$, $\tau_g = 100\ \mathrm{s}$ and $\Delta h^*/R = 80\ \mathrm{kK}$. A linear fit to these data gives the following equation:

$$\beta = 0.035 + 2.782(\bar{S}/\theta)\ (r^2 = 0.999) \qquad (6)$$

In order to determine β experimentally, therefore, it is proposed that the normalised dimensionless inflectional slope $\bar{S}/\theta$ be evaluated from the C_p^* signal, which is obtained experimentally by TMDSC for any given polymer during cooling through the glass transition region, and then compared with the graphical representation in Fig. 1 or inserted into Eq. (6).

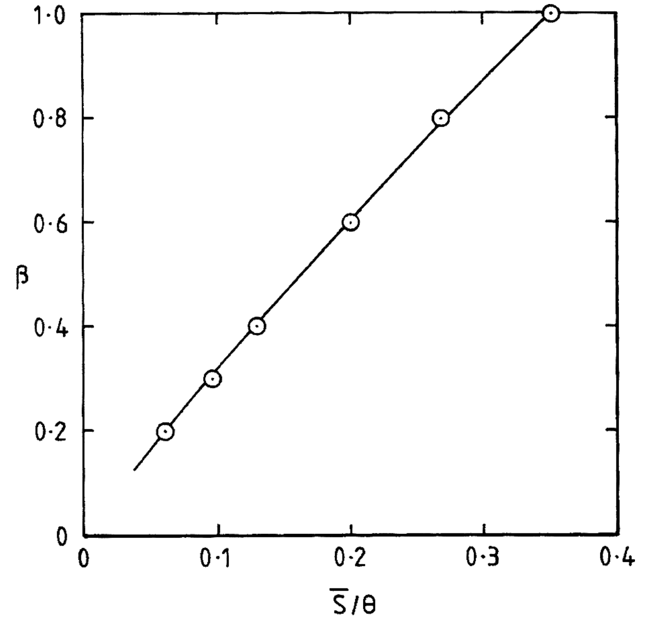

Fig. 1. Variation of the parameter β as a function of the normalised dimensionless inflectional slope $\bar{S}/\theta$ for a polymeric glass with the following material constants: $C_{p,l} = 1.6\,J\,g^{-1}\,K^{-1}$, $C_{p,g} = 1.3\ \mathrm{J\,g^{-1}\,K^{-1}}$, $\Delta C_p = 0.3\ \mathrm{J\,g^{-1}\,K^{-1}}$, $T_r = 373$ K, and $\tau_g = 100$ s.

3. Experimental

3.1. Materials

The epoxy resin was a commercial product based on diglycidyl ether of bisphenol-A (DGEBA) (Araldite F) with an epoxy equivalent of 188.8 g/equiv., cured by a polyethertriamine (Jeffamine T403) with an equivalent weight of 81 g/equiv. Three different epoxy-amine networks were prepared at different ratios (r) of amine/epoxy, $r = 0.8$, 1 and 1.5, which correspond to compositions per 100 epoxy (Araldite F) parts per weight of 34.3, 42.9 and 64.4 amine (Jeffamine T403) parts, respectively. The samples were cured at 60°C for 3 h followed by a postcure at 180°C for 2 h for the ratios 1 and 0.8, and at 150°C for 2 h for $r = 1.5$. The 'conventional' glass transition temperature (T_g) has been measured in all systems as the mid-point of the change of C_p in a DSC scan obtained by heating at $10\ \mathrm{K\,min^{-1}}$ immediately after cooling from a temperature $T_0 = T_g + 20\,K$ at $20\ \mathrm{K\,min^{-1}}$. The values of T_g for the three epoxies are shown in Table 1.

3.2. Calorimetric measurements

The temperature modulated DSC measurements were performed with a METTLER TOLEDO 821e equipped with an intracooler, and STAR© software was used for alternating DSC (ADSC) evaluation. The temperature and heat flow calibrations were performed using indium and zinc as standards.

Table 1
Conventional glass transition and enthalpy relaxation parameters (x, $\Delta h^*/R$ and β) for epoxy resins with the indicated stoichiometric ratios r. These values are reported in Ref. [17], and are shown here for the discussion of the new method for the evaluation of β

Ratio r	T_g (°C)[a]	x[b]	$\Delta h^*/R$ (kK)[c]	β[d]	θ ($\mathrm{K^{-1}}$)[e]
1	87.5	0.40 ± 0.06	116 ± 7	$0.3 < \beta < 0.4$	0.89
1.5	57.0	0.50 ± 0.02	89 ± 4	$0.3 < \beta < 0.4$	0.82
0.8	63.0	0.49 ± 0.03	85 ± 4	$0.3 < \beta < 0.4$	0.75

[a] Glass transition determined by conventional DSC at $10\ \mathrm{K\,min^{-1}}$ immediately after cooling at $20\ \mathrm{K\,min^{-1}}$.

[b] Nonlinearity parameter determined by the peak-shift method [10].

[c] Reduced apparent activation energy calculated from intrinsic cycles [4].

[d] Nonexponentiality parameter calculated by the method of Hutchinson et al. [8].

[e] Temperature dependence parameter of KAHR model [16].

The ADSC scans were performed at an underlying cooling rate of $0.5\ \mathrm{K\,min^{-1}}$, an amplitude of 0.5 K and various periods within the range 30–240 s. In order to calibrate the heat flow signal, correct the amplitude and eliminate the cell asymmetry, a blank run with an empty pan on the reference side and an empty pan plus a lid on the sample side was performed before the sample measurement.

The intrinsic cycles experiments had been performed on the same sample in an earlier study [17] using a Thermal Analyser Mettler TA4000 DSC30. They were obtained by cooling the samples from T_o at different rates (from -40 to $-0.5\ \mathrm{K\,min^{-1}}$) and immediately reheating at a constant rate of $10\ \mathrm{K\,min^{-1}}$. These experiments allow the estimation of the nonexponentiality parameter, β, by the 'conventional' method [8].

The sample mass for each resin was about 8–10 mg, and the same samples were used for the DSC and ADSC experiments. In both calorimeters, the scans were performed with a nitrogen gas flow of $50\ \mathrm{ml\,min^{-1}}$.

4. Results and discussion

The ADSC experiments were performed with an underlying cooling rate of $0.5\ \mathrm{K\,min^{-1}}$, a temperature amplitude of 0.5 K and for various modulation periods. Fig. 2 shows the curves of $|C_p^*|$ obtained from these resins with the same period of 60 s, while Fig. 3 shows the curves of $|C_p^*|$ for the resin with $r = 1$ for the full range of periods. It can be seen that the curves are shifted to higher temperatures as the period is decreased (or as the frequency increases), and that the change in C_p^* at the dynamic T_g remains essentially constant for all periods. These results are in agreement with the predictions of the theoretical simulation made using both the single parameter model of TMDSC applied to the glass transition region [18,19] and also the model with a distribution of relaxation times (see Fig. 6b of Ref. [13]). From the $|C_p^*|$ curves one can evaluate the slope at the point of inflection, which has been done here by making use of the derivative of the original curve and finding the maximum.

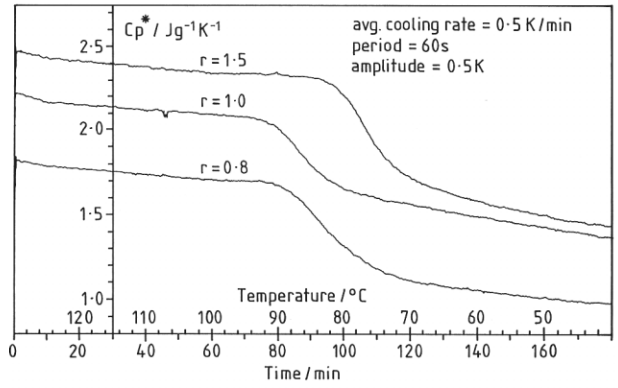

Fig. 2. Modulus of the complex heat capacity for the three epoxies obtained with an underlying cooling rate of 0.5 K min^{-1}, an amplitude of 0.5 K and a period of 60 s.

Table 2
Inflectional slope of C_p^* and variation of the modulus of C_p^* for the three epoxies obtained by TMDSC at different frequencies, an underlying cooling rate of 0.5 K min^{-1} and an amplitude of 0.5 K

	Inflectional slope (J g^{-1} K^{-2})			$\Delta\|C_p^*\|$ (J g^{-1} K^{-1})		
Period (s)	$r = 0.8$	$r = 1$	$r = 1.5$	$r = 0.8$	$r = 1$	$r = 1.5$
30	0.050	0.041	0.071	0.69	0.40	0.64
60	0.046	0.048	0.068	0.56	0.43	0.64
90	0.046	0.052	0.069	0.55	0.44	0.62
120	0.047	0.053	0.070	0.51	0.44	0.61
180	0.047	0.051	0.064	0.51	0.42	0.61
240	0.043	0.046	0.066	0.48	0.44	0.64

The values of these inflectional slopes for each resin and for each period are shown in Table 2, together with the values of $\Delta|C_p^*|$ at T_g. Since there is no significant systematic variation with frequency, the average values of the inflectional slope and $\Delta|C_p^*|$ have been determined, from which the normalised inflectional slope $\bar{S}$ is calculated. Making use of the values of the apparent activation energy for these resins, which have been determined in earlier work [17] and which are given in Table 1, together with the corresponding values of θ, the normalised dimensionless slope $\bar{S}/\theta$ has been determined, from which the values of the parameter β are obtained from the relationship in Fig. 1. The average values of the inflectional slope, of $\Delta|C_p^*|$ and of $\bar{S}/\theta$, as well as the parameter β calculated from the average values, are shown in Table 3.

It is observed that the values of β agree very well with the range of values previously estimated from the intrinsic cycles using conventional DSC, shown in Table 1. The values of β show a weak tendency to increase from the resin $r = 0.8$, with an epoxy excess, to the resin $r = 1.5$, with an amine excess. Taking into account the network structure of these resins, which has been discussed elsewhere [17,20], this variation would indicate that the distribution of relaxation times becomes broader in the resin $r = 0.8$, where the network presents some unreacted bulky epoxy groups situated at the ends of the chains, compared with the resin $r = 1.5$, where the network shows a branched structure as a consequence of the unreacted secondary amine groups. In other words, these results suggest that the distribution of relaxation times is slightly more heterogeneous in the epoxy with epoxy excess than in the epoxy with amine excess. Nevertheless, taking into consideration that the variation in β with r is only about 10%, within the uncertainties quoted, this conclusion is somewhat risky. Taking into account these uncertainties, it may be more reliable to conclude that the stoichiometry has only a small influence on the distribution of relaxation time.

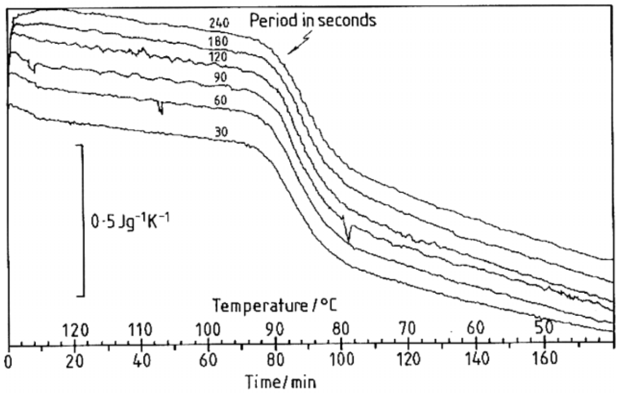

Fig. 3. Modulus of the complex heat capacity for the epoxy with $r = 1$ obtained with an underlying cooling rate of 0.5 K min^{-1}, an amplitude of 0.5 K and the indicated periods from 30–240 s.

5. Conclusions

An experimental method is presented for the evaluation of the nonexponentiality parameter β for structural relaxation. It requires the use of temperature modulated differential scanning calorimetry, and is based in the determination of the inflectional slope of the heat capacity C_p^* versus temperature, normalised and nondimensionalised. This

Table 3
Average values of the inflectional slope S (S_{avg}), variation of C_p^* ($\Delta|C_p^*|_{avg}$), normalised inflectional slope, $\bar{S}_{avg}$, normalised and dimensionless inflectional slope, $\bar{S}/\theta$, and parameter β

	$r = 0.8$	$r = 1$	$r = 1.5$
S_{avg} (J $g^{-1}K^{-2}$)	0.047 ± 0.004	0.049 ± 0.004	0.068 ± 0.004
$\Delta\|C_p^*\|_{avg}$ (J g^{-1} K^{-1})	0.55 ± 0.07	0.43 ± 0.02	0.63 ± 0.01
$\bar{S}_{avg}$ (K^{-1})	0.085	0.114	0.108
$\bar{S}/\theta$	0.113	0.128	0.132
β[a]	0.35 ± 0.08	0.39 ± 0.07	0.40 ± 0.04

[a] This parameter β has been calculated from the values of the normalised dimensionless slope and further application of the linear fit of Eq. (6). The uncertainty in β is a result of the experimental uncertainties in the slope, the variation of C_p^*, and the apparent activation energy (shown in Table 1).

method applied to a series of epoxy resins gives results in good agreement with the earlier work in which β was evaluated by an alternative technique.

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