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Effect of cooling rate and frequency on the calorimetric measurement of the glass transition

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Abstract

The glass transition of thermoplastics of different polydispersity and thermosets of different network structure has been studied by conventional differential scanning calorimetry (DSC) and temperature modulated DSC (TMDSC). The cooling rate dependence of the thermal glass transition temperature T_g measured by DSC, and the frequency dependence of the dynamic glass transition temperature T_α measured by TMDSC have been investigated. The relation between the cooling rate and the frequency necessary to achieve the same glass transition temperature has been quantified in terms of a logarithmic difference $\Delta = \log_{10}[|q|] - \log_{10}(\omega)$, where $|q|$ is the absolute value of the cooling rate in K s^{-1} and ω is the angular frequency in rad s^{-1} necessary to obtain $T_g(q) = T_\alpha(\omega)$. The values of Δ obtained for various polymers at a modulation period of 120 s (frequency of 8.3 mHz) are between 0.14 and 0.81. These values agree reasonably well with the theoretical prediction [Hutchinson JM, Montserrat S. Thermochim Acta 2001;377:63 [6]] based on the model of Tool–Narayanaswamy–Moynihan with a distribution of relaxation times. The results are discussed and compared with those obtained by other authors in polymeric and other glass-forming systems.

Keywords: Differential scanning calorimetry; Temperature modulated differential scanning calorimetry; Glass transition

1. Introduction

The glass transition is a universal phenomenon which is observed in a wide variety of non-crystalline materials such as silicate glasses, organic polymers, chalcogenides, as well as in low molecular weight compounds [1]. The glass transition is usually studied by cooling the material from the liquid state, or the so-called rubber-like state, at a sufficiently high cooling rate to avoid crystallization. During this process of vitrification, the system changes from a thermodynamic equilibrium (metastable) state to a non-equilibrium state, that is the glassy state.

Since its introduction in the sixties, differential scanning calorimetry (DSC) has been one of the more widely used techniques to study the glass transition by heat capacity measurements [2]. This technique permits the determination of a glass transition temperature T_g, and it is well known that this transpires to be dependent on the cooling rate. The T_g measured by conventional DSC is sometimes called the thermal glass transition temperature, in order to distinguish it from the dynamic glass transition temperature, which is measured by dynamic techniques such as dynamic mechanical thermal analysis (DMTA) or dynamic electric analysis (DEA) [3–6]. The dynamic glass transition is related to the relaxation process associated with the transition, which is frequency dependent. As this relaxation is usually called the α relaxation, the dynamic glass transition will be denoted as T_α.

Although the use of DSC for the measurement of the complex heat capacity had been demonstrated some 20 years earlier by Gobrecht et al. [7], the technique of temperature modulated differential scanning calorimetry (TMDSC) was first commercialised by TA Instruments, and its potential was demonstrated by Reading and co-workers in 1993 [8,9]. A major advantage is that it enables us to measure in the same experiment both the thermal T_g and the dynamic T_α. For given conditions of underlying cooling rate, amplitude and modulation period, TMDSC allows the determination of the thermal T_g from the total heat flow signal, which is essentially the same signal as that obtained at the same rate by conventional DSC, and also the dynamic T_α. This T_α is determined from the heat capacity signal, which is frequency dependent.

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When the glass forming material is cooled down, it undergoes a vitrification phenomenon, which depends on the cooling rate, and a relaxation process, which depends on the measuring frequency. For a typical underlying cooling rate, the T_α is usually observed at a temperature a few degrees higher than the T_g [3–5,10,11].

There is a relation between the cooling rate and the frequency which has been discussed by many authors [3–6,12–17]. From Donth's fluctuation model of the glass transition [13,14], the frequency can be related to the cooling rate by the following equation:

$$\omega = 2\pi f = \frac{|q|}{a\delta T} \quad (1)$$

where ω is the angular frequency, which can be calculated from the measuring frequency f or the modulation period t_p ($\omega = 2\pi f = 2\pi/t_p$), $|q|$ is the absolute value of the cooling rate, δT is the mean temperature fluctuation (which can be obtained from the dispersion of the relaxation), and a is a constant. TMDSC has been used to determine the cooling rate and the frequency necessary to achieve the same glass transition $T_g = T_\alpha$, but there is some inconsistency regarding the value of the constant a found for different glassy materials: the theoretical value of $a \approx 1$ [13,14,16] should be compared with experimental values of $a = 4.3 \pm 2$ [5] and $a = 6 \pm 3$ in thermoplastics and inorganic glasses [3,4,16], while the quoted uncertainties in the values of a for the individual glasses in Ref. [4] in fact give rise to extreme values of 0.5 ('standard' silicate glass) and 11.0 (polystyrene). Furthermore, when the product $a\delta T$ is considered the discrepancies appear even greater, as will be shown below.

The objective of this paper is to examine carefully the relationship between the cooling rate and the frequency which yield the same glass transition temperature. The techniques used are DSC and TMDSC, which give T_g and T_α respectively. The study is performed using thermoplastics of different polydispersity and thermosets of different network structure.

2. Experimental

2.1. Materials

The thermoplastic samples were a commercial polydisperse polystyrene ($M_w = 293{,}000$, $M_n = 200{,}000$, $M_w/M_n = 1.46$) and an anionic polystyrene, which is practically monodiperse ($M_w = 394{,}000$, $M_n = 392{,}000$, $M_w/M_n = 1.005$). In this work, the samples of polydisperse and monodisperse polystyrene are denoted as PS Pd and PS Md, respectively.

The thermosets were three epoxy-amine systems and a powder coating. The epoxidic systems were an epoxy resin based on diglycidyl ether of bisphenol-A (DGEBA) (Araldite F) with an epoxy equivalent of 188.8 g equiv^{-1}, cured by a polyethertriamine (Jeffamine T403) with an equivalent weight of 81 g equiv^{-1}. Three different epoxy-amine resins were prepared at different stoichiometric ratio $r = |A|/|E|$, where $|A|$ and $|E|$ are respectively the number of gram-equivalents (equiv) of amine and epoxy monomers. One system had the stoichiometric ratio $r = 1$, and the other two were non-stoichiometric with either excess of epoxy ($r = 0.8$) or excess of amine ($r = 1.5$). The samples were cured at 60 °C for 3 h followed by a postcure at 180 °C for 2 h for the stoichiometric ratios 1 and 0.8, and at 150 °C for 2 h for $r = 1.5$.

The powder coating was a physical blend of a lightly branched carboxyl-terminated polyester and triglycidylisocyanurate (TGIC), with a polyester/TGIC weight ratio of 93/7, which was fully cured by submitting the samples to a heating ramp of 10 K min^{-1} up to 260 °C. In this process, an increase of 8 °C was observed in the T_g of the powder coating [18].

2.2. Thermal analysis

For the polymer samples described in the preceding section, the thermal glass transition temperatures (equal to the fictive temperature) measured on heating in the DSC at 10 K min^{-1} (immediately after cooling at −10 K min^{-1}) and the dynamic glass transition temperature measured by TMDSC using a modulation period of 60 s (amplitude of 0.5 K and underlying cooling rate of −1 K min^{-1}) are shown in Table 1. Two points should be stressed here concerning the thermal glass transition measured by DSC. First, ideally it should be measured on cooling, but for reasons associated with temperature calibration it is usual to deduce it from measurements made during heating, making use of the concept of fictive temperature, explained in more detail below. Second, the glass transition temperature depends on the cooling rate (as does the fictive temperature also), and therefore any quoted value of T_g should be accompanied by the associated cooling rate, as is the case in

Table 1
Thermal and dynamic glass transition temperatures, reduced apparent activation energies, logarithmic differences for a period of 120 s, cooling rates to obtain $T_g = T_\alpha$ for a period of 120 s, and experimental values of $a\delta T$

	T_g DSC (°C)[a]	T_α $\lvert C_p^*\rvert$ (°C) (60 s)	$E_{a(DSC)}/R$ (kK)[b]	$E_{a(TMDSC)}/R$ (kK)[b]	Δ(10, Ks^{-1}, rad s^{-1}) (120 s)	q for $T_g = T_\alpha$ (K min^{-1})	$a\delta T$ (K)
PS Md	105.1	105.2	91	91	0.21	5.0	1.6
PS Pd	94.6	96.9	81	96	0.81	20.8	6.4
Powder coating	78.2	79.2	127	111	0.48	9.5	3.0
Epoxy $r = 0.8$	62.6	62.3	86	87	0.14	4.2	1.4
Epoxy $r = 1$	85.85	86	122	101	0.44	9.5	2.7
Epoxy $r = 1.5$	55.7	56.6	92	81	0.41	8.1	2.6

[a] These values of T_g were obtained as fictive temperatures on heating at 10 K min^{-1} immediately after cooling at −10 K min^{-1}.

[b] Experimental error ± 10 kK.

Table 1, where the choice of $-10\ \mathrm{K\ min}^{-1}$ is somewhat arbitrary.

The calorimetric analyses, both conventional DSC and TMDSC, were performed using a Mettler Toledo 821e equipped with an intracooler. The temperature and heat flow calibrations were made with standards of indium and zinc. The sample weight was approximately 6–8 mg and all the calorimetric scans, for both DSC and TMDSC, were made with a nitrogen gas flow of $50\ \mathrm{mL\ min}^{-1}$. The same sample was used for both the DSC and TMDSC analyses.

In order to study the effect of the cooling rate on T_g by conventional DSC, the samples were submitted to so-called intrinsic cycles (cooling and heating through the transition region without any annealing at the lower temperature). The system at a temperature above the T_g was cooled at a controlled rate q through the transition region until a lower temperature within the asymptotic glassy region was obtained, and was then immediately heated at a rate of $10\ \mathrm{K\ min}^{-1}$. These cycles were successively performed at several cooling rates from -20 to $-0.5\ \mathrm{K\ min}^{-1}$. Since there is no annealing at the lower temperature, the glass transition temperature of the glass formed at any cooling rate is equal to the fictive temperature of the glass at the start of the heating scan in the DSC. The fictive temperature is the temperature at which the particular glassy structure would appear to be in equilibrium if immediately removed there [19], and it can be evaluated from the DSC heating scan using software based upon the 'equal areas' algorithm proposed by Richardson and Savill [20] and by Moynihan et al. [21]. A value of the fictive temperature was calculated from the heating scan for each cooling rate. As is shown subsequently in this paper, these values allowed the calculation of the apparent activation energy.

The TMDSC measurements were performed at an average cooling rate of between -1 and $-0.25\ \mathrm{K\ min}^{-1}$, with an amplitude of 0.5 K and a period of between 30 and 300 s, which correspond to frequencies of 33 and 3.3 mHz, respectively. It is important that the absolute value of the cooling rate be reduced as the period increases; thus, for periods from 30 to 90 s the maximum cooling rate was $-1\ \mathrm{K\ min}^{-1}$, for periods from 120 to 180 s the cooling rate was $-0.5\ \mathrm{K\ min}^{-1}$, while for periods from 240 to 300 s the cooling rate was $-0.25\ \mathrm{K\ min}^{-1}$. The STAR software was used for the evaluation of the data from the alternating DSC (ADSC), which is the TMDSC technique commercialised by Mettler Toledo. In order to calibrate the heat flow signal, correct the amplitude and eliminate the cell asymmetry, ADSC requires a blank with an empty pan on the reference side and an empty pan plus a lid on the sample side, under the same conditions as for the sample measurement. For ADSC measurements, τ_{lag} was set to 0.

A Fourier analysis of the heat flow cycles enabled the total heat flow, the heat capacity and the phase angle to be obtained. According to the approach of Schawe [22], a complex heat capacity may be defined as $C_p^* = C_p' - iC_p''$, where C_p' and C_p'' are respectively the real and imaginary parts of the heat capacity. The modulus of the heat capacity is defined as the ratio of the heat flow amplitude, A_ϕ, and the heating rate amplitude, $A_q (A_q = A_T\omega)$:

$$|C_p^*| = \frac{A_\phi}{A_q} \tag{2}$$

The real and imaginary parts of the heat capacity are respectively defined as $C_p' = |C_p^*|\cos\delta$ and $C_p'' = |C_p^*|\sin\delta$, where δ is the phase angle, which is very small in the case of a relaxation process associated with a glass transition. As a consequence, the values for $|C_p^*|$ and C_p' are practically indistinguishable, and the shape of C_p'' is very similar to that of the phase angle. In the glass transition interval, the $|C_p^*|$ signal shows a sigmoidal variation with temperature, its value being frequency dependent but independent of the underlying cooling rate provided that there is no interaction of the vitrification process. In this paper, the dynamic glass transition T_α of the different polymers was determined from the $|C_p^*|$ signal as the temperature at which the value of $|C_p^*|$ lies midway between its asymptotic glassy and liquid-like values.

3. Results

Fig. 1 shows the intrinsic cycles for the monodisperse polystyrene that permit, for each cycle, the determination of the fictive temperature, T_f, of the glass at the start of the heating scan, which is the same as the glass transition temperature for the previous cooling rate. The dependence of T_f on the cooling rate in these intrinsic cycles allows the determination of the apparent activation energy, E_a, using the following equation proposed by Moynihan et al. [21]:

$$\frac{E_a}{R} = -\left[\frac{\partial \ln|q|}{\partial(1/T_f)}\right]_{\Delta H=0} \tag{3}$$

where $\Delta H = 0$ means that there is no enthalpy loss due to physical ageing because the heating is performed immediately

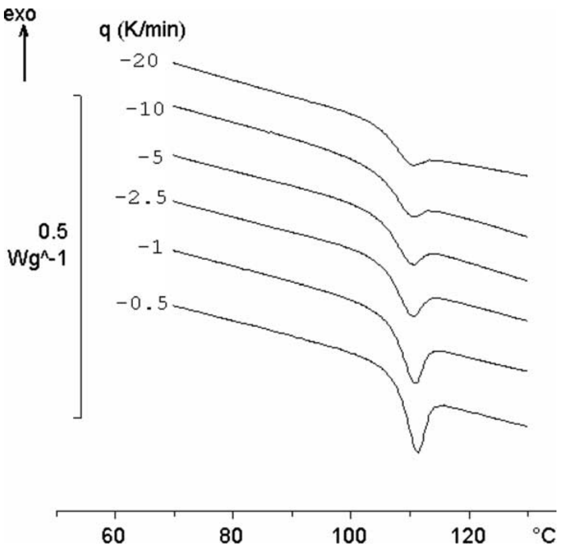

Fig. 1. DSC curves for the monodisperse polystyrene obtained by heating at $10\ \mathrm{K\ min}^{-1}$ immediately after cooling at the rates indicated in $\mathrm{K\ min}^{-1}$: -20, -10, -5, -2.5, -1, -0.5.

after the cooling. The values of this apparent activation energy determined by DSC, $E_{a(DSC)}$, are shown in their reduced form $E_{a(DSC)}/R$ in Table 1 for the different polymeric systems. A typical experimental uncertainty in these values of reduced apparent activation energy is of the order of ±10 kK. It can be seen that the epoxy-amine resin at the stoichiometric ratio and the powder coating show the highest values of $E_{a(DSC)}$. These values are comparable to those found in other epoxy-diamine systems, whose values lie between 97 and 125 kK [23], or in an epoxy-anhydride system, whose value is 132 kK [24].

On the other hand the dynamic glass transition decreases as the modulation period increases, or equivalently as the measuring frequency decreases, as illustrated in Fig. 2 for the non-stoichiometric epoxy-diamine resin. In fact, the dependence of the log of the frequency on the reciprocal of the temperature is nonlinear and fits the Vogel–Tammann–Fulcher (VTF) equation. Nevertheless, over a narrow range of frequencies, such as is the case for TMDSC where the interval of frequencies is between 3.3 and 33 mHz, a linear relation between the log of frequency and the reciprocal of the temperature may be obtained. The negative slope of the resulting straight line is a reduced apparent activation energy, $E_{a(TMDSC)}$, the values of which are similar to those obtained by DSC intrinsic cycles [25,26], as can be seen in Table 1. The high values of $E_{a(DSC)}$ and $E_{a(TMDSC)}$ for the stoichiometric epoxy resin ($r=1$) and the powder coating indicate a weak dependence of the glass transition temperature on the cooling rate and the frequency, respectively, for these polymers.

As an illustration of the difference between the thermal glass transition (vitrification) on cooling in DSC and the dynamic glass transition during cooling in TMDSC, we show these two responses for the monodisperse polystyrene sample in Fig. 3. The DSC cooling curve was obtained for a cooling rate of $-10\ \mathrm{K\,min^{-1}}$, while the TMDSC curve was obtained for an underlying cooling rate of $-1\ \mathrm{K\,min^{-1}}$, an amplitude of 0.5 K, and a period of 60 s, conditions for which $T_g=T_\alpha$, according to Table 1. It should be noted, however, that the DSC curve does not have a calibrated temperature scale, as the calorimeter was calibrated for the determination of the fictive temperature during heating rather than cooling, and it is for this reason that the two curves do not display the same transition temperature, the DSC curve being displaced by 2.5 K to lower temperatures. Nevertheless, the comparison of the DSC and TMDSC curves provides a useful illustration of the important difference between the gradual vitrification process seen in the DSC curve and the much more abrupt change from a liquid-like response to a glassy response seen in the TMDSC curve as the temperature is reduced.

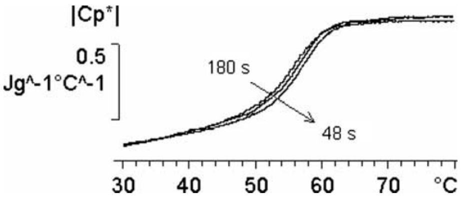

Fig. 2. Effect of the modulation period on the modulus of the heat capacity $|C_p^*|$, for the non-stoichiometric epoxy-diamine system ($r=1.5$), obtained at an underlying cooling rate of $-0.5\ \mathrm{K\,min^{-1}}$, an amplitude of 0.5 K, and the indicated modulation periods of 48, 60 and 180 s.

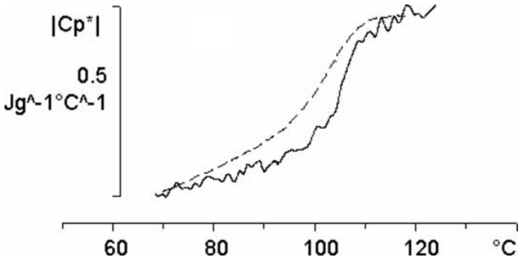

Fig. 3. Superposition of conventional DSC cooling scan (dashed line) at $-10\ \mathrm{K\,min^{-1}}$ and TMDSC scan (full line) with underlying cooling rate $-1\ \mathrm{K\,min^{-1}}$, amplitude 0.5 K, and period 60 s, obtained for monodisperse polystyrene. Note that temperature scale for DSC scan is not calibrated. The original $\mathrm{W\,g^{-1}}$ ordinate scale for DSC was divided by the heating rate ($10\ \mathrm{K\,min^{-1}}$) to superpose on the $\mathrm{J\,g^{-1}\,K^{-1}}$ ordinate scale for TMDSC.

The separate effects of the cooling rate and the frequency on the glass transition temperature are combined in Figs. 4 and 5 for the different polymeric systems studied here, where the log of the absolute cooling rate $|q|$ and the log of the angular frequency are plotted against the reciprocal of each of the glass transition temperatures, T_g and T_α, respectively. Note that the left hand axis (log frequency) and right hand axis (log cooling rate) both have the same scale. In theory, therefore, it should be possible to shift the data for TMDSC vertically to superpose onto the data for DSC in order to establish the corresponding values of frequency and cooling rate that will yield the same glass transition temperature (dynamic and thermal respectively). As was shown above, however, while both dependences appear linear and can be fitted to an Arrhenius relationship within the range of experimental variables used, the apparent activation energies for TMDSC and DSC can differ slightly (cf. Table 1), though not significantly if we accept the typical uncertainty of ±10 kK for both $E_{a(DSC)}$ and $E_{a(TMDSC)}$. This means that the same vertical shift will not lead to superposition of these lines over the whole temperature range. Accordingly, we arbitrarily select an angular frequency ω of $0.0524\ \mathrm{rad\,s^{-1}}$ (modulation period of 120 s) for which the dynamic glass transition temperature is T_α, and determine the cooling rate q (in units of $\mathrm{K\,s^{-1}}$) for which T_g is equal to this value of T_α. From this pair of values of ω and q we evaluate the logarithmic difference Δ defined as:

$$\Delta(10,\ \mathrm{Ks^{-1}},\ \mathrm{rad\,s^{-1}}) = \log_{10}[|q|] - \log_{10}[\omega] \tag{4}$$

The nomenclature for Δ is used specifically to distinguish this value of Δ from others that would result when different units are used for q and/or ω, or when a different logarithmic base is used [6]. The procedure is illustrated for the polydisperse polystyrene in Fig. 4.

The values of Δ obtained thus for the various polymers included in the present study are listed in Table 1, where it can be seen that they lie between 0.2 and 0.8, approximately. For further reference, the actual values of the cooling rates required to achieve $T_g=T_\alpha$ for a period of 120 s are also listed in

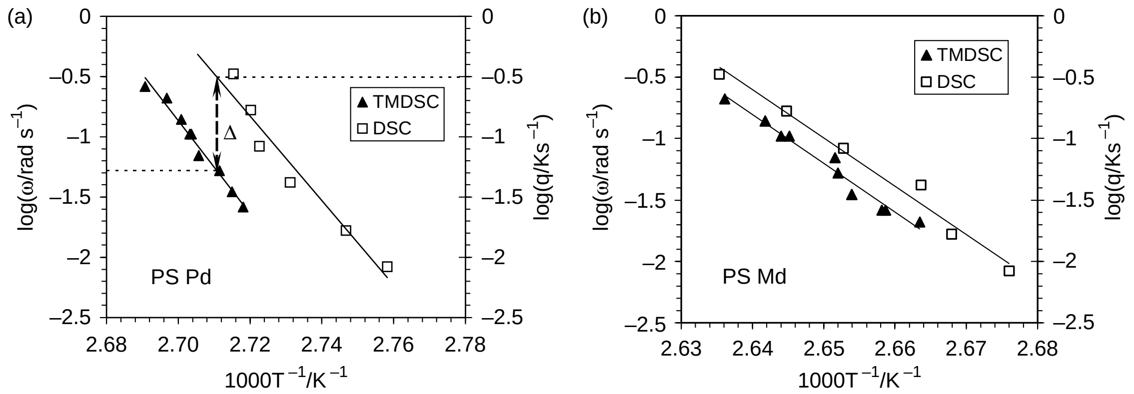

Fig. 4. Dependence of the dynamic T_α(▲) and the thermal T_g (□) on $\log_{10}$(angular frequency) and $\log_{10}$(cooling rate), respectively, for the thermoplastic polymers: polydisperse (PS Pd) and monodisperse polystyrene (PS Md), respectively. The lines correspond to the linear regression for each set of data.

Table 1. Clearly, the larger is the logarithmic difference Δ, the faster must be the cooling rate in order to achieve a thermal glass transition temperature equal to the dynamic glass transition temperature. More generally, Δ represents in some way the relationship between the thermal and dynamic glass transitions. In this respect, Schick and co-workers [3,4,16] have used Donth's fluctuation dissipation theorem for the glass transition [5,13,14] to derive the relationship given by Eq. (1). It is a simple matter to determine $a\delta T$ from Δ, therefore, and the resulting values are listed in the last column of Table 1.

Furthermore, the mean temperature fluctuation, δT, can be estimated from the TMDSC experiments, being given approximately as the half-width of the peak in the phase angle [4,16]. As an example, Fig. 6 shows the phase angle, corrected for heat transfer effects [27,28], obtained for the stoichiometric epoxy resin on cooling at -0.5 K min^{-1} with an amplitude of 0.5 K and a period of 60 s. From the peak half-width we obtain an approximate value of 5 K for δT for this sample, and hence using the value of $a\delta T$ from Table 1 we estimate $a \approx 0.5$. Although a is considered to be a constant of

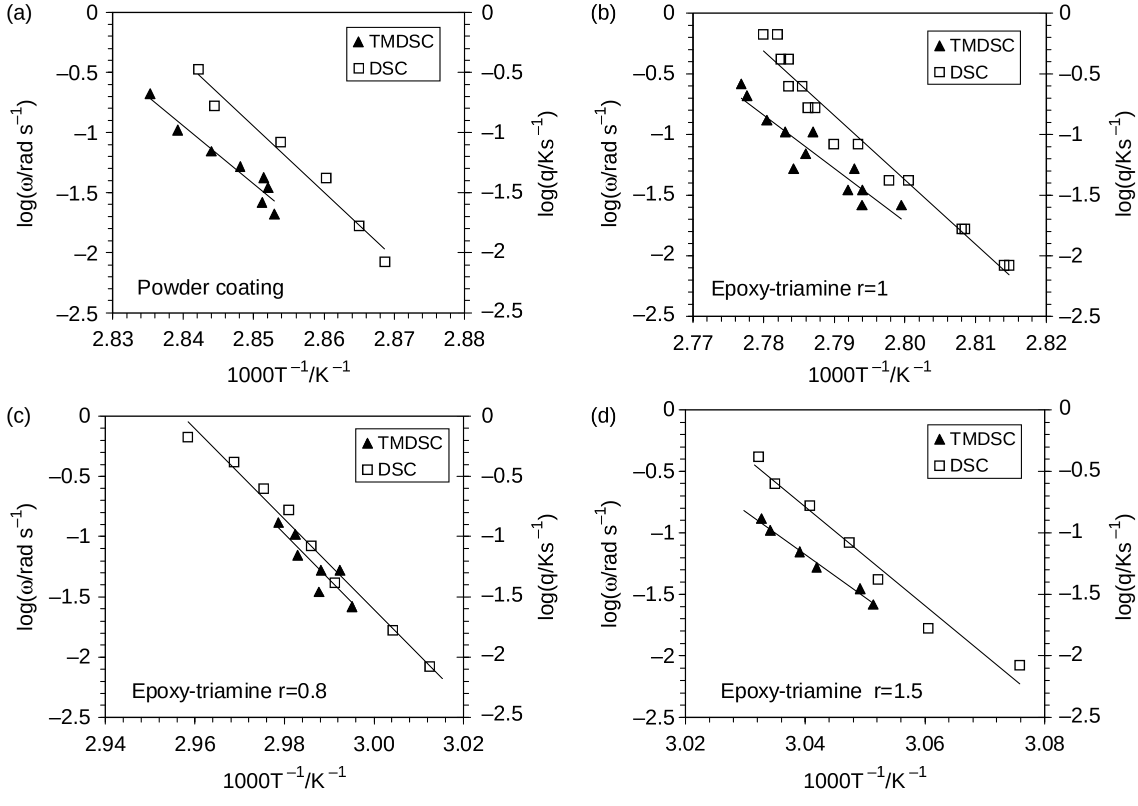

Fig. 5. Dependence of the dynamic T_α(▲) and the thermal T_g (□) on $\log_{10}$(angular frequency) and $\log_{10}$(cooling rate), respectively, for the thermosets: powder coating, epoxy-triamine with stoichiometric ratio ($r=1$) and non-stoichiometric ratios ($r=0.8$ and $r=1.5$). The lines correspond to the linear regression for each set of data.

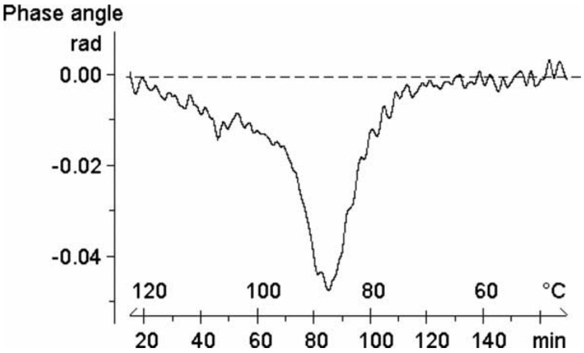

Fig. 6. Corrected phase angle for the epoxy-triamine with stoichiometric ratio ($r=1$) obtained by TMDSC on cooling at $-0.5\ \mathrm{K\ min^{-1}}$ with an amplitude of 0.5 K and a period of 60 s. The half-width of the peak is 5 K.

the order of unity [13,14], values reported are generally somewhat larger, usually in the range 6 ± 3 [3,4,16], which is significantly greater than our value of 0.5. Furthermore since typical values of $a\delta T$ are considered to lie in the range 15 ± 5 K [3,4] it is interesting to enquire why the experimental values listed in Table 1 are well outside this range.

Recently, Hutchinson and Montserrat [6] performed a numerical simulation of the glass transition region as observed by TMDSC, from which they obtained values of $\varDelta(10,\ \mathrm{Ks^{-1}},\ \mathrm{rad\ s^{-1}})$ and $a\delta T$ for glasses with different structural parameters. The simulation was based on the Tool–Narayanaswamy–Moynihan (TNM) model with a distribution of relaxation times based on the stretched exponential response function of the Kohlrausch–Williams–Watts (KWW) form. The structural parameters investigated were the non-exponentiality parameter β, which is inversely related to the width of the spectrum of relaxation times, and the non-linearity parameter x, which describes the relative contribution of temperature and structure to the relaxation time [29]. The simulation gives values of $\varDelta(10,\ \mathrm{Ks^{-1}},\ \mathrm{rad\ s^{-1}})$ that increase as the values of β and x decrease (greater non-exponentiality and non-linearity, respectively). More precisely, values of $\varDelta$ between 0.36 and 1.34 are found for the pair of values $\beta=1$, $x=1$ and $\beta=0.2$, $x=0.2$, respectively, which are limiting values of β and x used in the simulation. In particular, for a glassy system with 'typical' values of $\beta=0.4$ and $x=0.4$, the simulation yields $\varDelta(10,\ \mathrm{Ks^{-1}},\ \mathrm{rad\ s^{-1}})=0.92$. This result is somewhat greater than all the experimental values found for the polymers in this work (Table 1), and particularly so for the monodisperse polystyrene and the epoxy with $r=0.8$; indeed, the experimental values of $\varDelta(10,\ \mathrm{Ks^{-1}},\ \mathrm{rad\ s^{-1}})$ for these two polymers lie below the lower limit of theoretical simulation values (0.36) obtained for $\beta=1$ and $x=1$. Some possible reasons for this discrepancy are now considered.

4. Discussion

Before proceeding to examine our present results in more detail, though, it is useful to compare them with other results presented in the literature. In particular, Schick and co-workers [4] have reported values of the logarithmic difference (referred to as log Y by these authors) for polyetherketone, polystyrene, polyvinyl acetate, poly(n-butyl methacrylate) with 2% styrene, semicrystalline polyetheretherketone (PEEK), and for three inorganic glasses. For all these glassy materials, these authors found $\varDelta(10,\ \mathrm{Ks^{-1}},\ \mathrm{rad\ s^{-1}})$ to lie between 1.0 and 2.0 (when the quoted uncertainties in these values are taken into account). It is immediately evident that these values of $\varDelta$ are much greater than ours (Table 1). Moreover, many of these values are beyond the upper limit of our theoretical simulation values (1.34) obtained for $\beta=0.2$ and $x=0.2$, and most are near this limit. In contrast, Jiang [30] finds $\varDelta(10,\ \mathrm{Ks^{-1}},\ \mathrm{rad\ s^{-1}})$ to be 0.74 for PS and 1.17 for polycarbonate (PC), in much closer agreement with our values.

The use by Schick et al. of a triangular (saw-tooth) rather than sinusoidal temperature modulation is of no consequence, since they analysed the first harmonic only of the Fourier transform. Similarly, their use of a smaller temperature amplitude (0.2 K) compared with ours (0.5 K) should also be of no consequence, since the temperature amplitude does not have an influence provided that it remains sufficiently small, as we believe is the case here. On the other hand, their use of a slower underlying cooling rate ($-0.5\ \mathrm{K\ min^{-1}}$) compared with ours, which in some cases is $-1\ \mathrm{K\ min^{-1}}$, for the same modulation period of 60 s, could play a significant role.

Under ideal circumstances, from the point of view of identifying the dynamic glass transition separately from the thermal transition, these two transitions should be completely separated. This situation can be approached in TMDSC either by increasing the frequency of modulation, which shifts the dynamic T_g to higher temperatures, or by reducing the underlying cooling rate, which shifts the thermal T_g to lower temperatures. The former is not practical, since there is a limit to the extent to which the modulation period can be reduced (usually considered to be 30–60 s) while retaining control over the temperature of the sample. Accordingly, in this respect, a reduced cooling rate offers the better solution, and the slower cooling rate used by Schick et al. means that their analysis is likely to have better separated the dynamic and thermal transitions, all other things being equal.

However, it must be pointed out that all other things are not equal, and in particular that this reasoning must take into account the effects of different values of the parameters β and x which control the kinetics of structural relaxation. The most significant of these effects is that of β, for which a reduction in β leads to a broadening of both the dynamic and thermal transitions. This implies that glasses with lower values of β would require an ever greater separation of the thermal and dynamic transitions if they are not to interact with each other. An interaction of this kind would result in an average relaxation time, at any temperature, less than it would have been if the glass-former had remained in the liquid-like state, and hence would result in a broadening of the dynamic transition as the reduction in $|C_p^*|$ towards its glassy state value would be inhibited. The consequence of this would be a reduction in T_α as measured by the midpoint of the dynamic transition, and hence a reduction in the value of $\varDelta$.

A further consequence of this interaction would be that the apparent activation energy derived from the frequency dependence of T_α would be smaller than that derived from the cooling rate dependence of T_g. Although in certain cases this might appear to be evident in our data, in particular for the powder coating and the epoxies with $r=1$ and $r=1.5$ (Fig. 4), as well as in the data obtained for PS and PC by Jiang [30], who used similar periods and cooling rates to those used in the present work, this conclusion would be difficult to justify in the light of the estimated experimental error of ±10 kK given in Table 1. Furthermore, such an interpretation would be clouded by a non-Arrhenius temperature dependence, since the downward curvature of a typical VTF expression would naturally imply a lower apparent activation energy for the dynamic transition occurring in a higher temperature interval. Indeed, Schick and co-workers [4,16] make use of just such a non-Arrhenius fit to their data when obtaining their values of Δ.

The product $a\delta T$, which is related to the logarithmic difference, can be calculated by Eq. (1) or directly by the relation $\Delta=\log_{10}(a\delta T)$. The calculated values of $a\delta T$ for the polymers shown in Table 1 are between 1.4 and 3 K, except for the polydisperse polystyrene where it is 6.4 K. The theoretical values obtained by simulation can be found in Table 2 of Ref. [6], where it can be seen that they lie between 2.3 K (for $\beta=1$ and $x=1$) and 21.9 K (for $\beta=0.2$ and $x=0.2$). In contrast, Schick et al. [4,16] found values of $a\delta T$ ranging from 10 to 80 K for different amorphous thermoplastics (when the uncertainties in their log Y values are included), while their values for $a\delta T$ for semicrystalline PEEK and for inorganic glasses could be as large as 100 K.

The rather low values of $a\delta T$ found here (1.4 K for epoxy with $r=0.8$ and 1.6 K for PS Md) are believed to arise from an interaction between the dynamic and thermal transitions. This was discussed above with respect to the selection of cooling rates and modulation period, and serves as a useful illustration of the need to pay particular attention to these experimental conditions in order to obtain unequivocal results. However, this may not always be as straightforward as might appear, since the extent of interaction between dynamic and thermal transitions is influenced by the very same parameter, $a\delta T$, that is being determined in order to compare the behaviour of different glass-formers. Similar comments about the influence of vitrification on the thermal relaxation transition were made earlier by Schawe [31].

On the other hand, the deviations found by Schick and co-workers, with values of $a\delta T$ greatly in excess of the typical 15 ± 5 K, require further comment. Although these authors argue that the constraint imposed by the crystalline lamellae in PEEK restricts the mobility of the amorphous regions and leads to a broadening of the transition and hence a larger value of δT, the average temperature fluctuation, this would not appear to explain the large values found for poly(*n*-butyl methacrylate), nor for the inorganic glasses. Indeed, in the context of the concept of strength and fragility of glass-formers, it is the more fragile polymers such as PVC and PMMA which display a broad relaxation. However, the results found by Schick and co-workers [4] suggest that, in their inorganic glasses, it is the silicate glasses, denominated DGG-STG1 (a 'standard' glass; the details of the composition can be found in Ref. [4]) and Na_2O–$2SiO_2$ and normally considered to be strong glass-formers, which in fact display the greatest average temperature fluctuations, in other words the widest transitions, while the calcium potassium nitrate (CKN) glass, normally considered to be a fragile glass former, has a much sharper transition as evidenced by a smaller value of δT. This provides a good illustration of the anomalies that remain to be resolved in respect of the comparison of the dynamic and thermal glass transitions.

It is also interesting to note that the value of $a\approx0.5$ found here for the stoichiometric epoxy resin is rather closer to the anticipated value of unity [13,14] than are the values of a derived from the $a\delta T$ values quoted by Schick and co-workers [3,4,15]. While we have not evaluated δT for the other polymers in the present study, the TMDSC phase angle curves for these other polymers do not show significant narrowing or broadening in comparison with that for the stoichiometric epoxy resin, and for this reason we believe that values of a would reflect closely the variations displayed by $a\delta T$, and hence would remain close to unity for all the polymers in this study.

Furthermore, values of a close to but slightly less than unity also emerge from our earlier theoretical modelling study [6]. Estimating δT as the half-width of the phase angle peaks in Fig. 9 of Ref. [6], for which $\beta=0.4$ and $x=0.4$, one finds $\delta T\approx6$ K. For these same values of β and x, Table 1 in the same reference gives $a\delta T=4.16$ K, from which one obtains $a\approx0.7$.

The values of Δ or $a\delta T$ allow the calculation of the frequency which corresponds to a given cooling rate in order to achieve the same temperature of glass transition. Assuming a rate of 10 K min^{-1}, which is the rate most frequently used in DSC, an equivalent frequency has been calculated for the polymers in this work. From the frequency values, the corresponding time scale may be obtained. The calculation gives values of the time scale from 50 s for the non-stoichiometric epoxy ($r=0.8$) to 230 s for the polydisperse polystyrene. The monodisperse PS shows a value of 60 s, and the other thermosets show values of 121 s for the powder coating, 106 s for the stoichiometric epoxy and 92 s for the epoxy with $r=1.5$. On the other hand the values of $a\delta T$ quoted by Schick lead to time scales between 475 s (PEEK) and 1900 s (PnBMA). According to the commonly accepted guideline that an amorphous polymeric material with a time scale of about 100 s may be regarded operationally as a glass formed at a cooling rate of about 10 K min^{-1}, it seems that the time scales obtained for the polymers of the present work are consistent with the vitrification of the system.

In summary, we would like to emphasize that the dynamic and thermal transitions are different phenomena but that the latter can have an influence on the former if the experimental conditions are not carefully selected. In some thermal analytical techniques, such as dielectric thermal analysis, for example, the frequency range is often sufficiently high to ensure that there is no interaction between dynamic and thermal transitions. On the other hand, for TMDSC this is generally not the case, and the same may also be true for dynamic mechanical thermal analysis, for which the loss and storage moduli and tan δ may be influenced by an underlying thermal glass transition (a typical cooling or heating rate being 4 K min^{-1}), particularly when low frequencies are used.

The relationship between these two phenomena, quantified here by the logarithmic shift Δ, has important implications for a physical understanding of the glass transition, as has been pointed out in particular by Donth [5,13,14] in respect of his fluctuation dissipation ideas. For example, despite the difficulties associated with the interaction of the thermal and dynamic transitions and the sensitivity of Δ to the experimental uncertainty in T_α, it is quite clear that there are 'intrinsic' differences in the values of Δ obtained for the various polymers studied here. In fact, it was mentioned above that the value of $a\delta T$ for polydisperse polystyrene (6.4 K) is in good agreement with the theoretical modelling calculations, which give $a\delta T=$ 7.3 K when the values of $\beta=0.456$ and $x=0.48$ are used (taken from Refs. [32,33], respectively). If we overlook for the present the 'anomalously' low value of $a\delta T=1.6$ K for monodisperse polystyrene, then it is pertinent to ask whether it is significant that the cross-linked systems all have values of $a\delta T$ noticeably smaller than that for the polydisperse thermoplastic. The data available here are insufficient to answer this question, particularly in the light of experimental uncertainty and the problem of the interaction of the dynamic and thermal glass transitions, but we believe that the question is worth asking and that the response to it could be enlightening in respect of the glass transformation process.

Finally, although our earlier theoretical analysis [6] interprets these variations in Δ in terms of some parameters (β and x) of the phenomenological TNM model, there are some indications that the analysis may be inadequate despite its ability to describe rather well the important features of the glass transition, both thermal and dynamic. For example, the usefulness and indeed the appropriateness of a phenomenological model such as TNM with its Arrhenius temperature dependence is nowadays often called into question, and we note in this context the analysis of TMDSC made by Schick and co-workers [34] where they make use of an 'extended' TNM model in which the Arrhenius temperature dependence is replaced by a VTF dependence. An alternative would be to investigate other theoretical approaches, such as those based upon ideas of configurational entropy [35]. It remains to be seen what interpretation such alternative approaches can place upon the significantly larger values of Δ (or of $a\delta T$) obtained by Schick and co-workers [4,16], which fall outside the ranges of values predicted from the theoretical analysis [6] and which call for an adequate explanation.

5. Conclusions

The use of DSC and TMDSC for a range of polymeric glass-forming materials has shown clearly the different phenomena associated with thermal and dynamic glass transitions. Comparison of the transition temperatures T_g and T_α, respectively, permits the evaluation of a logarithmic shift Δ which quantifies the relationship between cooling rate and frequency. Comparison of our experimental results with an earlier theoretical analysis indicates that, in some cases, the choice of underlying cooling rate may have led to an interaction of the thermal transition with the dynamic transition, resulting in a reduction of the values of Δ obtained. This possible interaction is an important aspect which may have been overlooked in other thermal analytical techniques such as DMTA. Nevertheless, taking into consideration this possible interaction, our results are largely consistent with the earlier theoretical treatment and suggest that there are intrinsic differences between the various glass-formers in respect of the correspondence between the cooling rate and frequency dependences of the thermal and dynamic glass transitions, respectively. These intrinsic differences could provide important information regarding the physical phenomena underlying the glass transition, but this approach is somewhat hindered by the rather great sensitivity of Δ to experimental uncertainty in the transition temperatures as well as by possible inadequacies in the theoretical treatment.

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