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STUDYING THE GLASS TRANSITION BY DSC AND TMDSC

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Abstract

First, the principal features of the glass transformation process in polymers are reviewed, and then it is shown how they are manifest in conventional DSC, and the quantitative analysis of typical DSC data is discussed in terms of the Tool–Narayanaswamy–Moynihan (TNM) model. Subsequently, the way in which the glass transition is manifest in Temperature Modulated DSC is presented, and the effects of both experimental and material parameters are discussed. In conclusion, the two techniques are compared in terms of the information they provide about the glass transformation process.

Keywords: DSC, glass transition, TMDSC

Introduction

The glass transformation process is common to many different classes of materials, including metals, polymers and inorganic compounds. The most widely used technique for studying the glass transition is differential scanning calorimetry (DSC), though there are several other techniques available including, for example, dilatometry and dynamic mechanical and dielectric spectroscopy. Recently, the technique of Temperature Modulated DSC (TMDSC) has been developed, with potential for enhanced analysis of many aspects of the thermal response of materials, including in particular the glass transition. In this paper we review the general features of the response of glasses in both DSC and TMDSC and show how they can be modelled theoretically and what information can be gained from these analyses. Although this treatment will be illustrated mainly by reference to the response of polymer glasses, this should not conceal the fact that most of the observations made here are common to all glass-forming systems. We begin the review by describing the principal features of the glass transition as they are manifest in DSC.

Principal features

The universality of the glass transformation process implies that there are a number of features which are common to all materials. We review here five which may be considered to be the most representative.

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Non-equilibrium state

The glassy state is a non-equilibrium state. The implication of this is that a glass in any state will spontaneously attempt to approach equilibrium, and this is easily demonstrated by the comparison of two DSC scans, being the last stages of two separate thermal cycles, as follows. The first cycle involves cooling at rate q_1 from an equilibrium state above the glass transition temperature T_g, annealing at temperature T_a some few degrees below T_g, and then reheating at rate q_2 in the DSC. The second cycle is identical except for omitting the isothermal annealing stage. The two DSC scans are quite different: the first has a significant endothermic peak superimposed on the increase in heat capacity from a glassy (C_{pg}) to a liquid-like (C_{pl}) value, whereas the second has only a very small peak [1, 2]. This behaviour is most clearly represented on an enthalpy *H vs*. temperature *T* plot, such as that shown in Fig. 1. The cooling stage of each cycle defines $T_g(q_1)$ in the usual way; the annealed glassy state is one of lower enthalpy than the unannealed state, because the non-equilibrium glass attempts to approach an equilibrium state defined by H_∞, and may be identified by the fictive temperature T_f, which may be found by the methods of Richardson [3] or Moynihan [4]; the reheating scans in the DSC follow quite different paths, with the annealed glass showing a significant 'overshoot', as a result of the different initial states before heating.

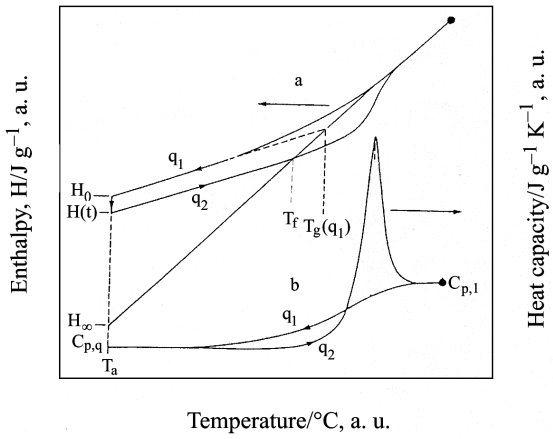

Fig. 1 Schematic illustration of the isobaric variation of a – enthalpy *H* and b – heat capacity C_p with temperature *T* during a typical thermal cycle involving cooling, annealing, and reheating

Rate (or time) dependence

The glass transformation process, and in particular the temperature identified as the glass transition temperature T_g, is rate dependent. This is easily demonstrated by cooling the same glass-former at different rates through its transformation region before scanning in the DSC at a common rate (for example 10 K min^{-1}). Such experiments, illustrated for example by Fig. 8 in [5], show an endothermic peak that in-

creases in magnitude as the cooling rate decreases, which can be interpreted on an *H–T* diagram to demonstrate that $T_g(q_1)$ decreases as the cooling rate q_1 decreases. One can also note that for the faster cooling rates, and in particular those that exceed the heating rate, the peaks are small in size and the peak temperature initially decreases before increasing as the cooling rate decreases; such peaks are called 'upper peaks', and will be referred to again later in the evaluation of the so-called non-exponentiality parameter β.

Relaxation process

If the glass is held isothermally, it will exhibit a relaxation process. This is, in fact, nothing other than the approach to equilibrium mentioned earlier, and is clearly evident in the DSC scans on glasses annealed for different lengths of time, such as those shown in Fig. 2. As the annealing time increases, the endothermic peaks increase in magnitude and shift to higher temperature. The enthalpy loss associated with each annealing time is obtained from the difference in areas under the annealed and unannealed scans, and usually shows a rather linear dependence on logarithmic annealing time within a typical experimental time scale. This observation forms part of the so-called peak shift method for the evaluation of a second material parameter (in addition to β mentioned above), the non-linearity parameter *x*. In fact, these two parameters describe the kinetics of the relaxation process, and are the last two features of common interest.

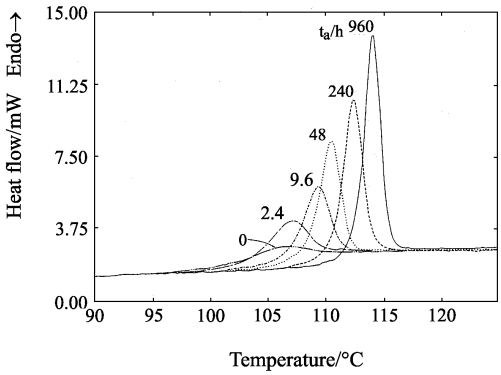

Fig. 2 DSC scans on polystyrene, illustrating the shift of the peak endotherm temperature with annealing time, indicated against each curve. The experimental conditions were: q_1=20 K min^{-1}, T_a=85°C, q_2=10 K min^{-1}. Reproduced from [6], with permission

Non-exponentiality

The isothermal relaxation process described above is non-exponential. This is most clearly demonstrated by reference to dilatometric data, for example the classic experiments of Kovacs [7], since DSC data are always more scattered than volume recovery data in this respect. Examination of the inflectional slope of such isothermal relaxation data following a quench from equilibrium at a higher temperature shows that

the interval between the onset and endset times of the sigmoidal relaxation curve is significantly greater than the 1.18 decades of an exponential decay.

Non-linearity

The evidence for non-linearity in the relaxation kinetics is not so obvious from a direct observation of DSC traces, though it is in fact implied by the shift of the peak temperature with increasing annealing time, mentioned earlier and illustrated in Fig. 2. In contrast, it is very clearly evident from dilatometric studies, again particularly from the classic work of Kovacs [7], in which initial departures from equilibrium of equal magnitude but opposite sign lead to quite different relaxation responses. The implication of non-linearity in the kinetics is that the relaxation time depends not only on the temperature T but also on the glassy structure, identified by the fictive temperature T_f.

In closing this review of the principal features of the manifestation of the glass transition, it can be noted that Malek [8] has shown how these last two features of non-exponentiality and non-linearity can be separated in an appropriate analysis of isothermal relaxation data. Almost certainly, though, the relatively large scatter in DSC data means that such analysis should be performed on dilatometric rather than calorimetric data.

Theoretical model

The theory most commonly used to analyse glassy state relaxation behaviour is referred to as the Tool–Narayanaswamy–Moynihan (TNM) model [4, 9–11], though other models are of equal merit, in particular that based upon the original idea of Adam and Gibbs [12–14]. The TNM model is phenomenological, and separates the temperature and structure (or fictive temperature) dependence of the relaxation time by means of the non-linearity parameter x ($0 \leq x \leq 1$), according to the equation:

$$\tau(T,T_f) = \tau_g \exp[x\Delta h^*/RT + (1-x)\Delta h^*/RT_f - \Delta h^*/RT_g] \quad (1)$$

where τ_g is the relaxation time in equilibrium at T_g. It should be noted that in the limit of $x=1$ there is no non-linearity, and hence only a temperature dependence of τ, and also that in equilibrium, for which $T_f=T$, the equation reduces to an Arrhenius temperature dependence with an apparent activation energy Δh^*.

The feature of non-exponentiality is most easily and most commonly introduced into the analysis by means of the so-called stretched exponential response function:

$$\phi = \exp[-(t/\tau)^\beta] \quad (2)$$

where β ($0 \leq \beta \leq 1$) is the non-exponentiality parameter.

This theoretical model provides a rather good description of the experimentally observed response of glasses, though it must be said that it is far from perfect. Some immediate problems that can be identified are the lack of physical significance for the parameter x and the equilibrium Arrhenius behaviour which should really be WLF,

Williams–Landel–Ferry [15], or VTF, Vogel–Tammann–Fulcher [16–18], in form. It is, however, possible to address these problems, for example through a modification of the configurational entropy approach [19, 20]. The usefulness of modelling the glassy response has been in determining how the important material parameters (Δh^*, x, β) vary with controlled differences in the chemical nature of the glass-former, for example tacticity [21], degree of crosslinking in thermosets [22], crosslink length [23], side groups [24], and network modifiers in inorganic glasses [25]. The question is: how to evaluate these material parameters?

One approach is to apply the theoretical model for the appropriate thermal history and to adjust all the parameters simultaneously to obtain the best fit to sets of experimental data in the form of DSC heating scans. This is what is referred to as curve-fitting, and has particularly been used by Hodge [26] as well as others. An alternative is to evaluate each parameter independently by suitable DSC experiments. The apparent activation energy Δh^* can be found, independently of β and x, from the dependence of T_g on cooling rate, a good illustration being provided by Fig. 9 in [27]. The non-linearity parameter x can be obtained, essentially independently of both β and Δh^*, by the so-called peak shift method [28]. This relies upon the determination of the variation of both enthalpy loss and endothermic peak temperature with annealing time in experiments in which the glass-forming material is cooled at constant rate to an annealing temperature approximately 10 K below T_g, annealed for lengths of time which should ideally extend to approximately 1000 h, and then reheated in the DSC at constant rate (for example 10 K min^{-1}) to give the endothermic peak. A good illustration of this method applied to polystyrene is given in [2]. Finally, the non-exponentiality parameter β can be estimated from the normalised height of upper peaks (mentioned earlier) as a function of the prior cooling rate (for example, [29]). These particular thermal cycles, involving cooling rates equal to or faster than the heating rate, effectively eliminate the non-linearity since there is very little overshoot (as implied by the small endothermic peaks), and hence very little departure from equilibrium at the endothermic peak temperature where the normalised peak height is evaluated.

Temperature modulated DSC

In TMDSC, the temperature is defined as a function of time t by:

$$T=T_0+q_{av}t+A_T \sin(\omega t) \tag{3}$$

where T_0 is the initial temperature, q_{av} is the underlying heating or cooling rate, A_T is the amplitude of the temperature modulations, and ω is the modulation frequency ($=2\pi/t_p$ where t_p is the period of modulation). The modulated heating rate is therefore defined by:

$$q = q_{av}+A_T\omega \cos(\omega t) \tag{4}$$

The corresponding modulated heat flow HF is Fourier transformed on the basis of a sliding single cycle of the heating rate modulations, from which an average value

of heat flow <*HF*> , also referred to as the total heat flow HF_{tot}, an amplitude of heat flow A_{HF}, and a phase angle ϕ between the heat flow and the heating rate are obtained.

One procedure for data analysis involves the definition of the reversing heat flow HF_{rev} as being equal to the amplitude A_{HF} scaled by the ratio of the underlying heating rate to the amplitude of the temperature modulation, and hence allowing the definition of the so-called non-reversing heat flow $HF_{non\text{-}rev}$ as the difference between the total and reversing quantities:

$$HF_{non\text{-}rev} = HF_{tot} - HF_{rev} \tag{5}$$

Whilst this might at first sight appear to be logical, care needs to be exercised in the interpretation of data in this way, since HF_{rev} and HF_{tot} are rather different in their dependence on the experimental variables: in particular, HF_{rev} is dependent on ω in regions where transitions take place, whereas HF_{tot} is dependent on q_{av} but independent of ω. For this reason we prefer the analysis procedure [30–32] that is based upon the complex heat capacity, C_p^*, which is a function of frequency and may be expressed in terms of real and imaginary parts corresponding to the components in-phase and out-of-phase, respectively, with the heating rate modulations:

$$C_p^*(\omega) = C_p'(\omega) + iC_p''(\omega) \tag{6}$$

The magnitude of C_p^* may be expressed as:

$$\left|C_p^*\right| = A_{HF} / A_q \tag{7}$$

where A_q is the amplitude of the heating rate ($=A_T\omega$), and the in-phase and out-of-phase components are:

$$C_p' = \left|C_p^*\right| \cos\phi \tag{8}$$

$$C_p'' = \left|C_p^*\right| \sin\phi \tag{9}$$

The glass transition is manifest in TMDSC by characteristic features in each of the evaluated quantities: <*HF*>, C_p^*, C_p', C_p'' and ϕ. These are shown in Fig. 3 by the results obtained by Montserrat for an epoxy resin under the following modulation conditions: q_{av}=1 K min^{-1}, A_T=1 K, t_p=60 s [33]. The characteristic features are as follows. The average heat flow <*HF*> very closely resembles that for conventional DSC under the same conditions, showing the usual endothermic peak on passing through the transition region (though the peak is very small because the heating rate of 1 K min^{-1} is much slower than the usual rate of 10 K min^{-1} used for conventional DSC), but includes some superimposed ripples which result from the Fourier transformation procedure [34]. If this average heat flow is divided by the underlying heating rate q_{av}, it yields an average heat capacity $C_{p,ave}$ equivalent to that from conventional DSC. The complex and in-phase heat capacities are almost identical, because the phase angle ϕ is small (Eq. (8)), and show a sigmoidal change from glassy to liquid-like values with no endothermic peak. Both the out-of-phase heat capacity and the phase angle display a negative peak in the same temperature interval as the sigmoidal change in C_p^*.

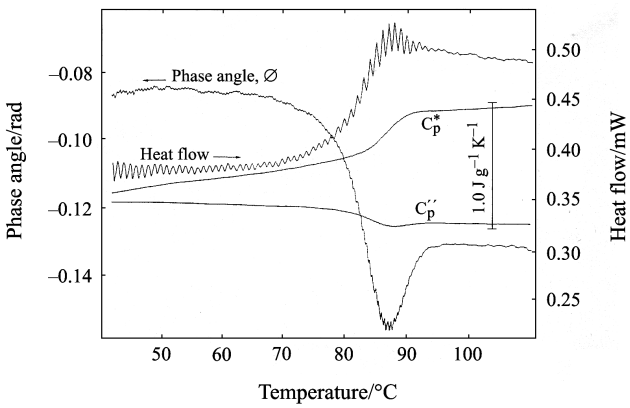

Fig. 3 Alternating DSC scan (Mettler-Toledo ADSC) through the glass transition region of a fully cured epoxy resin using the following conditions: q_{av}=1 K min^{-1}, A_T=1 K, t_p=60 s. Reproduced from [6], with permission

Effects of experimental parameters

The experimental parameters relevant to TMDSC are A_T, q_{av} and ω (or t_p). The effects of each of these on the manifestation of the glass transition again display a characteristic behaviour. *i*) The amplitude of temperature modulation A_T has no significant effect on the evaluated quantities; the only requirement is that it not be so large as to prevent the sample from following the prescribed temperature programme, bearing in mind that the maximum and minimum values of the modulated heating rate are $q_{av} \pm A_T\omega$. In studies of the glass transition by TMDSC, unlike studies of crystallisation and melting behaviour, it is not important that the heating rate modulations be heat only or cool only; heat-cool modulations are perfectly acceptable. *ii*) The underlying cooling rate q_{av} (rather than the heating rate, for which one additionally needs to consider the initial glassy state) has a direct influence on <*HF*> and hence on $C_{p,ave}$ in respect of the temperature $T_g(q_{av})$ at which the transition occurs, in exactly the same way as for conventional DSC, but has no effect on C_p^* (if q_{av} is kept within a reasonable range). *iii*) Conversely, the modulation frequency has a direct influence on A_{HF} and hence on C_p^* (as well as C_p', C_p'' and ϕ) in respect of the temperature $T_g^*(\omega)$ at which the sigmoidal change occurs, but has no effect on $C_{p,ave}$.

All of these observations can be described by the TNM theoretical model together with the stretched experimental response function and the input temperature programme [35]. One note of caution should be sounded, however. The theoretical model predicts phase angles of zero in the asymptotic and equilibrium glassy states, whereas the experimental data in Fig. 3 clearly show non-zero (and different) values in these regions. The explanation lies in the effect of heat transfer, which introduces an additional 'instrumental' phase angle; however, it is possible to correct the data for this effect by an appropriate treatment of the experimental data [36–39], which must be applied, of course, if any quantitative interpretation is to be made, in particular of

C''_p. The theoretical modelling also allows the effects of the experimental parameters to be studied, and it is found [35] that all of the experimental observations can be reproduced: no effect of A_T; a shift of $C_{p,ave}$ curves to lower temperatures as q_{av} decreases, as for conventional DSC, with no effect on C^*_p; a shift of C^*_p and ϕ to higher temperatures as ω increases, with no effect on $C_{p,ave}$.

Effects of material parameters

Furthermore, the advantage of theoretical modelling is that it permits the examination of the effects of the material parameters, in particular of x and β, on the response. It can be shown [35] that the non-linearity parameter x has a significantly different effect on $C_{p,ave}$ from that on C^*_p: as x increases within its range of zero to unity, the transition in $C_{p,ave}$ from liquid to glassy values on cooling is found to become narrower while the transition in C^*_p remains essentially unaffected. The reason for this lies in one of the fundamental aspects of TMDSC, namely that there are two different time scales in operation: $C_{p,ave}$ is observed on the time scale of the cooling (or heating) rate, whereas C^*_p is observed on the time scale of the modulation period. Under 'ideal' conditions, the transition in C^*_p occurs in equilibrium over a temperature interval centred on $T^*_g(\omega)$, lying somewhat higher in temperature than the transition interval in $C_{p,ave}$, which is centred at $T_g(q_{av})$ and which represents the departure from equilibrium into the glassy state (Fig. 4). Since the transition in C^*_p is essentially an equilibrium transition, therefore, one would not expect any effect of non-linearity, and this explains why there is no effect of x on C^*_p. It should be noted, however, that the complete separation of the transition intervals centred on $T^*_g(\omega)$ and $T_g(q_{av})$ must be considered as an 'ideal' situation, since they are functions of two different independent variables, ω and q_{av}. The correspondence between these two transition temperatures is of considerable interest, and is believed to provide information about the size of the co-operatively rearranging region that is active in the glass transformation process [40], but this aspect is beyond the scope of the present paper.

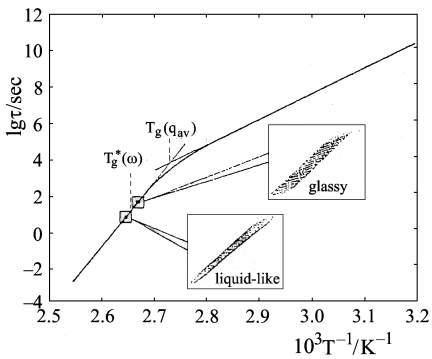

Fig. 4 Illustration of the dependence of log (relaxation time) on reciprocal temperature during cooling through the glass transition region. Full line shows dependence for conventional DSC, while points represent the start and finish of the transition in TMDSC, with the insets showing the difference between the glassy and liquid-like responses

The effect of the non-exponentiality parameter β contrasts with that of x in that as β increases within its prescribed range of zero to unity, both $C_{p,ave}$ and C_p^* become narrower in respect of their transition interval. The inflectional slope of C_p^* as a function of temperature therefore depends on β but is independent of x, and hence provides a new means of experimentally determining the value of β. An illustration of this procedure is given in [41].

Comparison of DSC and TMDSC

Conventional DSC in the glass transition region allows the evaluation of the important kinetic parameters by the judicial choice of suitable experiments. The dependence of the glass transition temperature on the cooling rate provides a direct means of evaluating the apparent activation energy Δh^*. Annealing experiments lead to the determination of both enthalpy loss and endothermic peak temperature as a function of annealing time, from which the non-linearity parameter x can be found, essentially independently of the other parameters, by means of the peak shift method. Finally, an estimate of the non-exponentiality parameter β can be obtained from the upper peak heights in the same experiments as are used for the determination of Δh^*.

TMDSC has been seen to provide essentially the same information as for conventional DSC, through the average quantities $\langle HF \rangle$ and $C_{p,ave}$, from which in principle one could evaluate the various parameters as for DSC. However, as a result of the temperature modulations and the Fourier transformation procedure, the data obtained by TMDSC in this respect are subject to greater errors than those for DSC, and consequently it is not recommended that TMDSC be used for these purposes. Nevertheless, TMDSC does provide other information through the complex heat capacity C_p^* and associated quantities. For example, the frequency dependence of $T_g^*(\omega)$ is an alternative approach to the evaluation of Δh^* [42]; this has the advantage of covering a different temperature range from that for $T_g(q)$, but the disadvantage that experimental considerations limit the range of frequencies to only about one decade, whereas the cooling rate can be varied easily over more than two decades. In addition to this frequency dependence, the correspondence between frequency and rate in respect of the transition temperature, as mentioned above, is of considerable interest in respect of the information that it can provide about the co-operative relaxation process. A distinct advantage of TMDSC is also afforded in the evaluation of β independently of x through the inflectional slope of C_p^*. Besides these, there is also the out-of-phase heat capacity C_p'' which displays a characteristic behaviour in the transition region. At present, though, the interpretation of C_p'' remains unclear, and it also suffers from the need (unlike for C_p^* and C_p') to make an appropriate correction to the phase angle to allow for heat transfer effects before it can be evaluated quantitatively, as a result of its dependence on ϕ (Eq. (9)).

Conclusions

The response of glasses in both conventional and TMDSC shows a number of characteristic features which can be described rather well by a theoretical model involving three important parameters: the apparent activation energy Δh^*, the non-linearity parameter x, and the non-exponentiality parameter β. Appropriate experiments in conventional DSC can be used to evaluate Δh^* and x independently of the other parameters, and also allow an estimate of β to be made. While TMDSC is not recommended for the evaluation of x, it can be used to determine Δh^* from the frequency dependence of $T_g^*(\omega)$, though the range of frequencies is limited. On the other hand, this technique provides interesting information for comparison with the rate dependent $T_g(q)$ from conventional DSC. One advantage that TMDSC does have over conventional DSC, however, is in the independent evaluation of β from the inflectional slope of the C_p^* curves as a function of T on cooling.

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