

Amorphous polymers

Interpretation of structural recovery of amorphous polymers from DSC data

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Abstract: The response of amorphous polymers on heating at constant rate in the differential scanning calorimeter is analysed as a function of the whole thermal history of the polymer. First, it is shown that a quantitative analysis of the data should make allowance for thermal gradients in the sample, which tend to broaden the response. Subsequently, the data are interpreted on the basis of the Tool-Narayanaswamy approach and involving three material parameters: an activation energy, Δh^* ; a parameter x ($0 < x \leq 1$), determining the relative contributions of temperature and structure to the retardation times; and an exponent β ($0 < \beta \leq 1$) of the stretched exponential response function, which is inversely proportional to the width of the distribution of retardation times. The activation energy can be found from the dependence of the glass transition temperature on cooling rate, or from the shift of the endothermic peak temperature with heating rate in intrinsic thermal cycles with fixed ratio of cooling to heating rate. The latter cycles provide also a means of correcting the data for thermal lag in the sample. The parameter x can be found from the dependence of the endothermic peak temperature on either annealing time or heating rate, provided that the glass is well annealed prior to scanning. On the other hand, if the glass is only poorly annealed, a quite different endothermic peak is observed, the height of which is sensitive to the parameter β . These material parameters are evaluated for polystyrene and polyvinylchloride, and are compared with those obtained for an inorganic glassy system in order to provide some insight into their physical significance.

Key words: Glasses; structural recovery; DSC; glass transition; enthalpy relaxation

Introduction

The use of differential scanning calorimetry (DSC) is widespread in the study of the thermal properties of polymers, and, in particular, in the investigation of the behaviour of amorphous polymers in the glass transition region. Most commonly, this involves heating the polymer glass through the transition region at a constant rate and observing the response. However, this heating scan is, alone, insufficient to allow a useful interpretation of the data, because the glass at the start of the heating scan is not in an equilibrium state. In other words, the response on heating depends on the state of the glass, and in a very intricate way, as will be shown below. The details of this response,

however, provide a rich source of information from which a better understanding of the glass transformation process may be derived. Fundamental to this interpretation, therefore, is a knowledge of the thermal history of the polymer glass.

The usual approach is to adopt a three-step thermal cycle (Fig. 1) in which: i) the polymer is cooled at constant rate q_1 from the equilibrium melt to a temperature T_1 in the asymptotic glassy region; ii) the glass is annealed at T_1 such that the enthalpy reduces by an amount δ_H ; and iii) the glass is reheated at constant rate q_2 until an equilibrium melt is again achieved. This last stage corresponds to the usual DSC heating scan, and results in the well-known endothermic peak occurring at a temperature T_p .

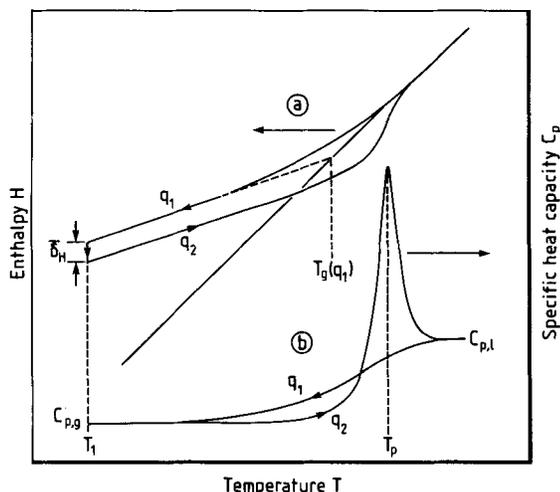


Fig. 1. Schematic illustration of the variation of enthalpy (a) and specific heat (b) with temperature in a three-step thermal cycle

The state of the annealed glass prior to reheating can be characterised by the fictive temperature, T_f , while the state of the glass formed on cooling at rate q_1 is characterised by the glass transition temperature, $T_g(q_1)$. It is clear that the peak temperature T_p is neither the fictive temperature nor the glass transition temperature; in fact, T_p is a function of the experimental variables defining the thermal cycle, namely q_1 , δ_H and q_2 (T_p is independent of T_1 provided T_1 lies within the asymptotic glassy region, as is the case here). It is the dependence of T_p on these experimental variables which forms the basis for the interpretation of DSC data discussed here.

Theoretical dependence of T_p

In addition to the experimental variables, T_p will depend also upon those material parameters which control the rate of structural recovery in the glass. These parameters characterise the two important features of structural recovery [1]: a dependence of retardation times τ_i on both temperature (T) and structure (T_f), and the existence of a distribution of retardation times. Commonly, the first is expressed by an equation often attributed to Tool [2] and Narayanaswamy [3]:

$$\tau_i = A_i \exp \left[\frac{x \Delta h^*}{RT} + \frac{(1-x) \Delta h^*}{RT_f} \right], \quad (1)$$

in which x ($0 < x \leq 1$) determines the relative contributions of temperature and structure to the retardation times, and Δh^* is an activation energy. An equivalent equation was proposed by KAHR [4, 5]:

$$\tau_i = A_i \exp[-\theta T - (1-x)\theta \delta_H / \Delta C_p], \quad (2)$$

in which ΔC_p is the difference between the heat capacities of the liquid and glass, and θ is related to Δh^* by:

$$\theta = \frac{\Delta h^*}{RT_g^2}. \quad (3)$$

The second feature of structural recovery can be represented either as a discrete distribution, as in the KAHR model [5], or as a continuous spectrum using the stretched exponential response function:

$$\phi(t) = \exp[-(t/\tau_0)^\beta], \quad (4)$$

in which β ($0 < \beta \leq 1$) is inversely proportional to the width of the distribution and τ_0 is given by Eq. (1) or (2).

The dependence of T_p on each of the experimental variables defines a set of shifts:

$$\hat{s}(Q_1) = \theta \left(\frac{\partial T_p}{\partial \ln |q_1|} \right)_{T_1, \delta_H, q_2} \quad (5)$$

$$\hat{s}(D) = \Delta C_p \left(\frac{\partial T_p}{\partial \delta_H} \right)_{q_1, T_1, q_2} \quad (6)$$

$$\hat{s}(Q_2) = \theta \left(\frac{\partial T_p}{\partial \ln q_2} \right)_{q_1, T_1, \delta_H}. \quad (7)$$

For well-annealed glasses, these shifts can be shown [6] to be inter-related and strong functions of x :

$$-\hat{s}(Q_1) = \hat{s}(Q_2) - 1 = \hat{s}(D) = F(x), \quad (8)$$

in which the caret signifies a so-called "main peak" and where the dependence of $F(x)$ on x defines the "master curve". For poorly annealed glasses, on the other hand, one finds [6]:

$$s_u(Q_1) + s_u(Q_2) = 1; \quad s_u(D) = 0, \quad (9)$$

in which the subscript u signifies an "upper peak" and where the shifts are essentially independent of x .

The difference between main and upper peaks for well and poorly annealed glasses, respectively, is crucial to a full interpretation of DSC data.

Experimental dependence of T_p

Intrinsic cycles

Intrinsic cycles are a special case of those illustrated in Fig. 1 in which $\bar{\delta}_H = 0$. Since the fictive temperature of the glass at T_1 can be found for intrinsic cycles, either by an algebraic [7] or graphical [8] method, the activation energy Δh^* is readily determined from the slope ($= -\Delta h^*/R$) of the linear relationship between $\ln|q_1|$ and $1/T_f$.

These same intrinsic cycles allow another means of evaluating Δh^* at the same time as providing a method of correcting the data for thermal lag in the sample. It can be shown theoretically [5] that intrinsic cycles for which the ratio (ρ) of cooling rate to heating rate is constant should be superposable by means of a shift along the temperature axis by an amount dependent upon θ (or Δh^*):

$$\left(\frac{\partial T_p}{\partial \ln q_2} \right)_{\rho, \bar{\delta}_H=0} = \theta^{-1} = \frac{RT_g^2}{\Delta h^*} \quad (10)$$

In practice, though, superposition cannot exactly be achieved because the DSC response broadens at faster heating rates as a result of thermal lag in the sample [9]. The theoretical invariance of the endothermic peak shape, however, enables correction factors to be determined for each heating rate, and then θ or Δh^* can be found from the corrected peak temperature shifts. Interestingly, for some ionically conducting iodomolybdate glasses with different amounts of silver iodide, a trend of reducing thermal lag was observed as the AgI content increased, implying that the thermal conductivity was mirrored by the ionic conductivity, both increasing with AgI content [10].

Well annealed glasses

In contrast to the use of intrinsic cycles for the evaluation of Δh^* , the evaluation of x requires well annealed glasses. Under such circumstances, the evaluation of any of the shifts defined in Eqs. (5) to (7) permits the determination of x from Eq. (8) and the master curve. For example, for polystyrene (PS) the dependence of T_p (corrected for thermal lag in the sample) on $\bar{\delta}_H$ is shown in Fig. 2. It is clear that for well annealed glasses (large $\bar{\delta}_H$) there is a linear dependence of T_p on $\bar{\delta}_H$ from which $\hat{s}(\bar{D})$ and hence x may be evaluated. This approach has been applied to other polymer glasses, including polyvinylchloride (PVC), as well as to the inorganic

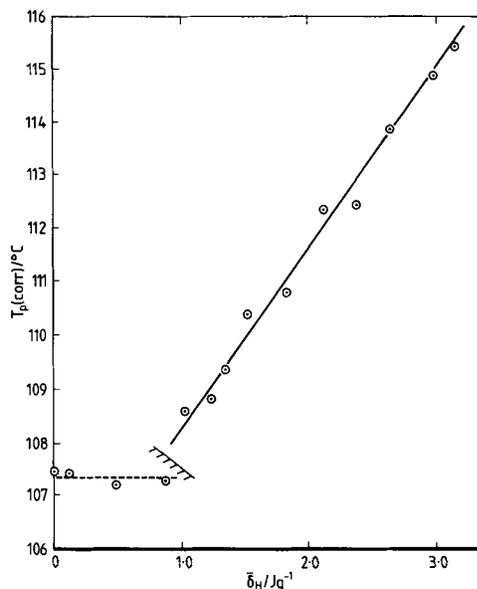


Fig. 2. Corrected peak temperature versus $\bar{\delta}_H$ for PS, obtained from a set of DSC traces with cooling rate -20 K/min, annealing temperature 85°C , heating rate 15 K/min and annealing times up to 960 h

system of iodomolybdates with 40, 50, and 60 mol % of AgI, and the values of x (and other parameters) are tabulated further below.

Poorly annealed glasses

It is also evident from Fig. 2 that the linear relationship between T_p and $\bar{\delta}_H$ does not hold for small $\bar{\delta}_H$, as indicated by the break in the line. This is because the peak in this region of small $\bar{\delta}_H$ is an upper and not a main peak, resulting from the reheating of a poorly annealed glass. Furthermore, the peak temperature is essentially independent of $\bar{\delta}_H$, as predicted by Eq. (9). This distinction between main and upper peak is also well illustrated by examining the dependence of T_p on cooling rate in intrinsic cycles: a very slow cooling rate corresponds to a well annealed glass, whereas a fast cooling rate will yield a poorly annealed glass. Figure 3 shows this for an inorganic glass: for slow cooling rates the slope is negative, from which $\hat{s}(Q_1)$ (Eq. (5)) could be obtained and hence x evaluated through Eq. (8), whereas for fast cooling rates the slope is positive and gives $s_u(Q_1)$, independent of x for these upper peaks.

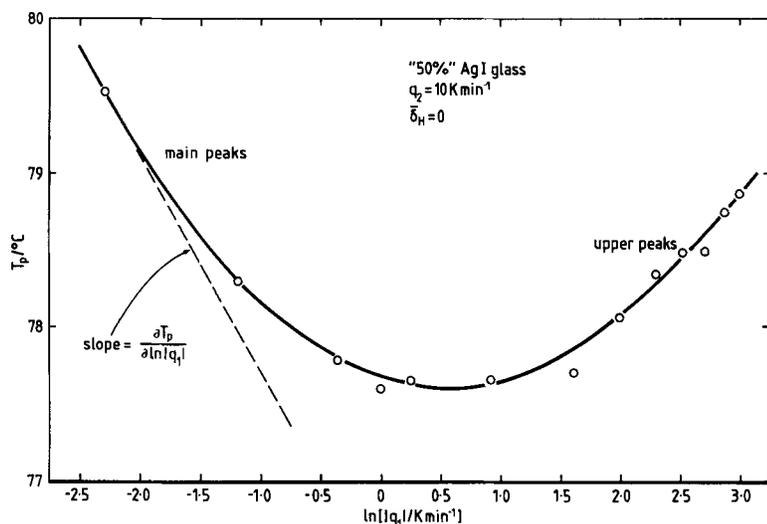


Fig. 3. Dependence of T_p on \log (cooling rate) for an inorganic glass in intrinsic cycles with heating rate 10 K/min

It is interesting to examine the magnitude of the upper peaks. Defining a normalised peak height, C_{pu}^N , as the height of the peak at the upper peak temperature, T_u , divided by ΔC_p at T_u , one can obtain information about the breadth of the distribution of retardation times as follows. C_{pu}^N depends on both cooling and heating rate (more precisely, on the ratio ρ) and has a minimum value of unity. Its theoretical variation is shown in Fig. 4, for various values of β and x [11]. For all values of these parameters, the height diminishes with increasing ρ , an effect which has been observed in PS [11] and in several inorganic glasses. Furthermore, given a value of x obtained by the peak-shift method, a comparison of experimental values of C_{pu}^N with this theoretical variation will provide an estimate of β for any glass.

For PVC this approach yields some interesting results, since no upper peak is observed for $\rho \geq 1$ approximately; there is only a sigmoidal "step change" in C_p , as has been reported on several occasions. The implication is that β for PVC must be very small, which is indicative of a very broad distribution. This result and those for PS and the inorganic system are summarised in Table 1 together with the other parameter values.

Results and discussion

In order to attempt to interpret the meaning of these parameter values, particularly of x and β , one can seek some correlations between them. For both

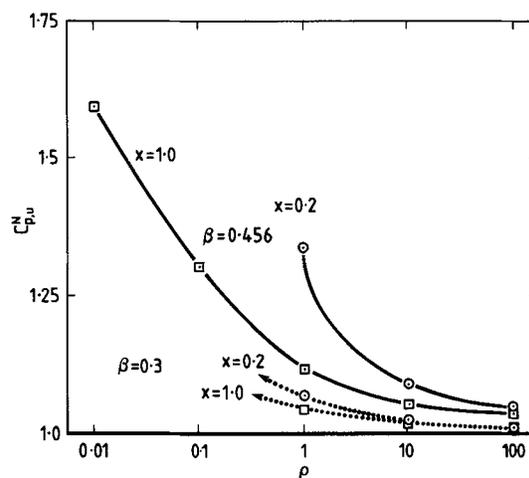


Fig. 4. Theoretical dependence of C_{pu}^N on ρ for intrinsic cycles for values of x and β indicated

Table 1. Values of the material parameters Δh^* , x , β and ΔC_p for some polymer and inorganic glasses

	PVC	PS	$(AgI)_y(Ag_2MoO_4)_{1-y}$		
			40%	50%	60%
x	0.27	0.46	0.50	0.54	0.65
$\Delta h^*/kJ \cdot mol^{-1}$	1100	580	640	505	360
$\Delta C_p/Jg^{-1} K^{-1}$	0.335	0.281	0.164	0.139	0.099
β	< 0.3	0.456	> 0.456 — increasing with y		
		< β	< 0.6		

polymers and for the inorganic glasses, higher values of x are associated with lower values of Δh^* , a correlation that has been observed before [12]. On the other hand, they also correlate with lower values of ΔC_p , implying that for increasing x there is less of a difference between melt and glass structure. This has led to the term "continuity parameter" for x , measuring the degree to which the melt structure is retained in the glass [10]. This is consistent with a cluster-tissue model for inorganic glass [13], in which increasing AgI content leads to increasing amounts of tissue (or melt-like structure) in the glass; at the same time, the ionic conductivity of the glass also increases, which is explained on the basis of transport of silver ions in the tissue of the glass.

Similar correlations can be seen for the parameter β . In particular, β decreases with increasing Δh^* in both the polymer and inorganic glasses. This inverse correlation, which has been noted before [12], suggests that low values of β , and hence broad distributions, result from an increased degree of cooperativity of molecular motion perhaps involving a larger number of chain segments. The larger values of β for the inorganic glasses is consistent with the idea that structural recovery in these materials is less co-operative than in polymers [12].

Conclusions

These results show that the C_p traces obtained by DSC on amorphous polymers (or, indeed, any glasses) are a rich source of information for the interpretation of structural recovery. However, some care must be exercised in their analysis, for a number of reasons. First, a quantitative analysis must allow for the effects of thermal lag in the sample. Second, different experimental conditions can give rise to very different responses, which reflect quite different material characteristics. In particular, will annealed glasses give C_p peaks which occur at

temperatures dependent primarily upon the parameter x , which controls the influence of structure on the retardation times, whereas poorly annealed glasses give C_p peaks whose magnitude is strongly dependent upon the parameter β , which provides a measure of the breadth of the distribution of retardation times. The evaluation and interpretation of these material parameters for a wide range of glasses, both polymeric and inorganic, is considered to be a useful approach towards a better understanding of the amorphous state.

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