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SIMULATION OF THE GLASS TRANSITION

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Abstract

Enthalpic relaxation has been used to model the development of the glass transition in polymers, using kinetic parameters determined separately. For this purpose the Kohlrausch-Williams-Watt stretched exponential function, relating the extent of relaxation, $\Phi(t)$, to time t and an average relaxation time, τ_a, i.e.

$$1-\Phi(t)=\exp(-t/t_a)^{\beta}$$

where β is inversely related to the breadth of the relaxation spectrum, has been adopted. The relaxation time dependence on temperature was taken to follow the modified Arrhenius relationship,

$$\tau_a = A\exp\left[\frac{X\Delta H}{RT}+\frac{(1-X)\Delta H}{RT'}\right]$$

where T is the storage and T' the fictive temperature, X is the structure factor and ΔH the activation enthalpy. Both have been found to describe the process of enthalpic relaxation in polymer glasses and a direct comparison has been made with the change in specific heat observed with different cooling rates in DSC experiments. The effect of variables, such as activation enthalpies, pre-exponential factors, and the non-linear factors such as X and β on the observed T_gs and the temperature range over which the transition occurred have been determined.

Keywords: DSC, enthalpic relaxation, glass transition, physical ageing

Introduction

When a liquid is cooled at a constant rate a temperature is eventually reached at which the molecular relaxations become too slow for the equilibrium conformations to be maintained within the time scale of cooling and so the liquid cannot continue to exhibit equilibrium properties following the decrease in temperature. A glass then forms and the molecular conformation become fixed at this temperature. In a chain-like molecule the concerted long ranged segmental motions is considered to stop at least in the time scale imposed by the cooling rate. This description of the glass forming process is kinetic in nature, and the measured glass transition temperature, T_g, is cooling rate dependent and is a thermally activated process.

If, however, the glass is stored at temperatures below T_g these molecular conformations will continue to occur at very slow rates which are temperature dependent and material properties, such as enthalpy and density, will decrease with storage time towards the extrapolated equilibrium value [1]. This process is called enthalpic relaxation and it suggests that the glass transition is kinetic in nature.

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The aim of this paper was to determine if the kinetics of physical ageing can be used to describe the onset of glass formation and determine the glass transition temperature, T_g. A model of the transition was created using the stretched exponential function using the kinetic parameters established for the enthalpic relaxation of the glass and known values for the relaxation time, τ, as well as determining the effect of the various model parameters on the predicted values of T_g. A finite element approach has been used to calculate the glass transition observed on cooling at different rates in a DSC.

The kinetics of physical ageing

Cowie and Ferguson [2] adopted a multi-relaxation model for enthalpic relaxation assuming that it was due to the relaxation of a distribution of processes, each process being characterised by its own relaxation time, τ. The overall relaxation of the glass towards equilibrium, $\varphi(t)$, at time t, was the sum of the relaxation of the individual processes, such that

$$1-\varphi(t)=\sum_{\tau=-\infty}^{\tau=\infty}\rho(t)\exp\left(-\frac{t}{\tau}\right)\mathrm{d}\tau \tag{1}$$

where $\rho(t)$ is the fractional concentration of one process with relaxation time τ.

This summation has only been solved in a closed analytical form for a limiting case, and is usually approximated by the stretched exponential form of the Kohlrausch [3], Williams and Watt [4] relaxation function, such that

$$1-\varphi(t)=\exp\left(-\frac{t}{\tau}\right)^{\beta} \tag{2}$$

where τ is now the average relaxation time and β an inverse measure of the breadth of the distribution of the processes involved in the relaxation, such that $1.0>\beta>0$.

The concept of a non-linearity parameter, X, such that $1.0>X>0$, in the relaxation of glasses was first introduced by Tool [5], Narayanaswamy *et al.* [6] and Moynihan *et al.* [7] for inorganic glasses in a modified form of the Arrhenius dependence of τ' with temperature, T, such that

$$\tau'=A\exp\left[\frac{\Delta H}{R}\left(\frac{X}{T}+\frac{1-X}{T'}\right)\right] \tag{3}$$

where ΔH is the activation enthalpy, A is a pre-exponential factor and T' is the fictive temperature. This equation separates the temperature and structure dependences of the relaxation time.

Hodge [8, 9] has used Eqs (2) and (3) to model the effects of physical ageing on the shape of the glass transition and the ageing endotherms observed in PVC on subsequent heating with some success. However, in all cases pre-transition rather than post transition ageing peaks were observed. We attribute this to the course temperature scale adopted by Hodge, i.e. 1 K, in his calculations and we have accordingly used a finite element approach in the present analysis.

The simulation of the glass transition

It is generally observed that the dependence of T_g on cooling rate has the same activation enthalpy as that of enthalpic relaxation and it has been suggested [10] that enthalpic relaxation is an extension of glass formation. Accordingly we have used the kinetic relationships for enthalpic relaxation as a model for the formation of the glass on cooling. The liquid was considered to cool at a rate, R, from a temperature T and the effective glass transition temperature, or fictive temperature, T', used to monitor the transition since if $T=T'$ then the system is a liquid. If $T<T'$ the liquid is converting to the glass and if T' does not change on further cooling the glass has formed.

A finite element calculation was used to follow the change in fictive temperature on cooling. The cooling rate, R, defined the dwell time, dt at each temperature, T,

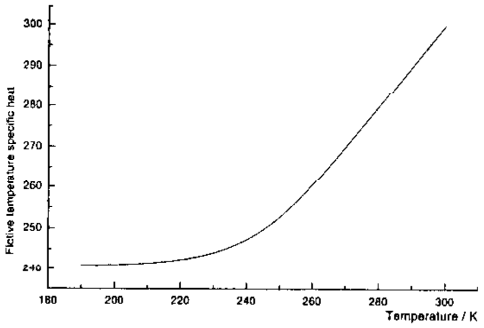

Fig. 1 Computer simulation of the glass transition; the development of the fictive temperature on cooling

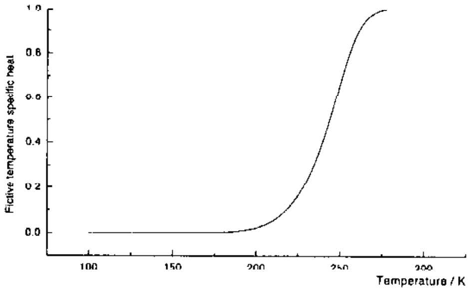

Fig. 2 Computer simulation of the glass transition; change in the fictive temperature specific heats on cooling

and so the extent of relaxation, dφ, which develops at each temperature is defined by the KWW function. The relaxation time at each temperature is given by the modified Arrhenius relationship, i.e. Eq. (3). The change in fictive temperature, dT', accompanying a change in temperature, dT, was then calculated for each temperature, T, since dT'=dT(1−φ(T,dt))

A fictive heat capacity was defined, C'_p =dT'/dT, for the liquid C'_p =1.0 and for the glass C'_p =0.0. During the conversion from liquid to glass, C'_p changes from 1.0 to 0.0.

The enthalpic relaxation rate parameters used in these calculations were those measured for polyhydroxybutyrate [11], which has T_g about 270 K as measured by DSC. Using the experimentally determined rate parameters for enthalpic relaxation, the activation enthalpies and pre-exponential factors listed in Table 1, were used to calculate the fictive temperature on cooling at different rates. These showed the clas-

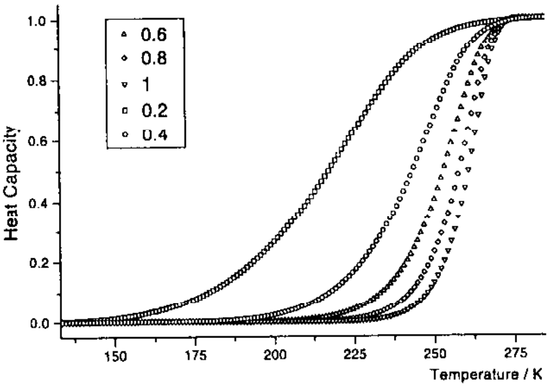

Fig. 3 Computer simulation of the glass transition; the effect of varying the value of β on the breadth of the glass transition

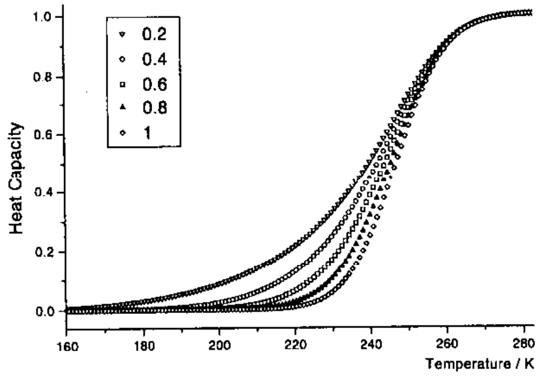

Fig. 4 Computer simulation of the glass transition; the effect of varying the value of X on the breadth of the glass transition

sical variation of properties with temperature expected on cooling (Fig. 1), with two distinct temperature dependences corresponding to the liquid and glass. Extrapolation of the two linear regions was used to measure the T_g from the intercept. The fictive temperature heat capacities also exhibited the characteristic step function at T_g, (Fig. 2). It was observed that the value of the T_g varied with cooling rate as determined and exhibited an Arrhenius temperature dependence corresponding to the value of the activation enthalpy selected. The individual values of T_g changed according to the values selected for ln$A$, ΔH_a and the X parameter, Table 1.

Table 1 The effect of selected variables on the calculated value of T_g

ΔH_a/kJ mol^{-1}	T_g^*/K	T_g^{**}/K	ln$A$	T_g^*/K	T_g^{**}/K
Effect of varying the activation enthalpy			Effect of varying ln$A$		
300	277.8	279.7	–200	147.3	148.2
250	323.1	234.3	–150	191.7	163.3
200	185.3	187.3	–100	274.1	191.8
150	140.6	140.7			
for ln$A$=–117, X=0.37 and β=0.38			ΔH_a=258 kJ mol^{-1}, X=0.37 and β=0.38		
X	T_g^*/K	T_g^{**}/K	β	T_g^*/K	T_g^{**}/K
Effect of varying X			Effect of varying β		
1.0	246.9	246.4	1.0	259.0	215.7
0.80	245.3	244.8	0.80	256.3	242.0
0.60	243.0	242.8	0.60	250.7	250.7
0.40	240.1	241.7	0.40	241.0	256.3
0.20	236.0	238.4	0.20	218.0	258.7
ln$A$=–117, ΔH_a=258 kJ mol^{-1} and β=0.38			ln$A$=–117, ΔH_a=258 kJ mol^{-1} and X=0.37		

T_g^* measured from intersection of fictive temperatures of liquid and glass; T_g^{**} measured by Aras and Richardson's method [12]

The effect of altering both β and X on the shape of the glass transition and the temperature range over which it occurred was considered. Lowering β, corresponding to a broadening of the relaxation distribution, lowered the value of T_g determined, and produced a wider range over which the transition was observed (Fig. 3), from over 100 K for a β value of 0.2 to 30 K for 1.0. X had a similar effect (Fig. 4) and it was not possible to separate the individual contribution from both β and X.

Discussion

The kinetics of enthalpic relaxation have been used to compute the glass transition on cooling and in general describes what is observed in DSC measurements. The temperature range over which the transition is observed is closely related to the breadth of the relaxation spectrum, β, and to structure parameter X. It is apparent that these parameters could be determined directly from the breadth of the transition as determined by DSC.

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