The physical ageing of amorphous and crystalline polymers

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Abstract: Changing the degree of crystallinity has a pronounced effect on the mechanical behaviour and fracture toughness of a polymer due to the crystallites acting as points of reinforcement and constraining the amorphous regions domains between crystallites. This is apparent in that the relaxation of the glass in a partially crystalline polymer the presence of increasing amounts of the crystalline regions progressively reduces the rate and extent of physical ageing which can develop and also the glass transition temperature, T_g, is raised by the presence of crystallinity. Enthalpic relaxation can be measured at temperatures above the T_g of the unconstrained amorphous regions.

INTRODUCTION

Amorphous "solids" are generally considered to have the molecular organisation of a liquid with localised short range order up to a few nm but no 3-dimensional order (1). While the liquid state is thermodynamically stable above the melting point on cooling it will harden to a glass if it does not crystallise at the glass transition temperature, T_g. This transition occurs with no change in order or structural reorganisation of the liquid and is not a thermodynamic first order process since there is no change in entropy, enthalpy or volume (2,3). There is, however, a step change in the first derivatives of these parameters with temperature. A generalised example of this can be seen in Figure 1 where the specific heat of a crystallisable polymer, such as polyether ether ketone (4) or polyethylene terephthalate (5), is shown as a function of temperature. The temperature of the transition, T_g, can clearly be identified by the step in specific heat and DSC, and DTA are convenient methods for determining the value of T_g. However, complications do arise in DSC in that the use of different heating and cooling rates, or ageing the glass make this determination of T_g incorrect and the temperature of the step change in C_p is no longer a measure of T_g, (6).

At temperatures below T_g amorphous materials are not in thermal equilibrium (2) and physical properties, such as specific volume, enthalpy and entropy which are greater than the equilibrium values decrease towards the equilibrium values at rates which decrease with the degree of undercooling from the T_g. There appears to be a limiting temperature range in which these changes are observed, (7). At the same time material properties, such as yield stress, tensile and flexural module, increase progressively and the fracture toughness, impact strength and compliance decrease, (3,8) While the change in material properties with time is generally called physical ageing, the changes in thermal properties is attributed to enthalpic relaxation. There is some agreement that there is a close correlation between physical ageing, glass formation and enthalpic relaxation in that the increased energy to fracture tensile specimens on ageing relates directly to the changes in enthalpy of the glass in relaxing towards the equilibrium values (9) and the activation energy of glass formation is very similar to that of enthalpic relaxation. However, the ageing of glasses as measured by changes in creep characteristics appear to occur over a wider temperature range than can be measured by DSC, dilatometry or changes in mechanical properties and it is very apparent that measurement of creep may not be measuring the same portion of the overall relaxation spectrum of the glass as either enthalpic relaxation or glass formation and that there is a contribution from the β process, (9) particularly at temperatures 50 K or more below T_g.

Clearly the variability of material properties implies that enthalpic relaxation has considerable commercial importance and for this reason it has been widely studied by thermal analytical techniques (10) DSC is well suited for the measurement of the extent of enthalpic relaxation since it directly measures changes in specific heat, and on integration the enthalpy, of the glass with extent of ageing.

THE DSC OF CRYSTALLISABLE POLYMERS

From a study of a range of different homopolymers and copolymers it is obvious that amorphous crystallisable polymers exhibit several transition in their DSC curves, see Fig. 1. The low temperature transition, observed as a step change in the specific heat, is a transition from glass to liquid, i.e. the glass transition at T_g. The second, at temperature, T_c, is that of liquid to solid and is an exothermic process, the heat evolved being determined by the extent of crystallinity which develops and the thermodynamic heat of fusion. The third transition is that of solid to liquid at T_m, and is associated with melting. It is an endothermic process and in polymeric materials it is not uncommon for several melting endotherms to be observed. The transition temperatures are characteristic for each polymer and the enthalpy changes in crystallisation and fusion are measures of the degree of crystallinity which develops within the polymer sample.
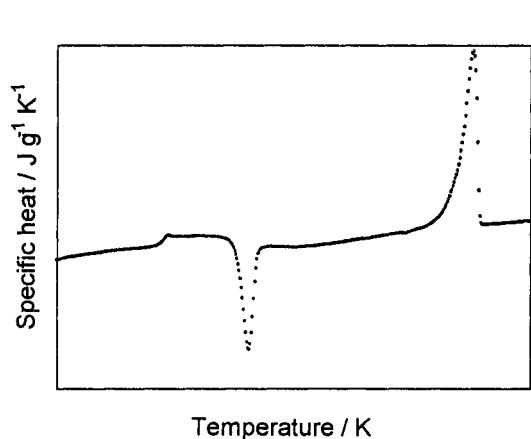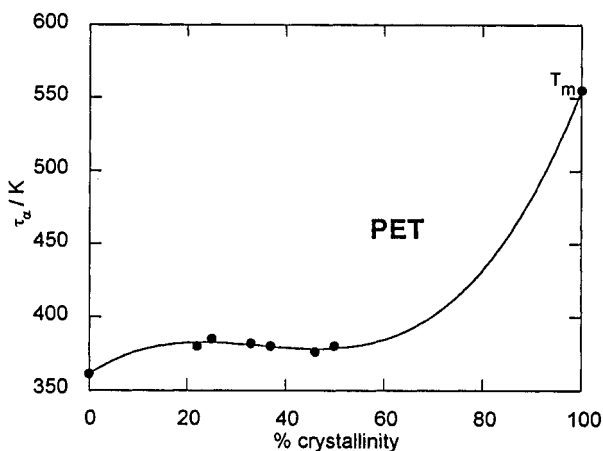

Fig. 1 DSC curve of amorphous crystallisable polymer.

Fig. 2 Change in T_g, T_α with crystallinity measured by DMTA.

The size of the step change in the specific heat at the glass transition temperature, $\Delta C_p(T_g)$, is a measure of the increase in number of rotational modes of the main chain segments which become active at the transition. The dependence of the transition temperature on rate of cooling during glass formation exhibits an Arrhenius dependence from which the overall activation enthalpy of the glass forming process can be determined. This is in the range 0.25 -2.5 MJ mol^{-1} for many polymers and is consistent with 10-20 monomer units being involved in the concerted segmental motion associated with the glass forming process.

On crystallisation, the size of step change in C_p at the transition becomes less obvious, in that the $\Delta C_p(T_g)$ is greatly reduced and T_g moves to higher temperatures. DSC becomes insensitive to these minor specific heat changes and the transition soon becomes lost in the background DSC curve of the partially crystalline polymer, particularly if there is any melting or recrystallisation occurring. The two phase model of amorphous and crystalline regions, conventionally used to account for the dependence of material properties, such as specific volume, on the degree of crystallinity, cannot account for this behaviour and the non-linear response of $\Delta C_p(T_g)$ to the degree of crystallinity. Composite models in which adjacent crystalline regions alter the properties of the amorphous material can account for this dependence on crystallinity and it is apparent that some part of the amorphous matrix is constrained by the crystallites, and so does not contribute to $\Delta C_p(T_g)$ of the amorphous.

Since DSC relies on the step change in C_p it lacks the required sensitivity to determine the T_g at high degrees of crystallinity. Accordingly, similar studies were repeated using dynamic mechanical and dielectric thermal analysis, DMTA and DETA. The temperature corresponding to the maximum in tan δ was used as a measure of T_α and assuming it was a measure of T_g. The frequency dependence of T_α was used to determine the activation enthalpy. Crystallinity reduces the value of tan δ_{max} and shifts T_α to higher values. The T_g apparently reaches a maximum value at about 40% crystallinity and decreases as the crystallinity increased further, see Fig. 2. However, in a study of the effect of crystallisation temperature it was found that for the same degree of crystallinity samples crystallised at higher temperatures exhibited lower T_α values than those produced at low crystallisation temperatures. While these measurements were made on PET similar behaviour has been observed with PEEK and this seems to be a general feature of partially crystalline polymers.

The critical size nucleus increases with temperature depending on the reciprocal degree of supercooling from the melting point but for the same degree of crystallinity the amorphous regions between the lamellae must be larger and correspondingly less constrained than in material containing small crystallites. The dependence of the T_α on the degree of crystallinity is closely dependent on the fine details of the polymer morphology and hence crystallisation temperature and thermal treatment.

ENTHALPIC RELAXATION.

Annealing a glass in a temperature range close to but below the glass transition temperature results in a progressive decrease in the enthalpy of the glass with ageing time which is recovered as an endotherm on the glass transition on reheating the glass above the transition temperature, see Fig. 3.

The extent of enthalpic relaxation, $\Phi(t)$, with time, t, can be characterised by the difference in enthalpy between the aged and quenched glasses and related to an average relaxation time τ_0, by the Williams-Watts stretched exponential function (11),

$$\Phi(t) = \exp[-(t/\tau_0)^\beta] \qquad (1).$$

where β is an inverse measure of the breadth of the relaxation spectrum and is in the region of 0.3-0.6 for many organic glasses. The characteristic relaxation time, τ_0, is dependent both on the ageing temperature, T_a, and the structure of the glass through the fictive temperature, T_ϕ, and the structural parameter, x such that

$$\tau_0 = A \exp[x/RT_a + (1-x)/RT_\phi] \Delta H^* \qquad (2).$$

where A is the pre-exponential factor and ΔH^* the activation enthalpy for enthalpic relaxation. In the DSC analysis of enthalpic relaxation,

$$\Phi(t) = 1 - (\Delta H_t / \Delta H_\infty) \qquad (3).$$

where $\Delta H_\infty = \Delta C_p (T_g - T_a)$ is the maximum extent of physical ageing.
This relationship between ΔH_∞, ΔC_p and $\Delta T = (T_g - T_a)$ is usually valid over small values of ΔT, from 10 to 20 K.
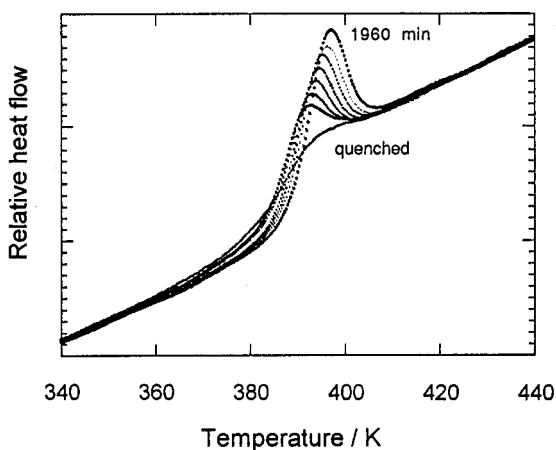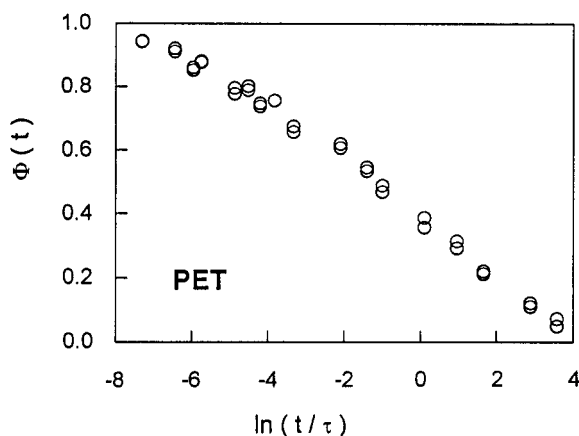

Fig. 3 Enthalpic relaxation.

Fig. 4 Williams-Watts fit of extent of physical ageing against reduced time.

Physical ageing or enthalpic relaxation is measured in amorphous material at different supercooling below the glass transition temperature and is accompanied with the development of endothermic peaks on the glass transition, see Fig 2. ΔH_t is measured by integration of the difference between the quenched and aged DSC curves The extent of enthalpic relaxation, $\Phi(t)$ is then 1 - ($\Delta H_t / \Delta H_\infty$) and β and τ_0 determined from a curve fit of $\Phi(t)$ against the reduced time, t/τ_0, see Fig. 4 The determination of β by this means is reasonably accurate to $\pm$ 0.02 and consistent over the temperature range studied.

The values of β vary from polymer to polymer but in the case of polyethylene terephthalate β was observed to be 0.35 The temperature dependence of the relaxation time, τ_a, gave an activation energy of 350±50 kJ mol^{-1} which compared with 400±100 kJ mol^{-1} from the frequency dependence of T_g measured by DETA (12). An overall Arrhenius dependence of reciprocal glass transition temperature against log of relaxation time measured over 10 decades from DETA to ageing results show the same general trend, see Fig. 5, and indicates very clearly that glass formation and enthalpic relaxation are all manifestations of the same phenomenon.
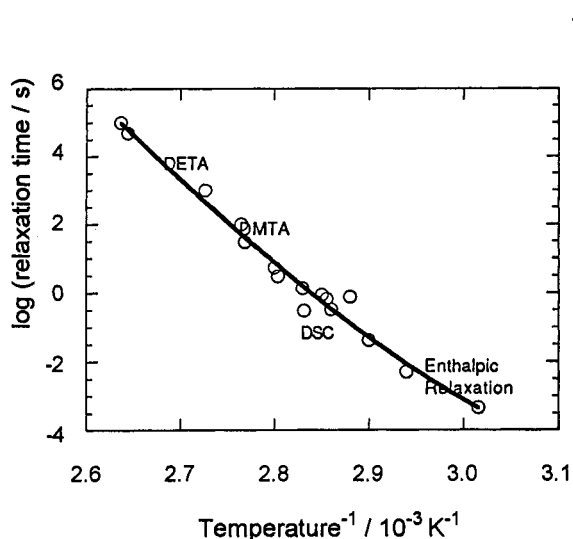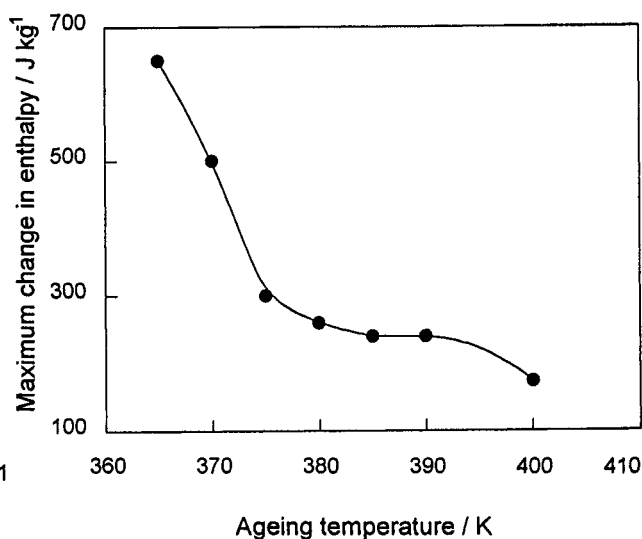
Fig. 5 Arrhenius plot of the relaxation time τ_a.

Fig. 6 The physical ageing of crystalline Polyphenylene Sulphide

A plot of this maximum in the enthalpy of ageing against T_a extrapolated to a value of T_g some 40-50 K above that of the amorphous material, see Fig. 6.

Crystallisation of polyphenylene sulphide raised the value of T_g such that it can be aged up to 40 K above the amorphous T_g. The sample studied was crystallised at a temperature close to the melting point such that it would not anneal during the subsequent ageing experiments. Samples were quenched from the crystallisation temperature and subsequently aged at various temperature, T_a. Baseline corrections were made using material which had been cooled directly to T_a and then immediately reheated without ageing. A series of endotherms developed whose intensities increased with log t_a up to a maximum.

CONCLUSIONS

It has been observed that crystalline regions constrained the amorphous regions in partially crystalline polymers and this has a marked effect on the glass transition and the mobility of the chain segments in the non-crystalline regions such that the observed T_g is raised well above that of the completely amorphous sample. This allows enthalpic relaxation to occur at higher temperatures. It is apparent, however that the morphology, in particular the size of the lamellar crystals, primarily determines the value of T_g and so enthalpic relaxation characteristics.

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