letters

Comment on 'Structure and thermal history dependent enthalpy relaxation at the glass transition of semicrystalline polymers' by S. Z. D. Cheng *et al.*

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In a recent paper by Cheng *et al.* on enthalpy relaxation in semicrystalline polyimides[1], several errors are made in the data analysis that invalidate the results. Some of these errors seem to be increasingly common in the field (e.g. in papers by Oguni *et al.*[2] and by Cowie and Ferguson[3]), and we feel obliged to draw attention to them.

The method for obtaining the β parameter in the Williams–Watts (WW) function is inappropriate for non-linear relaxations, because $\phi(t)$ is determined by the non-linearity parameter x as well as β, i.e. the average retardation time τ is time dependent and not constant. The linear relation reported for $\log[-\ln(1-\Delta H/\Delta H_\infty)]$ *versus* $\log t_a$ is not compelling evidence for the vaidity of the linear WW function because the doubly logarithmic ordinate is a weak function of the argument, and because the Narayanaswamy (N) and WW expressions (i.e. non-linear WW) happen to produce a decay function that closely resembles the linear WW form with a lower β parameter (see below). The way in which non-linearity can be subsumed into non-exponentiality is readily illustrated by introducing an explicit time dependence for the enthalpy retardation time (i.e. non-linearity) into the WW function. Suppose for example that

$$\tau = \tau_0 t^\mu \tag{1}$$

where μ is the relaxation time shift factor introduced by Struik[4]. The Narayanaswamy reduced time is then

$$\zeta \equiv \int_0^t \frac{dt'}{\tau} = \frac{t^{1-\mu}}{(1-\mu)\tau_0} \tag{2}$$

and the non-linear WW function is given by

$$\phi(t) = \exp(-\zeta^\beta) = \exp\left[-\left(\frac{t}{\tau'}\right)^{\beta'}\right] \tag{3}$$

where

$$\beta' = (1-\mu)\beta \tag{4}$$

and

$$\tau' = (1-\mu)\tau_0 \tag{5}$$

Equation (1) is not completely accurate over the entire annealing time, but serves to make the point that neglecting the time dependence of τ can give a function that is similar to the linear WW form but has spurious τ and β parameters that do not correspond to the linear values. This assertion is confirmed by an explicit calculation of $\phi(t)$ using the WW and N expressions. Consider a pre-annealing cooling rate of $100\ \mathrm{K\ min^{-1}}$ and define $t = 0$ at the start of annealing. For $\Delta h^*/R = 50$ kK, $x = 0.5$, $\beta = 0.7$, $T_g = 385$ K, and $T_a = 335 = T_g - 50$ K, which with the exception of β are those cited for the $n = 3$ polyimide, one obtains an almost linear plot for $\log\{-\ln[1-\phi(t)]\}$ *versus* $\log t_a$ with a slope of ~0.35, in agreement with Figure 5 in reference 1. A similar value for β' (0.39) is obtained by iterative least squares fitting of $\phi(t)$ directly, so that the apparent value, β', is only 50% of the true value, β. We suggest that the decreases in β' with annealing temperatures reported by Cheng *et al.* may be artifacts of the incorrect data analysis.

The procedure for evaluating x is also inappropriate, because the value of τ is incorrect for the same reason that β is [e.g. equations (4) and (5) above]. For the N + WW calculation cited above, for example, the true average retardation time increases by about two orders of magnitude for a 90% decrease in $\phi(t)$. The evaluation procedure used by Cheng *et al.* for obtaining x from τ is therefore inconsistent, because the non-linearity parameter is being evaluated from data produced by a method that neglects non-linearity.

These incorrect procedures for evaluating both x and β invalidate the discussion of changes in these parameters with chain flexibility, since these changes may be artifacts of the data analyses.

Another error is evident from the estimate of the maximum excess enthalpy that can be lost on annealing, ΔH_∞. The authors do not state the functional form used to obtain ΔH_∞ from the extrapolation $1/t_a \to 0$, but it is clearly incorrect because it produces the unphysical result that ΔH_∞ is independent of annealing temperature. In terms of fictive temperature, the starting value of $T_f' \equiv T_g$ is constant for a particular polymer and cooling rate (neglecting the minute amount of relaxation occurring during cooling in the glassy state between annealing temperatures), and since the equilibrium enthalpy is given by $T_f = T_a$ the quantity $T_f' - T_a$ ($\approx \Delta H_\infty/\Delta C_p$) decreases in direct proportion to T_a. Thus the values for ΔH_∞ are incorrect, and these in turn would produce incorrect forms for $\phi(t)$. Furthermore, the relation cited by the authors relating $\phi(t)$ and ΔH_∞ is only completely accurate for an instantaneous temperature step. For a finite cooling rate the previous history should be incorporated by integrating the time dependence of τ during cooling, as shown by Narayanaswamy and done in the calculation cited above. These errors in ΔH_∞ compound those produced by the neglect of non-linearity in evaluating β and τ.

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