letter

Thermally activated deformation of polymers. Comments on a paper by Zhu and Zhu

Dear Sir

We have some reservations about the formulations and ideas presented in a paper by Zhu and Zhu[1]. These are discussed below.

(1) If V_a is the volume involved in an activation event (presumably the difference between the volume of the activated state and that of the normal state), $V_a\tau$ (τ is the applied shear stress) is not the work done by τ during the process of activation and hence the free energy of activation ΔG will not be reduced by that amount. This is due to the fact that a shear stress will not do any work unless there is a corresponding shear strain involved. Let this strain be γ_a (a tensorial component corresponding to τ) and let it be uniform within V_a. Then ΔG is reduced by $V_a\gamma_a\tau$ during the activation process. The product $V_a\gamma_a$ is the activation shear strain volume Ω_a. If γ_a is not uniform, a spatial integration is needed and if Ω_a varies with τ an integration with respect to τ is needed as discussed before[2,3]. Now experimentally only Ω_a can be evaluated from a change of stress with strain rate. V_a can be estimated only by assuming a γ_a or vice versa.

(2) Zhu and Zhu[1] assumed that the shear strain produced by each activation event is:

$$\gamma_p = \beta_2 \frac{V_a}{V_m} \times \frac{\lambda}{\lambda_1} \qquad (1)$$

where λ/λ_1 is the shear strain produced in V_a after the completion of the activation event, V_m is the volume of the molecular chain and β_2 is a factor used to convert the local strain to the system strain, namely, the number of activation events within the molecular chain per unit time interval. Since V_a should be Ω_a or $V_a\gamma_a$, this assumption is really:

$$\gamma_p = \beta_2 \frac{V_a\gamma_a}{V_m} \times \frac{\lambda}{\lambda_1} \qquad (2)$$

which, when combined with their equation (2), gives the following strain rate:

$$\dot{\gamma}_p = \gamma_p \nu_\tau = \beta_1\beta_2 \left(\frac{kT}{h}\right)\left(\frac{V_a\gamma_a}{V_m}\right)\left(\frac{\lambda}{\lambda_1}\right) \exp\left(-\frac{\Delta G}{kT}\right)\sinh\left(\frac{\Omega_a\tau}{kT}\right) \qquad (3)$$

The minus sign in front of ΔG is missing in their equation (4); their V_a has been replaced by Ω_a which was assumed constant in order to obtain the hyperbolic sine function. Then they assumed a value of 2 for $\beta_1\beta_2\lambda/\lambda_1$. The justification was that the rate equation will not be affected much whether the value 2 is 0.2 or 20. Unfortunately the activation entropy calculation depends directly on that assumption. For example, a factor of 10 increase in the pre-exponential reduces the activation entropy by $R\ln(10)$ per mole where R is the gas constant.

(3) In deriving their equations (12) and (13) they assumed ΔH, V_a and ΔS to be constants (not varying with either temperature or strain rate). However, their Figures 4, 5 and 6 show clearly that these quantities vary with both temperature and strain rate. However, if expressed properly[2], these quantities do not have to be assumed constant in order to evaluate them.

(4) While their equation (14) was derived by Ferry[4] from the WLF equation except for a sign in the denominator:

$$\Delta H_m = \frac{2.303RC_1C_2T^2}{(T-T_g+C_2)^2} \qquad (4)$$

their equation (15) was their own creation. They used the idea that $T_g - C_2$ is a thermodynamic transition temperature so that:

$$\Delta S_m = \Delta H_m/(T_g - C_2) \qquad (5)$$

at this temperature. In this case since ΔH_m approaches infinity so does ΔS_m at $T = T_g - C_2$. Furthermore this idea does not give ΔS_m at other temperatures. Their equation (15) shows:

$$\Delta S_m = \frac{\Delta H_m}{T^2}(T_g - C_2) \qquad (6)$$

at other temperatures. This equation requires justification.

(5) The flow of a liquid is homogeneous on the molecular scale but the flow of a solid is inhomogeneous. Shear bands and crazes are clearly visible even by human eyes. To regard the plastic deformation of glassy polymers as a viscous flow of a supercooled melt will not help us understand their differences. In fact Zhu and Zhu do not really have any evidence for this similarity.

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