

Modification of Robertson's equation for the yield stress of a glassy polymer

Recently, Robertson [1] has developed a model based on a molecular interpretation of yield in glassy polymers. The model predicts the yield stress, explains cold-drawing (or strain-hardening) and also can be used to interpret the viscosity [2] of a glassy system over a wide range (10^2 to 10^{15} P). The Fulcher [3] or Williams-Landel-Ferry [4] equation can accurately describe the viscosity only in the temperature range near T_g . In this viscosity region, Robertson describes the glass as being in the mixed flexed-bond and unflexed-bond states. However, when the glassy state is at a higher viscosity region (about 10^{10} to 10^{15} P) or at a lower viscosity region (about 10^2 to 10^5 P) it exists either in an unflexed-bond state or in a flexed-bond state, respectively. Therefore, the glass exhibits a higher activation energy in the higher viscosity region, and a lower activation energy in the lower viscosity region [2, 5].

In Robertson's model, he proposed that there are only two rotational conformational energy states; the *trans* low-energy state and the *cis* high-energy state, which he terms the "flexed-bond" state. Applying a stress will cause the energy difference between the two conformational states of each bond to be less than the original energy difference ΔE . This result causes the fraction of elements in the high-energy *cis* state to increase. Robertson also concluded that yielding is caused by a stress-induced liquid structure involving molecular transformations from the *trans* state to the *cis* state of the glassy system. Robertson introduced an energy balance equation to account for a liquid structure induced isothermally at the temperature θ_1 by an applied stress as

$$\sigma_s \cdot \epsilon_s + \sigma_n \cdot \Delta\alpha(\theta_1 - T_g) = \rho \cdot \Delta C_p(\theta_1 - T_g) \quad (1)$$

where σ_s and σ_n are the shear and normal components of the stress, ϵ_s is the shear strain, ρ is the density, $\Delta\alpha$ and ΔC_p are the excess thermal expansivity and the excess heat capacity of the liquid over that of glass, and T_g is the glass transformation temperature. By applying the foregoing concept, Robertson could predict the yield stress of a glassy polymer very reasonably. The model also explained the experimental result observed by

Whitney [6, 7] that a polymer expands just before yielding, even when the applied stress is uniaxial compression. This is because the *cis* state, or the "flexed bond" configuration, is induced when a stress is applied to the glass. The "flexed bond" expands the structure and creates more 'free volume.'

One of the most likely sources of strain-hardening is strain-induced crystallization. This phenomenon can also be explained by Robertson's model. As mentioned above, the yield is caused by an applied stress which induces, isothermally, the liquid structure corresponding to the temperature θ_1 . This places the glass in a state of "fictive temperature" θ_1 which is higher than the glass transformation temperature, T_g ; therefore, the viscosity decreases to a value which is low enough to permit crystallization. The result might be partial crystallization after yield. At temperatures just below T_g , some glassy polymers show yield and strain-softening followed by strain-hardening. Partial crystallization after yield would explain this phenomenon.

The dependence of physical properties in the glassy state upon thermal and mechanical history has also been studied by Davies and Jones [8], and by Hsich [9, 10], among others. Hsich [9, 10] has pointed out that the structure-dependent physical properties of glass are characterized not only by external thermodynamic variables such as temperature and pressure but also by internal thermodynamic ordering parameters. This is why the glass transformation temperature, T_g , is used as the initial temperature state of a glassy polymer in Robertson's energy balance equation, even though the data were collected at room temperature. (By definition, the internal state of glass structure has been frozen at the fictive temperature, T_f . The fictive temperature of the glassy polymers which were studied by Robertson is very close to T_g .) Davies and Jones have developed a relationship between a temperature jump and a change in hydrostatic pressure applied to a glass in order to cause the same change in the glassy structural state. The relationship can be written as

$$P = - \left(\frac{\Delta C_p}{T_g \cdot V \cdot \alpha} \right) \Delta T \quad (2)$$

where V is the specific volume, i.e. $V = 1/\rho$. This

relationship between applied pressure and a temperature jump is similar to the concept proposed by Robertson that applying a stress will cause the frictive temperature, T_f , of a glassy polymer to change.

However, it appears that the energy balance equation, i.e. Equation 1, used by Robertson should be modified in the second term. Although the effect of the normal component of stress on the calculation of the yield stress is small, the error of the calculation of the angle between the yielding plane and the stress is relatively large. As pointed out by Robertson, the calculated angle never deviated from 45° by more than about 2.5° ; however, larger deviations have been observed by Whitney [6, 7]. The error of Equation 1 in the second term can be shown by rearranging Equation 1 as

$$\sigma_n = \frac{\rho \cdot C_p}{\Delta\alpha} - \frac{1}{\Delta\alpha} \frac{\sigma_s \epsilon_s}{(\theta_1 - T_g)}. \quad (1a)$$

In the limiting case when the shear component, σ_s , is equal to zero, the second term in Equation 1a vanishes (because $\theta_1 - T_g \neq 0$, i.e. the rise in temperature is caused by the normal stress component, σ_n). For a glass system $\rho\Delta C_p/\Delta\alpha$ is a constant, while σ_n is not. Decreasing or increasing the normal component stress, σ_n , does not affect the values of $\Delta\alpha$ and ΔC_p . Equation 1a thus requires modification as shown below.

Because there is a similarity of the behaviour between the normal component stress and hydrostatic pressure, the study of glass structural relaxation by Davies and Jones [8] permits one to conclude that a more adequate relationship between the normal component stress, σ_n , and the temperature dependence of the glass structure could be written as

$$\sigma_n \cdot T_g \cdot \Delta\alpha = \theta \cdot \Delta C_p (\theta_1 - T_g). \quad (1b)$$

Therefore, the equation of the energy balance proposed by Robertson [1] can be modified as follows

$$\sigma_s \cdot \epsilon_s + \sigma_n T_g \Delta\alpha = \rho \cdot \Delta C_p \cdot (\theta_1 - T_g). \quad (1c)$$

The calculation of the angle between the yielding plane and the stress axis now becomes

$$\theta = \frac{1}{2} \tan^{-1} \left[\pm \frac{\rho \Delta C_p (\theta_1 - T_g)}{\sigma_{12} T_g \Delta\alpha} \right]. \quad (3)$$

Also, the equation for calculating the uniaxial stress σ_{11} required to induce the same liquid structure that is induced by a simple shear stress σ_{12} can be rewritten as

$$\sigma_{11} = \sigma_{12} \sin \theta \cos \theta \pm \frac{\sigma_{12} T_g \Delta\alpha}{\rho \Delta C_p (\theta_1 - T_g)} \sin^2 \theta. \quad (4)$$

The deviation of the angle θ from 45° will be larger using the modified equation than the value calculated from the unmodified equation. Therefore, use of the modified equation is expected to improve the agreement between the calculated and experimental results for the angle θ .

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