

instance, the opposed models for elastin (globular model [5] or random chain model [3, 4]), the nature of the diffusion processes in the aortic wall and the strain analysis around aortic bifurcations (with particular relevance to atherosclerosis), are the subject of continuing research.

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## Comment on "The compression yield behaviour of polymethyl methacrylate over a wide range of temperatures and strain-rates"

The relationship between the yield stress in either compression ( $\sigma_c$ ) or tension ( $\sigma_T$ ) and log strain-rate ( $\dot{\epsilon}$ ) has been shown by Duckett *et al.* [1] and Bauwens-Crowet [2] to have a definite curvature when a sufficient range of strain-rate is considered. This curvature was ascribed [2] to the possibility that at high strain-rates or low temperatures a second co-operative yield process begins to dissipate significant energy. Thus the deviation from linearity arises from the addition of two stress components, the first arising from processes which operate under all conditions and the second from a process which is only significant under conditions of low temperature or high strain rate and which was associated with the  $\beta$  mechanical relaxation. The object of this communication is to suggest that it may not be necessary to invoke two processes to explain the observed curvature.

A number of workers, including Haward and Thackray [3] have suggested that in order to account for the observed recovery of a polymer before and after yield it is necessary to consider that some of the applied stress is borne by an elastic recovery element and that this reduces the

effective stresses on the time dependent flow process. In fact such an approach has been used by Bauwens-Crowet [2] to represent the  $\beta$  relaxation process. It is suggested that the effective shear stress  $\tau^*$  may, therefore, be described as

$$\tau^* = \tau_a - \tau_r \quad (1)$$

where  $\tau_a$  is the applied stress and  $\tau_r$  the stress borne by the elastic recovery process, i.e. the recovery stress. The effect of allowing for this extra stress term will be to cause a vertical shift to the curves of  $\tau_a$  (or  $\tau_a/T$ , where  $T$  is the absolute temperature).

It has also been noted [3] that a co-operative movement of a number of polymer segments would be necessary to permit significant flow in a solid amorphous polymer. If it is necessary for  $n$  such segments to move co-operatively during the yield process then it is possible to derive an expression for the rate at which such co-operative movement can take place in terms of the energy distribution statistics of the individual segments.

Following previous workers [2] the activation energy barrier for viscous flow for an individual polymer segment is put equal to  $Q$ . The probability  $p$  that a given segment occupies an energy level  $Q$  above its zero energy state is

$$p_1 = p_0 \exp(-Q/kT) \sinh(\tau^*v^*/2kT) \quad (2)$$

where  $p_0$  is a constant including the translational partition function and  $v^*$  is the activation volume. The probability  $p_n$  that all  $n$  of the segments which have to move co-operatively simultaneously occupy an energy level  $Q$  above the zero energy level is

$$p_n = \{p_0 \exp(-Q/kT) \sinh(\tau^* v^*/2kT)\}^n. \quad (3)$$

If  $\epsilon_0$  is the macroscopic shear strain resulting from one such co-operative movement of  $n$  polymer segments, then the macroscopically observed shear strain-rate  $\dot{\gamma}$  will be given by

$$\dot{\gamma} = K[\exp(-Q/kT) \sinh(\tau^* v^*/2kT)]^n \quad (4)$$

where  $K$  is a constant which includes  $\epsilon_0$ , a transmission coefficient and a frequency factor.

If, following previous workers [1, 6, 9], yield is defined as the load when the displacement rate arising from the viscous strain-rate  $\dot{\gamma}$  just matches the displacement speed in a conventional test, then the relationship between  $\dot{\epsilon}$  and  $\sigma_c$  or  $\sigma_t$  should be

$$\dot{\epsilon} = K'[\exp(-Q/kT) \sinh(\sigma^* v^*/2kT)]^n. \quad (5)$$

There is some similarity between this approach and that of Robertson [6] in that both consider the effect of applied stress on a number of segments and introduce a multiplying term before the function of stress in the  $\sigma/\log \dot{\epsilon}$  relationship. However, this treatment avoids the consequence of the Robertson treatment that for those segments which are unfavourably oriented with respect to the applied stress, the effect of such stress would be to decrease the equilibrium fraction of segments in the upper energy state and hence to

decrease the mobility of such segments. Such a consequence would appear to be inconsistent with the results of Litt and Koch [7].

Bauwens-Crowet [2] has determined the compressive yield stress for PMMA over a wide range of temperatures and strain-rates and showed that the curves of reduced yield stress against log strain-rate for various temperatures may be superimposed by shifting along a slanting line, that is when vertical and horizontal shifts are applied to each curve there is a linear relation between these shifts for any given temperature. This linearity may be expected on the basis of the results of Rusch and Beck [8] who have shown that the yield strain decreases with temperature while the present authors have shown in work to be published that the recovery stress increases with strain.

In order to use the values of applied stress  $\sigma_a$  instead of  $\sigma^*$  in Equation 5 it is necessary to ensure that  $\sigma_x = 0$ . This may be achieved by shifting to the glass transition temperature  $T_g$  where the yield stress and hence  $\sigma_x$  tends to zero. Using  $T_g = 100^\circ\text{C}$ , Equation 5 was fitted to the master curve from [2] using a computer to optimize the parameters. The resulting fit is excellent (Fig. 1) and the resulting value for the activation volume  $v^*$  is  $61 \text{ \AA}^3$  which is comparable to that expected for a single polymer segment, estimated by Robertson [6] as  $140/2 = 70 \text{ \AA}^3$ .

A similar approach was used with the tensile yield data for PVC determined by Bauwens-Crowet *et al.* [9]. Again a good fit is obtained and the value of  $v^* = 180 \text{ \AA}^3$  is reasonable for a segmental flow volume (Fig. 2).

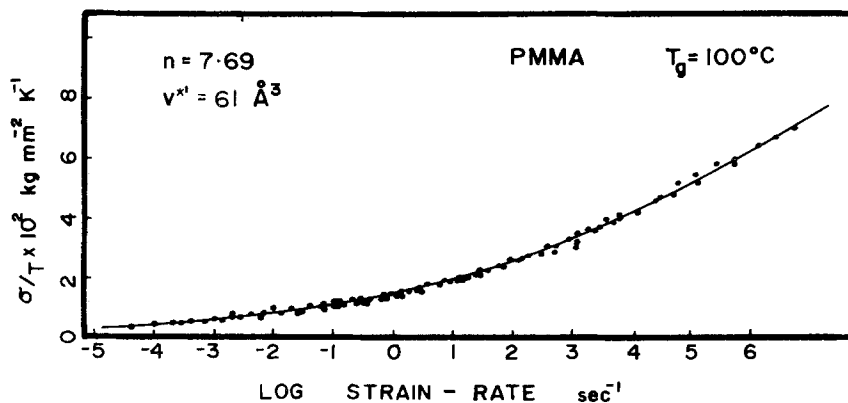


Figure 1 Master yield stress curve for PMMA [2] reduced to  $100^\circ\text{C}$  and theoretical curve from Equation 5. Optimum values of the parameters are given.

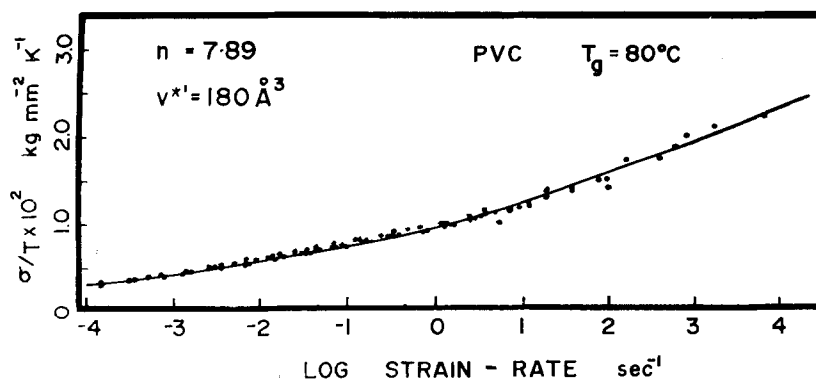


Figure 2 Master yield stress curve for PVC [9] reduced to 80°C and theoretical curve using Equation 5. Optimum values of the parameters are given.

In conclusion, it has been demonstrated that a mechanism for yield in glassy polymers based on the simultaneous movement of a number of segments leads to a treatment which corresponds very well with the reported yield data for PMMA and PVC, providing that a stress shift to account for the effects of stored elastic energy is included. The mechanism predicts very realistic values for the segmental flow volume and may help to explain the anomalously high values frequently observed in work on polymers.

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## Reply to "Comment on 'The compression yield behaviour of polymethyl methacrylate over a wide range of temperatures and strain-rates'"

We have described previously [1-3] the yield behaviour of glassy polymers assuming the existence of two rate processes,  $\alpha$  and  $\beta$ . The  $\beta$  rate process has been attributed to the molecular movement associated with the  $\beta$  loss peak, well known to influence the mechanical properties such as relaxation modulus and creep compliance. The activation energy  $Q_\beta$  related to this process was found to be in good agreement with the values reported from other types of measurements for

five glassy polymers studied by Roetling [4] and ourselves [1-3]. Moreover, using Bauwens' treatment [5, 6], from the position and the width of the  $\beta$  loss peak, it was possible to determine the range of experimental conditions where the  $\beta$  contribution to the yield stress becomes significant and to locate where the master yield stress curve exhibits a definite curvature. This correlation has been established for PVC [5], PC [6] and PMMA [3].

Fotheringham and Cherry have preferred to give an interpretation of the yield behaviour which ignores such a  $\beta$  contribution, we take this opportunity to reply to their comments by the following three points.

(1) *Building the master curve.* These authors adopt the same procedure as we in building the master yield stress curve but, to justify the vertical shifts used to generate this master curve, they invoke the existence of a recovery stress borne at yield by an elastic element. Therefore, from their point of view, this recovery stress:

(a) must decrease linearly with  $T$ , the absolute temperature, throughout the whole range of temperatures explored;

(b) does not depend on the imposed strain-rate (although this quantity varies in the proportion of 1 to  $2.5 \times 10^4$  for each isothermal yield stress curve). The behaviour of this elastic element has yet to be confirmed experimentally and its nature must be discussed.

(2) *Linear behaviour.* Our proposed approach leads to the following relation for the viscosity at small stresses:

$$\eta = \text{const. } T \cdot \exp \frac{Q}{RT} \quad (1)$$

where  $Q$  equals  $Q_\alpha$  or  $Q_\beta$  according to the range of temperatures explored. Equation 1 is the expression of the viscosity related to the linear behaviour of high polymers.

As Fotheringham and Cherry consider that  $n$  segments take part in viscous flow, their expression of the viscosity at yield does not reduce to linear viscosity at small stresses.

(3) *Shape of the master curve.* Both conceptions imply that the master curve admits a slanting asymptote at high stresses and strain-rates. However, from our treatment it can be seen that the master curve exhibits another linear part at moderate stresses and strain-rates; this straight portion is related to the case where the observed yield stress reduces to:

$$\frac{\sigma}{T} = \frac{\sigma_\alpha}{T} = \text{const.} \left( \ln \dot{\epsilon} + \frac{Q_\alpha}{RT} + \text{const.} \right) \quad (2)$$

In the master curve obtained for PMMA and PVC, this straight portion is rather narrow and, therefore, these examples are of no help to settle the question, but the case of PC is more interesting. For this high polymer the data fit a set of parallel straight lines from 20 to 120°C [1]. Moreover, using tensile creep and impact tests it is possible to extend the study of the tensile yield stress to strain-rates which cannot be reached in tension tests, we have thus measured the yield stresses related to strain-rates varying from  $10^{-8}$  to  $10^2 \text{ sec}^{-1}$ . From room temperature to 80°C, the data obtained on PC fit Equation 2 over ten decades of strain-rates [7]; this experimental fact cannot be explained by Fotheringham and Cherry's treatment. We are of the opinion that the master yield stress curve of PC exhibits such a wide straight part, simply because, for this polymer, the  $\beta$  transition is located far below the glass transition.

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## Thermal behaviour of silver amalgam

Long, needle-like, six-faced single crystals of silver amalgam, silver-grey in colour, grow on the surface of mercury placed in 0.02 N AgNO<sub>3</sub> solution. Some aspects of the growth features of these crystals have been reported by Sake Gowda and Madaiah [1]. The stoichiometry of the compound, the powder diffraction data, and the cell constants, have already been reported by Nirmala and Sake Gowda [2]. A

brief literature survey has been given in the above paper [2] with the intention of comparing the author's results with the earlier work.

Silver amalgam crystals obtained by the above method crystallize in the space group P6<sub>2</sub> or P6<sub>2</sub>22 or their enantimorphic complements. The lattice parameters obtained from Weissenberg patterns were used to index the powder pattern of silver amalgam crystals unambiguously [2]. The thermal behaviour of silver amalgam crystals grown from