

# Rubber toughening of plastics

## Part 10 *Effects of rubber particle volume fraction on the kinetics of yielding in HIPS*

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Measurements of tensile yield stress, compressive yield stress and kinetics of tensile creep have been carried out for a series of HIPS polymers containing "salami" structure rubber particles of median diameter  $1.6\ \mu\text{m}$ , which account for 35, 22.5, 17.5, 10.5 and 3.5% of the total volume, respectively. Deformation is due to multiple crazing in tension and shear yielding in compression; the dependence of yield stress upon rubber particle volume fraction is similar but not identical in the two cases. Eyring plots of  $\log$  (creep rate) against applied stress are used to determine stress concentration factors for each member of the series, and the results are discussed in terms of the Goodier equations for an isolated spherical inclusion, and the Ishai-Cohen model for average stress concentrations.

### 1. Introduction

Part 9 [1] described in detail the characterization of internal structure in a particular HIPS polymer, including the determination of the volume fraction,  $\phi$ , of composite rubber particles in the polymer. A series of materials with the same internal structure but varying values of  $\phi$  was obtained by melt-blending the parent HIPS polymer with polystyrene of a similar molecular weight to that of the matrix of the original material.

This series of HIPS polymers, therefore, makes it possible to compare mechanical properties on the basis of the particle volume fraction. The effects of changing  $\phi$  on the low-strain modulus, dynamic mechanical properties and notched Charpy impact resistance of these polymers have already been described [1]; this paper extends the study to the consideration of yield mechanisms and the effects of the volume fraction on the kinetics of tensile yield.

### 2. Experimental details

#### 2.1. Materials

The parent material for this series of HIPS polymers contains 8.5 wt% polybutadiene chains and 2 wt% plasticizer. The weight average molecular weight,  $M_w$ , of the polystyrene matrix is 196 000 and that of the polystyrene used for blending is 232 000. The volume fraction values are 35% for the parent polymer and 22.5, 17.5, 10.5 and 3.5% for the blends, each value being accurate to  $\pm 0.5\ \text{vol}\%$ .

A description of the blending method can be found in [1]. The materials were compression moulded into 3 mm thick sheets at  $200^\circ\text{C}$ . At the end of each moulding cycle, the heaters were switched off and the press was allowed to cool slowly to room temperature in order to standardize the thermal history of the sheets.

Specimens for tensile tests, tensile creep and compressive tests were milled out of the finished sheets.

#### 2.2. Methods

Determinations of yield stress values in tension and in compression were carried out on a Nene Instruments (Wellingborough, UK) tensile testing machine, at a crosshead speed of  $0.5\ \text{mm}\ \text{min}^{-1}$  and at  $23^\circ\text{C}$ . Broad-waisted dumb-bell tensile specimens were milled from the sheets to dimensions of  $13\ \text{mm} \times 3\ \text{mm}$  in the gauge length, according to ASTM D638. Yield was taken to be the point of marked deviation from linearity of the stress-strain curve, and an average of five readings was taken for each result.

Compression testing was carried out on 40 mm wide strips of sheet, using a Rocol ASP graphite lubricant applied to 6 mm wide dies before each test. The basic apparatus used was similar to that introduced by Williams and Ford [2]. The ratio of test-piece width to die breadth was greater than 4, to eliminate edge effects and thus ensure plane strain conditions. Yield was again taken to be the point of marked deviation from linearity, as some of the materials did not show a peak load, but a point of inflexion. Six tests were performed for each result.

Tensile creep tests were carried out at  $20^\circ\text{C}$  and 60% r.h. using the method described in earlier papers in this series [3, 4]. Volume strain,  $\Delta V$ , was calculated from longitudinal strain,  $e_3$ , and lateral strain,  $e_1$ .

### 3. Results

Tensile yield in the HIPS polymers was accompanied by the formation of white bands, perpendicular to the tensile axis, at elongations above 1%. Small cracks eventually initiated at the sides of the specimen, leading to ultimate tensile fracture without necking. The

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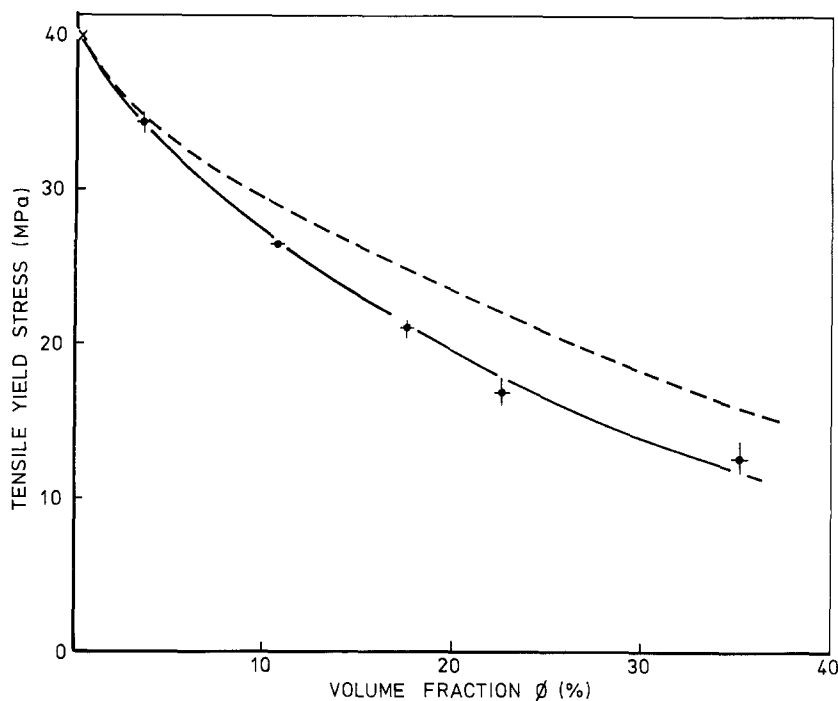


Figure 1 Dependence of the tensile yield stress on  $\phi$ . — Experimental; --- Ishai-Cohen model.

HIPS blend containing the lowest volume fraction of rubber particles, 3.5%, appeared to yield and break simultaneously without significant whitening. Unmodified polystyrene exhibited no whitening and failed by catastrophic fracture without yielding. In this case, the maximum load was used to calculate the breaking stress of the material.

Tensile yield stress depends on the rubber volume fraction,  $\phi$ , as shown in Fig. 1. Error bars indicate the scatter in the data. All of the materials yield in compression, but only the unmodified polystyrene and the HIPS blend with 3.5% rubber particles exhibit a true post-yield load drop. Representative compressive load-deflection traces for PS and for HIPS with low and high values of  $\phi$  are shown in Fig. 2. Yielding is not accompanied by whitening, but further

compression results in whitening at the die edges where bulging produces tensile stresses. Fig. 3 shows the dependence of the compressive yield stress on  $\phi$  for this series of materials. Error bars indicate the observed scatter in measurements.

Fig. 4a shows a representative tensile creep curve for the parent HIPS polymer at a stress of 11.8 MPa. The basic pattern of creep is characteristic of a polymer deforming by crazing: after the initial elastic response that occurs when the specimen is loaded, the cross-sectional area,  $A$ , remains constant; during the initial part of the test, elongation,  $e_3$ , and volume strain,  $\Delta V$ , also show little change, but at the end of this "induction period" both rise rapidly to give a constant strain rate  $de_3/dt$  which is equal to  $dV/dt$ . Fig. 4b, in which the volume strain is plotted against corresponding values of elongation, reinforces the point that deformation in HIPS is due to crazing, with no detectable contribution from shear processes, since shear yielding would reduce the slope of the line below 1.0.

The induction period  $\tau$  is defined by drawing tangents to the initial and final sections of the creep curves of  $\Delta V$  against  $t$ , and marking where the two lines cross. The reciprocal of  $\tau$  defines a rate which can be used in analysing the kinetics of deformation. The other important rate quality for HIPS is the steady-state rate of volume change  $(dV/dt)_{\max}$ , measured between 2% and 5% extension. Eyring plots of  $\log \tau^{-1}$  and of  $\log(dV/dt)_{\max}$  against the applied stress,  $\sigma$ , are presented in Figs. 5 and 6.

#### 4. Discussion

The tensile yield behaviour of HIPS has been extensively documented, but few systematic studies of deformation behaviour as a function of one specific structural parameter have been published. Our work shows that the dependence of tensile yield stress on the effective volume fraction of rubber is non-linear and of the form that might be expected on the basis of the Ishai-Cohen effective area model [5].

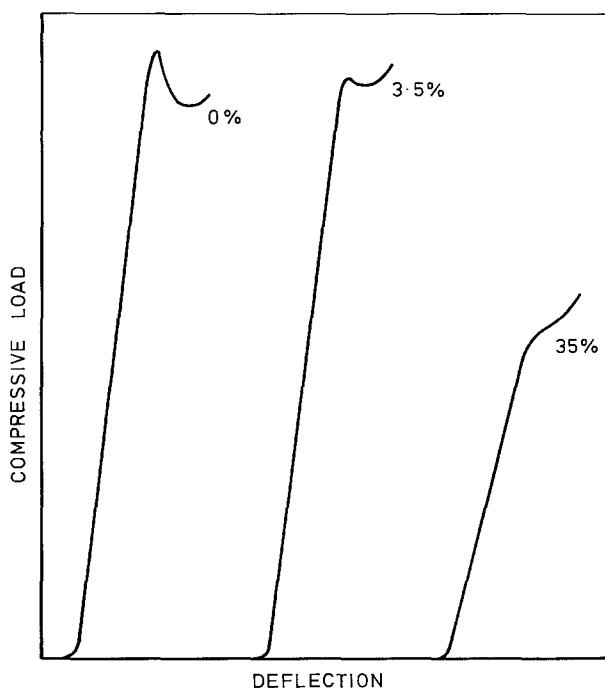


Figure 2 Changes in the compressive load-deflection curve characteristics with changing rubber volume fraction (nominal units).

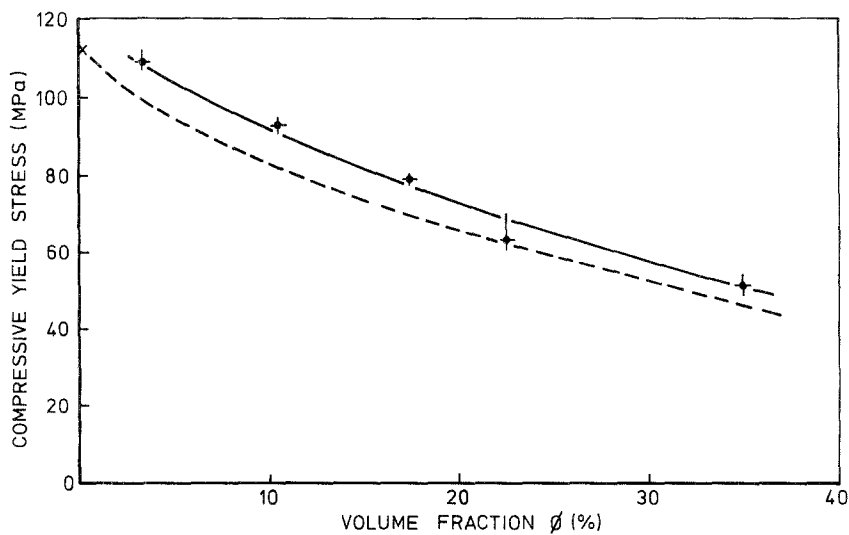


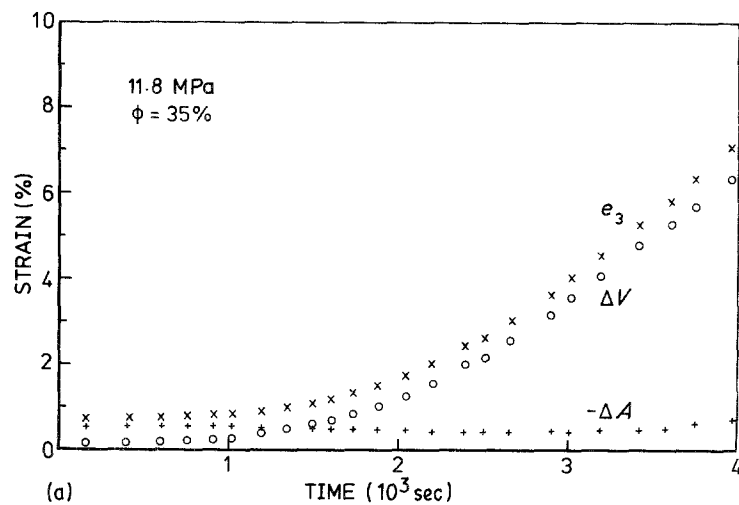
Figure 3 Dependence of the compressive yield stress on  $\phi$ . — Experimental; --- Ishai-Cohen model.

$$\sigma_{yt}(\phi) = \sigma_{yt}(0) (1 - 1.21 \phi^{2/3}) \quad (1)$$

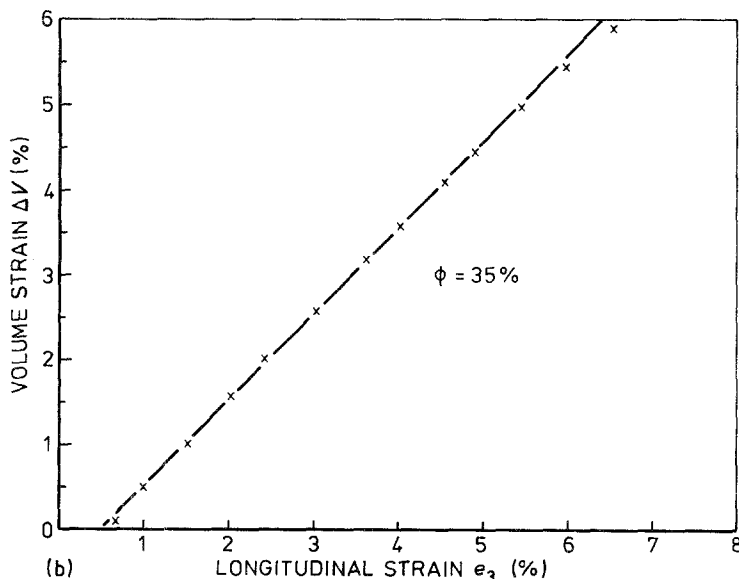
where  $\sigma_{yt}(\phi)$  is the tensile yield stress of a composite containing a volume fraction,  $\phi$ , of voids or low modulus inclusions, and  $\sigma_{yt}(0)$  is the yield stress of the matrix.

The compressive yield behaviour of HIPS is much less well documented [6, 7], possibly because of the experimental difficulties associated with compression testing of polymers. Williams [8] has studied some of

the errors arising from plane strain compression testing of polymers. He suggests that friction between specimen and dies, and the restraining forces resulting from large elastic deformation of polymeric materials are the two main sources of error. Our use of a graphite-based lubricant followed trials which showed that it could be both reproducibly applied and that consistently low friction could be achieved. The effects of elastic deformation can be allowed for by using several different die breadths and extrapolating to infinite die



(a)



(b)

Figure 4 (a) Creep curve for the parent HIPS polymer at a stress of 11.8 MPa. (b) Relationship between volume strain and elongation.

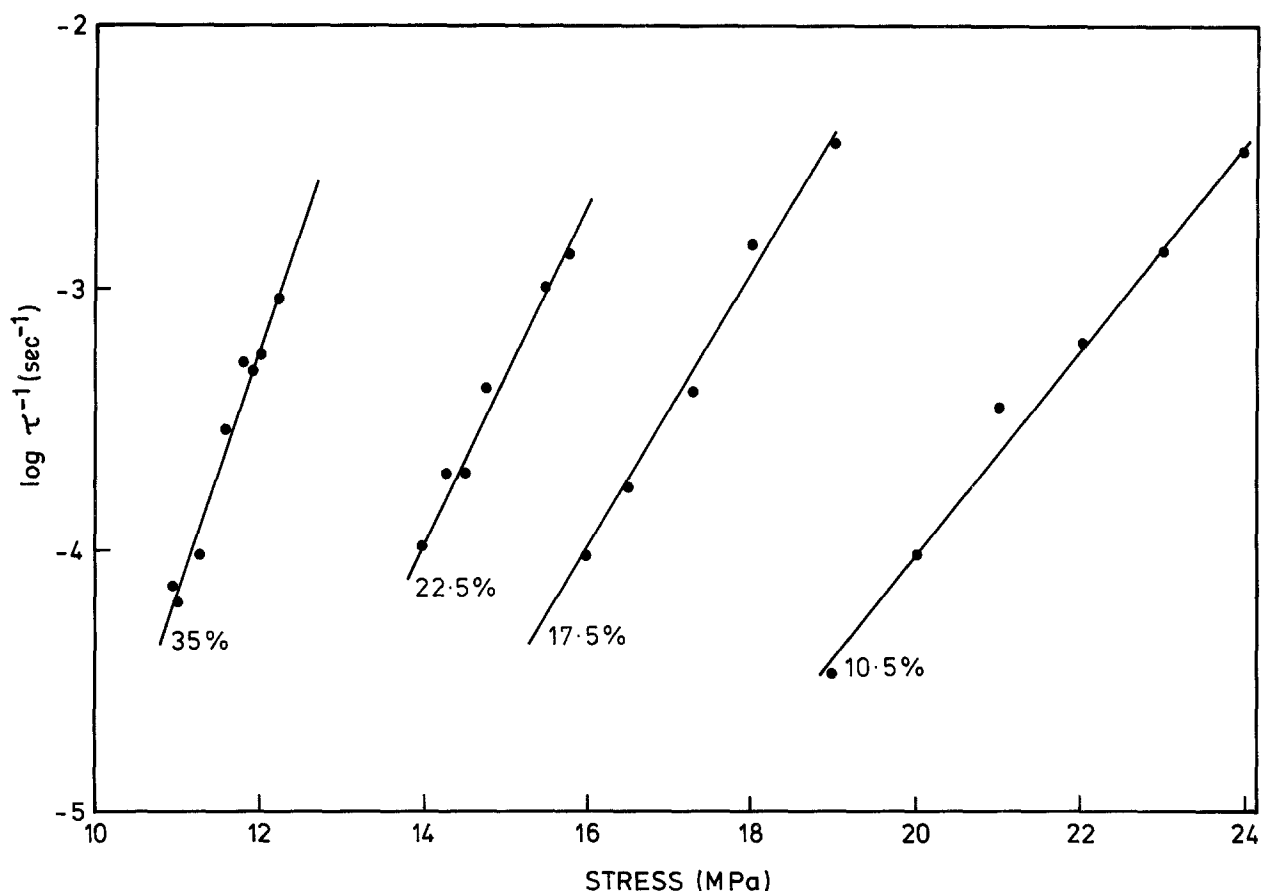


Figure 5 Eyring plots of  $\log(\tau^{-1})$  against applied stress.

breadth. No such extrapolation was carried out here: all of the compression tests reported in this programme used the same die breadth of 6 mm. Sample-to-sample variation is indicated by the error bars on the graph in Fig. 3; the frictional effects are negligible in comparison, but all of the compressive yield stress values are shifted up from their true value by an unknown amount, due to the elastic deformation effects

mentioned above. It is estimated that the elastic deformation effect in this series of materials could cause a systematic error as high as +10 MPa in the compressive yield stress values; however, it is assumed that comparisons between materials remain valid.

The disappearance of a post-yield load drop at rubber particle volume fractions above 3.5% seems to be a genuine effect of rubber particle spacing, but the

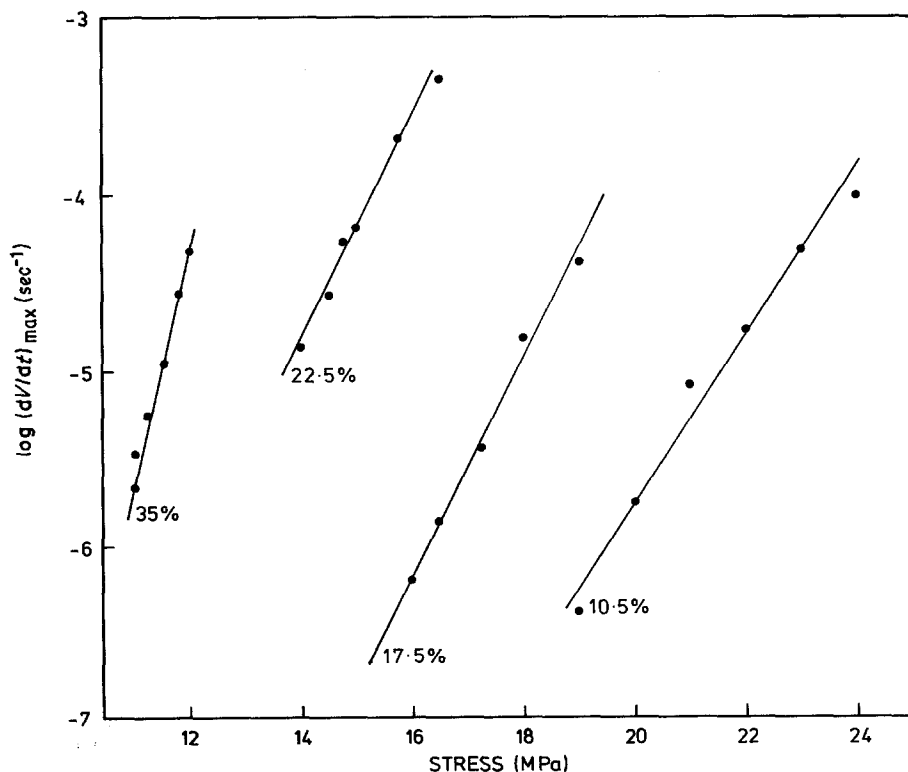


Figure 6 Eyring plots of  $\log (dV/dt)_{\max}$  against applied stress.

exact cut-off volume fraction in a given material will undoubtedly be determined by the test conditions.

The mechanisms of tensile and compressive yielding in HIPS are, of course, entirely different. In tension, the material deforms by crazing, a process not possible under compressive stress conditions: instead, the material deforms by shear yielding. It is interesting to note that, despite this fundamental difference in mechanisms, the dependence of the yield stress on  $\phi$  is in both cases qualitatively of the form predicted by the Ishai–Cohen equation, using as reference points the yield stress of unmodified polystyrene in tension. The Ishai–Cohen equation is based on a simplified model for stress concentrations produced by spherical holes in a continuous matrix. There is, therefore, no reason to expect a quantitative agreement between the model and a real material which contains rubber particles well bonded to the matrix. The fact that the model overestimates the yield stress in tension, whereas it underestimates the yield stress in compression at any given rubber volume fraction, is probably a reflection of the above-mentioned difference in the yield mechanisms in the two types of test. The size of the rubber particles appears to influence the effects of different mechanisms on the yield stress, as the following paper in this series will demonstrate [9].

The measurements of yield stress provide only a partial description of the effects of the rubber volume fraction on the yield behaviour in HIPS. Detailed studies of tensile creep of these HIPS polymers provide two kinetic parameters, the reciprocal induction time,  $\tau^{-1}$ , and the maximum rate of volume increase  $(dV/dt)_{\max}$ , which can be compared as functions of stress and of the rubber volume fraction. The creep data are plotted in Figs. 5 and 6 according to the Eyring equation, which can be written

$$\kappa = Q \exp(-\Delta H/kT) \exp(V^*\sigma/kT) \quad (2)$$

where  $\kappa$  is a rate coefficient,  $Q$  is a constant,  $\Delta H$  and  $V^*$  are activation enthalpy and activation volume for the deformation process,  $\sigma$  is stress,  $k$  is Boltzmann's constant and  $T$  is temperature. In the simplest case of a flow process occurring homogeneously throughout a material under uniform stress, the flow rate is proportional to the rate coefficient,  $\kappa$ . In HIPS, deformation is more complex: crazes are initiated in regions of high stress concentration, extend and grow into regions of lower stress concentrations, and finally reach a stage at which no further growth is possible. Kinetic schemes to describe these processes have been proposed by Bucknall [10], Argon *et al.* [11] and Sjoerdsma and Heikens [12].

Despite the presence of polystyrene subinclusions, the rubber particles are substantially lower in modulus than the surrounding matrix, which therefore has regions of high stress concentration close to the particles. Stresses in these regions are not only higher in magnitude but also somewhat different in character from the applied stress,  $\sigma_\infty$ : using the Goodier equations it can be shown that application of a uniaxial tension produces a state of triaxial tension near the equators of the rubber particles [10, 13]. As the major principal stress,  $\sigma_1$ , is a factor of approximately 8

higher than the two minor principal stresses,  $\sigma_2$  and  $\sigma_3$ , there is some justification for neglecting the effects of triaxiality, and expressing the stress concentration in terms of a scalar stress concentration factor,  $\gamma$ , defined as  $\sigma_1/\sigma_\infty$ . Processes occurring in regions of high stress concentration can then be represented by the modified Eyring equation

$$\kappa = Q \exp(-\Delta H/kT) \exp(\gamma V^*\sigma_\infty/kT) \quad (3)$$

A more general form of the equation would enable the rate coefficient  $\kappa$  to be calculated under any combination of principal stresses, but in the absence of a generally accepted criterion for crazing under multi-axial loading is not possible to formulate the Eyring equation in this way at present.

The Goodier equations give exact values for the stress concentrations around an isolated spherical inclusion in an isotropic matrix [13]. Maximum values of  $\gamma$  calculated on this basis for a rubber particle in a polystyrene matrix are between 1.90 and 2.05, depending upon the moduli assigned to the particle. These theoretical values of  $\gamma$  are independent of particle size, but it should be noted that in a typical HIPS  $\gamma$  falls from 1.92 to 1.80 over 0.02 units of particle radius [14]. This means that a significant fall in stress occurs over a range of 1 nm when the rubber particle diameter is 0.1  $\mu\text{m}$ . The applicability of a continuum elastic analysis to particles of this size or smaller is, therefore, questionable.

Stress concentrations are of course higher when the rubber particles are present at finite concentration. Broutman and Panizza have obtained an approximate solution to this problem using finite element analysis [15]. A simpler approach, which has nevertheless proved applicable to a number of particulate composites [3, 4], is the Ishai–Cohen effective area model [5]: the crack, craze or shear band is assumed to follow a surface of least resistance passing through the equator of each debonded (or low modulus) particle in its path, thus minimizing the area of matrix surface involved. The average stress concentration factor is then given by

$$\bar{\gamma} = (1 - 1.21\phi^{2/3})^{-1} \quad (4)$$

which gives  $\bar{\gamma} = 2.5$  at  $\phi = 0.35$ . Maximum stress concentrations near the rubber particles are, of course, much higher than these average values, especially where the rubber particles are relatively close together. Since the average stress in the matrix is  $\bar{\gamma}\sigma_\infty$  the maximum value of  $\gamma$  can be obtained approximately by using this average stress in place of  $\sigma_\infty$  in applying the Goodier equations. This would indicate stress concentration factors of about 5 for the parent HIPS polymer with  $\phi$  equal to 35%.

Values of  $\gamma V^*$  (Equation 3) were obtained from the slopes of the straight line graphs in Figs. 5 and 6, using rate coefficients  $\kappa$  corresponding to the reciprocal induction time,  $\tau^{-1}$ , and to the maximum rate of volume increase,  $(dV/dt)_{\max}$ , respectively. Stress concentration factors in HIPS have been calculated on the assumption that  $\gamma$  is 1.0 in polystyrene and using a figure of 1.4 nm<sup>3</sup> for the apparent activation volume  $\gamma V^*$  of crazing in unmodified polystyrene. This figure

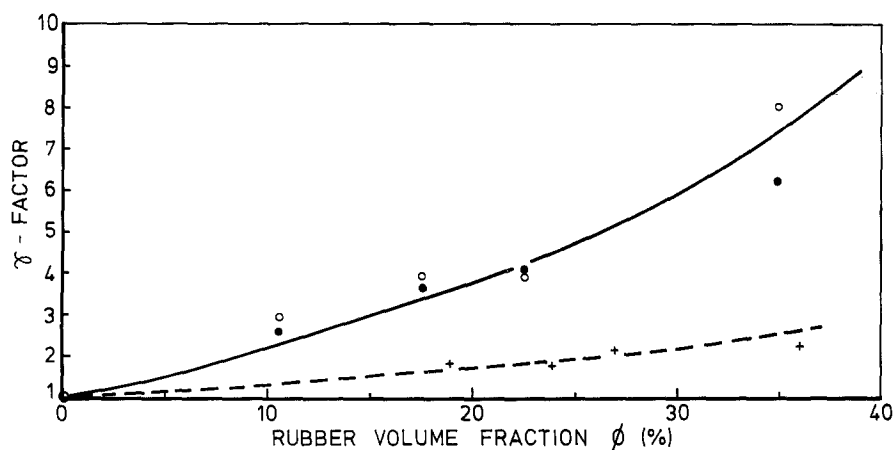


Figure 7 Stress concentration factor  $\gamma$  as a function of  $\phi$ . ●, HIPS ( $\tau^{-1}$ ); ○, HIPS  $((dV/dt)_{\max})$ ; +, RTPMMA. ---- Ishai-Cohen model.

was calculated by Bucknall [10] from data on crazing in polystyrene obtained by Maxwell and Rahm [16] using a light reflection method. (It should be noted that the numerical values for  $\gamma V^*$  given in [10] are different from those given in the present paper because of a difference in the exact definition of  $V^*$ .) Since there is no reason why the activation volume  $V^*$  for crazing in polystyrene should vary from one material to another, it is concluded that the differences in the slopes of the Eyring plots for HIPS of different rubber volume fractions are due to different stress concentration factors  $\gamma$  operating on the rate-controlling step.

The  $\gamma$  values are plotted against  $\phi$  in Fig. 7 which compares the results for the HIPS series with those for a series of rubber toughened poly(methyl methacrylate) (RTPMMA) materials [17]. The two sets of rubber-modified polymers differ completely in their mechanisms of deformation: whereas creep in HIPS is dominated by multiple crazing, in PMMA and the RTPMMA series it is due almost entirely to shear yielding. Furthermore, the pattern of creep is entirely different: in the PMMA materials, strain increases

linearly with the cube root of time, according to the Andrade equation. These differences probably account for the divergence between the two sets of results in Fig. 7. The results can best be interpreted by assuming that the rate-controlling step in HIPS is craze initiation in regions of high stress concentration near the rubber particles, where  $\gamma$  might well exceed 5 at high volume fractions of particles. By contrast, the rate-controlling step in RTPMMA appears to be propagation rather than initiation of shear bands, so that the relevant value of  $\gamma$  is determined by the average stress in matrix, and is therefore significantly lower [17]. According to this explanation,  $\gamma$  for HIPS contains a built-in factor of 2, which applies even when the volume fraction of particles is very low, since it derives from the stress concentrations around an isolated particle, but which does not apply to RTPMMA or other shear-yielding toughened polymers, because localized stress concentrations do not play a significant part in the creep of these materials.

The calculated values of  $\gamma$  in HIPS are, of course, dependent upon a literature value for the activation

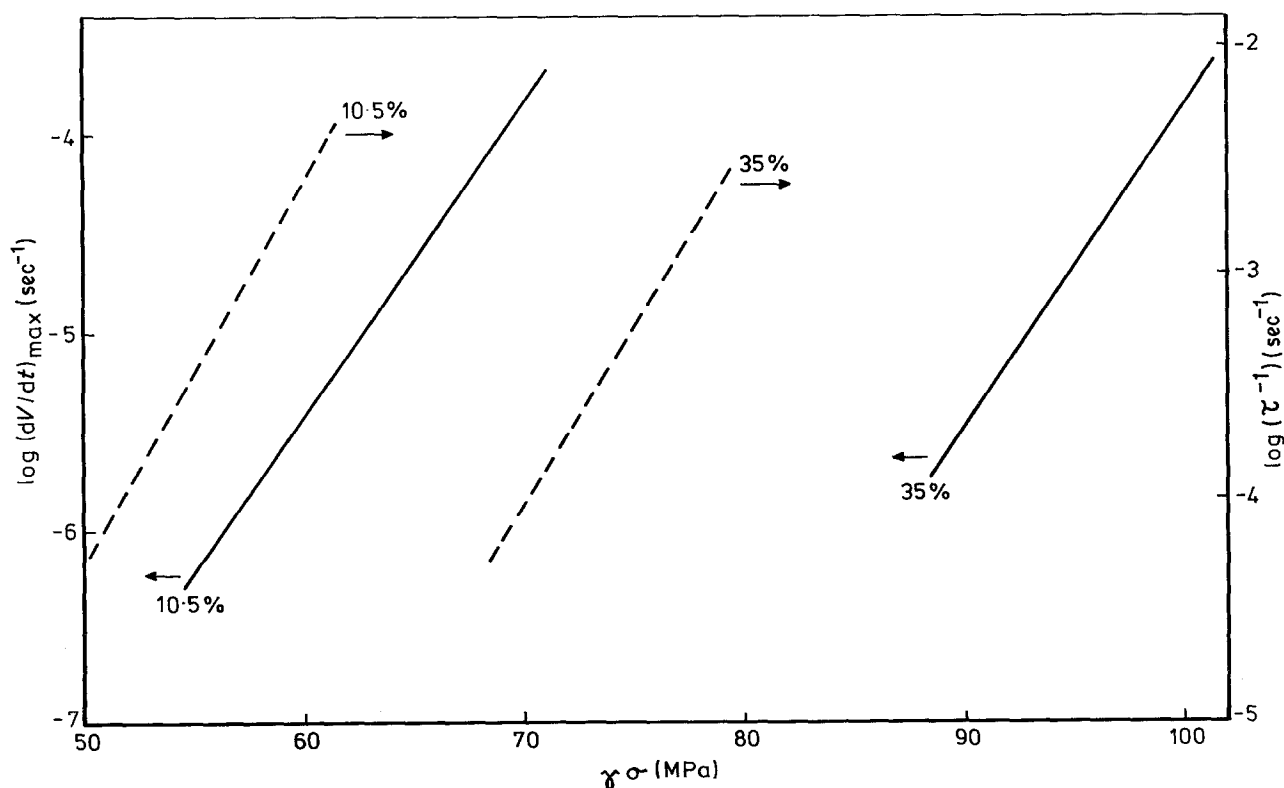


Figure 8 Eyring plots of  $\log(\tau^{-1})$  and  $\log(dV/dt)_{\max}$  against  $\gamma\sigma$ .

volume of polystyrene, which was measured by a quite different experimental method from the volume strain test used in the present work. The results for the PMMA series, on the other hand, are all direct determinations based on the same creep method. Consequently, it is possible that some of the difference between the two curves originates from the use of a low value for  $V^*$  of polystyrene.

The effects of volume fraction,  $\phi$ , upon rates of crazing are not confined to changes due to an increase in  $\gamma$ . If  $\log(\tau^{-1})$  and  $\log(dV/dt)_{\max}$  are plotted not against  $\sigma$  but against  $\gamma\sigma$ , as in Fig. 8, the curves for higher rubber contents are below those for low rubber contents. It is unlikely that an increase in  $\phi$  would reduce the pre-exponential factor  $Q$ , and another explanation is therefore required. The most likely reason for the shift is that the average size of craze or volume of craze material generated by each initiation event decreases with increasing  $\phi$  because of interaction between crazes and neighbouring particles or other crazes. In terms of reaction kinetics, this is equivalent to saying that the rate of termination increases with the rate of initiation.

## 5. Conclusions

This paper has concentrated upon a single structural parameter in HIPS, the rubber particle volume fraction  $\phi$ ; other factors, including particle size distribution and internal morphology, have been kept constant. The study has characterized relationships between mechanical properties and  $\phi$ , but has also raised some unanswered questions concerning the kinetics of crazing. These results have been used as a basis for a more comprehensive examination of structure-property relationships, including particle size effects, which will be reported in future papers.

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