Crazing within glassy occlusions in rubber particles of toughened glassy polymers: a micromechanical investigation

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The possibility that crazing initiates within glassy occlusions in rubber particles of toughened glassy polymers has been explored theoretically. A micromechanical analysis of the stress distribution and of some craze initiation factors has been performed using an elementary, single particle model. The results show that this possibility falls within theoretical predictions, if dilation is assumed to be the dominant factor in craze initiation criteria.

INTRODUCTION

Toughening by inclusion of rubber particles in glassy polymers is a well-consolidated technology. Whatever the mechanism of yielding and fracture may be, the toughening action is believed to be due to absorption of energy by the composite material through internal crazing arising from stress concentrations induced by the soft rubber inclusions (see, for example, refs 1 and 2). This phenomenon is generally thought to be localized in the glassy matrix regions surrounding the rubbery particles.

However, the particles themselves are known to be composite, in turn occluding substantial amounts of glassy material. It is therefore of interest to investigate the effect that glassy sub-inclusions have on stress distribution and the role that they may play in craze initiation phenomena inside the composite material.

In previous papers[3–5] we have carried out a micromechanical analysis of an elementary, single-particle model of rubber-toughened glassy polymers, in which the rubbery particle had composite nature. The particle embedded in the glassy polymer matrix was assumed to be made of a single spherical glassy occlusion enveloped by a concentric, spherical rubber shell. Thermal stresses induced by the two phase particle[3], and the stress distribution in the matrix around the particle under an applied uniaxial tension[4] were first analysed. A number of different mechanical factors, which have frequently been thought to govern craze initiation, were then calculated[5] still under uniaxial tension and in the matrix region surrounding the particle, where crazing is usually thought to occur. Results showed that the highest values of these factors in the matrix are found either at the pole or at the equator of the particle[5].

A corresponding analysis may now be interesting for the glassy occlusion of the particle. It has been indicated that crazing may also occur within the glassy occlusions (or sub-inclusions) in high impact polystyrene when the fraction of occluded polystyrene is high[6,7]. Furthermore, a recent experimental investigation[8] points to the possibility that crazes initiate at the sub-inclusion/rubber interface within the composite particle. This possibility is of particular practical interest, because an appropriate design of the material would offer a means of absorbing energy within the heterophasic particles even before the matrix reaches the critical point of its incipient failure.

The aim of the present work is to explore this possibility theoretically using the elementary model presented in previous publications[3–5].

The model

The model assumed for the two phase rubbery particle embedded in the glassy polymer matrix[3–5] is represented in *Figure 1.* The component materials are postulated to be perfectly homogeneous, isotropic and linearly elastic, neglecting any time-dependence of the viscoelastic properties. Using these assumptions, the only relevant material constants are the ratio between two elastic moduli, (say the shear moduli G_1 and G_2) and the Poisson ratios ν_1 and ν_2 of the two compoennt materials, 1 and 2. Since the analysis was carried out numerically, we had to assign specific values for these constants. Indicating the glassy polymer by index 1 and the rubber by index 2, the following values were taken[3–5] as characteristic of this pair of materials: $G_1/G_2 = 10^3$, $\nu_1 = 0.35$, $\nu_2 = 0.49982$ (the Poisson ratio of rubber, ν_2, being close to the limiting value of 0.5, is more critical and needs to be realistically specified[9]). Furthermore, perfect adhesion is postulated at the interfaces of different materials.

The choice of this single-occlusion, single-particle model in relation to craze initiation was justified and extensively commented upon in ref 5. It may be worth recalling that while it sacrifices the multiplicity of sub-inclusions, it preserves other topological features which may be envisaged as relevant in the real composite particle: discrete nature of sub-inclusion, continuity of rubber within the inclusion, embedding of sub-inclusion in the rubber matrix. In this way, every phase of the material maintains its individual characteristics, and the local analysis of crazing factors can be considered as being meaningful.

It may also be worth recalling that the hypothesis of

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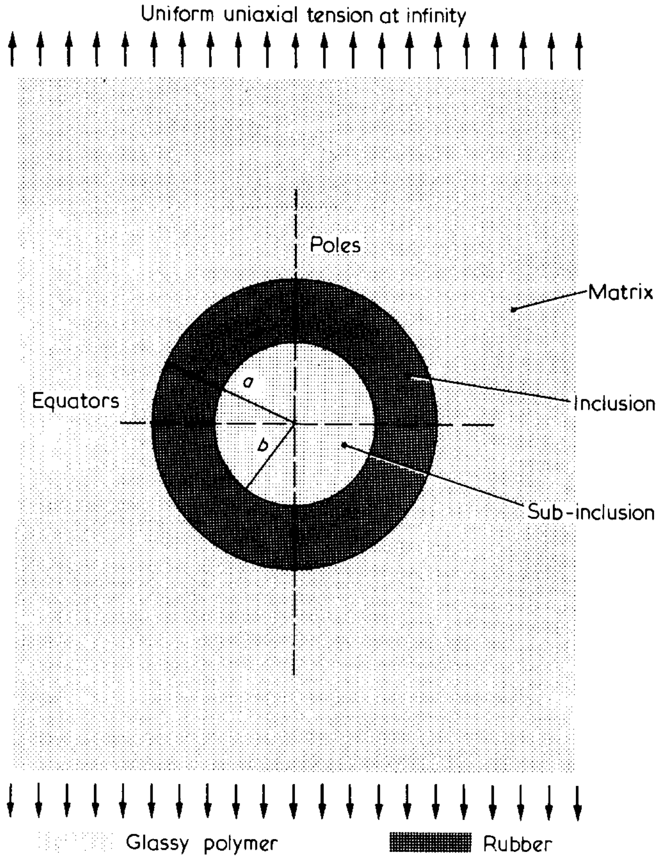

Figure 1 Elementary model assumed for a single, composite rubbery particle embedded in glassy polymer

linear elasticity makes the analysis valid up to the point of incipient craze formation at best, so that when crazing takes place at some site, the hypothesis of linear elastic behaviour throughout the composite material fails, and the correct meaning of the analysis is lost.

RESULTS AND DISCUSSION

The craze initiation factors examined are listed in the first column of *Table 1*. The reader is referred to our previous paper[5] and to the original papers quoted therein for an explanation of the craze initiation criteria involving these factors.

Each of these can be expressed in terms of stress or strain tensor components. For the convenience of the reader, the relevant general relations and the basis for the calculation in the specific case of the model system here considered are given in the Appendix. Each of the factors examined was computed at any point inside and the glassy sub-inclusions, at different ratios b/a of the radii of sub-inclusion and inclusion, respectively. For any given value of b/a in the interval $0 < b/a < 1$, the spatial distribution of each craze initiation factor was displayed by drawing a contour level map of its values on a generic meridian plane of the model.

These maps showed that maxima occurring in the craze initiation factors happen to be localized either at the centre or at the pole of the sub-inclusion, as reported in *Table 1*. For comparison, in the same Table the location of the maxima of the same factors in the glassy matrix (at the inclusion–matrix interface) is also indicated[5].

While the location of the maximum of each of the factors in the sub-inclusion does not vary, whatever the relative size of sub-inclusion and inclusion, the values of the maxima depend on b/a. These values, normalized with respect to the corresponding values at infinity, are reported as a function of b/a in *Figure 2*, together with the values of the absolute maxima in the matrix region surrounding the particle, for comparison.

For every factor examined, except dilation, the maximum value inside the glassy sub-inclusion is constantly lower than the maximum value outside the particle, over the entire b/a range.

Dilation, however, shows an inversion at $b/a = \sim 0.88$: in the lower range of b/a a higher (equatorial) maximum is reached in the matrix, while for $b/a > 0.88$ the maximum at the pole of the sub-inclusion overcomes the one in the matrix. As a consequence, every criterion of craze initiation based on dilation would make it possible for crazing to occur firstly inside the glassy occlusion, if its relative size were sufficiently high.

CONCLUSIONS

In spite of the simplicity of the elementary model of composite rubber particle assumed, interesting indications emerge from the present analysis.

(1) The possibility that crazing can initiate inside the composite rubber particles, within the glassy domains of matrix material occluded, indicated by experiment, falls within theoretical predictions based on the assumption that dilation is the dominant factor of craze initiation.

(2) Should this possibility become substantiated by general experimental evidence, criteria based on dilation would become apparent as the most appropriate for predicting craze initiation phenomena.

The present results are controlled by specific values of the material constants. It seems interesting to extend the analysis to a number of combinations of different values, covering a spectrum of realistic cases. This work is in progress.

Table 1 Location of maxima of different craze initiation factors as a function of b/a*

	Sub-inclusion (This paper)		Matrix (Previous paper[5])	
	b/a	Location	b/a	Location
Maximum principal stress, σ_{max}	0–1	Pole	0–1	Equator
Maximum principal strain, ϵ_{max}	0–1	Centre	0–0.93 0.93–1	Equator Pole
Dilation, Δ	0–1	Pole	0–1	Equator
(Total) strain energy density, W_S	0–1	Centre	0–0.91 0.91–1	Equator Pole
Maximum principal shear stress, τ_{max}	0–1	Centre	0–0.91 0.91–1	Equator Pole
Distortion energy density, W_D	0–1	Centre	0–0.90 0.90–1	Equator Pole

* Ratio of the shear elastic moduli of the two component materials $G_1/G_2 = 10^3$, Poisson's ratio of the glassy polymer $\nu_1 = 0.35$, Poisson's ratio of the rubber $\nu_2 = 0.49982$

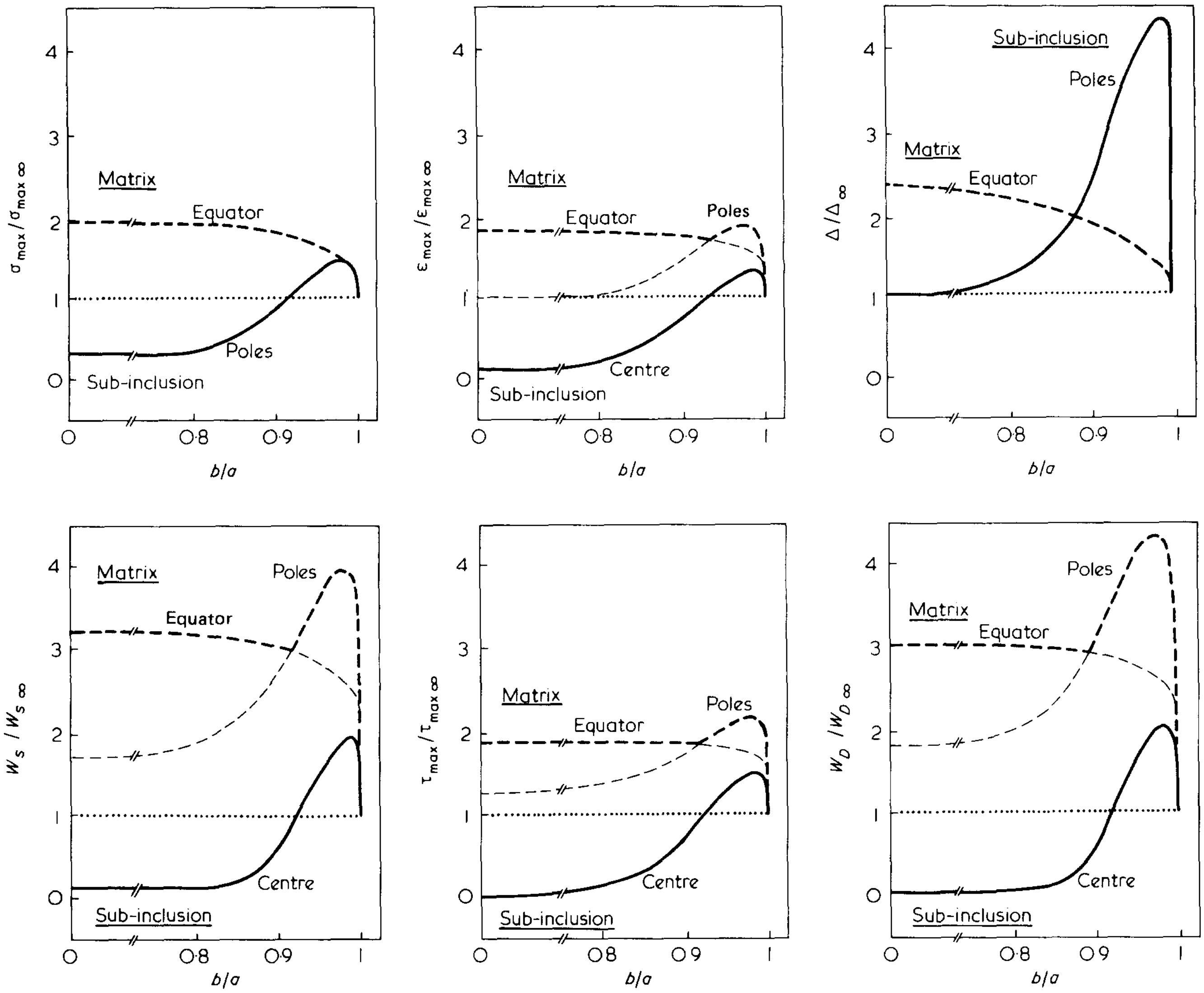

Figure 2 Maxima of the maximum principal stress, σ_{max}, maximum principal strain, ϵ_{max}, dilation, Δ, total strain energy density, W_S, maximum principal shear stress, τ_{max}, and distortion energy density, W_D, in the glassy sub-inclusion (full lines) and in the glassy matrix around the particle (broken lines: heavy-absolute maximum, light-relative maximum) as function of ratio *b/a* of the radii of the sub-inclusion and of the inclusion, respectively

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APPENDIX

If σ_1, σ_2, σ_3 denote the principal stresses, τ_1, τ_2, τ_3 the principal shear stresses, and ϵ_1, ϵ_2, ϵ_3 the principal strains at a point, the following general relations hold:

$$\tau_1 = 1/2|\sigma_1 - \sigma_2|$$

$$\tau_2 = 1/2|\sigma_2 - \sigma_3|$$

$$\tau_3 = 1/2|\sigma_3 - \sigma_1|$$

and, applying Hooke's law:

$$\epsilon_1 = (1/E)\,[\sigma_1 - \nu(\sigma_2 + \sigma_3)]$$

$$\epsilon_2 = (1/E)[\sigma_2 - \nu(\sigma_1 + \sigma_3)]$$

$$\epsilon_3 = (1/E)[\sigma_3 - \nu(\sigma_1 + \sigma_2)]$$

where E and ν denote the Young's modulus and the Poisson's ratio, respectively, of the material at the same point.

We then call:

$$\sigma_{max} = \max(\sigma_1, \sigma_2, \sigma_3)$$

$$\epsilon_{max} = \max(\epsilon_1, \epsilon_2, \epsilon_3)$$

$$\tau_{max} = \max(\tau_1, \tau_2, \tau_3)$$

The dilation Δ, the total strain energy density W_S, and the distortion energy density W_D can be expressed as:

$$\Delta = \epsilon_1 + \epsilon_2 + \epsilon_3$$

$$W_S = (1/2E)\cdot[-\nu(\sigma_1 + \sigma_2 + \sigma_3)^2 + (1 + \nu)(\sigma_1^2 + \sigma_2^2 + \sigma_3^2)]$$

$$W_D = (1/3\,G)\cdot(\tau_1^2 + \tau_2^2 + \tau_3^2)$$

where G denotes the shear elastic modulus of the material.

The evaluation of the quantities $\sigma_{\max}$, $\epsilon_{\max}$, $\tau_{\max}$, Δ, W_S and W_D implies that the stress tensor components are first computed. In our case, it is convenient to assume a spherical coordinate system (r, θ, ψ) with its origin at the centre of the particle and the polar axis coincident with the symmetry axis (oriented as the applied stress direction). It turns out that the only non-zero stress tensor components are σ_{rr}, $\sigma_{\theta\theta}$, $\sigma_{\psi\psi}$, $\tau_{r\theta}$ and these are related to the principal stresses as follows:

$$\sigma_{1,2} = \frac{1}{2}(\sigma_{rr} + \sigma_{\theta\theta}) \pm \frac{1}{2}\left[(\sigma_{rr} - \sigma_{\theta\theta})^2 + 4\tau_{r\theta}^2\right]^{1/2};\ \sigma_3 = \sigma_{\psi\psi}$$

Using Goodier's work on a single spherical domain[10], the general solution of the field equations of elasticity (or otherwise the non-zero stress tensor components as well as the non-zero displacements at a point) can be expressed in the present case (two concentric spherical domains) through twelve constants to be determined from continuity conditions at the interfaces[11,12,4]. This requires the solution of a set of twelve equations which can be practically performed numerically using a digital computer.

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