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A predictive model for particulate filled composite materials

Part 2 *Soft particles*

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Our predictive model for particulate filled composite materials is applied to epoxy resin toughened by rubber spheres. Good agreement is found between predicted values of stiffness and experimental measurements. The variability of yield stress with volume fraction is explained. The observed fracture processes, including rubber cavitation, are explored; the importance of thermal stresses is highlighted. The fracture behaviour of these materials is discussed in the light of these predictions.

1. Introduction

Polymeric materials toughened by addition of rubber are being increasingly used both as adhesive materials and as the matrices of fibre reinforced composite materials. The rubber forms discrete spheres in a polymer matrix. The mechanism of toughening has been the subject of much controversy in the literature. The toughening may not take place for high speed impact tests [1] or in the presence of a constraint such as thin bond adhesive application [2]. It is, therefore, of considerable importance that the source of the toughness is elucidated. This source of the toughness may be found by examination of stress distributions which can be provided by our theoretical model.

The deformation and fracture behaviour of rubber toughened epoxy resin has recently been reviewed and investigated by Kinloch and his coworkers [3–5] and by Yee and Pearson [6, 7]. Results of both mechanical studies and microscopic observations from both these studies show that deformation occurs via voiding and cavitation of the rubber particles, with shear yielding in the resin matrix. An alternative model for the toughening of these materials arising from the tearing of rubber particles has been proposed [8]; the shortcomings of this approach have been fully discussed [3, 6].

Our results presented here do not include full examination of thermal stresses arising from curing. The difference in thermal expansion coefficients for rubber and epoxy resin means that the rubber sphere will be in hydrostatic tension after cooling. The properties of these materials are very sensitive to conditions of curing [9], which must indicate sensitivity to thermal stresses. Thermal stresses in fibre reinforced composites have been found to relax even when the material is left at zero stress; this relaxation is shown by changes in specific damping capacity [10] and acoustic emission behaviour [11]. Such relaxation might occur more rapidly under conditions of stress. Our analysis shows that the fracture processes for these materials may be dependent on thermal stresses (Section 5). There is urgent need for further theoretical and experimental investigation of thermal stresses and their possible relaxation.

2. Analysis

The method of analysis was identical to the method described for the hard particles [12]. The method of analysis has been fully described by Davy and Guild [13]. Finite element analysis is carried out for a sphere centred in a cylinder of resin, as shown in Fig. 1, using axisymmetric elements for the plane ABCD. The deformed grid shape is constrained as shown. The finite element analysis package used is LUSAS, running on an ICL 2988 computer. A statistical model of a particulate filled composite has been developed [13]; the model assumes that the spheres are randomly distributed, but they are not allowed to overlap. The statistical analysis allows results from finite element analyses, that is results from analyses of a sphere within a cylinder of resin, to be related to an overall volume fraction of randomly distributed spheres. The property values are calculated from combining results from three different finite element analyses, and are presented as bounds. These bounds arise from the statistical variability of the microstructure, which has been modelled to consist of varying size cylinders; the bounds are described as "equal stress" and "equal strain" bounds, dependent on the assumption made regarding the load distribution to the different cylinders.

The material properties used were those proposed by Maxwell [14] and are shown in Table I. Finite element analysis was carried out for the primary grids and for the grids necessary to calculate the dispersion factors. Dispersion factors must be applied to numerical

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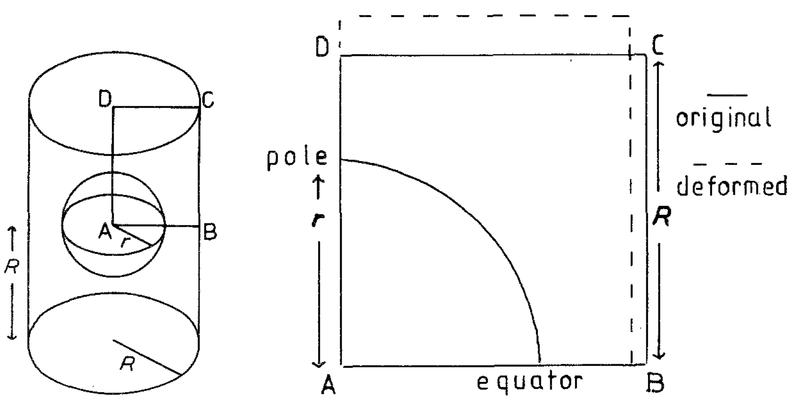

Figure 1 The finite element model.

results to allow for the effect of the variability of the distribution of the spheres [13]; results from finite element analysis may be directly associated with volume fraction after the application of dispersion factors. As in our previous paper [12], most graphical results presented have been fully calculated and are accurately associated with volume fraction. Contour diagrams, however, were obtained from finite element analysis of the primary grid only; the values are not, therefore, numerically accurate. All stress results are expressed as stress concentration factors, that is as the ratio of the local stress to the average stress applied to the composite.

3. Young's modulus

The predicted variation of Young's modulus of epoxy resin reinforced with varying volume fractions of rubber spheres is shown in Fig. 2. Fig. 2 includes the theoretical values calculated assuming regular hexagonal packing [15]. The near linear relationship between this property and volume fraction leads to very similar results for the two methods of prediction [16]. The measured Young's modulus [14] for epoxy resin reinforced with 15% volume fraction of rubber spheres is also included. The value shown is the mean value measured at different temperatures, the modulus value being expressed as the ratio of the composite to matrix modulus; the error bar shown is one standard deviation.

This measured value is significantly higher than the predicted range. We postulate that the lack of precise numerical agreement could arise from the description of the rubber properties required by LUSAS, and our assumption here that the phases are perfectly separated. The predicted values of overall modulus are relatively insensitive to precise value of rubber modulus. The modulus value used was 0.0004 GPa; the predicted overall modulus value increased by only 7% for an increase in rubber modulus of two orders of magnitude. The predicted overall modulus is found to decrease by a similar amount if the Poisson's ratio of the rubber is decreased from the value used, 0.499, to 0.4. The properties of the rubber could probably best be described using a Poisson's ratio of 0.5, but this causes problems for the finite element analysis. The higher experimental value compared with our theoretical predictions therefore probably arises from some stiffening of the rubber via the epoxy, from the inadequate description of the Poisson's ratio of the rubber, and from incomplete phase separation leading to a lower rubber volume fraction than expected from the formulation.

TABLE I Constituent material properties

Epoxy resin matrix		Rubber sphere	
Young's modulus *E* (GPa)	Poisson's ratio	Young's modulus *E* (GPa)	Poisson's ratio
3.21	0.35	0.0004	0.499

Our theoretical predictions are compared with experimental results from Yee and Pearson [6] in Fig. 3. We note that the almost linear relationship between Young's modulus and volume fraction shown in Fig. 3 is of the same form as the relationship measured experimentally by Yee and Pearson [6]. Further, their experimental results show an approximate 30% decrease in Young's modulus for about 20% volume fraction of rubber; the magnitude of this decrease is in agreement with our predicted decrease (Fig. 3).

Our model predicts that the overall modulus of the composite is relatively insensitive to the modulus of the rubber. This result raises questions regarding the work which has been presented as justification of the theory of rubber tearing as the major source of

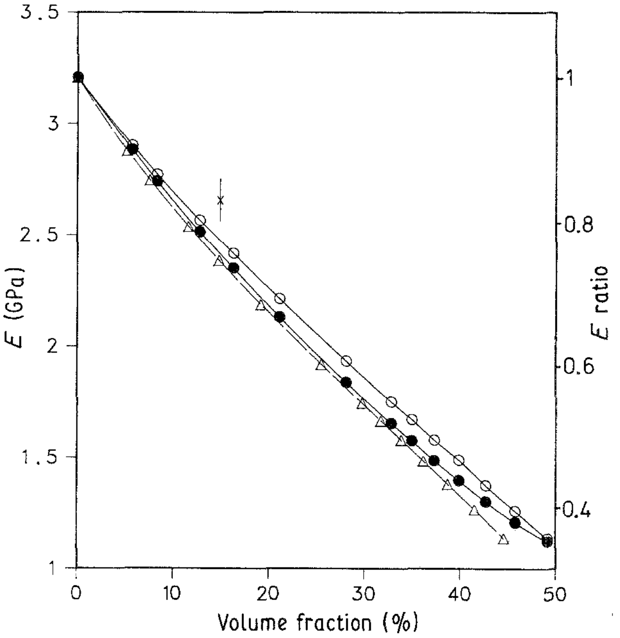

Figure 2 Variation of Young's modulus, *E*, with volume fraction for epoxy resin filled with rubber spheres (● equal stress predicted values using our model, ○ equal strain, △ predicted values assuming regular hexagonal array, x experimental value, with error bar [14]).

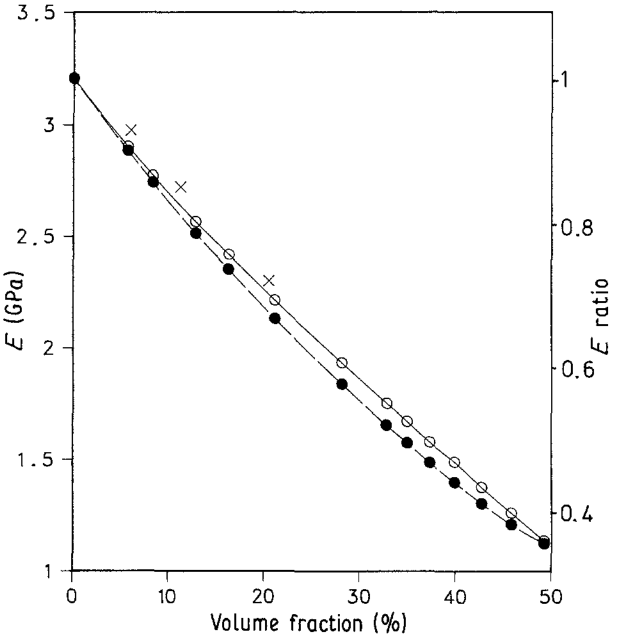

Figure 3 Variation of Young's modulus, E, with volume fraction for epoxy resin filled with rubber spheres (● equal stress predicted values, ○ equal strain, x experimental values [6]).

toughening in these materials [17]. Radiation treatment was used to increase the cross-link density of the rubber, thus increasing the tear energy. This parameter was considered to be the only material property changed by the radiation treatment, thus the toughening peak at mid-dose was attributed to the point when both deformation and tearing of the particles occurred. We note however that an increased Young's modulus of the composite with dose was measured; our results show the insensitivity of the composite modulus to rubber modulus and we therefore propose that the change in composite modulus must indicate a very large change in rubber modulus. Radiation is, therefore, changing the stress distributions, and the measured toughening peak represents the most favourable distribution. This effect will be considered in detail in a future paper [18].

4. Stress distributions

4.1. Concentration of direct stress

Fig. 4 shows the contour diagram for the concentration of the applied stress, σ_{yy}, for the primary grid for 21.1% volume fraction of rubber. Maximum stress concentration is found at the interface at the equator of the sphere. Examination of other contour diagrams confirmed that this is the maximum principal stress in the system. The value of this maximum stress concentration factor varies sharply with volume fraction of rubber spheres, as shown in Fig. 5. The position of maximum stress concentration, at the equator of the sphere, is in agreement with previous theoretical predictions and experimental results [19]. Crack growth is attracted to the equator of the sphere.

4.2. Stresses at the interface

Stresses around the interface were converted to polar coordinates; uncorrected values for the same grid are shown in Fig. 6. The shear stresses in both the resin matrix and the rubber sphere are zero. The only high

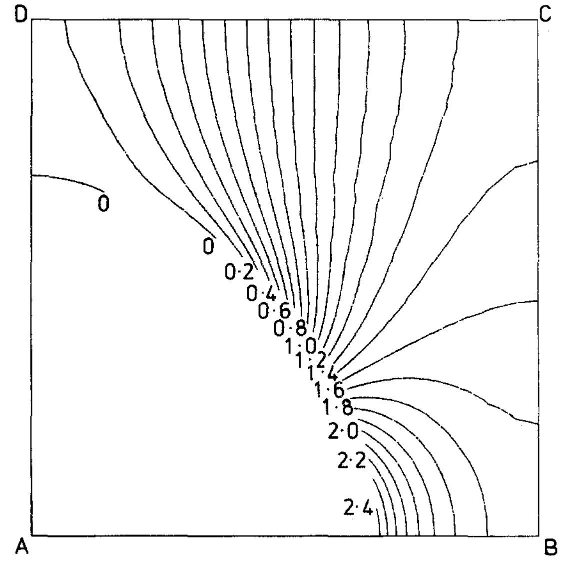

Figure 4 Contours of stress concentration factor of applied stress, σ_{yy}, for primary grid for epoxy resin filled with 21.1% volume fraction of rubber spheres.

stress is the tangential stress in the resin matrix, which has its maximum, the maximum stress in the system, at the equator of the rubber sphere. The radial stresses in the resin and rubber are equal and constant around the interface; the tangential stress in the rubber is also identical. We note that the radial stress at the interface is far smaller than that found for epoxy resin filled with glass spheres [12]. This result indicates that for rubber spheres there is no tendency for debonding at the interface, in contrast to the tendency for debonding for the glass filled material.

Fig. 6 shows that very little stress is transmitted to the rubber; the rubber sphere is acting like a hole. This is confirmed in Fig. 7 which compares values of maximum stress concentration factor, at the equator, for epoxy resin containing holes or rubber spheres, for

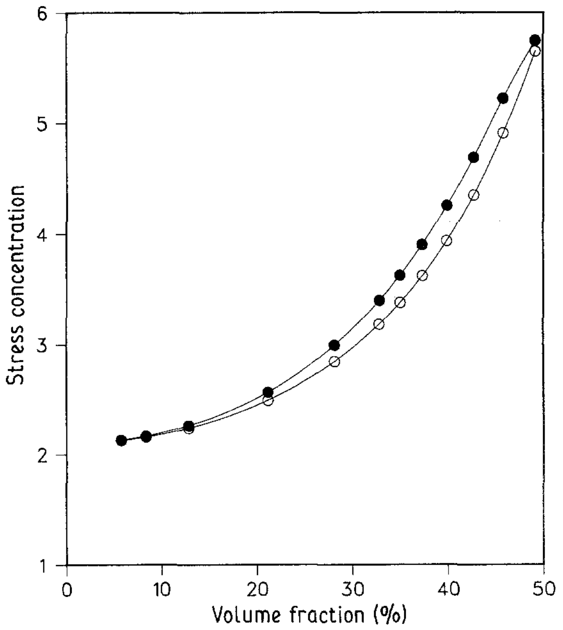

Figure 5 Variation of stress concentration factor of applied stress, σ_{yy}, with volume fraction of rubber spheres (● equal stress, ○ equal strain).

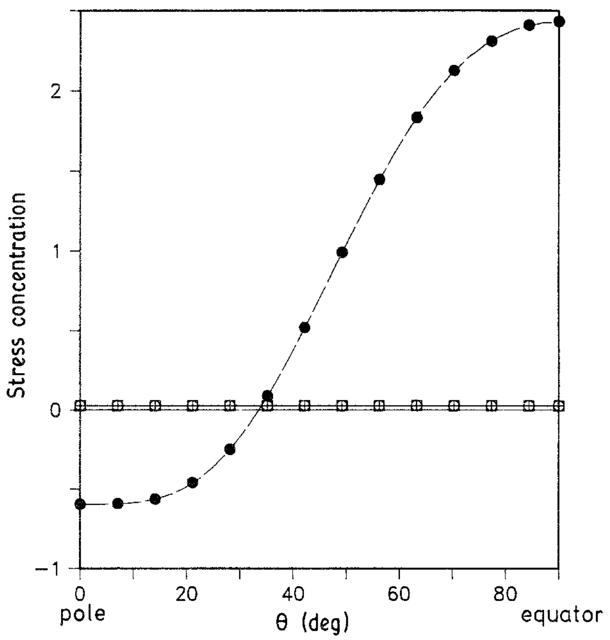

Figure 6 Variation of stress concentration factors of interface stresses, in polar coordinates, for primary grid for epoxy resin filled with 21.1% rubber spheres (□ radial stress in resin, ● tangential stress in resin, + radial stress in rubber, ○ tangential stress in rubber).

different finite element grids. The values are hardly changed by the presence of the rubber.

4.3. Hydrostatic stress in the rubber particle

Examination of the stresses in the rubber show that the whole particle is in uniform pure hydrostatic tension. The variation of this stress concentration factor of hydrostatic tension with volume fraction is shown in Fig. 8. The magnitude of this stress is uniform throughout the sphere within the accuracy of these predictions indicated by Fig. 8. Although the value of this stress concentration is about two orders of magnitude smaller than the maximum stress concentration in the resin (Fig. 6), its magnitude may be significant since the difference in moduli is around five orders of magnitude. The magnitude of the stress concentration of hydrostatic tension in the rubber increases with increasing volume fraction as shown in Fig. 8.

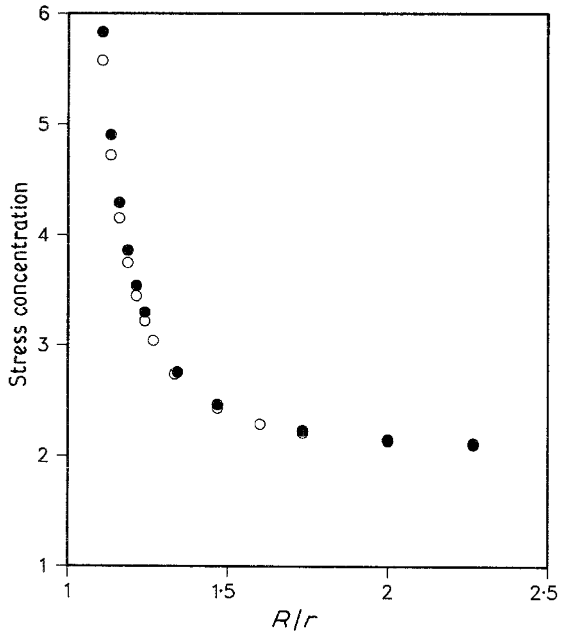

Figure 7 Comparison of stress concentration factor of applied stress at the equator for epoxy resin containing holes or rubber spheres (○ rubber sphere, ● hole).

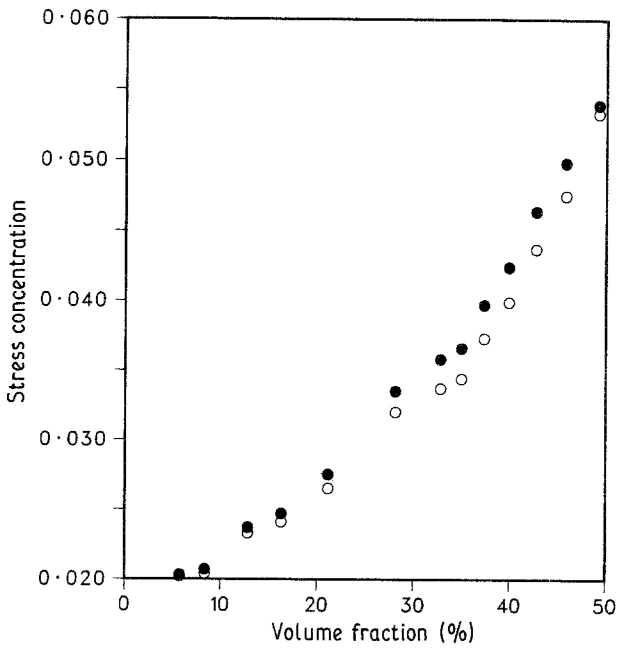

Figure 8 Variation of stress concentration factor of hydrostatic tensile stress in rubber sphere with volume fraction (● equal stress, ○ equal strain).

Thermal stresses from cooling of the composite also place the rubber particle in hydrostatic tension. Full examination of thermal stresses is beyond the scope of this paper, but a preliminary examination has been carried out. Cooling of the composite places the rubber sphere in hydrostatic tension, the value being almost constant between rubber volume fractions of 7% and 27%. The exact value of hydrostatic tension cannot be deduced from our results since the temperature dependence of the moduli cannot be included. We note however that cooling through 10° C assuming room temperature moduli predicts that the rubber particle will be at around 1 MPa hydrostatic tension; this may be an indication of the true value.

4.4. Concentration of yield stress

Contours of Von Mises stress for the same grid are shown in Fig. 9. The maximum Von Mises stress is found at the interface, at the equator of the sphere, the identical position to the maximum direct stress. The position of the maximum remains unchanged for different volume fractions, but the magnitude of the stress concentration factor increases sharply with increased volume fraction, as shown in Fig. 10. The magnitude of the hydrostatic stress at the equator is less dependent on volume fraction; there is little increase up to around 20% volume fraction and it then increases by a factor of 2 between 20 and 50% volume fraction.

Our finite element predictions may be directly compared with experimental values of yield stress. Experimental values of yield stress at varying volume fractions of rubber are available from Yee and Pearson [6]. Our predictions (Fig. 10) show that a stress concentration of yield stress, Von Mises

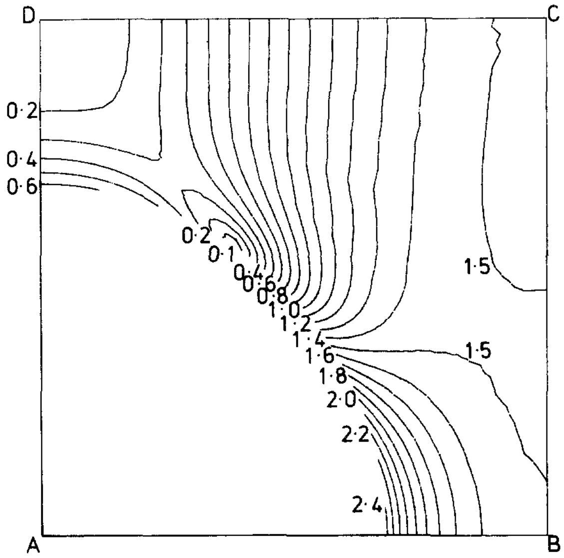

Figure 9 Contours of stress concentration factor of Von Mises stress, σ_V, for primary grid for epoxy resin filled with 21.1% volume fraction of rubber spheres.

stress, of almost 2 is found for a single rubber sphere. The experimental results do not show a very steep change in applied stress for yield at low volume fractions. We can however compare the change in applied stress required for yield between about 10% and 20% volume fraction of rubber. Our predictions show an increase in stress concentration factor from 2.05 to 2.30 over this range. Assuming that yield occurs when the stress within the material reaches a given level, and we note that hydrostatic stress over this range changes slowly, this increase in stress concentration factor predicts that the applied stress at 20% rubber volume fraction should be 89% of the applied stress at 10% rubber volume fraction; the decrease measured [6] was from 55 to 50 MPa, i.e. 91%. This excellent agreement gives further confidence to our predictions.

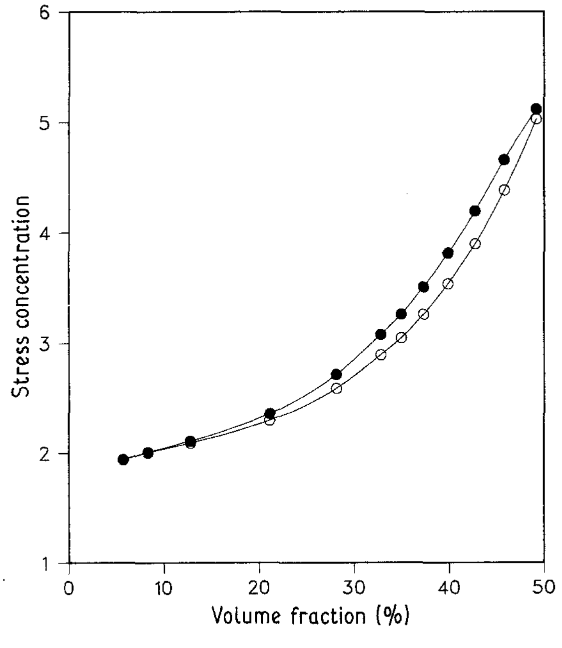

Figure 10 Variation of maximum stress concentration factors of Von Mises stress with volume fraction for epoxy resin filled with rubber spheres (● equal stress, ○ equal strain).

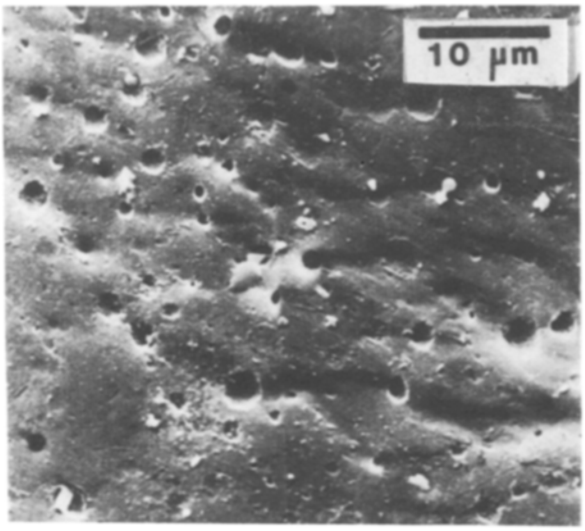

Figure 11 Polished surface of epoxy resin filled with rubber spheres showing shear bands forming from the equators of the rubber particles after deformation (courtesy Dr D. L. Maxwell) [14].

Shear bands in the resin would be expected to grow from the point of maximum concentration of Von Mises stress, predicted to be the equator of the sphere. This result is found on the side surfaces of deformed samples (Fig. 11). Shear bands growing from the equators of rubber particles are clearly visible.

5. Fracture behaviour

Yee and Pearson [6] describe the fracture processes to be cavitation of the particles followed by yield of the resin; they consider yield impossible until after cavitation. Our results, however, show that the rubber particle behaves very like a hole in respect to the stress distribution in the resin (Fig. 7) so cavitation should not be essential prior to yield.

Gent and Lindley [20] have shown that cavitation of rubber can occur at relatively low stresses. Their analysis was later extended to include surface energy effects for small holes [21]. Surface energy effects are important for initial holes smaller than 0.1 μm radius. The hydrostatic stress required for cavitation from an initial hole with radius greater than about 0.1 μm has been shown to approximate to the modulus of the rubber [22], i.e. about 0.4 MPa. For an initial hole of radius 0.01 μm the stress required for cavitation increases by a factor of 40. Schwier *et al.* [23], in their experimental investigation of polystyrene filled with polybutadiene rubber spheres, concluded that intrinsic cavitation of rubber spheres occurred at about 60 MPa overall hydrostatic tension.

Our preliminary examination of thermal stresses has found that the rubber sphere is subjected to some hydrostatic tension from cooling, perhaps of the order of 1 to 10 MPa. Our results in Fig. 8 predict that for 20% volume fraction of rubber the concentration factor of hydrostatic tension in the rubber is about 0.025. Shear band formation probably occurs at about 40 MPa stress for epoxy resins [14]; our model predicts that this average applied tensile stress would subject the rubber spheres to a further 1 MPa hydrostatic tension. Doyle [24] used finite element analysis to also show that the rubber particle would be subjected to

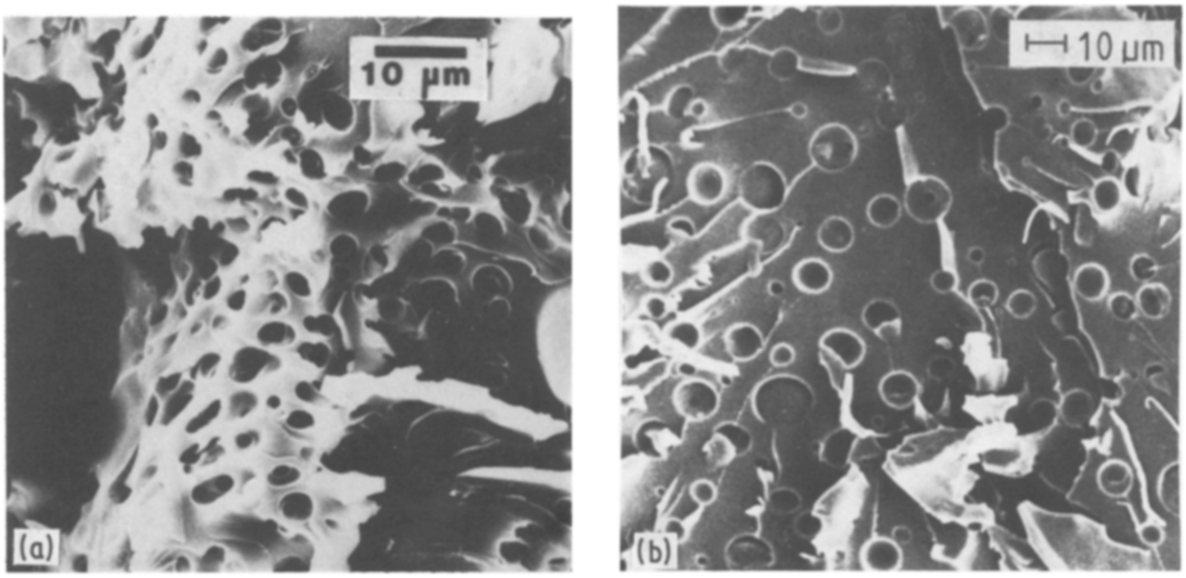

Figure 12 Fracture surfaces of polymers filled with rubber spheres showing rubber cavitation (a) epoxy resin (courtesy Dr D. L. Maxwell [14]), (b) polyurethane (courtesy Dr J. L. Stanford [25]).

additional hydrostatic tension by the presence of a crack or shear band.

Cavitation of rubber particles has been clearly observed by many workers including Yee and Pearson [6] and Maxwell [14] in rubber-modified epoxy resins and by Stanford and his coworkers [25] in their studies of rubber toughened polyurethane. Examples of cavitation of rubber particles on fracture surfaces are shown in Fig. 12 and it can be seen that cavitation is generally found to initiate from the centre of the sphere. Our predictions do not indicate a preferred point of initiation but it is clear that they show that the imposition of an overall tensile stress of the order of the matrix yield stress places the rubber particles in sufficient hydrostatic tension to initiate cavitation from small flaws. These flaws may be areas of rubber which are not fully polymerized and which could not be observed using conventional microscope techniques. There is some argument as to whether or not the cavitation of the rubber particles is necessary before shear bands form. Clearly our results show that the two processes can take place independently although the exact stress levels for shear band formation and cavitation will depend upon the values of stress required to form matrix shear bands and cause rubber cavitation for the system in question. Yee and Pearson [6] report seeing cavitation before matrix yielding whereas the fracture surfaces in Fig. 12 result from complex deformation and so do not give any information on this point.

Epoxy resins reinforced with rubber spheres may be described as inherently tough materials since the position of maximum stress concentration, where a crack would be attracted, is at the equator of the sphere; the sphere would be a barrier to further crack growth. However, Fig. 5 shows that the magnitudes rise very sharply at high volume fractions. A simple description of toughness could be that yield is the preferred mechanism to crack growth. Fig. 5 shows the very high stress concentration of applied stress at high volume fractions; crack growth could become more preferred at high volume fractions leading to decreased toughness. This effect was noted by Kunz *et al.* [26] who found a rapid increase in toughness until around 5 pbw (parts by weight) rubber, around 10% volume fraction, followed by a plateau. A similar effect was found by Spanoudakis and Young [19] for epoxy resin reinforced with glass spheres treated with a release agent; the sphere must be behaving as a "stable hole", and stress distribution in the resin must be similar to our predictions here; the observed crack growth for glass spheres treated with a release agent supported the expected maximum stress concentration at the equator of the sphere. They found that fracture toughness decreased with volume fraction above about 30% for this material, although for glass spheres coupled to the resin matrix the toughness increased throughout the range of volume fraction.

Stress distributions in the matrix for resin containing rubber spheres has been found to be very similar to those for resin containing holes. Shear band formation in the resin would occur very similarly for the two materials. However, epoxy resin containing holes is known to be a very poor material. We therefore postulate that shear band formation is not the only important fracture mechanism for this material. Our results have shown that cavitation of the rubber particles is likely to occur, in agreement with experimental observations; after cavitation the rubber may be stretched. The presence of thermal stresses, causing the rubber sphere to be in hydrostatic tension, may be necessary for cavitation to occur; such stress may be very different when the material is used as a composite matrix or as thin bond adhesive.

It appears that the processes of rubber cavitation and stretching may make important contributions to the overall fracture energy. The magnitude of these contributions is dependent on the modulus of the rubber. This effect will be studied theoretically in our future paper [18], but could also be a subject of fruitful experimental study. Further contribution to the fracture energy of epoxy resin containing rubber spheres may arise from the physical presence of the rubber which would act as a crack stopper to a growing crack attracted to the equator of the sphere by either the concentration of direct stress or the initiation of shear bands.

6. Concluding remarks

Our combination of finite element analysis and spatial statistical techniques allows results from finite element analysis to be applied to real composite materials. Comparison of our predictions with experimental results for epoxy resin reinforced with soft particles provides valuable insights into the mechanical behaviour of these materials. The importance of thermal stresses has been highlighted; the implication of our model that their presence is required for high toughness needs further theoretical and experimental investigation. The design of optimum particulate reinforced materials in terms of the desired volume fraction of filler and constituent material properties may now be considered.

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