The sequence of initiation of the toughening micromechanisms in rubber-modified epoxy polymers

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(*Received 5 February 1992; revised 16 June 1992*)

Numerical finite element analyses have shown how the sequence of initiation between the two main mechanisms of toughening observed in rubber-toughened epoxy polymers is strongly dependent upon the properties of the rubbery particle and, in particular, the value of Poisson's ratio. A high Poisson's ratio of the dispersed second phase favours the initiation of internal cavitation before localized shear yielding of the epoxy matrix.

(**Keywords: toughening; epoxy polymers; Poisson's ratio**)

Introduction

Thermosetting epoxy polymers are frequently toughened by the incorporation of a secondary rubbery phase. This second rubbery phase is typically present at a volume fraction of ~0.1–0.2 and consists of spherical particles possessing a diameter of a few micrometres in size which are chemically grafted to the matrix. The following toughening mechanisms have been identified: (1) localized shear yielding of the epoxy matrix, with the shear bands running between rubber particles[1,2]; (2) internal cavitation, or debonding, of the rubber particles[1–5] which enables plastic void growth in the epoxy matrix[6,7]; and (3) bridging of the crack surfaces by the rubber particles[8], which is not usually of major importance.

Studies of these mechanisms have revealed that the sequence in which the various mechanisms come into play is very important. For example, it has been noted[6,7] that if cavitation or debonding of the rubber particles is delayed until the matrix epoxy begins to strain-harden, then the plastic void growth mechanism may be suppressed. However, there has been a debate as to whether cavitation or shear yielding occurs first in the process zone ahead of a crack tip during the fracture of a typical rubber-modified epoxy[2]. The present communication considers such aspects of the toughening of rubber-modified thermosetting polymers.

Finite element analysis studies

The sequence between shear yielding of epoxy matrix and cavitation of rubber particles has been studied using a finite element analysis[6,7,9]. The analysis models the two-phase rubber-modified epoxy polymer as a periodic array of spherical rubber particles embedded in the glassy epoxy matrix, which is subjected to plane-strain loading[7,9]. Due to the periodic symmetry, a structure containing only two particles was selected for analysis and an elastic analysis was employed. The volume fraction of spherical rubber particles was taken to be 0.19 and, as in many rubber-toughened epoxies, it has been assumed that grafting has occurred across the rubbery particle/epoxy matrix interface to a sufficient degree to prevent the particle from debonding from the matrix.

Effect of Poisson's ratio, ν_r, of the rubbery particle. The maximum hydrostatic stress inside the rubber particle and the maximum von Mises stress (sometimes also referred to as the 'effective stress' or 'equivalent stress') in the epoxy matrix were calculated using different values of Poisson's ratio for the rubber particle. The following properties were assumed in the calculations[7]: Young's modulus of epoxy, $E_e = 3.2$ GPa; Poisson's ratio of epoxy, $\nu_e = 0.35$ and Young's modulus of rubber, $E_r = 2.0$ MPa. The maximum von Mises stress in the epoxy matrix occurs at the rubbery particle/matrix interface. *Figure 1* shows P_Y as a function of ν_r, where P_Y is the calculated maximum hydrostatic stress inside the rubber particle at a value of the applied load when the maximum von Mises stress in the epoxy matrix just attains the uniaxial yield stress, σ_y, of the matrix material. (For this numerical analysis the value of σ_y was taken[7]

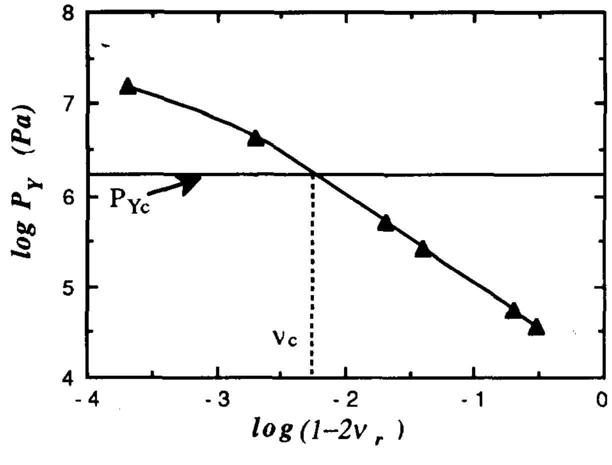

Figure 1 The relationship between the maximum hydrostatic stress, P_Y, in the rubber particle when yielding initiates in the epoxy matrix and the Poisson's ratio, ν_r, of the rubber particle; the horizontal line is the value of the critical cavitational hydrostatic stress ($P_{Yc} = 5E_r/6$)

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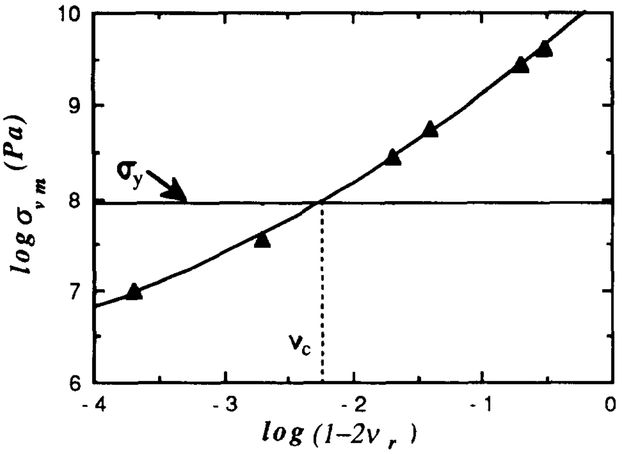

Figure 2 The relationship between the maximum von Mises stress, σ_{vm}, in the epoxy matrix when the applied load is just sufficient to initiate cavitation of the rubbery particles (i.e. when the cavitational hydrostatic stress, $P_Y = P_{Yc} = 5E_r/6$) and the Poisson's ratio, ν_r, of the rubber particle. (When the maximum von Mises stress, σ_{vm}, in the epoxy matrix equals the uniaxial yield stress, σ_y, then localized shear yielding is assumed to be initiated)

to be 88 MPa.) This value of applied load was selected since it represents the value at which localized plastic shear bands will initiate in the epoxy matrix. The x-axis parameter was conveniently chosen to be $\log(1-2\nu_r)$, which changes from minus infinity for an ideally incompressible rubber particle ($\nu_r = 0.5$) to zero when $\nu_r = 0.0$.

Now, a simple criterion[10] for cavitation in a rubber-like solid is that the cavitation occurs when the hydrostatic stress reaches a critical value, P_{Yc}, given by $5E_r/6$. This criterion is based upon the elastic expansion of a microscopic precursor void present in the rubber-like solid. (Although, it is recognized that when the volume of the rubber-like solid material is very small then an additional restraint on its expansion becomes significant, arising from its own surface energy, so that cavitation becomes more difficult[11].) Hence, the critical value of the hydrostatic stress for cavitation is independent of the Poisson's ratio of rubber particles and for the present paper it is taken to be given by $5E_r/6$, especially since no quantitative assessment for the role of the surface energy term is possible. The value of $5E_r/6$ is shown by the horizontal line in *Figure 1*. Clearly, there exists a critical value of the Poisson's ratio, ν_c, which has a value of 0.497. When ν_r is below ν_c, then localized plastic shear yielding precedes cavitation of the rubbery particles. However, when ν_r is above ν_c, it is predicted that cavitation will occur before shear yielding.

The above analysis may also be undertaken by calculating the maximum von Mises stress, σ_{vm}, in the epoxy matrix at the critical applied load when the rubbery particles will start to cavitate. This critical applied load was deduced by assuming that the hydrostatic stress inside the rubbery particle which had to be achieved for cavitation was given by $5E_r/6$, i.e. is equal to the value of P_{Yc} shown in *Figure 1*. Now, when σ_{vm} in the epoxy matrix equals the σ_y of the epoxy, localized shear yielding would be initiated; and the value of σ_y is shown as a horizontal line in *Figure 2*. From the data shown in *Figure 2* it is predicted that when ν_r is >0.497 cavitation of the particles will initiate first; since the value of σ_{vm} is below that of σ_y and the applied loads are, therefore, insufficient to cause shear yielding of the epoxy matrix before cavitation of the particles occurs. However, when ν_r is <0.497, the value of σ_y needed for shear yielding is attained at applied loads below those required to cause cavitation; hence shear yielding will now initiate first. Thus, there is general agreement between *Figures 1* and *2* which represent different approaches to the same problem.

Several points of interest arise from the analyses presented in *Figures 1* and *2*. First, a typical 'pure' rubber particle has a bulk modulus[12] of ~2 GPa and, with a Young's modulus of 2 MPa, this gives a Poisson's ratio of 0.49983. For such particles it is therefore predicted that cavitation of the particles will occur before shear yielding of the matrix material is initiated. Second, this observation is in agreement with the results reported by Parker *et al.*[13]. These workers employed rubber particles which were preformed before being added to a polycarbonate matrix and, from subsequent fracture experiments, they concluded that cavitation preceded localized shear yielding. The pure rubbery particles they employed would possess a ν_r approaching 0.5 and the observed sequence of events would be as predicted. Third, however, in the case of rubber-toughened epoxies, the problem will be complicated by the fact that ν_r will be dependent on the amount of epoxy matrix trapped inside the particles, since the particles form by an *in situ* phase separation process. Indeed, for the Poisson's ratio of the dispersed rubbery particles to fall as low as 0.497 either a very high degree of crosslinking would have to be present (which is very unlikely in the present materials) or epoxy matrix would have to be trapped inside the particle, as suggested above. The amount of such trapped epoxy matrix would have to be of the order of 20%, which is entirely feasible. Consequently, the exact sequence of initiation of the two micromechanisms could be different for different formulations of rubber-toughened epoxy polymers. Indeed, various groups of workers have debated as to which micromechanism occurs first and, since they examined different formulations tested at various rates and temperatures, the above analyses suggest that their respective observations might all be correct.

Effective of modulus, E_r, *of the rubbery particle*. It should be noted that the above value of ν_c was calculated by employing the properties of the particular rubber-toughened epoxy used in the current experimental work[7]. Further, cavitation was again assumed to occur when the maximum hydrostatic stress inside the rubber particle reached a value of $5E_r/6$ and localized shear yielding of the epoxy matrix to occur when the von Mises yield criterion was satisfied. Obviously, any modification of the cavitation or yield criteria may give a different value of ν_c. Also, changes in the assumed mechanical properties of the two phases will cause variations in the value of the calculated ν_c. Such changes in the properties may arise from different materials or curing conditions being used, or a different test rate or temperature being employed. For example, as shown in *Figure 3*, a series of curves are obtained by assuming different values for E_r.

In *Figure 3* again the relationship between σ_{vm} in the epoxy matrix when the applied load is just sufficient to initiate cavitation of the rubbery particles (i.e. when the critical cavitational hydrostatic stress, $P_{Yc} = 5E_r/6$) and ν_r is shown, but now for different values of E_r. Again,

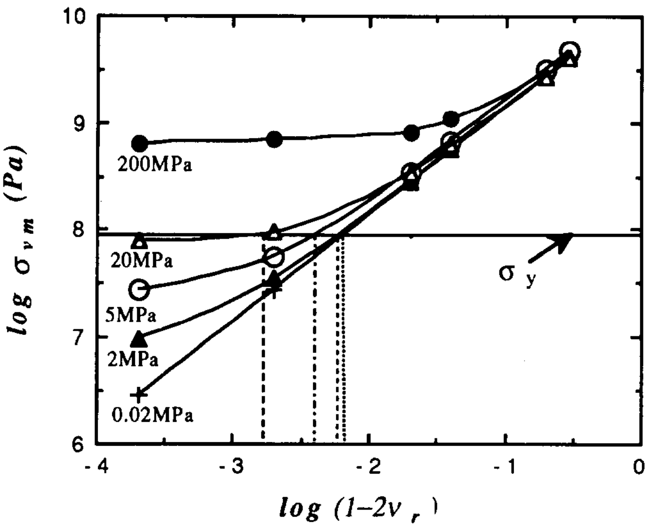

Figure 3 The relationship between the maximum von Mises stress, σ_{vm}, in the epoxy matrix when the applied load is just sufficient to initiate cavitation of the rubbery particles (i.e. when the cavitational hydrostatic stress, $P_Y = P_{Yc} = 5E_r/6$) and the Poisson's ratio, v_r, of the rubber particle for various values of the Young's modulus, E_r, of the rubbery particle

when σ_{vm} in the epoxy matrix equals σ_y then localized shear yielding is assumed to be initiated. It may be seen that a decrease in the value of E_r from 2 to 0.02 MPa results in a small decrease in the value of v_c from 0.4970 to 0.4966. By contrast, a small increase in E_r from 2 to 5 MPa induces an increase in v_c from 0.4970 to 0.4980. A further increase in the modulus to 20 MPa shifts v_c to an even higher value of 0.4992. When E_r is around 200 MPa, the calculation predicts a v_c approaching 0.5 in value. The importance of these results is that it will be recalled that at values of v_r below v_c then localized plastic shear yielding precedes cavitation of the rubbery particles, but when v_r is above v_c it is predicted that cavitation will occur before shear yielding. Again the range of Poisson's ratios discussed here is considered to be possible due to inclusion of trapped epoxy matrix in the rubbery particle. Thus, the sequence of initiation of the toughening mechanisms is dependent upon the modulus of the rubbery particles, as well as the Poisson's ratio of the particle. Indeed, the data shown in *Figure 3* predict that the internal cavitation of a rubbery particle may be suppressed by increasing its Young's modulus. This is consistent with Sue's[14] recent observation on toughened epoxy polymers which contained relatively rigid rubbery particles.

Concluding comments

The numerical analyses have shown how the sequence of initiation between the two main mechanisms of toughening observed in rubber-toughened epoxy polymers is strongly dependent upon the properties of the rubbery particle and, in particular, the value of Poisson's ratio. A high Poisson's ratio of the particle favours the initiation of internal cavitation, before localized shear yielding of the epoxy matrix, and a somewhat lower Poisson's ratio vice versa. The predictions from the analysis are in general agreement with the limited published work on this topic but more detailed measurements of the Poisson's ratio of the rubbery phase are required, as well as of the kinetics of the different micromechanisms, in order to enable more exact correlations between theory and experiment.

Acknowledgement

The authors are grateful to the British Council for providing a studentship to Y. Huang.

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