FRACTURE OF PARTICULATE COMPOSITES BASED ON POLYMETHYLMETHACRYLATE

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INTRODUCTION

The strength of many ceramic materials containing dispersions of elastic particles can be explained by considering the interaction between particle and crack front [1]. Theories of particle strengthening of brittle materials emphasize the energy to create fracture surface and the energy expended in increasing the length of the crack front [1, 2, 3]. The crack progresses unhindered through the matrix when the crack front breaks away from the particles, and the fracture surface energy of the composite is given by

$$\gamma_c = \gamma_m + \left(\frac{\Gamma}{\lambda}\right) \qquad (1)$$

where γ_m is the fracture surface energy of the unreinforced matrix, Γ is the line energy per unit length of crack front, λ is the average distance between particles.

This paper describes the results of an experimental study on the effects of second phase particles upon the fracture behaviour of an acrylic polymer. The results are discussed in terms of crack front-particle interaction. First, the effects of barium sulphate ($BaSO_4$) particles upon the plane-strain fracture toughness K_{IC} and fracture surface energy γ_c of a brittle polymer composite based on polymethylmethacrylate (PMMA) have been evaluated. Second, the occurence of subcritical (slow) crack growth has been investigated at values of stress intensity factor K_I less than K_{IC}. Crack velocity-stress intensity factor diagrams have been constructed as a function of the volume fraction of $BaSO_4$. Finally, glass spheres have been dispersed in the acrylic matrix and a second series of experiments have been carried out to determine the effects of glass particles upon K_{IC}, γ_c and sub-critical crack growth. Fracture mechanics experiments were carried out in air and in physiological environments, namely saline solution and a blood serum.*

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* An acrylic material based on PMMA and containing $BaSO_4$ particles (10% by weight) is widely used for the reconstruction and replacement of injured and diseased bones and joints in the human body.

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MATERIALS

A surgical acrylic bone cement based upon PMMA has been used as a matrix material. In it have been dispersed particles of $BaSO_4$ having a mean diameter, $\bar{d}$, of 0.9 µm. Five samples were fabricated with increasing amounts of $BaSO_4$ in increments of 5% (by weight) to a maximum of 20% (corresponding to a maximum particle volume fraction, V_p, equal to about 0.06). A second batch of samples were fabricated with increasing amounts of glass spheres, ($\bar{d}$ = 75 µm), in increments of 10% (by weight) to a maximum of 50%, (corresponding to $V_p \simeq 0.30$). The samples were fabricated into plates 2 mm thick.

SPECIMEN DESIGN AND ANALYSIS

Double-torsion (DT) specimens were machined from the plates, (Figure 1). A detailed description of specimen geometry and experimental technique has been presented in [4, 5]. The stress intensity factor K_I associated with a crack in a DT specimen is proportional to the applied load P, and is independent of crack length [5]:

$$K_I = \alpha P \qquad (2)$$

where α is a geometrical constant. For fast fracture, $P = P_{crit}$, and $K_I = K_{IC}$.

Constant Displacement (Load Relaxation Method)

In a fixed displacement test, the crack growth rate is proportional to the rate of load relaxation;

$$\left(\frac{da}{dt}\right)_y = V = -\left[\frac{P_{i,f}}{P^2}\right]\left[\left(a_{i,f} + \frac{C}{\beta}\right)\left(\frac{dP}{dt}\right)_y\right] \qquad (3)$$

where $P_{i,f}$ is the initial (or final) load, P is instantaneous load at time t, $a_{i,f}$ is the initial (or final) crack length, y is displacement, and β and C are values of gradient and intercept, respectively, of a compliance analysis calibration curve.

Constant Load Method

If the load P is held constant, then the average crack velocity is

$$V = \left(\frac{\Delta a}{\Delta t}\right)_P \qquad (4)$$

where $\Delta a = (a_f - a_i)$ and Δt is the increment in time for cract extension.

RESULTS AND DISCUSSION

Slow continuous crack growth was observed in both particulate composites at values of $K_I < K_{IC}$.

Acrylic Containing $BaSO_4$ Particles ($\bar{d}$ = 0.9 µm)

Figure 2 shows V(K) diagrams for the acrylic composite containing different amounts of $BaSO_4$. Two principle effects can be seen:

(1) increasing V_p has shifted the V(K) curve towards the left of the diagram, and

(2) the slope of the V(K) curve has decreased from 28 for the acrylic material to 24 for the particulate composite, ($V_p \simeq 0.06$).

There appears to be a critical value of K_I of the order of 0.8 $MPa \cdot m^{1/2}$ where the V(K) curves converge. This apparent critical value of K_I may be considered for all practical purposes to correspond to a threshold value of K_I below which no cracking occurs, at least for $V_p \leqslant 0.06$. It was found impossible to separate the data points collected in air from those obtained in saline solution and blood serum, (Figure 3).

Figure 4 shows the effect of V_p upon K_{IC} and γ_c. These material parameters have decreased in value by about 25% after the addition of about 6% $BaSO_4$. The value of Young's modulus, E, was essentially unaffected by the dispersion of $BaSO_4$.

Lange [6] has demonstrated that for silicon nitride (Si_3N_4) containing a dispersion of silicon carbide (SiC) particles, a critical particle size d_{crit} exists (∿ 10 µm) before a toughening effect is observed. For $d < d_{crit}$, an increase in V_p resulted in a decrease γ_c for the Si_3N_4 composite, a phenomenon that was observed for the $BaSO_4$ filled acrylic composite, (Figure 4). Lange described this as a "dilution effect". If the "toughness" of $BaSO_4$ is considerably less than the toughness of the matrix, then the fracture energy of the composite would be less than the fracture energy of the matrix (providing $d < d_{crit}$). One may therefore expect that where a decrease in γ_c occurs, the V(K) curve will shift to the left, as shown in Figure 2.

Acrylic Containing Glass Spheres ($\bar{d}$ = 75 µm)

Figure 5 shows V(K) diagrams for different volume fractions of glass spheres. Two principle effects of the spherical particles can be seen:

(1) the V(K) curve has shifted towards the right of the diagram as V_p increased to a critical value $V_{p(crit)}$ of approximately 0.20, and

(2) for $V_p > V_{p(crit)}$, the V(K) curve has moved towards the left of the diagram.

The slope of each curve is essentially constant at about 28. There does not appear to be a threshold value of K_I below which no crack growth occurs, at least over the range of K_I values that have been investigated. Measurements of E, K_{IC} and γ_c as a function of V_p are shown in Figure 6. E continued to increase with V_p whilst K_{IC} and γ_c both reached a maximum value at $V_p \simeq 0.20$. This critical value of V_p is similar to $V_{p(crit)}$ which was measured in the subcritical crack growth study.

A peak in the fracture energy curve for $Al_2O_3 \cdot 3H_2O$ particles, ($\bar{d}$ = 12 µm), dispersed in an epoxy resin matrix [7], and glass spheres, ($\bar{d}$ = 35 µm), dispersed in a similar epoxy resin matrix [8] has been previously seen. In both of these studies, maxima occurred at about $V_p = 0.20$. The reported increase in γ_c (at $V_p < V_{p(crit)}$) may be due to crack front-partical interaction effects.

Figure 7 shows a plot of γ_c for the acrylic-glass sphere composite as a function of the inverse of particle spacing* λ. The value of the intercept is equal to the fracture surface energy of the unfilled acrylic material, (equation 1). The experimental data begins to deviate from the theoretical prediction (equation 1) at $V_p \simeq 0.20$. For values of $V_p > V_{p(crit)}$ (corresponding to an inter-particle spacing $\lambda < 250$ μm), particle-crack front interaction has been less effective as a toughening mechanism.

Note that the glass spheres which have an average diameter of about two orders of magnitude greater than that of the $BaSO_4$ particles have exhibited the reverse effects on the acrylic material when compared to $BaSO_4$

Inherent Flaw Size

From a knowledge of the fracture stress, σ_f, and K_{IC}, the inherent flaw size, a_o, responsible for fracture can be estimated:

$$a_o = \frac{1}{Y^2}\left(\frac{K_{IC}}{\sigma_f}\right)^2 \qquad (5)$$

where Y is a dimensionless parameter which depends on the geometry of the flaw. If $Y \simeq 1.12\sqrt{\pi}$ for a spherical crack at the surface, then the effect of glass spheres on a_o is seen in Figure 8. There is no correlation between a_o and λ as suggested by Hasselman and Fulrath [10]; they proposed that λ limits the crack size within the composite. The simple linear relationship between a_o and V_p was found also by Lange [6] for the Si_3N_4/SiC system provided $d > d_{crit}$, where $d_{crit} \simeq 10$ μm.

If the formation of a crack in a particulate composite requires a critical amount of stored elastic strain energy within the particles and surrounding matrix, (as suggested by Davidge and Green [11]), then this pre-requisite for cracking must therefore be dependent on V_p. Since one of the assumptions of the Davidge-Green model is that the strain energy field of a given particle is not affected by an overlapping field of an adjacent particle, then it can be shown [11] that the inter-particle spacing λ must be equal to or greater than twice the particle diameter; it corresponds in this case to particle volume fractions $V_p \leqslant 0.20$. For the acrylic-glass sphere composite, λ_{crit} is therefore about 250 μm which is a factor of three greater than d. The critical volume fraction $V_{p(crit)}$ at which the experimental data in Figure 7 begins to deviate from the theoretical prediction (equation 1) is about 0.20. Thus, cracks will form more easily in the acrylic particulate composite containing glass spheres when $V_p > V_{p(crit)}$ or $\lambda < \lambda_{crit}$. They will initiate at lower stresses than predicted using equation 1 when $V_p > V_{p(crit)}$ (or $\lambda < \lambda_{crit}$) without necessarily propagating catastrophically, as found for both the particulate composites based on PMMA.

ACKNOWLEDGEMENTS

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* The spacing λ between spherical particles of equal size d can be estimated [9]; $\lambda = 2d(1 - V_p)/3V_p$.

REFERENCES

1. LANGE, F. F., Phil. Mag., 22, 1970, 983.
2. FRIEDEL, J., "Fracture", edited by Averbach et al, J. Wiley, New York, 1959.
3. EVANS, A. G., Phil. Mag., 27, 1972, 1327.
4. BEAUMONT, P. W. R. and YOUNG, R. J., J. Material Science, 10, 1975, 1334.
5. EVANS, A. G., J. Material Science, 7, 1972, 1137.
6. LANGE, F. F., J. Amer. Ceram. Soc., 56, 1973, 445.
7. LANGE, F. F. and RADFORD, K. C., J. Material Science, 6, 1971, 1197.
8. BROUTMAN, L. J. and SAHU, S., Mat. Sci. Eng., 8, 1971, 98.
9. FULLMAN, R. L., Trans. AIME, 197, 1953, 447.
10. HASSELMAN, D. P. H. and FULRATH, R. M., J. Amer. Ceram. Soc., 49, 1966, 68.
11. DAVIDGE, R. W. and GREEN, T. J., J. Material Science, 3, 1968, 629.

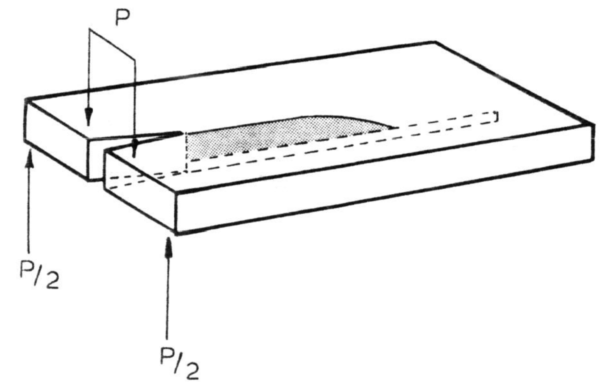

Figure 1 Schematic Representation of DT Specimen and Loading Configuration

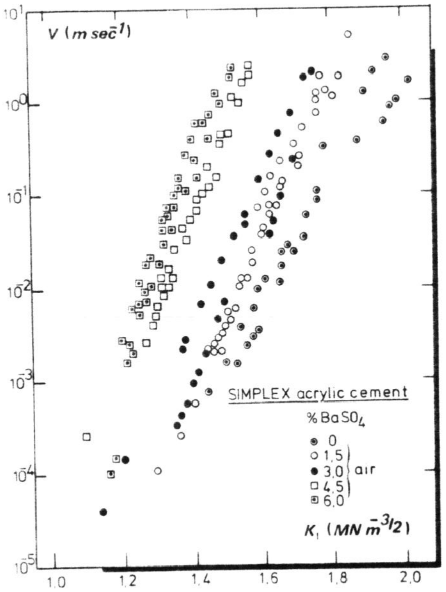

Figure 2 V(K) Diagram for Acrylic Bone Cement for Different Amounts of $BaSO_4$

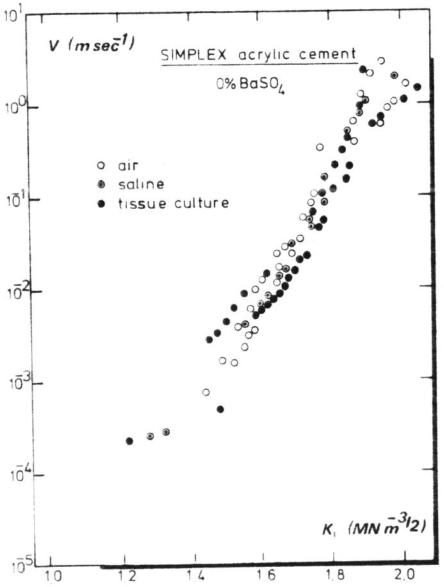

Figure 3 V(K) Diagram for Acrylic Bone Cement in Air, Saline Solution and Blood Serum

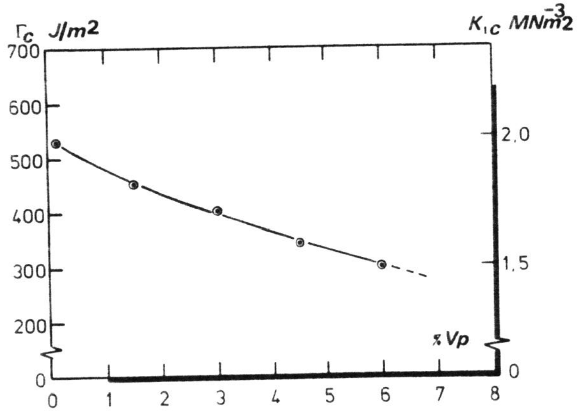

Figure 4 Fracture Surface Energy γ_C and Plane-Strain Fracture Toughness K_{IC} of Acrylic Bone Cement as a Function of Volume Fraction of $BaSO_4$

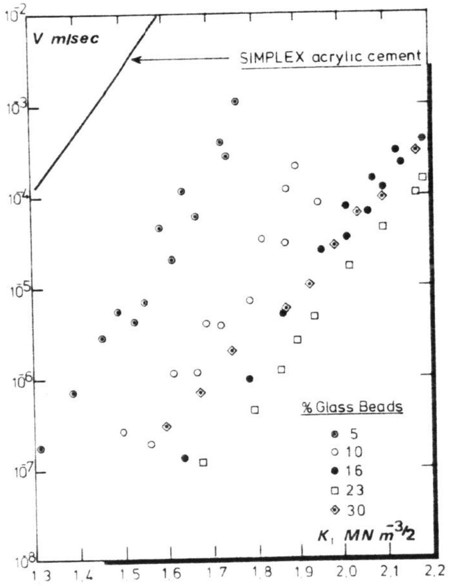

Figure 5 V(K) Diagram for Acrylic Bone Cement Composites for Different Volume Fractions of Glass Spheres

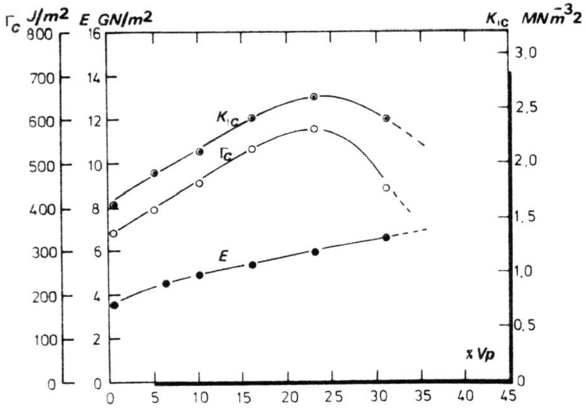

Figure 6 The Effect of Volume Fraction of Glass Spheres Upon Fracture Surface Energy γ_c, Plane-Strain Fracture Toughness K_{IC} and Young's Modulus E of Acrylic Bone Cement Composites

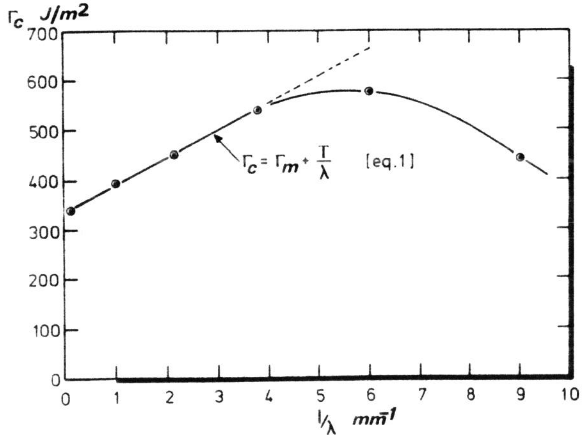

Figure 7 The Effect of Inter-Particle Spacing Upon the Fracture Surface Energy of Acrylic Bone Cement-Glass Sphere Composites

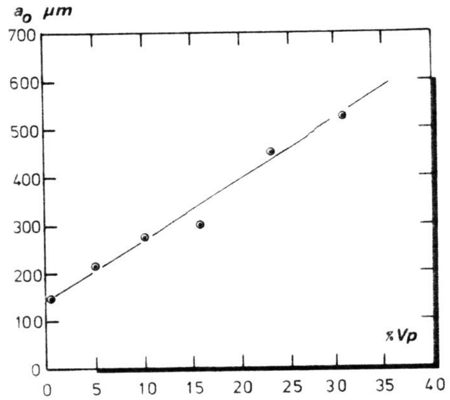

Figure 8 The Effect of Volume Fraction of Glass Spheres Upon the Inherent Flaw Size of Acrylic Bone Cement Composites