

The influence of particle size on the tensile strength of particulate-filled polymers

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The tensile strengths of a particulate-filled rigid polyurethane resin are presented at varying volume fractions and a wide range of particle sizes. These results are compared with existing theories of the strength of particulate-filled composite systems. A linear relationship is proposed to exist between the mean particle diameter and the tensile strength at a given volume fraction. A method of normalizing data is presented which removes the stress-concentration effects of finite particle sizes and allows comparison of the data with a simple equation relating tensile strength and volume fraction. The effects of particle size and volume fraction in relation to crack propagation are discussed, and the proposed method of analysis is shown to give similar results when applied to published data.

1. Introduction

The inclusion of particulate fillers in polymeric materials is an established practice in the polymer industry. Their inclusion can enhance such properties as modulus and fracture toughness, while reducing the overall cost of a component. The use of solid spherical glass fillers has been common in this field and a number of investigations have been made into their mechanical properties [1-5].

Interest has recently been shown in the use of hollow glass or thermoplastic microspheres as fillers for polymeric materials. The resulting composite materials, known as syntactic foams [6], are finding increasing use in such diverse applications as furniture [7], ablative heat shields [8], and in deep submergence vessels [9]. Their combination of low density, strength and modulus properties make them interesting materials for study.

This paper describes the production of composites by the inclusion of hollow and solid glass microspheres of various diameters and volume fractions in a rigid cross-linked polyurethane resin. The strength of these composites is evaluated with respect to the existing theories of particulate reinforcement.

2. Theory

The studies published on the experimental and theoretical strength relationships for polymeric

materials filled with solid particles [1-5, 10] have, in general, taken one of two main approaches in explaining the tensile strength variation with volume fraction.

One approach, as expressed by Sahu and Broutman [10], is to assume that the composite fails when one element fails due to stress concentrations around the filler. It follows from this assumption, that the composite strength should decrease rapidly with the first addition of filler, and remain essentially at that level with further additions of filler. The experimental results presented by Sahu and Broutman [10] did not give good agreement with the theoretical predictions.

The second approach is to assume that the strength of a particulate-filled polymeric composite is determined by the effective decrease in the cross-sectional area of the load-bearing polymer matrix due to the presence of the filler [2-5, 11]. Assuming no adhesion between the matrix and the spheres (i.e. no stress transfer), and no stress concentration effects, then

$$\sigma_c = \sigma_m(1 - a\phi^n) \quad (1)$$

where σ_c and σ_m are the tensile strength of the composite and matrix respectively, and ϕ is the volume fraction of filler, a and n are constants which depend on the particular geometric model of the composite and the assumed plane of fracture. In

the model in which spheres are randomly distributed but the fracture path deviates through the equatorial plane of all spheres which are encountered, then $a = 1.21$ and $n = \frac{2}{3}$. If the spheres are randomly distributed and the fracture path is perfectly planar, (i.e. non-deviated), then $a = 1.0$ and $n = 1.0$. Most of the experimental investigations show an intermediate dependence of tensile strength on volume fraction between the upper bound of $a = 1.0$ and $n = 1.0$ and the lower bound of $a = 1.21$ and $n = \frac{2}{3}$.

Piggot and Leidner [12] have shown that an equation of the form

$$\sigma_c = A\sigma_m - b\phi \quad (2)$$

may be used to represent the experiment data in certain cases, where A is a factor expressing the stress concentration caused by the presence of spheres in the matrix and b is a constant. They have shown that Equation 2 can give almost identical values to a two thirds power law expression, at volume fractions greater than 0.2.

Little work has been published on the strength of hollow-sphere filled polymers. Okuno and Woodhams [13] have derived an equation for such systems which predicts a linear relationship between composite strength and volume fraction of filler. The basis of the relationship is the additivity of the strengths of a polymer foam and the hollow sphere, which gives

$$\sigma_c = \sigma_m \left[k_0 - \left(\left[k_0 - \frac{\sigma_g}{\sigma_m} \phi_g \right] \phi_f \right) \right] \quad (3)$$

where k_0^{-1} is the stress concentration factor, σ_g is the strength of the solid phase of the hollow sphere, ϕ_g and ϕ_f are the volume fractions of the solid phase and void respectively. In this case it is assumed that there is sufficient stress transfer between the matrix and the spheres to cause fracture of the sphere walls in the fracture path. There is photographic evidence that this assumption is valid.

None of the preceding equations take account, directly, of the influence of filler size on the strength of the composite. It is known that, for a given volume fraction, the strength is reduced as particle size is increased. Some workers [13] attribute this to an increase in the stress concentration factor with increase in particle size.

A number of attempts have been made to apply a Hall-Petch [14-15] type of relationship to sphere filled polymer composites, at constant vol-

ume fraction of filler. This relationship was originally derived to describe the dependence of the yield strength of a polycrystalline material on the reciprocal of the square root of the grain size. Hojo *et al.* [16] have shown a linear relationship between tensile strength and the reciprocal of the square root of the particle diameter. Alter [17] took published data for a number of thermoplastic polymeric composites and showed a linear relationship between tensile strength and the reciprocal of the particle diameter. Alter proposed that this function expressed a dependence of tensile strength on the surface-to-volume ratio of the filler. Baldwin [18] has shown that in the case of polycrystalline metals, tensile strength may vary directly with particle diameter.

So there appear to be three possible relationships between fracture strength σ_c and mean particle diameter d at a given volume fraction of particles:

$$\sigma_c = kd + c \quad (4)$$

$$\sigma_c = k'd^{-1} + c' \quad (5)$$

$$\text{or } \sigma_c = k''d^{-\frac{1}{2}} + c'' \quad (6)$$

where k, k', k'', c, c', c'' are the slopes and intercepts of the respective straight lines.

3. Materials

3.1. Matrix

The matrix material was a highly cross-linked rigid polyurethane [19] thermosetting resin (ICI Daltomer 3) produced by the reaction of a diphenylmethane di-isocyanate (ICI Polymeric grade DNR) with a low molar mass, branched oxypropylated glycerol (ICI Daltocast 3).

To avoid the formation of bubbles due to the evolution of carbon dioxide in the resin, the polyol was dehydrated *in vacuo* at 110°C before use. The isocyanate was also degassed *in vacuo* at room temperature to remove dissolved carbon dioxide and air. All equipment and fillers used in the preparation of the resin and composites were carefully dried at 115°C for 15 min prior to use.

The resin was produced by mixing, in approximately stoichiometric ratio, the hot polyol with the cold isocyanate. The mixture was then cast into a mould consisting of two aluminium sheets separated by a rubber gasket. After gelation, which occurred in approximately 5 min, the resin was cured in an oven for 45 min at 110°C.

TABLE I Average diameters and densities of the fillers

	d (μm)	ρ (kg m^{-3})
Solid Spheres	21	2480
	85	2480
	216	2480
Hollow Spheres	43	485
	55	485
	77	485
	80	540
	116	705
	141	705

3.2. Fillers

The solid spheres were obtained without adhesion promoter from Platichem Ltd., Esher, Surrey, England. The hollow microspheres were obtained without adhesion promoter from Fillite Ltd., Runcorn, Cheshire, England.

Average particle diameters d and densities ρ are shown in Table I.

3.3. Preparation of composites

Composites were produced by mixing a weighed quantity of liquid resin with a weighed quantity of filler to provide a uniform slurry which was cast into a pre-heated mould. The cure cycle was identical to that of the unfilled resin.

4. Experimental procedure

Test pieces were cut from the cast sheets with a bandsaw, the cut edges being carefully ground with silicon carbide paper. The volume fraction of filler was calculated from the measured density of impact test pieces, assuming volume additivity. Tensile strength was measured on a Howden Tensometer with specimens to BS.305A with a cross-head speed of 30 mm min^{-1} . An average of at least three specimens, usually five, for each volume fraction were taken; exceptions to this were composites containing solid beads of $216 \mu\text{m}$ diameter where gross sedimentation reduced the number of specimens to one. Average particle size was computed using a Cambridge Metals Research 'Quantimet' quantitative microscope. Particle densities were determined using a pycnometer.

5. Results

The tensile strengths of solid-sphere filled composites are shown as a function of volume fraction of filler in Fig. 1. Figs. 2-4 show the tensile strength of hollow-sphere filled composites as a function of volume fraction of filler. In all cases the tensile

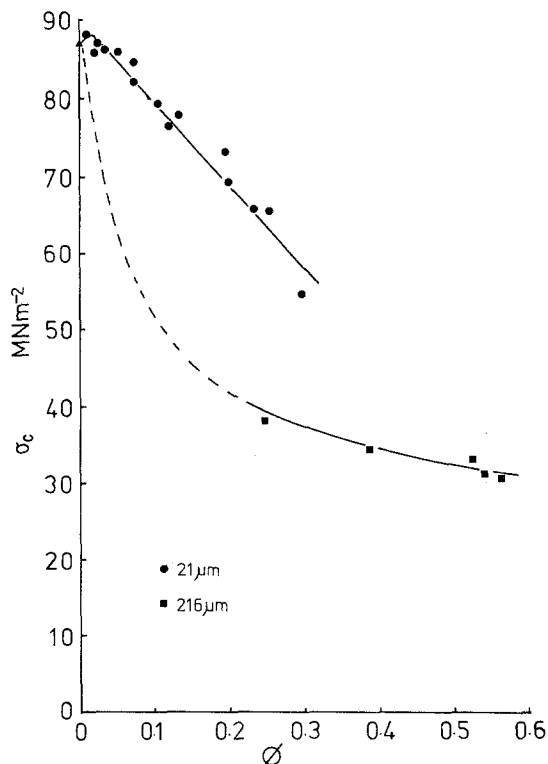


Figure 1 Tensile strength σ_c as a function of volume fraction ϕ for solid-sphere filled composites.

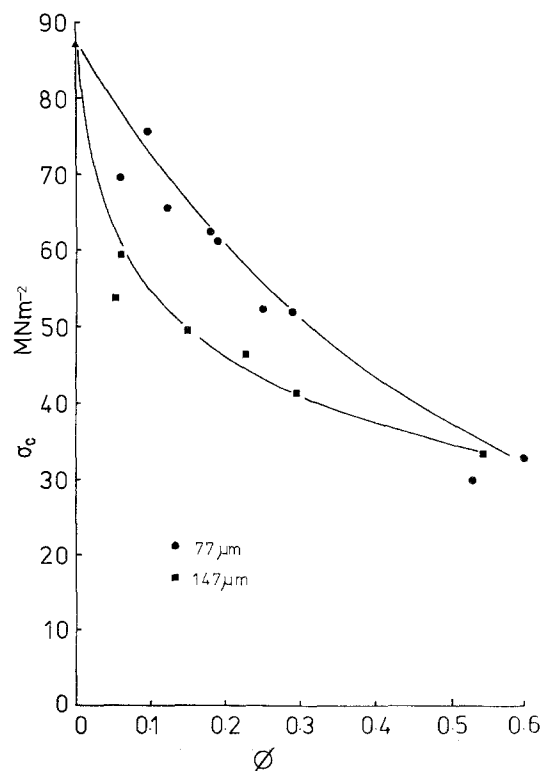


Figure 2 Tensile strength σ_c as a function of volume fraction ϕ for hollow-sphere filled composites.

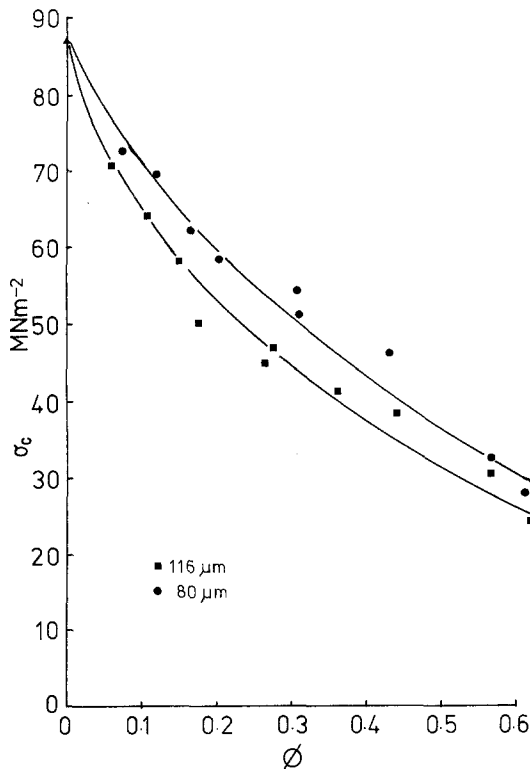


Figure 3 Tensile strength σ_c as a function of volume fraction ϕ for hollow-sphere filled composites.

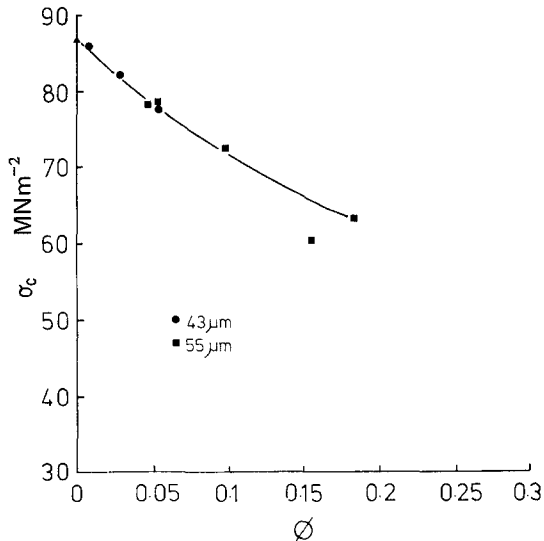


Figure 4 Tensile strength σ_c as a function of volume fraction ϕ for hollow-sphere filled composites.

strength decreases with increasing volume fraction. In order to investigate the effect of particle size on the tensile strength, values of composite tensile strength, as represented by points on the smooth curves drawn in Fig. 1-4, were taken for selected volume fractions. An attempt was made to fit these points by the Equations 4, 5 and 6 at each selected

TABLE II Correlation of experimental data with Equation 4.

$\sigma_c = kd + c$ (4)			
ϕ	Slope k (GN m ⁻³)	Intercept c (MN m ⁻²)	Correlation Coefficient
.05	-138	87.60	-0.92
.1	-167	82.48	-0.94
.15	-185	78.53	-0.97
.2	-180	73.45	-0.99
.3	-114	59.47	-0.98
.4	-69	47.81	-0.96
.5	-32	38.58	-0.81

TABLE III Correlation of experimental data with Equation 5.

$\sigma_c = k'd^{-1} + c'$ (5)			
ϕ	Slope k' (N m ⁻¹)	Intercept c' (MN m ⁻²)	Correlation Coefficient
.05	322	71.12	0.72
.1	409	62.18	0.77
.15	430	55.75	0.80
.2	413	50.42	0.84
.3	363	42.36	0.89
.4	840	32.06	0.95

TABLE IV Correlation of experimental data with Equation 6.

$\sigma_c = k''d^{-\frac{1}{2}} + c''$ (6)			
ϕ	Slope k'' (kN m ^{-3/2})	Intercept c'' (MN m ⁻²)	Correlation Coefficient
.05	107	63.19	0.78
.1	135	52.33	0.83
.15	143	45.40	0.86
.2	135	40.94	0.88
.3	113	34.99	0.93
.4	151	25.52	0.92

volume fraction of filler. The resultant values of the slopes k , k' , k'' , and the intercepts c , c' , c'' together with the correlation coefficients are shown in Tables II, III and IV. It can be seen that the best correlation between experimental data and theoretical equations is with Equation 4. Typical graphical representations of this procedure are shown in Figs. 5-7.

6. Discussion

The dependence of tensile strength on volume fraction for the sphere filled polyurethane composites follow a family of curves lying below the upper bound of Equation 1, (Fig. 8).

The factors thought to influence the variation

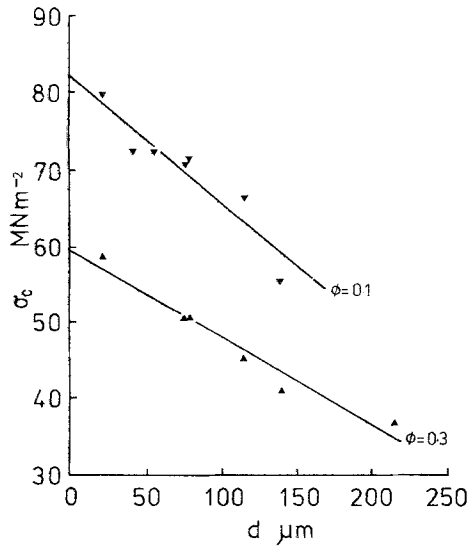


Figure 5 Tensile strength σ_c as a function of average particle diameter d at two volume fractions.

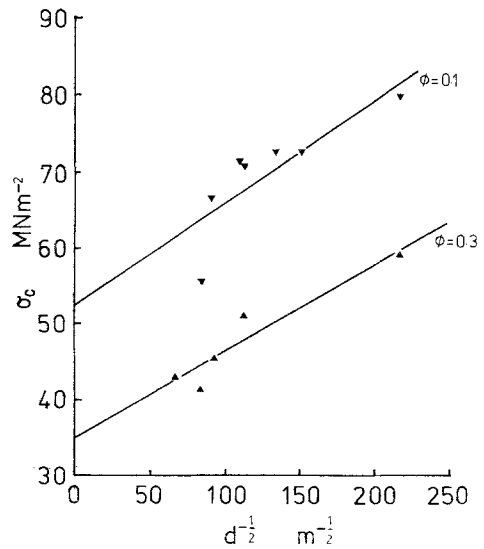


Figure 7 Tensile strength σ_c as a function of $d^{-1/2}$ at two volume fractions.

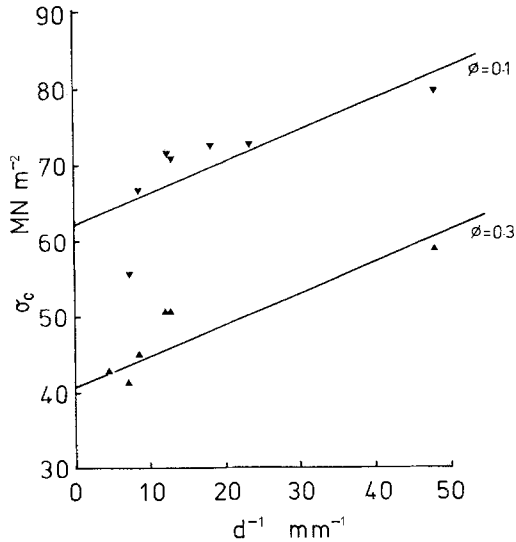


Figure 6 Tensile strength σ_c as a function of d^{-1} at two volume fractions.

of tensile strength with volume fraction of filler are (1) the effective decrease in cross-sectional area of the load-bearing matrix, (2) stress-concentrations set up by the presence of the filler particles, (3) mode of crack propagation through the composite during failure, (4) changes in modulus of the composite due to the presence of filler.

The composites containing the smallest spheres show behaviour closest to the upper bound in Fig. 8, and as the size of the spheres increase, the lower bound is approached. Within the limits of the experiments reported, the results given by both

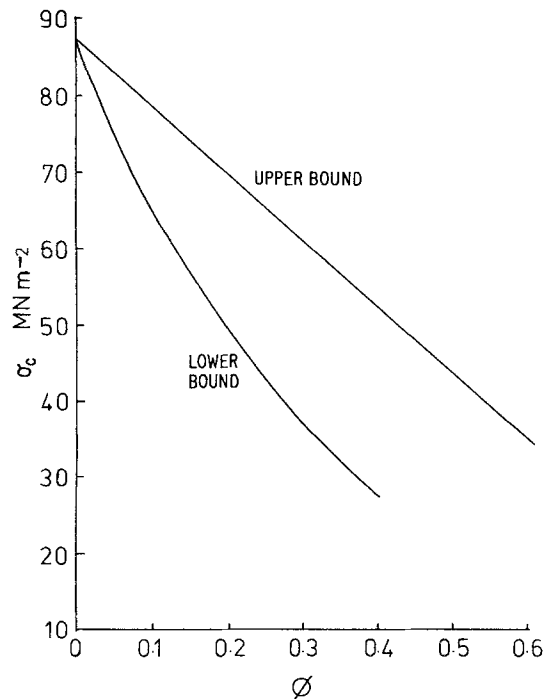


Figure 8 Upper and Lower bounds for the variation of Tensile strength σ_c with volume fraction ϕ as predicted by Equation 1.

the solid and hollow spheres appear to belong to the same family of curves. This would imply that whatever contributions are made to the tensile strength of the composite by (a) adhesion between the spheres and the matrix or (b) strength of the walls of the hollow spheres are both negligible in

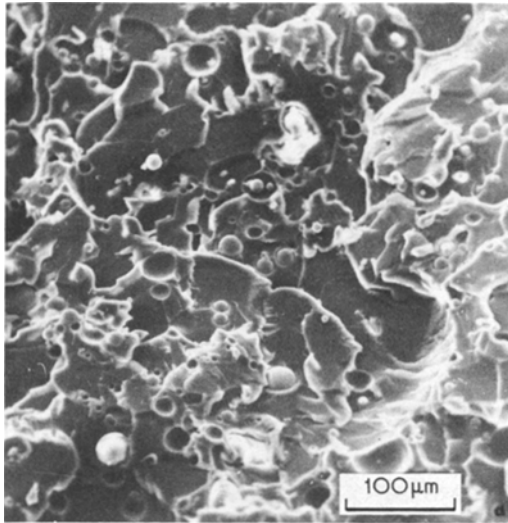


Figure 9 SEM of solid-sphere filled composites containing 21 μm diameter spheres, $\phi = 0.13$.

comparison to the contribution made by the strength of the matrix, or that both contributions are approximately equal. The former idea is supported by the fact that the spheres were not treated with an adhesion agent and SEMs show (Fig. 9) that little resin adheres to any of the solid spheres at the fracture surface. The hollow spheres (Fig. 10) are also seen to contain many flaws and imperfections in their walls, so may be presumed to make only a small contribution to the tensile strength of the matrix. The latter idea is supported

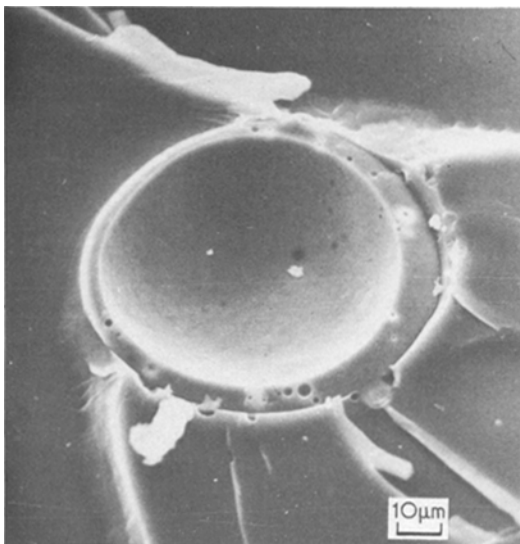


Figure 10 SEM of hollow-sphere filled composites containing 116 μm diameter spheres, $\phi = 0.18$.

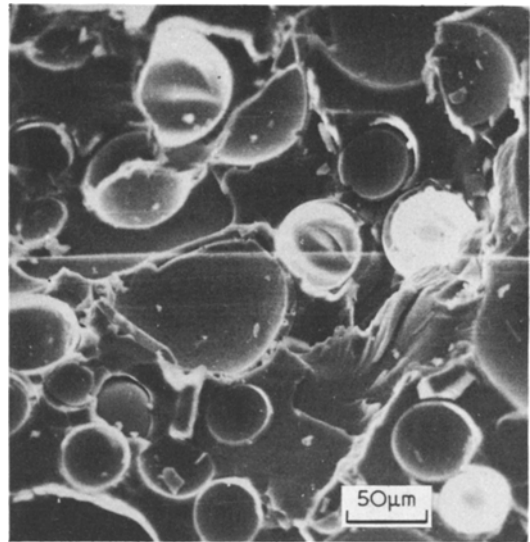


Figure 11 SEM of hollow-sphere filled composites containing 80 μm diameter spheres, $\phi = 0.3$.

by Fig. 11, which shows that in the hollow-sphere filled composites some spheres are fractured and others are debonded, indicating that the two processes may be equally preferred.

Linear equations such as those proposed by Piggot and Leidner [12] (Equation 2) or Okuno and Woodhams [13] (Equation 3) are seen to be ineffective in representing the data at low volume fractions of fillers, but may be considered as useful empirical equations for use at medium to high volume fractions of filler.

The problems encountered in defining the relationship of tensile strength to particle size have been discussed in the case of polycrystalline metals [18]. It may be considered that the observed relationship between tensile strength and particle size is a result of the influence of sphere size on the Griffith flaw size within the composite. It has been shown that calculated flaw size increases rapidly with increasing particle size [20].

The intercepts c on the tensile strength axis from Table II may be taken to represent the hypothetical tensile strengths of composites containing spherical fillers of infinitely small diameter σ_{α} at a series of given volume fractions of filler. Normalized intercepts are plotted against volume fraction of filler in Fig. 12, and fairly good correlation is observed between the points and the predicted upper bound of Equation 1.

It can be seen from Table II that the dependence of tensile strength on particle size increases with volume fraction of spheres to a maximum in the

region of 0.2 volume fraction, and decreases subsequently. This dependence is illustrated by plotting the slope, k , from the table against volume fraction of spheres in Fig. 13. Published data of Mallick

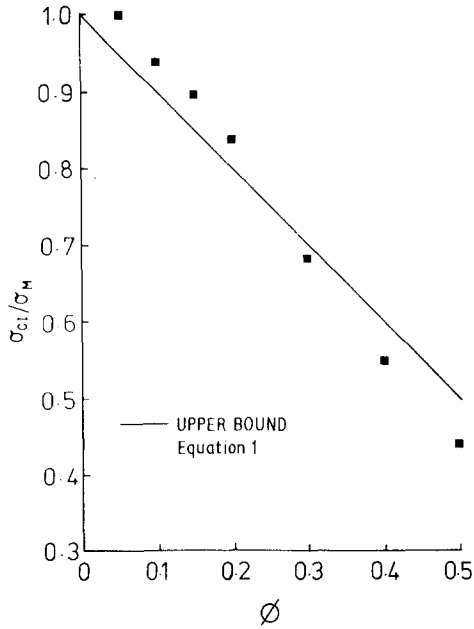


Figure 12 The ratio of intercept tensile strength σ_{CI} to unfilled matrix tensile strength σ_m as a function of volume fraction ϕ of filler.

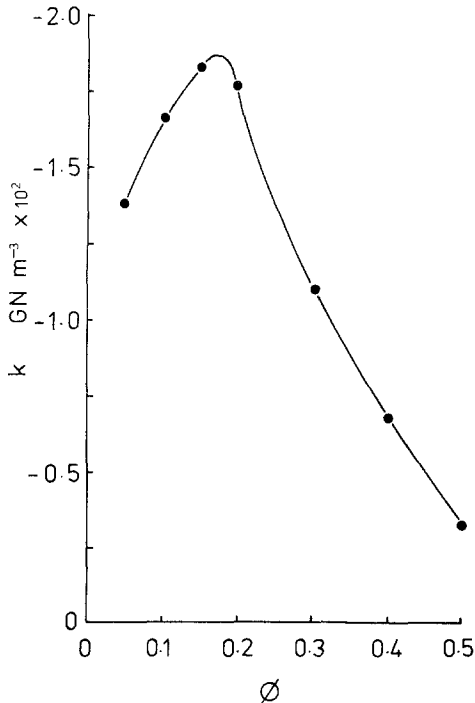


Figure 13 The slope k from Table II as a function of volume fraction ϕ of filler.

and Broutman [21], Lange and Radford [22], and Sahu and Broutman [23] show that glass-sphere filled brittle polymeric composites show an increase in fracture surface energy with increasing volume fraction up to a maximum at around 0.2 volume fraction of spheres, and that the increase in fracture surface energy is greater, the smaller the particle size. As the volume fraction of fillers increases above 0.2 the fracture surface energies decrease and the differences in fracture surface energies given by spheres of varying sizes also decreases. These results were explained [20–25] by assuming that as the crack front meets the dispersed phase it is momentarily pinned between two particles. Then, in a manner analogous to a pinned dislocation in crystalline materials, the crack front bows out and meets on both sides of the particle to break away. As the distance between the particles decreases, consistent with either an increase in volume fraction of spheres or a decrease in sphere diameter, the radius to which the crack front is bent also decreases. Therefore, the force required to bend the crack front into the arc of a circle also increases until crack pinning becomes unfeasible energetically, compared with other modes of crack propagation. At this point, crack propagation becomes continuous rather than discontinuous and fracture surface energy begins to decrease. The contribution of this fracture surface energy, which varies with volume fraction and particle size, may partially explain the variable slope of tensile strength against particle size shown in Fig. 13.

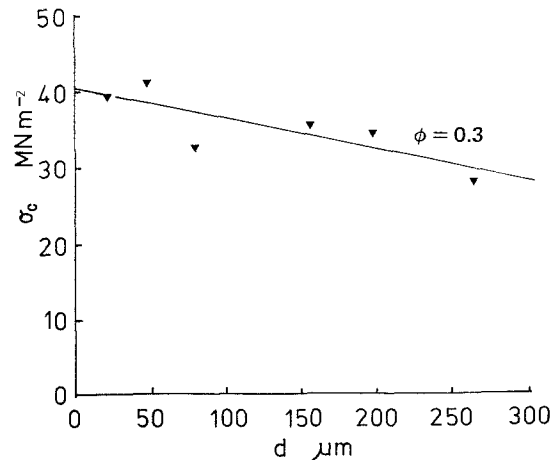


Figure 14 Tensile strength σ_c as a function of mean particle diameter d (Leidner and Woodham's data).

To investigate the possibility of applying the same approach with published results for other systems, the data of Leidner and Woodhams [26] for a polyester/glass system were analysed in a similar manner to that presented in this paper. In the absence of any data on the average particle sizes, the mid-points of the stated size ranges were taken as the mean particle diameters. A typical graph of tensile strength against mean particle diameter is shown in Fig. 14. Fig. 15 shows a plot

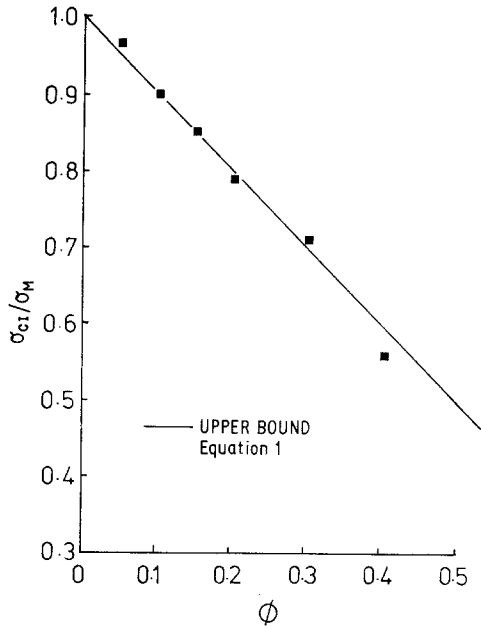


Figure 15 The ratio of Intercept tensile strength σ_{CI} to unfilled matrix tensile strength as a function of volume fraction ϕ of filler (Leidner and Woodham's data).

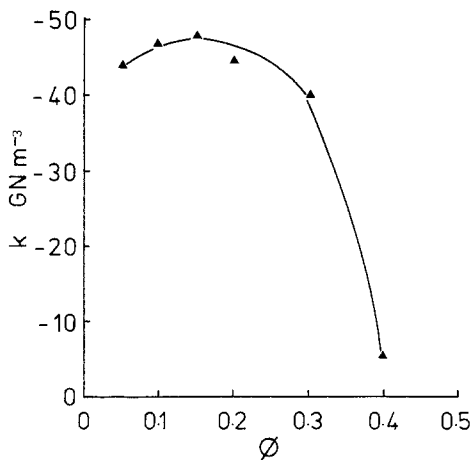


Figure 16 Slope k as a function of volume fraction ϕ of filler (Leidner and Woodham's data).

of normalized intercepts σ_{CI} calculated from Equation 4 against volume fraction of spheres. The points show good agreement with the upper bound of Equation 1. Fig. 16 shows a plot of k , the slope of tensile strength against particle diameter, against volume fraction of spheres. Again, a maximum is visible at 0.15 to 0.2 volume fraction of spheres.

It is proposed, therefore, that the strength of a particulate-filled polymeric composite can be expressed by

$$\sigma_e = \sigma_m(1 - \phi) - k(\phi)d$$

where d is the average particle diameter and k is the slope of the plot of tensile strength against mean particle diameter at the particular volume fraction in question.

7. Conclusions

In the case of low adhesion between filler and matrix, the tensile strengths of solid- and hollow-glass sphere filled rigid polyurethane composites decrease with increasing volume fraction of filler; greater decreases in tensile strengths being shown by the larger particles. At fixed volume fractions of fillers, there appear to be linear relationships between tensile strength and particle diameter. The intercepts obtained from the above relationships, representing the hypothetical tensile strengths obtainable with fillers of infinitely small particle size, when plotted against volume fraction, show good agreement with the upper bound of Equation 1. This form of Equation 1 simply represents the effective decrease in tensile strength due to the decrease in cross-sectional area of the load-bearing polymer, in the absence of any allowance for stress concentration factors caused by the presence of the spheres. The dependence of tensile strength on particle diameter passes through a maximum at about 0.2 volume fraction of spheres, which may reflect a change in crack propagation mode as the amount of filler increases. The published data of Leidner and Woodhams can be analysed to yield similar results.

Acknowledgements

The authors would like to thank The Polytechnic, Wolverhampton for the provision of a Research Assistantship to G. Landon.

References

1. A. S. KENYON and H. F. DUFFEY, *Poly Eng. Sci.* 7 (1967) 189.

2. L. E. NIELSON, *J. App. Polymer Sci.* **10** (1966) 97.
3. L. NICOLAIS, E. DRIOLI and R. F. LANDEL, *Polymer* **14** (1973) 21.
4. G. W. BRASSELL and K. B. WISCHMAN, *J. Mater. Sci.* **9** (1974) 307.
5. L. NICOLAIS, *Poly. Eng. Sci.* **15** (1975) 137.
6. T. M. FERRIGNA, 'Rigid Plastics Foams' (Rheinhold, 1967) p. 353.
7. D. I. NETTING, *Plastics, Design & Processing* **14** (1974) 26.
8. L. B. KELLER, *J. Cell. Plastics* **4** (1968) 418.
9. R. W. JOHNSON, P. W. MONTGOMERY and D. L. O'BRIEN, *Mater. Eng.* **66** (1967) 75.
10. S. SAHU and L. J. BROUTMAN, *Poly. Eng. Sci.* **12** (1972) 91.
11. L. NICOLAIS and L. NICODEMO, *ibid.* **13** (1973) 469.
12. M. R. PIGGOTT and J. LEIDNER, *J. App. Polymer Sci.* **18** (1974) 1619.
13. K. OKUNO and R. T. WOODHAMS, *J. Cell. Plastics* **10** (1974) 237.
14. E. O. HALL, *Proc. Phys. Soc. (London)* **B64** (1951) 747.
15. N. J. PETCH, *J. Iron. Steel Inst.* **174** (1953) 25.
16. H. HOJO, W. TOYOSHIMA, M. TAMURA and N. KAWAMURA, *Poly. Eng. Sci.* **14** (1974) 604.
17. H. ALTER, *J. App. Polymer Sci.* **9** (1966) 1525.
18. W. M. BALDWIN, *Acta Met.* **6** (1958) 141.
19. G. A. HAGGIS, *Polymers, Paint & Colour Journal* (1973) 879.
20. F. F. LANGE, *J. Amer. Ceram. Soc.* **54** (1971) 614.
21. P. K. MALLICK and L. J. BROUTMAN, *Mat. Sci. Eng.* **8** (1971) 98.
22. F. F. LANGE and K. C. RADFORD, *J. Mater. Sci.* **6** (1971) 1197.
23. L. J. BROUTMAN and S. SAHU, *Mat. Sci. Eng.* **8** (1971) 98.
24. F. F. LANGE, *Phil. Mag.* **22** (1971) 983.
25. A. G. EVANS, *ibid.* **26** (1973) 1327.
26. J. LEIDNER and R. T. WOODHAMS, *J. App. Polymer Sci.* **18** (1974) 1639.

Received 18 October and accepted 9 December 1976.