Strength *versus* composition of rigid matrix particulate composites

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Models proposed so far for the relationship between mechanical strength (stress to fracture) and filler content (volume fraction) of rigid matrix particulate composites are briefly reviewed. In the case of no adhesion between matrix and filler particles, for which regular, semiregular and random models have been formulated, a new semiempirical equation, based on the more realistic random structural view, is suggested as an attempt towards a unifying treatment of the subject. It is also shown that the same equation, properly modified on purely empirical grounds, can be used when adhesion between matrix and filler is present.

(Keywords: particulate composites; filled polymers; materials strength; constitutive equations)

INTRODUCTION

In polymer science, problems involving the relation between mechanical strength of particulate composites and structural and processing variables have received particular attention in the last two decades. A concomitant, practical interest in this subject has arisen mainly because of possible economies arising from the addition of mineral (or inorganic) fillers to known polymeric materials, increasingly to enlarge their potential and actual applications.

The quantitative relation between strength and relative amount of a particulate filler for composites with a rigid matrix has in particular been the object of many investigations; these have produced a number of theoretical or empirical equations that well fit the experimental results. The large number of these proposals appears to be the consequence not only of several difficulties implicit in the theory of fracture, but also of the widely diverse experimental behaviour of different materials, as well as of the general proneness of experimental fracture values to scatter.

In this paper, the present state of the suggested models is briefly reviewed, with reference also to parallel investigations in the metallurgical field, and two new unifying equations are presented, whose validity is checked also against new experimental results.

It is known that in order rationally to establish the relation between strength (stress to break) of composite and amount (volume fraction) of filler, two kinds of models have to be formulated, for the two cases of adhesion and no adhesion between filler particles and matrix.

CASE OF NO ADHESION

For absence of adhesion, all the models are based on two common assumptions, namely that the fracture follows a substantially planar section of the composite; and at the breaking strain the filler particles are completely detached from the matrix, so that they give rise to a corresponding number of holes in the matrix, and the strength of the composite depends solely on the matrix phase.

Area reduction models

For a derivation of 'simple' laws, an additional assumption is introduced, that the presence of the holes does not modify the level of the critical local state of maximum stress that causes the failure of the matrix phase.

In this case, the strength of the matrix phase (in the system matrix–holes) is equal to that of the matrix material (without holes). Then, the strength of the composite is due solely to that of the matrix, which occupies only a part, A_m, of the whole area, A_c, of the fracture surface of the composite.

If F is the breaking load, and σ_m the strength of the matrix material, the strength, σ_c, and the 'relative strength', σ_{rel}, of the composite can be expressed as:

$$\sigma_c = F/A_c = \sigma_m A_m/A_c \qquad (1)$$

$$\sigma_{rel} = \sigma_c/\sigma_m = A_m/A_c \qquad (2)$$

Different structural models may be formulated to calculate the geometrical ratio, A_m/A_c (area fraction of matrix), as a function of the filler (holes) volume fraction.

Regular models. Consider a mass of matrix material, with a volume fraction, Φ, of spherical holes, of equal radius, uniformly distributed. This uniform distribution may be postulated for simplicity as a regular array of spheres, like that of a crystallographic lattice. Generally, planar sections through these structures do not contain the same area fraction of matrix material. Under an equivalent state of stress it can be supposed that the fracture will take place along a planar section of minimal matrix surface area A_m^*, so that $\sigma_{rel} = A_m^*/A_c$.

For a simple cubic array, with one sphere of radius r in the unit cell, side l:

$$\Phi = \tfrac{4}{3}\pi(r/l)^3$$

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up to a maximum packing fraction ($r = l/2$):

$$\Phi_{\max} = 0.52(36)$$

The section of minimal matrix area A^*_m is that parallel to a cube face, passing through the centre, and the relative strength is easily calculated:

$$\sigma_{\mathrm{rel}} = 1 - 1.21\,\Phi^{2/3} \quad (0 \leqslant \Phi \leqslant 0.52) \qquad (3)$$

Equation (3) has been introduced for polymeric materials filled with glass spheres by Nicolais and Narkis[1], and for porous metals by Eudier[2].

For a body-centred cubic array, with two spheres in the unit cell:

$$\Phi = \tfrac{8}{3}\pi(r/l)^3$$

$$\Phi_{\max} = 0.68(02)$$

the section of minimal matrix area is diagonal, and

$$\sigma_{\mathrm{rel}} = 1 - 1.08\,\Phi^{2/3} \quad (0 \leqslant \Phi \leqslant 0.68) \qquad (4)$$

For a face-centred cubic array, with 4 spheres in the unit cell:

$$\Phi = \tfrac{16}{3}\pi(r/l)^3$$

$$\Phi_{\max} = 0.74(05)$$

the section of minimal matrix area is along every face, and

$$\sigma_{\mathrm{rel}} = 1 - 0.96\,\Phi^{2/3} \quad (0 \leqslant \Phi \leqslant 0.74) \qquad (5)$$

Similarly, for a hexagonal array, the corresponding equation is:

$$\sigma_{\mathrm{rel}} = 1 - 1.11\,\Phi^{2/3} \quad (0 \leqslant \Phi \leqslant 0.74) \qquad (6)$$

It may be seen, from these models, that with regular filling of equal spheres, for the given assumptions the following generalized equation holds:

$$\sigma_{\mathrm{rel}} = 1 - \alpha\Phi^{2/3} \qquad (7)$$

in which the parameter α assumes different values (1.21, 1.08, 0.96 and 1.11) for any of the possible main regular configurations (for close packed spheres), with a validity range from $\Phi = 0$ to the Φ value of the closest packing of any configuration ($\Phi_{\max} = 0.52$, 0.68, 0.74 and again 0.74). In *Figure 1*, equation (7) is represented in the forms given by equations (3) to (6) (lines A, C, D, B).

Semiregular models. A wider validity of the relation expressed by equation (7), compared with equation (3), has been recognized by several investigators.

As a matter of fact, a more realistic view might lead to conceive the hole configuration as a 'mixed' regular array, as if the fracture surface was lined with tiles of different regularities. In this case equation (7) might be taken as holding with an α value properly weighted among the values of the possible regular arrays (e.g. for loose or close random packing of spheres, $\Phi_{\max}$ values have been estimated in the range 0.60–0.64 (ref. 3), intermediate among those of the main regular arrays).

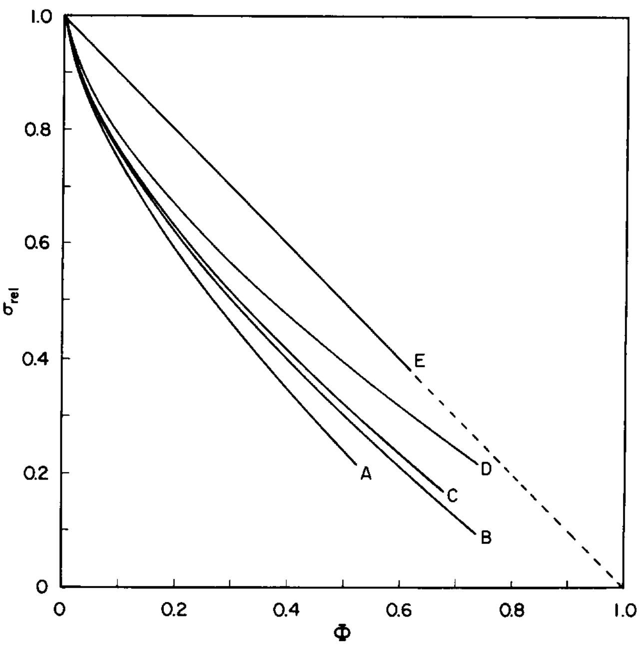

Figure 1 Theoretical values of relative strength (σ_{rel}) versus filler volume fraction (Φ) given by: equation (3), (A); equation (6), (B); equation (4), (C); equation (5), (D); and equation (9), (E)

With reference to porous metals or cermets, Butcher and Howlett[4], Ishimaru *et al.*[5] and Griffiths *et al.*[6] considered non-spherical pores, or pore arrangements other than the simple cubic one of equation (3), and theoretically or empirically found appropriate corrections of the parameter α in equation (7), with values differing from 1.21. Similarly for particular cases of polymeric materials, Nicolais and Nicodemo[7] suggested that α could usefully be considered to be an empirical parametric quantity. Furthermore Nicolais and Mashelkar[8], on the basis of 'major experimental evidence' proposed a generalization of the relation in the form:

$$\sigma_{\mathrm{rel}} = 1 - \alpha\Phi^{n} \quad (\alpha > 0;\ n < 1) \qquad (8)$$

although pointing out good fitting of various experimental results by taking $\alpha = 1.21$ and $n = 2/3$, i.e. by using equation (3); see *Figure 2*.

It is of interest to note that equations (3)–(7) were derived from the geometry of strictly regular systems with the aim of finding out the weakest planar section of the material. However, when the sphere packing is not near the closest one, they are equally valid for 'semiregular' (smectic) systems; in fact, on the third assumption, in the section of minimal matrix content found for any regular model the relative positions of the spheres can be supposed to vary in the plane towards a random configuration without affecting the material strength, provided that the matrix area fraction is kept constant. Thus, from a different viewpoint, on the assumptions made, and when dealing with fracture phenomena, the problem could be seen as that of finding the possible (not probable) section (or section portion) of minimal (not average) matrix content of the real (probably close to random) configuration.

This might explain the physical meaning of empirical determinations of the parameter α in equation (7), and of the circumstance that a value near 1.21 is frequently observed (as a lower bound?), being the section described

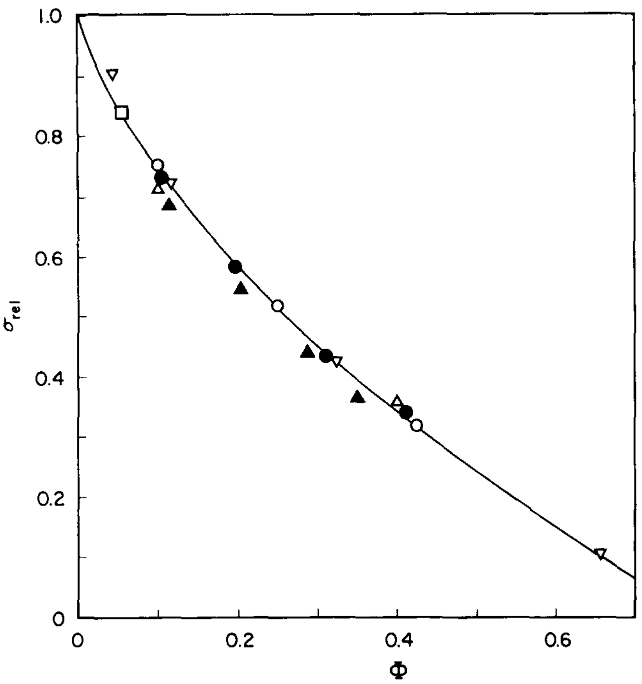

Figure 2 Experimental relative strength, as a function of filler volume fraction fitted to equation (3). The experimental results, with six composite materials, were taken from various authors: see ref. 8

by equation (3) that has the lowest matrix content and is the weakest of the main regular models. Furthermore, in this 'semiregular' picture, strict sphericity of the pores becomes unimportant, so that equation (7) can reasonably be related to composites with non-spherical filler particles. Similarly, to a first approximation it may be expected that in some cases the fracture surface can be not strictly planar; for these, the introduction of a generalized second parameter, *n*, in equation (8) may be justified.

In conclusion, the most practical method of solution based on regular models appears to be the use of the relation in the form mathematically indicated by these models but with the introduction of one or two empirical parameters, appropriately chosen for classes of filler materials to allow a wider range of good fitting of the experimental results.

Random model. A completely different structural approach is to consider a uniform, completely random system of holes of any shape. In this case the area fraction of matrix must be the same for any section through the system, and equal to the volume fraction of the matrix itself[9]. For this model equation (2) becomes:

$$\sigma_{rel} = 1 - \Phi \qquad (9)$$

and is represented by the diagonal straight line in *Figure 1*, with σ_{rel} values higher than those of the preceding models.

This simple law generally has been considered as an ideal, unattainable upper bound, since it was believed that, in addition to a matrix area reduction, critical effects ought in any case to be induced by the filler particles in the system, with a further decrease of the composite strength. However, very recently Danusso *et al.*[10] found that equation (9) is substantially obeyed in composites of polyester resins filled with $CaCO_3$ particles of a size of the order of a few micrometres. An example is reported in *Figure 3*.

This result could be expected from the comment of Landon *et al.*[11], on experimental data obtained with polyurethane filled with glass spheres, that equation (9) represents the law obeyed when the results with different particles sizes at constant Φ are extrapolated to zero size; but more precise was a previous conclusion by Lange[12] that critical filler effects should be prevented when the particle size went below a certain threshold value. In fact, for the polyester resins that they used, Danusso *et al.*[10] estimated an inherent flaw size of ~30–40 μm, i.e. much higher than the particle size, which explains the successful application to that case of the simplest (random) area reduction model.

Models including critical effects

When the addition of the filler particles gives rise to local defects that induce critical effects affecting the strength of the matrix (particulate inhomogeneities, additional cracks or flaws, air bubbles, etc.), the third assumption is no longer valid, and more sophisticated models must be formulated.

Although stress concentration problems have been solved, e.g. within elasticity theory, for particular geometries of holes or inclusions, satisfactory agreement of quantitative theoretical predictions of this kind with experimental results has not as yet been found for particulate composites[13].

The only practical way that now remains is to resort to empirical corrections of the area reduction models above.

Previous suggestions. For regular or semiregular models, and for polymeric foams, Masi *et al.*[14] suggested the introduction of a constant concentration factor reducing the matrix strength in equation (3). Following this suggestion, for a generalization equation (7) can be modified to the two-parameter form:

$$\sigma_{rel} = a(1 - b\Phi^{2/3}) \qquad (10)$$

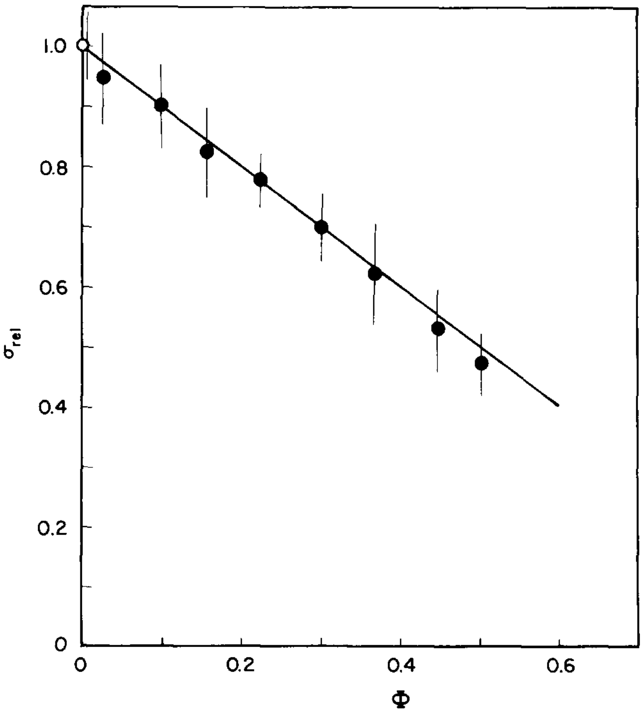

Figure 3 Relative strength of a polyester resin filled with $CaCO_3$; (———), curve calculated by equation (9)

or equation (8) to the three-parameter form:

$$\sigma_{\mathrm{rel}} = a(1 - b\Phi^n) \qquad (11)$$

With the same models, in the metallurgical field, for stress concentration effects only modifications implicit in the adjustment of α in equation (7) have been suggested[6,15].

For the random model, one- or two-parameter forms have been proposed at different times for porous metals. Balshin[16] suggested the following equation:

$$\sigma_{\mathrm{rel}} = a(1 - \Phi)^n \qquad (12)$$

and Pines and Suchinin[17] a one-parameter variant of equation (9):

$$\sigma_{\mathrm{rel}} = 1 - a\Phi \qquad (13)$$

whereas Bagshaw *et al.*[18] used the two-parameter equation:

$$\sigma_{\mathrm{rel}} = a(1 - b\Phi) \qquad (14)$$

which was subsequently suggested by Piggott and Leidner[19] for polymeric materials; it was given a theoretical interpretation by Leidner and Woodhams[20] on the basis of poor adhesion between matrix and particles.

The following one-parameter equation from a modified random model was instead suggested by Haynes[21] for porous metals:

$$\sigma_{\mathrm{rel}} = \frac{1 - \Phi}{1 + b\Phi} \qquad (15)$$

in which non-constancy of a 'reduction factor' versus Φ is taken into account.

A new unifying model. In order to simplify the rather complex picture that results from the numerous suggestions put forward so far, a new unifying model is now presented.

In the simplest, and essentially realistic equation (9), a critical effect coefficient, C, can be introduced:

$$\sigma_{\mathrm{rel}} = \frac{1 - \Phi}{C}$$

When critical effects are actually present ($C > 1$), it seems to be reasonable to regard C as dependent on Φ[13,21]. To a first approximation this dependence may be written as

$$C = a + b\Phi \qquad (16)$$

This leads to the general equation:

$$\sigma_{\mathrm{rel}} = \frac{1 - \Phi}{a + b\Phi} \quad \text{(no adhesion)} \qquad (17)$$

which is represented in *Figure 4* for various values of the adjustment parameters a and b.

With $a = 1$ and $b = 0$ (no critical effects) equation (17) becomes equation (9); with $a = 1$ and $b = 2$ it is practically equivalent to equation (3) (broken line in *Figure 4*); with $a = 1$ it becomes equation (15), and with different adjustments of a and b it can replace to a good approximation the remaining suggested equations, in particular equation (10) (see example in *Figure 4*).

Obviously, equation (17) gives good fitting of the experimental results of *Figures 2* and *3* (with $a = 1$ and $b = 2$, and with $a = 1$ and $b = 0$ respectively); and *Figure 5* shows, as an example, that it fits equally well (with $a = 1$ and $b = 0.80$) the results of Landon *et al.*[11], from polyurethane filled with hollow spheres, intermediate to those of *Figures 2* and *3*.

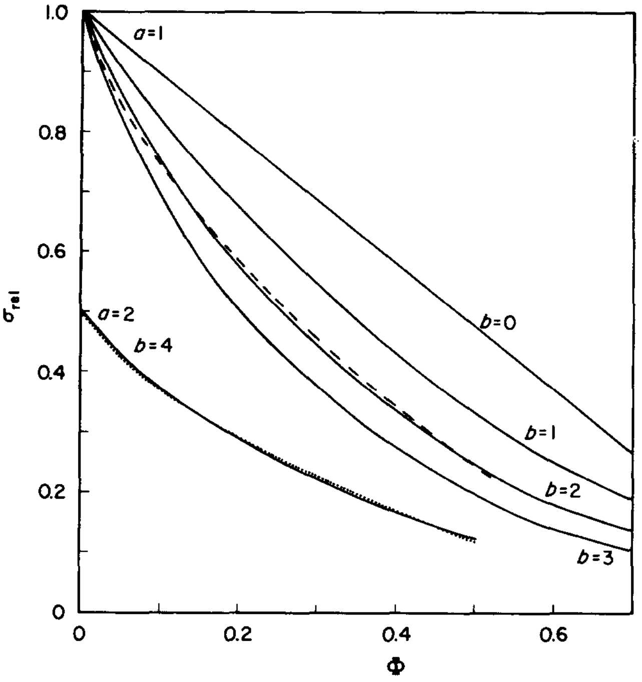

Figure 4 Relation between σ_{rel} and Φ as expressed by equation (17) with $a = 1$ or $a = 2$ and the indicated values of the parameter b. (– – –), equation (3); (·····), equation (10) with $a = 0.5$ and $b = 1.21$

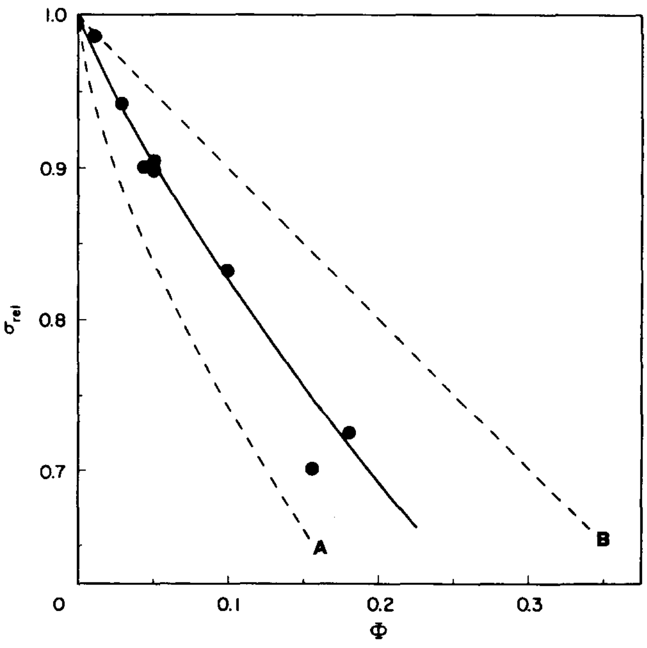

Figure 5 Fitting of experimental results from ref. 11 by equation (17) with $a = 1$ and $b = 0.80$. Broken lines: (A), equation (3); (B) equation (9)

CASE OF ADHESION

For the case of adhesion, two main models have been formulated with a special reference to polymeric matrix particulate composites.

According to Nielsen[22], a very simple model is suggested by assuming for the tensile strength rigorous Hookean behaviour up to breaking strains; then, $\sigma_c = E_c\varepsilon_c$, where E is the tensile modulus and ε is elongation to break, and ε_c may be expressed according to a simple model as:

$$\varepsilon_c = \varepsilon_m(1-\Phi^{1/3})$$

where ε_m is elongation to break of the matrix, so that:

$$\sigma_{rel} = \frac{E_c}{E_m}(1-\Phi^{1/3}) \tag{18}$$

The ratio E_c/E_m can be calculated according to one of the models already advanced for the modulus of particulate composites. In *Figure 6* two examples of equation (18) are represented (broken lines A and B) as calculated by Nielsen using for E_c/E_m the equations of Kerner and Eilers–Van Dijck respectively[22].

According to Leidner and Woodhams[20], on the basis of a micromechanical analysis of stress transfer between matrix and spherical particles, σ_c should decrease initially with Φ according to the same linear equation (like equation (14)) that they found for the case of no adhesion, but beyond a critical Φ value it should increase according to another linear equation.

Agreement with experimental results is somewhat problematic. As a matter of fact the results, though with various amplitudes for different materials and degrees of adhesion, show in general a nonmonotonic pattern with a decrease of σ_c at low Φ values, frequently steeper than that for the corresponding case of no adhesion, followed by a minimum and an increase.

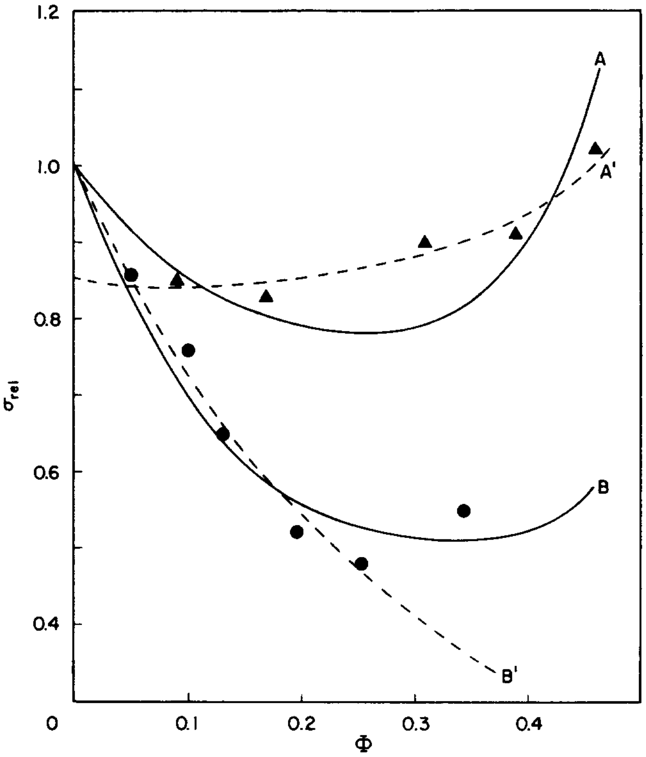

Figure 7 Fitting of experimental results from ref. 23 (▲) and from ref. 7b (●) by equation (20) or by equation (17) (see text)

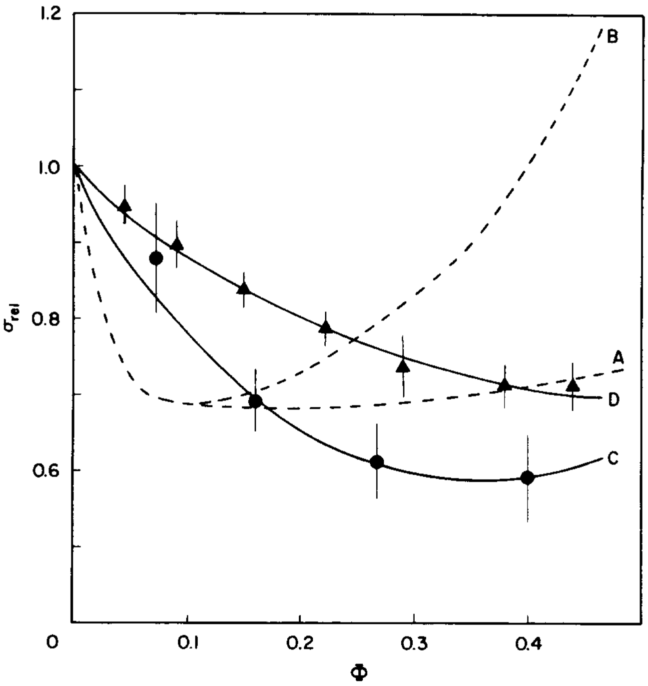

Figure 6 (A, B): relationship between σ_{rel} and Φ in the case of adhesion, as calculated by Nielsen[22] using, for the relative modulus, the equations of Kerner (A) and of Eilers–Van Dijck (B). (C, D): fitting by equation (20) of our experimental results with a modified polyester resin (●) (C: $a=1$, $b=2.20$, $c=-5.41$) and vinyl ester resin (▲) (D: $a=1$, $b=0.38$, $c=-1.90$) filled with $CaCO_3$

We suggest, on a purely empirical basis, an extension of our equation (17) to the case of adhesion, by which the condition expressed by equation (16) is extended with a quadratic third term:

$$C = a + b\Phi + c\Phi^2 \tag{19}$$

so that equation (17) becomes:

$$\sigma_{rel} = \frac{1-\Phi}{a+b\Phi+c\Phi^2} \quad \text{(adhesion)} \tag{20}$$

In *Figure 6* two examples are shown (full lines C and D) of the fitting by equation (20) of our results with a modified polyester resin and a vinyl ester resin respectively, filled with $CaCO_3$ particles sized about 3 μm (by putting $a=1$, $b=2.20$, $c=-5.41$; and $a=1$, $b=0.38$, $c=-1.90$, respectively).

Figure 7 shows the best fitting by equation (20) of the results of Spanoudakis and Young[23] on an epoxy filled with glass spheres (full line A: $a=1$, $b=1.01$, $c=-4.63$), and of the Nicodemo and Nicolais[7b] with SAN filled with Al particles (full line B: $a=1$, $b=3.96$, $c=-9.0$). It is interesting to observe that these two cases offer an example of typical difficulties that can arise in this kind of analysis. In fact, the results from ref. 23 could be better represented by equation (20) with $a=1.18$, $b=-1.07$ and $c=-0.70$ (broken line A'); on the other hand, the results from ref. 7b could be very well fitted by equation (17) (case of no adhesion, as indicated by the authors), if the experimental point at $\Phi=0.34$ were discarded (broken line B': $a=1$, $b=2.30$).

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