

## Misconceptions About Filled Polymers

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### Synopsis

The idea that, with filled polymers, length fraction, area fraction, and volume fraction of filler are different appears to have gained wide acceptance. The fallacy of this, except for special directions in ordered arrangements, is demonstrated. This misunderstanding has led to widespread misinterpretation of experimental results in this field.

### INTRODUCTION

The idea that length fraction depends on volume fraction to the one-third power appears to have first been applied to filled polymer systems by Bueche.<sup>1</sup> It was carried a stage further by Nielsen<sup>2</sup> who, in deriving his eq. (5), seems to have assumed that area fraction depends on volume fraction to the two-thirds power. The Nielsen treatment has since been widely quoted and applied (see, e.g., Sahu and Broutman<sup>3</sup> and Brassell and Wischmann<sup>4</sup>), sometimes with variations,<sup>5,6</sup> but still apparently based on the view that the different fractions have different values.

An understanding of the relationship between length fraction area fraction and volume fraction is a first important requirement if the mechanical properties of particulate composites are to be understood. It is interesting to note that in the metallurgical field, these relationships do seem to be well understood, and etched sections have been used for a long time in the determination of volume fractions of precipitates, and automatic methods for doing this have recently been perfected.<sup>7</sup>

### Relation Between the Fractions

Consider a material containing randomly dispersed particles of any shape and size. We will examine a cubic box of this composite which is sufficiently large to be representative of the whole material.

Any straight line long enough to traverse the box completely will have a length fraction of dispersed material which is the same as that of any other equally long line. In addition, any plane sheet of sufficiently large extent to divide the box completely will have the same area fraction of dispersed material as any other equally large plane sheet.

In particular, the line OX, and any line in the plane OXDY (see Fig. 1) will have this length fraction,  $L_f$ , say. Thus, the total area occupied by

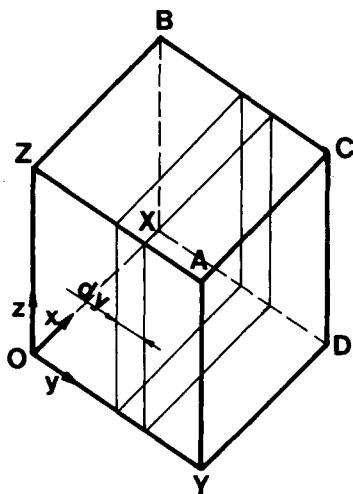


Fig. 1. Representative portion of filled polymer. The cube drawn is envisaged as being sufficiently large so that any plane in the cube has the same area fraction as any other plane when filler is randomly disposed.

particles sectioned by an element of area of width  $dy$  on the face OXDY is  $L_f ady$ ,  $a$  being the length of the sides of the box.

To calculate the area fraction of the face OXDY,  $A_f$ , say, we sum the area of particles over all the elements of thickness  $dy$  across the cube. This is done by making  $dy$  tend to zero and integrating, i.e.,

$$A_f = \frac{1}{a^2} \int_0^a L_f ady = L_f$$

since  $L_f$  is independent of  $y$ . Thus, area fraction is equal to length fraction.

Next, consider the total volume of the parts of particles lying between two parallel planes,  $dy$  apart and parallel to the face ACDY. This is  $A_f a^2 dy$ , so that the same reasoning as above gives

$$V_f = \frac{1}{a^3} \int_0^a A_f a^2 dy = A_f.$$

Thus,

$$L_f = A_f = V_f.$$

If, instead of considering a random arrangement, we consider an ordered one, we get a different result. Let the box in Figure 1 represent one unit cell of a primitive cubic lattice of spheres of equal radius,  $r$ , say ( $2r < a$ .) The box is assumed to have a sphere at the center. The volume fraction of spheres is  $4\pi r^3/(3a^3)$ . The area fraction varies according to the plane considered. For the plane AZBC (or any other face of the box), the area fraction is zero. For a plane going through the center of the box, and parallel to one of the faces, the area fraction is

$$A_f' = \pi r^2/a^2 = 1.2V_f'^{2/3}.$$

This is the formula used by Nicolais and Narkis<sup>5</sup> and by Cohen and Ishai.<sup>6</sup> For diagonal planes like OACX, the area fraction is

$$A_f'' = 2\pi r^2/a^2 = 1.7V_f^{2/3}.$$

Finally, for a plane in an entirely random direction, we have to consider many units of the structure to find the true area fraction. Such a plane (e.g., the one that crosses OX at  $a/\pi$ , OY at  $a/e$ , and OZ at  $a/\ln 2$ ) has an area fraction

$$A_f = 4\pi r^3/(3a^3) = V_f.$$

It is most unlikely that experimental samples ever have arrangements which have long-range order, however. To have high volume fractions, some ordering is necessary, but this is most likely to occur over relatively small volumes, and adjacent ordered volumes will normally be randomly oriented with respect to each other, just as polycrystalline metals have randomly oriented crystals. At low volume fractions, of course, even short-range order is unlikely, unless clumping occurs.

### PRACTICAL IMPLICATIONS

Effects of inclusions on strength must come about primarily as a result of particle shape and, to a lesser degree, on volume fraction and particle size.

When the inclusions are long well-bonded rods or fibers, great improvements in strength are possible. On the other hand, when they consist of poorly bonded or weak sheets of material, the matrix can be deprived of most of its strength even when the volume fraction of the inclusions is very small (e.g., hydrogen-embrittled zirconium). This weakening is due to stress concentrations, coupled with a size effect. Since Inglis<sup>8</sup> solved the stress field around an ellipse, and Griffith<sup>9</sup> showed that the size of elliptical cracks was also important, stress concentrations due to voids of a wide range of shapes have been worked out, and a number of solutions have been obtained for stresses around inclusions of various shapes.

In the case of rounded cracks and inclusions, the stress concentrations are much less severe than when they have sharp corners. However, Sahu and Broutman,<sup>3</sup> using finite element analysis, show that rigid inclusions with circular sections give stress concentrations which vary from just under 2 for  $V_f = 0.033$  to just under 3 for  $V_f = 0.489$ . Thus, considerable weakening can result from using poorly bonded spheres. The actual amount of weakening will also depend to some extent on the sphere size and the degree of brittleness of the matrix material.

As a first approximation, however, it is reasonable to assume that strength, or flow stress,  $\sigma$ , should depend on volume fraction to the first power rather than any other, when spherical, or approximately equiaxed and rounded inclusions are used, i.e.,

$$\sigma_p = a - bV_f \quad (1)$$

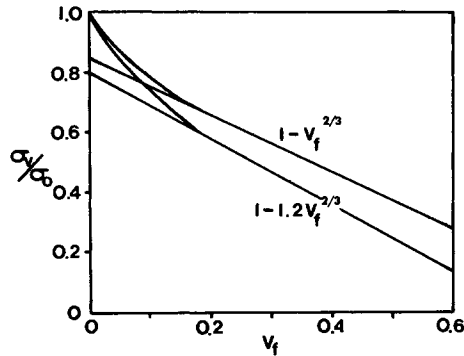


Fig. 2. Linear and two-thirds power laws compared. Both two-thirds power laws are indistinguishable from linear expressions for volume fractions greater than 0.2.  $\sigma_v$  = Strength of filled polymer;  $\sigma_0$  = strength of polymer without filler;  $V_f$  = volume fraction.

where  $a$  and  $b$  are influenced by the size, shape, modulus, and bonding of the inclusion particles, and by matrix strength and modulus.

Stress concentration effects can, of course, be very important even at vanishingly small volume fractions. Neglect of this can result in spurious agreement with the two-thirds power law. If weakening due to stress concentrations reduces the matrix strength to about 0.8 of its normal value, then

$$\sigma_v = 0.8 \sigma_0 - bV_f. \quad (2)$$

It can be seen from Figure 2, where eq. (2) is compared with two-thirds power expressions, that, between  $V_f = 0.15$  and 0.6, it is hard to choose between the first power and fractional power laws;  $\sigma_0$  is, of course, the matrix strength in the absence of voids or fillers.

### PRACTICAL EXAMPLES

Equation (2) fits the values for composite strength of Nicolais, Drioli, and Landel<sup>10</sup> much better than the two-thirds power law. Their experimental points are on a straight line which intersects the stress axis at  $0.7 \sigma_0$ , and the point at  $V_f = 0.12$  is a considerable distance away from the two-thirds power curve. Sahu and Broutman's<sup>3</sup> results for composite strength fit the first-power law, eq. (1), better than the fractional power law, and so do Ishai and Cohen's<sup>11</sup> and Brassell and Wischmann's<sup>4</sup> results for composite yield strength ( $b$  in eq. (1) can, of course, be negative).

Brassell and Wischmann's results for tensile strength fit first-power and fractional power laws equally well, and Nicolais and Narkis's<sup>5</sup> results for tensile yield strength also fit both equally well. Finally, Ishai and Cohen's<sup>11</sup> results for the yield stress of composites with voids fit the two-thirds power law slightly better.

## CONCLUSIONS

The interpretations of results of mechanical tests on filled polymers by many workers appear to have been based on a misunderstanding. The experiments on strength and yield stress of these composites fit a relationship of the type

$$\sigma = a - bV_f$$

somewhat better than relationships involving fractional powers of volume fraction.

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Received November 12, 1973