NOTES

The Effect of Spherical Inclusions on the Ultimate Strength of Polymer Composites

Recently, a number of papers have been dealing with the strength of filled polymeric systems.[1-3] At present, two empirically derived predictive equations have been developed. Leidner and Woodhams[1] and Piggott and Leidner[2] have proposed a general equation of the form

$$\sigma_u = a - bV_f \tag{1}$$

where σ_u is the ultimate strength of the composite, V_f is the volume fraction of particles present, and a and b are constants. Nicolais and Mashelkar[3] proposed an alternate equation of the form

$$\sigma_u = \sigma_0 - bV_f^n \tag{2}$$

where σ_0 is the ultimate strength of the unfilled matrix and n has been found to be $\frac{2}{3}$. The constant b is limited to positive values. A comparison between experimental results and the above equations is shown in Figure 1 (these curves are reproduced from Nicolais and Mashelkar[3]). Though eq. (2) fits the experimental data quite well, it is empirical in nature and does not lend itself to a model of the actual failure mechanisms.

Here, a model is presented which, thought resulting in an equation different in nature than either of the two above, fits the experimental data as well as eq. (2). Spherical particles of volume V_p are being added to a polymeric matrix (Fig. 2). Associated with each imbedded spherical particle is a volume of matrix, v_i, which is affected by the presence of the imbedded particle. On a unit volume basis, after the addition of N particles, let V_m be the volume of matrix material as yet unaffected by the presence of the particle. The subsequent random addition of a particle has associated with
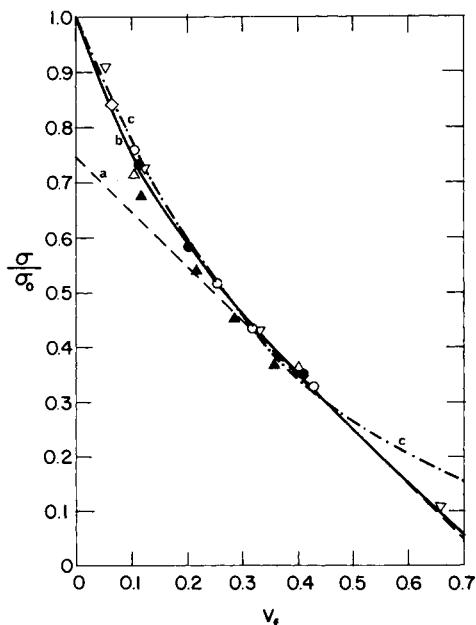

Fig. 1. Relative strength σ_u/σ_0 as function of filler volume fraction V_f. Data from reference 3: (a) eq. (1) drawn on the basis of the recommendations in reference 1; (b) eq. (2), with $b = 1.21$, from reference 3; (c) eq. (5), with $r = 2.66$.
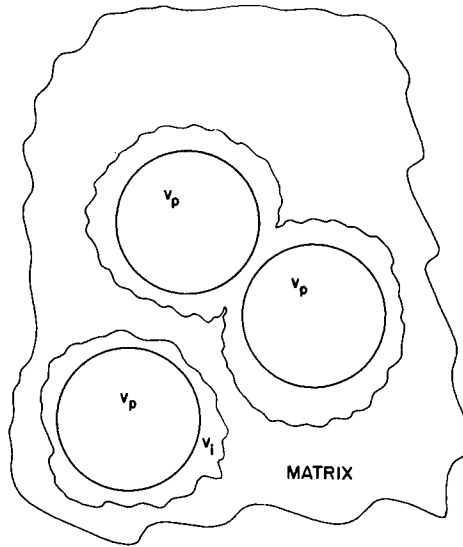
Fig. 2. Cross-sectional view of model of a composite containing spherical fillers.

it an included matrix volume v_i. However, the probability that this particle will affect unaffected matrix is V_m. Therefore, for the random addition of particles,

$$\frac{dV_m}{dN} = -(v_i + v_p)V_m$$

Integrating, and noting that N, the number of particles added, is simply V_f/v_p, where V_f is the volume fraction of particles, results in the expression

$$V_m = \exp(-rV_f), \qquad \text{where } r = (v_i + v_p)/v_p \tag{3}$$

As the composite is stressed, initial failure occurs in regions of affected matrix volume v_i, due to the initial presence of stress concentration factors. As the level of stress is increased, the mean strain magnification factor has been shown[4,5] to be

$$\frac{\epsilon'}{\epsilon} = \frac{1}{1-c} \tag{4}$$

where ϵ is the measured strain of the composite, ϵ' is the strain of the matrix material in the composite, and c is the volume fraction of nonmatrix matter.

At the point of failure, ϵ_u is the ultimate strain of the composite and ϵ'_u is the strain in the matrix at this ultimate point. Assuming that failure in the composite occurs because of failure in the matrix, the ultimate strain in the matrix at this point, ϵ'_u is the same value as the ultimate strain in the unfilled polymer, ϵ_0. The ultimate strain of the composite is thus governed by ϵ_0.

Noting that the stress is proportional to the strain, eq. (4) at the point of failure can be inverted and written as

$$\frac{\epsilon_u}{\epsilon'_u} = \frac{\epsilon_u}{\epsilon_0} = \frac{\sigma_u}{\sigma_0} = 1 - c \tag{5}$$

It is interesting to note the relationship between eq. (5) and eq. (1). They are comparable for the situation where $a = b = \sigma_0$ and $c = V_f$. However, as will be shown, c is not V_f.

As the stress (or strain) of this system is increased, initial failure occurs in those regions nearest the particle surface. Since these regions are no longer able to sustain the stress, they cannot effectively be considered as part of the matrix. Therefore, at (or near) the ultimate strength of the material, c includes both the particle volume fraction plus the total volume of matrix affected by the particles. Therefore, $1 - c$ is V_m. Combining eqs. (5) and (3) yields

$$\frac{\sigma_u}{\sigma_0} = \exp(-rV_f) \tag{6}$$

This expression differs considerably from either eq. (1) or eq. (2). A comparison of the three equations is shown in Figure 1.* As can be seen, it compared well with eq. (2) over the dominant region of volume fraction. Equation (1) was not meant to fit such varied data.[6]

Unfortunately, this model is valid over a limited range of volume fraction. It is known that at approximately 35–40 vol-%, included particles begin forming continuous chains. At higher concentrations, regions of affected matrix transverse the composite structure, altering the failure mechanism. As anticipated, the experimental values of $\sigma_u \sigma_0$ would be lower than projected by eq. (6). This is confirmed experimentally.

From the data, r is found to be 2.66. Using eq. (3) and noting that $v_p = 4\pi R^3/3$ and $v_i = 4\pi(R + \Delta r)^3/3$, the term $(1 + \Delta r/R)^3$ is found to be 1.66. Zeigler et al.[5] noted that eq. (4) could best be used when account is taken of "bound or immobilized matrix at the interface." Their correction term, $(1 + \Delta r/R)^3$, was found experimentally to be 1.75, close to the above 1.66.

It is interesting to note the variability of the data plotted in Figure 1. These results are independent of both particle size and material. This implies that failure in all these material occurs as a result of a common failure mechanism. This hypothesis will be investigated in the near future.

References

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* Data from reference 3. All the data points are presented in the reference.