Strain Magnification in Polymer Composites

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Synopsis

We consider two approaches to strain magnification in a composite material, point out that they apply to different situations, and caution against misapplication of the equations derived.

Strain magnification occurs when a sample of a deformable matrix containing essentially nondeformable particles is subjected to an elongation or compression. Barring the formation of voids, the total sample deformation has to be accommodated by the matrix; hence the strain in the matrix is larger than the measured overall strain.

In general, it is necessary to distinguish between the maximum strain, which would prevail between the closest points of approach of two neighboring particles, and the mean strain, which is obtained by averaging the strains over the entire range of particle separation distances. The former value would probably be relevant to failure properties of a composite; the latter would be the appropriate quantity to use for modulus, energy storage and dissipation.

Even though the particles in a composite are most likely randomly distributed, a number of authors have found it convenient to assume a particular spatial arrangement. Smith,¹ using a model of spheres in a closepacked array, predicts a strain magnification ϵ'/ϵ given by:

$$\epsilon'/\epsilon = 1/(1 - 1.105\varphi_{\mathbf{F}}^{1/s}) \tag{1}$$

where ϵ is the measured overall strain $(\Delta L/L_0)$, ΔL is the change in length, L_0 is the initial specimen length, ϵ' is the magnified strain in the matrix, and $\varphi_{\mathbf{F}}$ is the volume fraction of filler particles. This result gives the strain in the matrix along the line between centers of adjacent spheres, i.e., the maximum rather than the mean strain. A similar result is obtained by F. Bueche² using a model of cubical particles apparently in a cubic array. He gives the line fraction of polymer between two reference points in a filled system as $1 - \varphi_{\mathbf{F}}^{1/4}$; hence the line fraction of filler, $L_{\mathbf{F}}/L_0$, is $\varphi_{\mathbf{F}}^{1/4}$. This led Bueche to the conclusion that the magnified extension ratio α' is

$$\alpha' = (\alpha - \varphi_{\mathbf{F}}^{1/s})/(1 - \varphi_{\mathbf{F}}^{1/s})$$
⁽²⁾

where $\alpha = \epsilon + 1$ and $\alpha' = \epsilon' + 1$. This is equivalent to a maximum strain magnification given by

$$\epsilon'/\epsilon = 1/(1 - \varphi_{\mathbf{F}}^{1/2}) \tag{3}$$

The mean strain magnification can be obtained by considering many different models. We shall illustrate its derivation for spheres of radius R whose centers are randomly distributed in the matrix. A line passing through the composite will intersect only spheres whose centers are within a cylinder of radius R around that line, such as spheres B and C in Figure 1. The line fraction of filler, $L_{\rm F}/L_0$, is the total length of chords of spheres through which a line of unit length passes. The chord length, L in Figure 1, is $2(R^2 - r^2)^{1/2}$ for spheres with centers at distance r from the line. If P is the number of sphere centers per unit volume, then

$$L_{\rm F}/L_0 = \int_0^R 2(R^2 - r^2)^{-1/2} P \ 2\pi r dr = (4\pi P/3) \ R^3 \tag{4}$$

Since P is equal to the number of particles per unit volume, $3\varphi_F/4\pi R^3$, it follows that

$$L_{\rm F}/L_0 = \varphi_{\rm F} \tag{5}$$

This relation can be shown to hold not only for spheres but also for particles of any shape or orientation. Thus, to obtain the mean magnified extension ratio, eq. (2) should read:

$$\alpha' = (\alpha - \varphi_{\rm F})/(1 - \varphi_{\rm F}) \tag{2a}$$

A strain magnification ratio, ϵ'/ϵ , based on Bueche's concept of line fraction equal to cube root of volume fraction² has been used by a number of other authors³⁻⁵ to explain modulus increased in filled systems. The mean strain magnification, which is more appropriate for this problem, is

$$\epsilon'/\epsilon = 1/(1 - \varphi_{\rm F}) \tag{6}$$



Fig. 1. Physical model for calculation of line fraction of filler.

In order to take into account the effect of bound or immobilized matrix at the interface,⁶ eq. (6) is rewritten to include an effective radius correction. If Δr is the increase in particle radius, R, due to surface interactions, then

$$\frac{\epsilon'}{\epsilon} = \frac{1}{1 - \varphi_{\rm F} [1 + (\Delta r/R)]^3} \tag{7}$$

We have found that $[1 + (\Delta r/R)]^3$ is of the order of 1.75 for many systems of practical interest. By using this value, eq. (7) can then be expanded to

$$\epsilon'/\epsilon = 1 + 1.75\varphi_{\mathbf{F}} + (1.75\varphi_{\mathbf{F}})^2 + \dots$$
(8)

which, though derived from geometric considerations alone, is similar in form to the strain magnification equation of Mullins and Tobin⁷ which was based on an extension of hydrodynamic considerations of Guth.^{8,9}

References

1. T. L. Smith, Rubber Chem. Technol., 34, 123 (1961); Trans. Soc. Rheol., 3, 113 (1959).

2. F. Bueche, J. Appl. Polym. Sci., 4, 107 (1960).

3. L. E. Nielsen, J. Appl. Polym. Sci., 10, 97 (1966).

4. R. Shuttleworth, Europ. Polym. J., 4, 31 (1968).

5. B. M. E. Vander Hoff and E. J. Buckler, J. Macromol. Sci. (Chem.), A1, 747 (1967).

6. K. D. Ziegel, J. Colloid Interface Sci., 29, 72 (1969).

7. L. Mullins and N. R. Tobin, J. Appl. Polym. Sci., 9, 2993 (1965).

8. E. Guth and R. Simha, Kolloid-Z., 24, 266 (1936).

9. E. Guth, J. Appl. Phys., 16, 20 (1945).

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