The Strength of Polymeric Composites Containing Spherical Fillers

The papers dealing with the strength of polymeric composites have been increasing in recent years due to the increasing technological importance of composite materials. Leidner and Woodhams[1] recently presented some work dealing with the theoretical and experimental aspects of the strength of polymeric composites containing spherical fillers. Since the predictive equations proposed by these authors deviate significantly from the more traditional approach, we shall examine some aspects of their theoretical development and show that some of the assumptions made by these authors may have a doubtful validity.

Leidner and Woodhams[1] assume that the radial pressure exerted by the matrix on the bead due to the shrinkage of the resin on curing and due to the difference in coefficients of thermal expansion of the matrix and the filler is constant and independent of the volume fraction of the inclusions. Furthermore, they have performed experiments on cylindrical glass rod drawing to determine the resin–glass rod interface stresses, and they have assumed the same results to be valid for spherical fillers. This implies an assumption that the stresses are independent of the shape. A critical analysis, however, shows that both these assumptions are unlikely to be valid.

We shall demonstrate this point by making use of the results from the classical work of Laszlo,[2] who has solved the compound sphere and cylinder problem by an elementary application of the theory of elasticity. Laszlo shows that the thermal stresses for the compound sphere are given by

$$p = \frac{(\alpha_p - \alpha_f)\Delta t}{\left(\frac{1}{\nu_p} - 1 \Big/ \frac{2}{\nu_p} E_p\right) \frac{1 + 2v_f}{1 - v_f} + \frac{1}{E_p/\nu_p} + \left(\frac{1}{\nu_f} - 2\right) \Big/ E_f/\nu_f} \qquad (1)$$

In the case of shrinkage due to curing, the value of p could be calculated from eq. (1), but with $(\alpha_p - \alpha_f)\Delta t$ substituted by $(\Delta s)/3$, where Δs is the fractional change in the volume of the polymer due to curing shrinkage. Here, the subscripts p and f stand for the polymeric matrix and the filler, respectively; ν, E, α, and Δt are the Poisson ratio, the tensile modulus, the thermal expansion coefficient, and the temperature difference, respectively. The formula for the tangential and radial stresses for the compound cylinder case reported in reference 3 is quite complicated but is significantly different from that in eq. (1). An estimate of p for the single cylinder embedded in an infinite matrix is given by[3]

$$p = \frac{(\alpha_p - \alpha_f)\ \Delta t E_p}{(1 + \nu_p) + (1 + \nu_f)\dfrac{E_p}{E_f}}. \qquad (2)$$

We shall now perform calculations to demonstrate the strong dependence of the shape and the filler volume content on the total residual stresses. We assume the material constants to be $\alpha_p = 3 \times 10^{-5}$ in./in. °F, $\alpha_f = 2.8 \times 10^{-6}$ in./in. °F, $\Delta t = 126$°F, $E_p = 3 \times 10^5$ psi, $E_f = 1.1 \times 10^7$ psi, $\nu_p = 0.4$, $\nu_f = 0.2$. Volumetric shrinkage of about 3% has been assumed. The results of such calculations are shown in Table I.

It can be easily seen that the single cylindrical glass rod drawing experiment of Leinder and Woodhams[1] gives a total stress value of 3400 psi. Then, assuming a reasonable value of α (coefficient of friction) to be 0.5, we obtain $\tau = 1700$ psi, which is reasonably close to the value of 1540 psi reported by Leidner and Woodhams.[1] The same calculation performed for a single spherical filler, based on eq. (1) with $v_f \rightarrow 0$, gives a total residual stress value of 5700 psi, which is about 65% higher than the value obtained with the cylindrical rod. This clearly shows the importance of the shape which has been ignored by the authors. That p depends strongly on the volume fraction can also be seen from the calculations in Table I. Leidner and Woodhams' assumption that p is independent of volume fraction is thus likely to lead to serious errors, since the load carried by the beads will be a nonlinear function of the volume fraction.

Leidner and Woodhams[1] and Piggott and Leidner[4] propose to correlate their data on strength of polymeric composites with an equation of the form

$$\sigma_v = a - bv_f \qquad (3)$$

TABLE I
Influence of Shape and Volume Fraction on Residual Stresses (Expressed in psi) in Polymeric Composites

Volume fraction	Cylindrical shape			Spherical shape		
	$p_{thermal}$	$p_{shrinkage}$	p_{total}	$p_{thermal}$	$p_{shrinkage}$	p_{total}
0	850	2500	3350	1400	4300	5700
0.05	800	2400	3200	1350	4000	5350
0.5	450	1300	1750	600	2300	2900

where a and b are constants and b can assume either positive or negative values. Such a linear relationship can be found to be unrealistic in view of the discussion in the foregoing. In fact, the major experimental evidence in the literature suggests that a relationship of the type

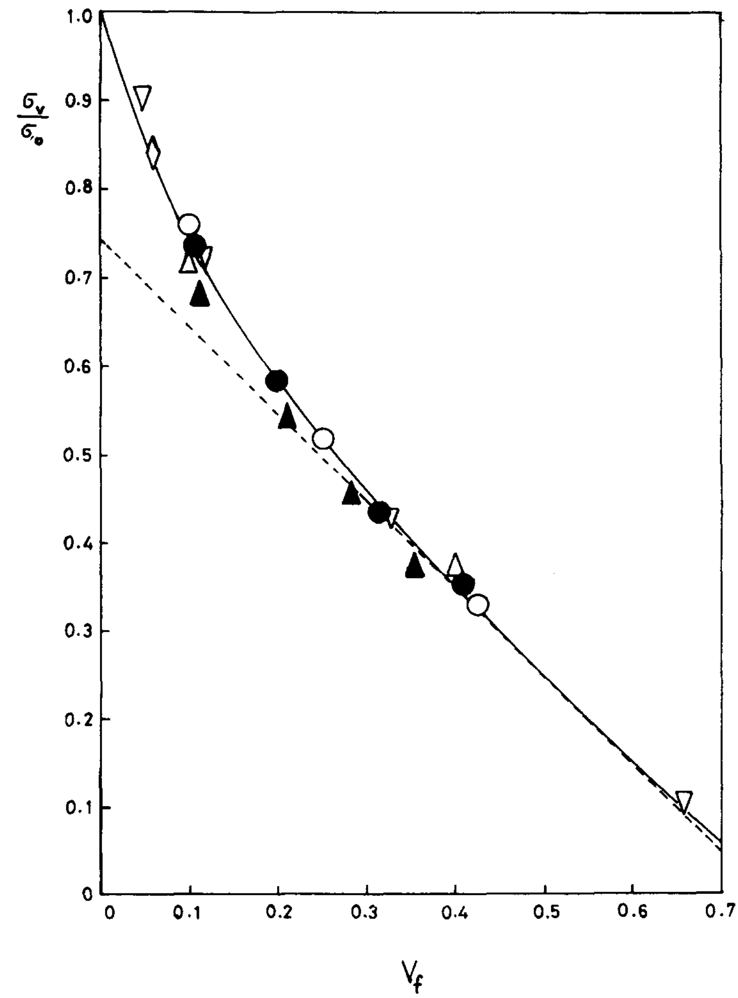

Fig. 1. Relative strength σ_v/σ_0 as a function of the filler volume fraction v_f: (▽) epoxy resin with voids (average values from ref. 8); (◇) SAN/Carbospheres (from ref. 10); (○) PPO/glass beads (from ref. 9); (●) epoxy/glass beads (from ref. 7); (△) SAN/glass beads (from ref. 5); (▲) ABS/glass beads (from ref. 6). Full line is drawn on the basis of $\sigma_v/\sigma_0 = 1 - 1.21\, v_f^{2/3}$. Dotted line is drawn on the basis of the recommendations in ref. 1.

$$\sigma_v = \sigma_0 - bv_f^n \quad (4)$$

(where $n < 1$) is likely to be more appropriate, with σ_0 being the strength of the unfilled matrix and only positive values of b being admissible. The latter condition implies that under no circumstances can the strength of the filled matrix be greater than the strength of the unfilled matrix. We shall examine this point in detail by considering experimental data on the strength of polymeric composites drawn from various sources.[5–10]

Figure 1 shows a plot of the relative strength σ_v/σ_0 as a function of the filler volume fraction V_f. The full line is drawn on the basis of eq. (4), with specifically $b = 1.21\sigma_0$ and $n = 2/3$. We have also drawn a dotted line on the basis of the prediction of eq. (3), which postulates a linear relationship. It is clearly seen that eq. (4) fits the data much better than does eq. (3). The criticism advanced by Piggott and Leidner[4] against a nonlinear relationship of the type used in eq. (4) thus appears to have a doubtful validity. Indeed, a linear relationship of the type shown in eq. (1) is likely to be decidedly inadequate at very small values of the volume fraction.

The preliminary evidence presented in this note is probably adequate to strengthen the validity of eq. (4). However, more work is in progress which analyzes stress situations, adhesion problems, and matrix responses in polymeric composites containing spherical fillers, which further validates the rationale of the correlation given in eq. (4).

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