

The Elastic Modulus of Particulate-Filled Polymers

Glass beads are stiffer than glassy polymers (moduli ratio of about 25), thus their inclusion in a polymeric matrix increases its modulus. Both treated and untreated glass beads give practically the same modulus values showing that the interfacial properties are not important to the modulus, a low-strain property. The effect of the bead size on the elastic modulus has not been reported in the literature; however, in a recent work the authors have found essentially similar moduli values for polysulfone and poly(methylmethacrylate) composites filled with either 4–44 μm or 149–250 μm glass beads. It is possible, however, that the modulus will change with bead diameter beyond the studied size range.

Several theories have been postulated for calculating the modulus of particulate systems from the properties of their components. Smith¹ has recently compared the experimental results for polyester–glass-bead composites² and epoxy–glass-bead composites³ with the theoretical equations of van der Poel,⁴ Budiansky and Hill,^{5,6} Hashin and Shtrikman,⁷ and Kerner.⁸ Kolarik *et al.*⁹ studied poly(2-hydroxyethylmethacrylate)–glass-bead systems and compared their results with a modified Kerner equation.¹⁰ Experimental results for epoxy–glass-bead composites were also reported by Ebdon *et al.*¹¹ and compared with the Kerner equation.⁸

A semiempirical single parameter equation describing the moduli of particulate systems has recently been formulated by Narkis¹² as follows:

$$E_c/E_p = 1/K(1 - \phi^{1/3}) \quad (1)$$

where E_c and E_p are the composite and polymer moduli, respectively; ϕ is the bead volume fraction, and K is an empirical parameter (apparently related to a stress concentration factor) with usual values in the range of 1.4–1.7. This equation has been verified using data generated by the authors and also taken from the literature for glass-bead-filled thermoplastic and thermosetting polymers.¹³ The equation is limited to rigid spherical inclusions and has been found applicable over the range of $\phi = 0.1$ – 0.5 , which is the range of practical interest (it is not valid in the lower concentration range).

The experimental data reported by Richard,² Smith,³ Kolarik *et al.*,⁹ and Ebdon *et al.*¹¹ are shown in Figure 1.

Figure 1(a) shows Richard's results for polyester–glass-bead composites. Equation (1) gives the best fit with $K = 1.36$. A value of $K = 1.6$ was previously reported¹³ for similar systems studied by Sahu and Broutman.¹⁴ The authors attribute this difference in K values and the rather low value of $K = 1.36$ to the considerable scatter of Richard's data. Another probable reason, of secondary importance, may be related to the different polyester grades used by the two researchers. Among the theoretical equations, the best overall agreement with Richard's data is provided by the van der Poel theory.

Smith's data for epoxy–glass-bead systems are shown in Figure 1(b). A value of $K = 1.57$ in eq. (1) gives the best fit with the experimental results. Epoxy–glass-bead systems were also studied by Mallick and Broutman,¹⁵ Sahu and Broutman,¹⁴ and Wambach.¹⁶ The calculated K values for these systems were found to be 1.70, 1.65, and 1.60, respectively,¹³ in good agreement with the value of 1.57 describing Smith's results. The van der Poel equation, among the various theoretical possibilities, again provides the best fit to the experimental results.

A value of $K = 1.55$ is used for the epoxy–glass-bead composites shown in Figure 1(c) describing the data of Ebdon *et al.*¹¹ The result agrees well with that used to describe Smith's data. Figure 1(c) also shows the insignificant effect of a coupling agent on the modulus.

Kolarik *et al.*'s results are shown in Figure 1(d). Equation (1) with $K = 1.40$ agrees very well with the experimental data. As shown, this equation gives a better fit than the modified Kerner equation.

In summary the wide applicability of eq. (1) has been confirmed using experimental data from various sources. The equation works well for glass beads or other rigid spheres ($0.1 < \phi < 0.5$) used for reinforcing thermoplastic, as well as thermosetting matrices.

In addition, using the data of Kolarik *et al.*,¹⁷ it is possible to analyze the temperature dependence of K for the glass-bead–rubber polyurethane system.

In Figure 2 the relative moduli of such composites are plotted as function of filler content for

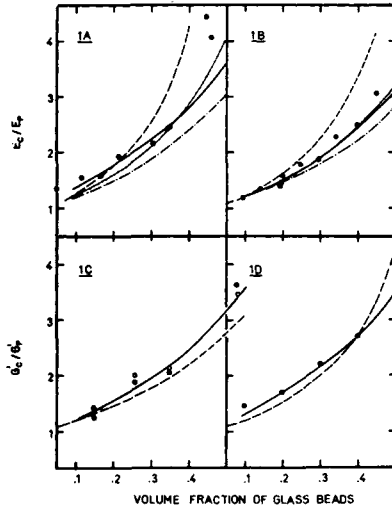


Fig. 1. Moduli ratio vs glass bead content. (a) Richard's data for polyester-glass-bead composites (ref. 2). - - -, Hashin and Shtrikman's highest lower bounds; —, van der Poel; —, Narkis, with $K = 1.36$; - - -, Budiansky-Hill. (b) Smith's data for epoxy-glass-bead composites (ref. 3). - - -, Hashin and Shtrikman's highest lower bounds; —, van der Poel; —, Narkis, with $K = 1.57$; - - -, Budiansky-Hill. (c) Ebdon et al.'s data for epoxy-glass-bead composites (ref. 11). - - -, Kerner; —, Narkis, with $K = 1.55$; O, uncoupled; ●, coupled. (d) Kolarik et al.'s data for poly(2-hydroxyethylmethacrylate)-glass-bead composites (ref. 9). - - -, modified Kerner; —, Narkis, with $K = 1.40$.

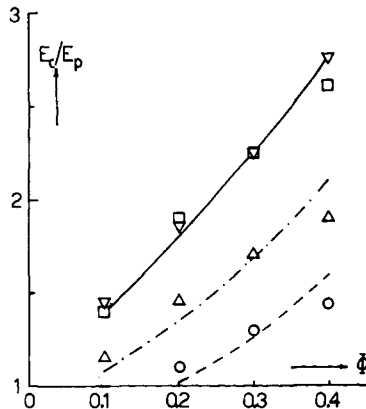


Fig. 2. Relative moduli of polyurethane-rubber-glass-bead composites (ref. 17) at various temperatures (O, $T = -80^{\circ}\text{C}$; Δ , $T = -20^{\circ}\text{C}$; \square , $T = 0^{\circ}\text{C}$; ∇ , $T = +80^{\circ}\text{C}$). The lines are the plots of eq. (1), with $K = 2.4$, - - -; $K = 1.8$, - · - · - ·; and $K = 1.35$, —.

different temperatures. The lines drawn through the experimental data represent eq. (1) with values describing the best fit. Once again, verification of the equation is assessed. It should be pointed out that the temperature dependence of K (as described later) was expected due to its assumed significance as a stress concentration factor. In fact, in Figure 3 the values of K are plotted as function of temperature and a rather sharp transition is observed in the temperatures of -50° – 0°C (the glass transition temperature of this polyurethane rubber is -28°C).

Figure 3 indicates that K is temperature independent below and above the transition region while it declines within this temperature transition region. It is interesting to note that K values were also temperature independent for poly(methyl methacrylate)-glass-bead and polysulfone-glass-bead systems in the temperature ranges of 24° – 85°C and 24° – 150°C , respectively (i.e., in the glassy re-

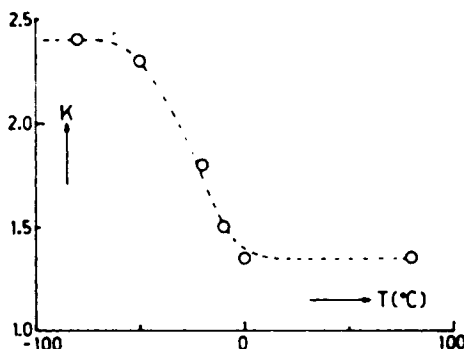


Fig. 3. K values vs temperature for polyurethane-rubber-glass-bead composites.

gion).¹⁸ A noteworthy difference exists, however, between the glassy polyurethane composite and the glassy thermoplastic composites in their values of K , namely, 2.4 and 1.4–1.7, respectively ($K = 1.35$ describes the rubbery polyurethane composite). It is assumed that the state of internal stresses in the polyurethane composite is changing markedly by transferring this system from glass to rubber and vice versa due to the significant variation of the polymer thermal expansion coefficient and the insignificant variation of this property for the glass beads. It is also believed that the levels of internal stresses in the glassy polyurethane composite and the glassy thermoplastic composites are significantly different reflecting the difference in their respective K values. Needless to say much more data covering the dependence of K on temperature over the glassy-transition-rubbery region are required before further elaboration of K behavior and significance is postulated.

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