Modulus Reinforcement in Elastomer Composites.
I. Inorganic Fillers

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Synopsis

The effect of various inorganic fillers on the storage modulus of four elastomers was determined experimentally. Results are interpreted using the Kerner equation, modified to include a parameter, B, in the volume fraction terms. This factor combines particle size and specific interaction effects, and in theory can be evaluated from energy dissipation measurements.

INTRODUCTION

In developing the final properties of an elastomer-based product, such as strength, modulus, cost, color, durability, etc., the filler plays a most important role. A wide variety of inorganic and organic materials have long been available, most familiar, of course, is carbon black, and these have been characterized quite extensively in terms of particle size, structure, density, and porosity. What is harder to characterize is the property often termed polymer–filler interaction. This term broadly includes the interfacial forces between the solid and elastomer, the orientation of the elastomer in the immediate vicinity of the filler surface, the formation of an "interphase" the properties and dimensions of which affect the composite properties, nucleation of crystallization, and other physicochemical phenomena.

Without a knowledge of this interaction, one may nevertheless make perfectly utilitarian selections of fillers for specific polymers. The usual technique is to blend various fillers, in varying amounts, with the elastomer and prepare vulcanizates for mechanical testing. The technique is laborious and time consuming. For some end uses, for example, very high concentrations of filler may be desirable from a cost and density viewpoint, and the high filler concentrations can often interfere with the usual vulcanization mechanism either by altering the chemical environment, participating in side reactions, or simply by removing active ingredients from the matrix elastomer by adsorption onto the filler surface. Furthermore, many ex-

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perimental polymers with great commercial potential are never properly evaluated simply because the curing chemistry has not been perfected.

In this paper we propose and evaluate a simple technique for determining quantitatively the polymer–filler interaction parameter, using gum stock elastomers, and only limited (low) concentrations of filler, this parameter possessing utility in predicting, a priori, the modulus of composites based on elastomer matrixes with inorganic fillers.

THEORY

Attempts to predict the modulus of elasticity at low extension, E', from filler content have included the well-known Guth[1] equation based on extensions of hydrodynamic arguments, a sedimentation volume treatment by Eilers,[2] the Sato-Furukawa approach,[3] and geometric theories by Nielsen[4] and by Zorll.[5] Each of the derived equations appears to satisfactorily describe the data at least of the individual author. None appears to be universally applicable, which is not surprising since none really approaches reinforcement within the admittedly complex mathematical framework of modern micromechanics. Only the equations of Kerner,[6] which themselves are extensions of the original work of Goodier[7] on a suspended single grain of material in a rubbery matrix, appear to be theoretically on very firm ground. The Kerner equation pertaining to modulus reinforcement in simple tension is

$$\frac{E'_c}{E'_0} = \frac{\{G'_F\varphi_F/[(7-5\nu)G'_0 + (8-10\nu)G'_F]\} + \{(1-\varphi_F)/[15(1-\nu)]\}}{\{G'_0\varphi_F/[(7-5\nu)G'_0 + (8-10\nu)G'_F]\} + \{(1-\varphi_F)/[15(1-\nu)]\}} \tag{1}$$

where E'_c is the modulus of the composite, ν is the Poisson ratio of the matrix, G'_F is shear modulus of filler (real part), G_0 is the shear modulus of unfilled matrix (real part), and φ_F is the volume fraction of the filler. Unfortunately, however, this equation does not describe the modulus of composites as a function of the volume loading of filler for any of the systems tested. Its failure to fit the data has probably been the main driving force for the derivations of many of the equations cited above, which, though empirical, follow in some cases more closely the variation of E' with φ_F.

Unwilling to totally abandon the Kerner equation simply because the data did not comply with it, we examined Kerner's approach in light of some current theories of composite materials. The only discrepancy seems to rest in the volume fraction of filler, φ_F. If one accepts the notion of a tightly adhering interphase as a result of specific physicochemical interactions between the filler and the polymer, then the true volume fraction of immobilized material, φ_e, will be greater than φ_F by some factor which could be included directly into Kerner's formalism.

In a previous contribution concerning energy dissipation,[8] a definition of φ_e was employed, i.e.,
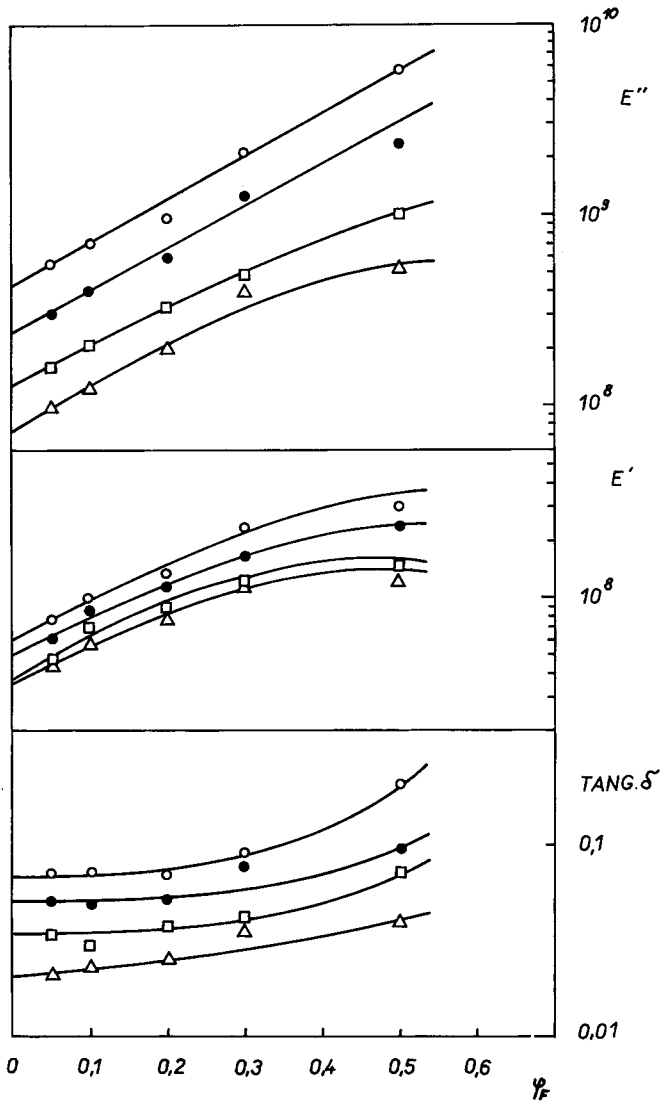
$$\varphi_e = \varphi_F(1 + \Delta R/R_0)^3 \tag{2}$$

Fig. 1. E', E'', and tan δ as a function of volume loading of filler: Neoprene with Bayrites, (O)110 Hz; (●) 35 Hz; (□) 11 Hz; (△) 3.5 Hz; all at 30°C.

where the term $\Delta R/R_0$ is the relative increase in particle diameter for spheres and can be estimated either from viscosity measurements of dispersions of the filler particles in fluid polymers (this is only practical when low molecular weight analogs of the elastomer can be prepared) or from comparison of the loss moduli E'' of filled and unfilled specimens, using the equation

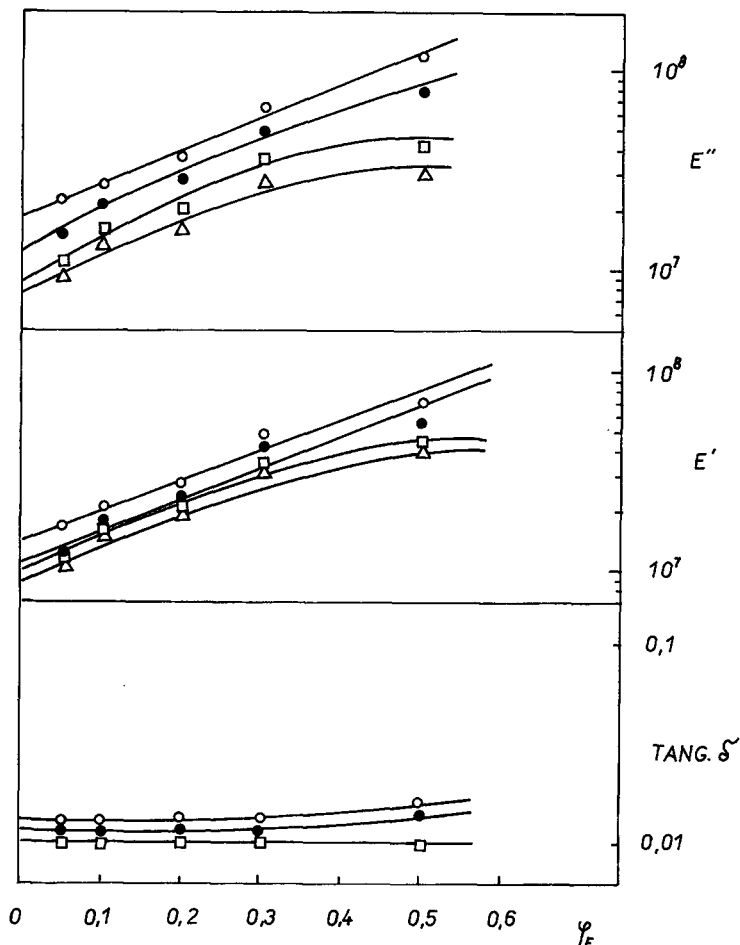$$E''_0/E''_c = 1 - \varphi_F(1 + \Delta R/R_0)^3. \tag{3}$$

Fig. 2. E', E'', and tan δ as a function of volume loading of filler: urethane with micro-beads, (O) 110 Hz; (●) 35 Hz; (□) 11 Hz; (△) 3.5 Hz.

Equation (3) was derived from the concept of "strain magnification," meaning the increase in local strain amplitude in the matrix caused by the inextensibility of the filler particles and their associated interphase of immobilized polymer, and was shown to be valid at least for one specific polyurethane elastomer using glass microbeads as filler particles. An extension of the strain magnification concept into modulus reinforcement was not attempted because it fails to take into account the role of the filler modulus which is significant when dealing with E' but negligible when considering energy dissipation E''.

The possibility that the Kerner equation could be "improved" by modifying the volume fraction term was then explored. Hence for φ_F we substitute $\varphi_F B$, where B represents the term $(1 + \Delta R/R_0)^3$. Equation (1), for rubbery matrices where $\nu = 0.5$, and $G_F \gg G_0$, becomes

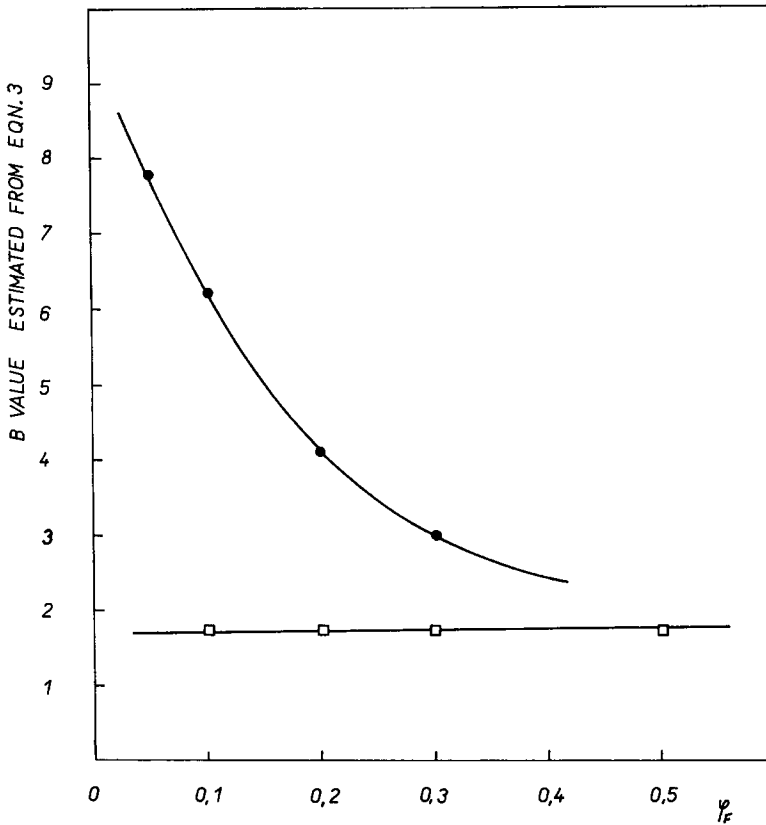$$E'_c/E'_0 = (1 + 1.5\,\varphi_F B)/(1 - \varphi_F B). \qquad (4)$$

Fig. 3. Variation of apparent B values from eq. (3) with volume loading of filler: Viton with (●) HiSil and (□) microbeads.

Somewhat similar "adjustments" have been proposed by Lewis and Nielsen[10] and by Ilavsky et al.[11]

A comparison with eq. (3) predicts that the loss tangent of a composite will decrease with increasing filler loading according to

$$\tan \delta_c = \tan \delta_0/(1 + 1.5 \ \varphi_F B),\qquad(5)$$

a situation that has been observed[10,13] experimentally in many composites.

EXPERIMENTAL

Four gum elastomers, three of them commercial products from Elastomer Chemicals Department of E. I. du Pont de Nemours and Co., one an experimental product, were employed. These were: Neoprene AD30, a polychloroprene elastomer; Viton AHV, a high-viscosity version of the fluorinated polymer; Nordel 1145, a copolymer of ethylene and propylene; and ECD 2957, poly(ether urethane).
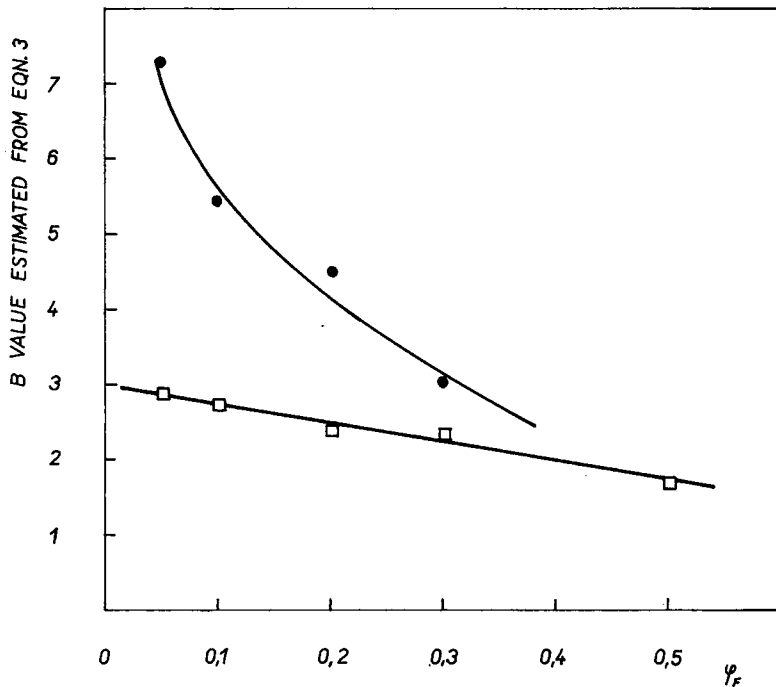
Fig. 4. Variation of apparent B values from eq. (3) with volume loading of filler: Urethane with (●) HiSil and (□) microbeads.

For fillers we used: HiSil 233, a "semireinforcing" powdered silica obtained from Cabot Co., density = 1.95; glass beads in the 20- to 60-μ particle size range obtained from Microbeads, Inc., density 2.5; and barium sulfate powder, "Bayrites," density 4.35.

Sample preparation was accomplished by mixing the filler and elastomer on a two-roll rubber mill and pressing slabs of approximately 0.100 in. in thickness, at 100°C to 120°C in a platen press.   Attempts were made to obtain φ_F values of 0.05, 0.1, 0.2, 0.3, and 0.5.   In some cases, however, the higher concentration could not be achieved because of crumbling of the elastomer–filler mixture.   In one case, Neoprene with HiSil, the polymer darkened and toughened during mill mixing, making specimen preparation impossible.   Final specimen preparation was required to reduce the size and thickness of the sample to approximately 2.5 cm × 1 cm × 0.1 cm and was accomplished by reheating in a small laboratory press.   Dynamic testing of the samples was accomplished with a Vibron Model DDV-II, Toyo-Measuring Instruments Co., Ltd., Tokyo, Japan.   Data were obtained at 30°C (well into the rubbery region for each elastomer tested) and at 110, 35, 11, and 3.5 Hz.

Typical curves showing the variation of E' and E'' and loss tangent with increasing filler concentration also as a function of test frequency are shown in Figures 1 and 2.   Values of E'_0 and E''_0 were obtained by extrapolation
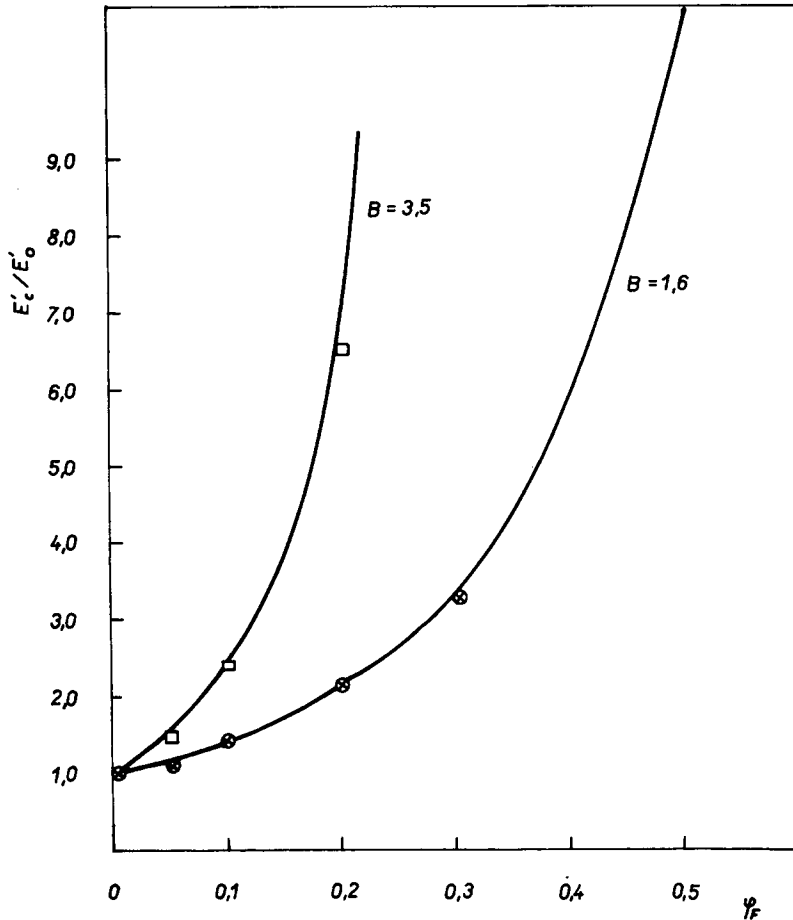
Fig. 5. Variation of reduced storage modulus with filler concentration: Urethane with (□) HiSil and (⊗) microbeads. Solid lines are from eq. (4).

to the $\varphi_F = 0$ axis, since direct evaluation on the Vibron was impossible owing to the very low stiffness of the unfilled elastomers.

RESULTS AND DISCUSSION

Using the E'' values obtained experimentally and eq. (3), a direct estimate of the interaction parameter B was made. It was immediately apparent that eq. (3), though applicable for a specific system of glass beads in a vibration-damping polyurethane,[8] and apparently for glass beads in Viton, did not posess any degree of universality. The B values generally decreased with increasing concentration, as shown in Figures 3 and 4. Hence, use of the strain magnification estimate of B to substitute into the modified Kerner equation was not possible. Instead, we used a curve-fitting approximation technique to obtain interaction parameter values directly from
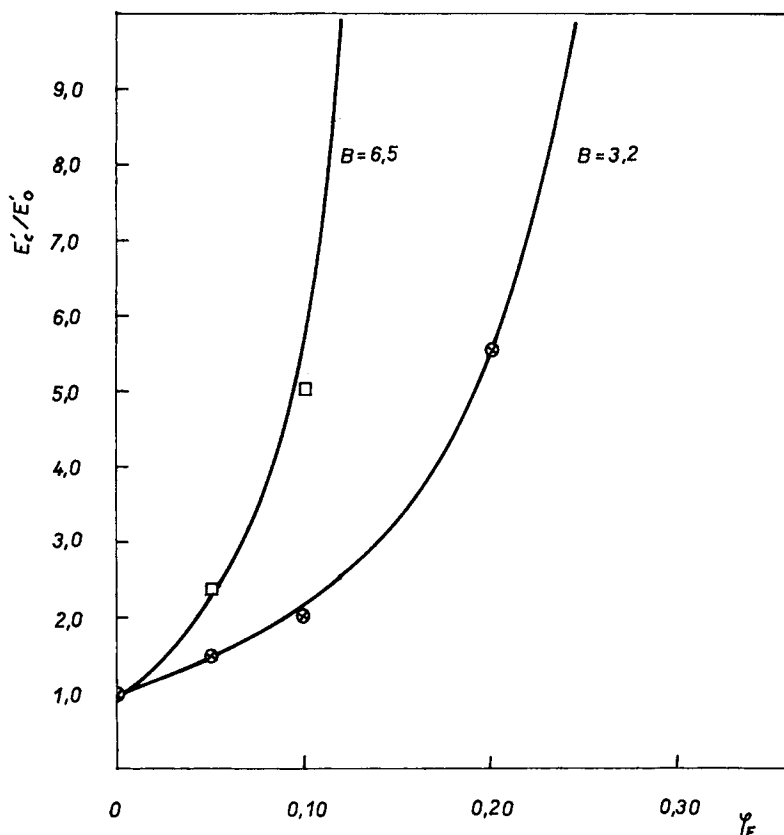
Fig. 6. Variation of reduced storage modulus with filler concentration: Nordel with
(□) HiSil and (⊗) microbeads.   Solid lines are from eq (4).

reduced storage modulus data.   The "goodness" of fit is amply illustrated
in Figures 5, 6, 7, and 8.

Thus, the modified Kerner equation appears to describe a variety of
elastomers with various fillers provided an interaction parameter correction
is applied to the volume fraction term.   Because of the sensitivity of this
technique, it would appear that accurate estimates of the B factor can be
made using only a few concentrations of filler, especially at the low loading
level, perhaps up to 20 vol-%.   It is, in fact, important to avoid high-
volume loadings because of the existence of a critical volume fraction φ_c,
above which not all the filler particles can be wetted by the elastomer
matrix.   This critical volume fraction is related to the parameter B.
When eq. (3) is applicable, φ_c is simply the reciprocal of B.   A value of
B of 6.5, for example, as observed with HiSil in Nordel, would predict a φ_c of
approximately 0.15, and it was indeed observed that for this polymer-
filler combination only a maximum of 10 vol-% filler was experimentally
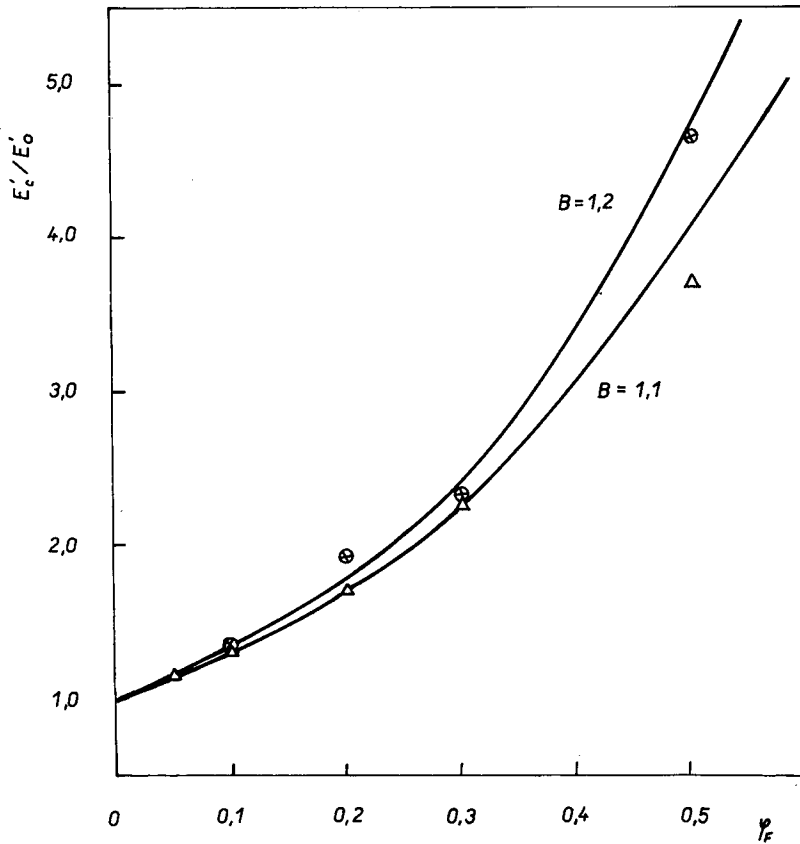feasible.

Fig. 7. Variation of reduced storage modulus with filler concentration: Neoprene with
($\otimes$) microbeads and ($\triangle$) Bayrites. Solid lines are from eq (4).

Examining now the failure of eq. (3) to describe the energy dissipation
properties of these composites, we recognize the rather drastic assumptions
made in the development of the original theory. It was demonstrated[9]
that the average strain magnification (disregarding the B factor) is indeed
linear with respect to φ_F, i.e.,

$$\epsilon_c/\epsilon_0 \;=\; [1 \;-\; \varphi_F]^{-1}$$

while the maximum magnification ratio is equal to $[1 - \varphi_F^{1/3}]^{-1}$, where ϵ_c
represents the strain, $\Delta L/L_0$, in the matrix of a filled polymer, and ϵ_0 that
in the pure elastomer. In deriving the ratio of energy dissipated in filled
and unfilled polymers, the important equation is

$$E''_c/E''_0 \;=\; \langle \epsilon_c{}^2/\epsilon_0{}^2 \rangle \,(1 \;-\; \varphi_F). \tag{6}$$

From the assumption that $\langle \epsilon_c{}^2/\epsilon_0{}^2 \rangle \;=\; \langle \epsilon_c/\epsilon_0 \rangle^2$, eq. (3) was derived, with the
admission that this was only a convenient simplification based on the ab-
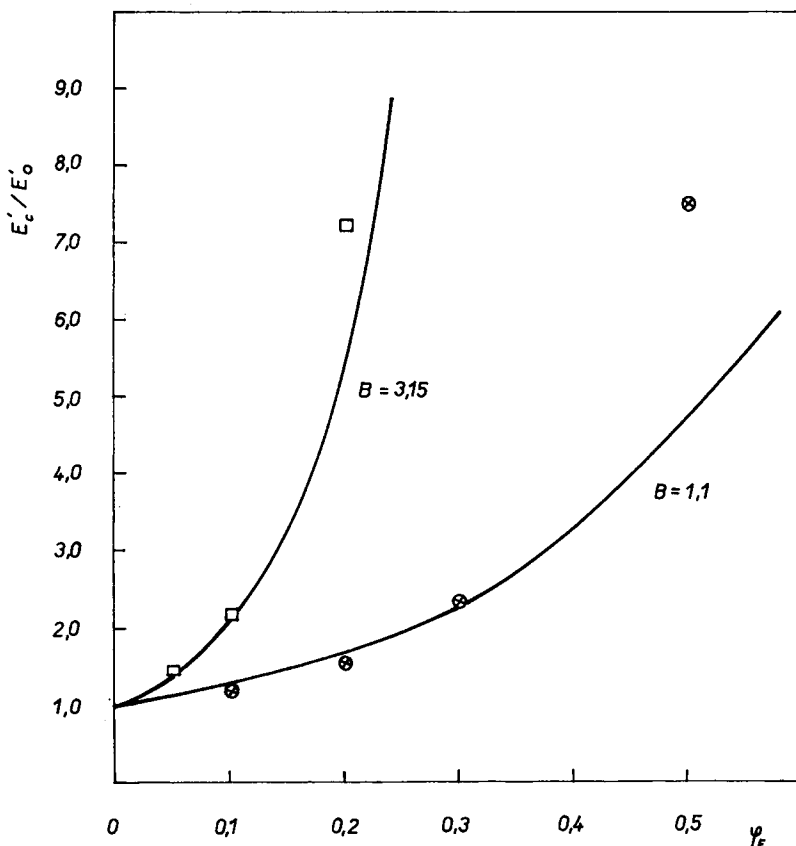sence of any more detailed theory.

Fig. 8. Variation of reduced storage modulus with filler concentration: Viton with
(□) HiSil and (⊗) microbeads.   Solid lines are from eq. (4).

It is possible, then, that the energy dissipation ratio can be more ade-
quately described by an expression where the power of φ_F, or $\varphi_F B$, is less
than unity.   A convenient empirical equation based on eq. (3) is

$$E''_c/E''_0 = [1 - (\varphi_F B)^n]^{-1}. \tag{7}$$

A plot of the logarithm of $1 - E''_0/E''_c$ versus the logarithm of φ_F yields the
exponent n as slope, and the interaction parameter B can be evaluated from
the intercept.   Figures 9, 10, and 11 reveal linearity in the log–log plots.
The Viton–HiSil system showed considerable nonlinearity.   A summary
of the B values and the exponent n is made in Table I. in comparison with
those B values obtained by the modified Kerner equation(4).

CONCLUSIONS

The Kerner equation, modified to include a volume correction term, has
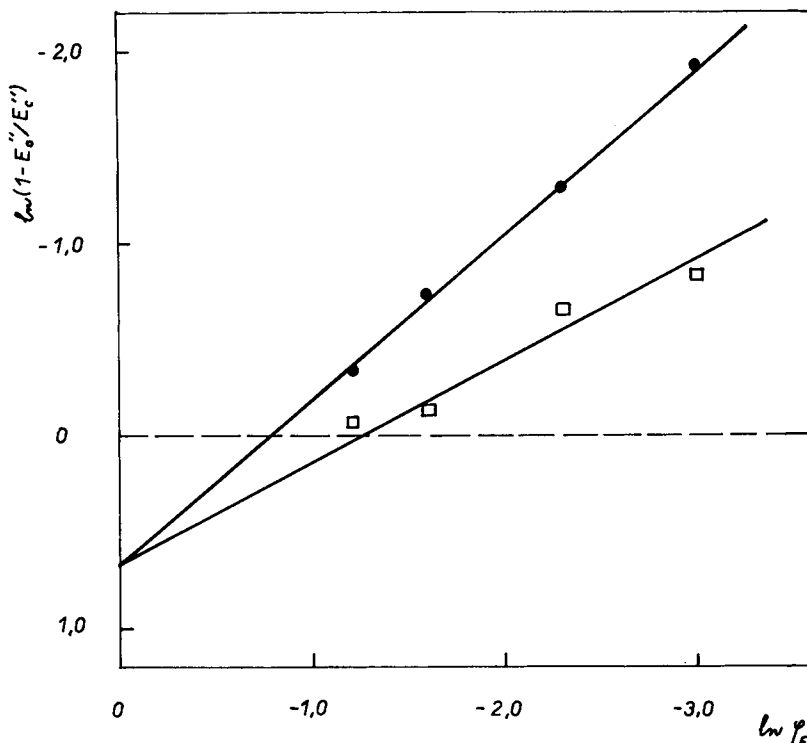been shown to accurately describe the variation of storage modulus E'_c

Fig. 9. Plot of logarithm of eq. (7):   Urethane with (●) microbeads and (□) HiSil.

with filler concentration.   The correction, or polymer–filler interaction term B, obtained from curve fitting is of fundamental importance in selecting fillers for various commercial end uses.

An equation derived in earlier work to describe the energy dissipation of composites has been modified to allow for variable power dependence of the

TABLE I
Interaction Parameter and Equation (7) Exponent

| | | B value | | Exponent. |
Filler	Polymer	Kerner eq.	Eq. (7)	n Eq. (7)
HiSil	urethane	3.15	3.5	.52
	Nordel	6.5	6.1	.52
	Viton	3.15	[b]	[b]
Microbeads	urethane	1.6	2.2	.85
	Nordel	3.2	4.2	.65
	Neoprene	1.2	.91	.60
	Viton	1.1	1.7[a]	1.0[a]
Bayrites	Neoprene	1.1	.91	.60

[a] Equation (3).
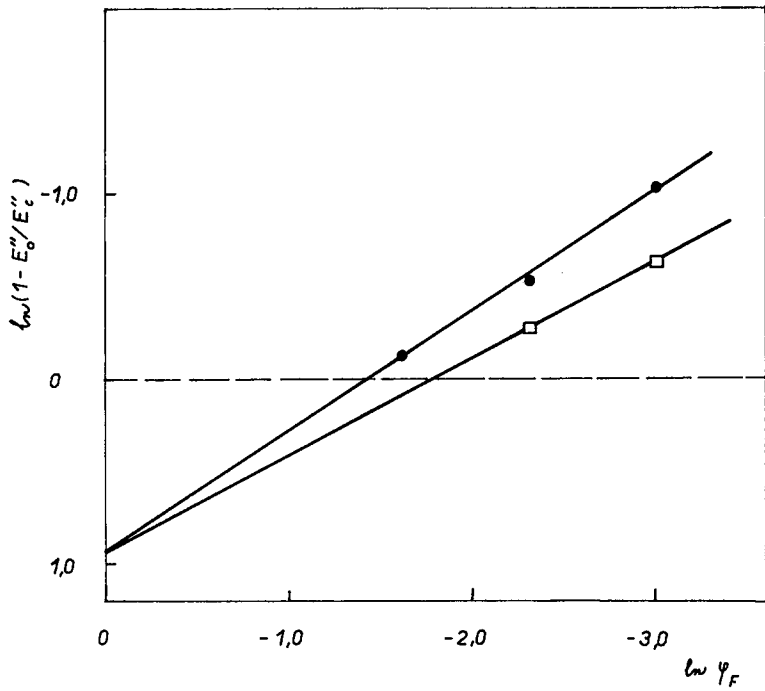[b] Equation (7) not applicable.

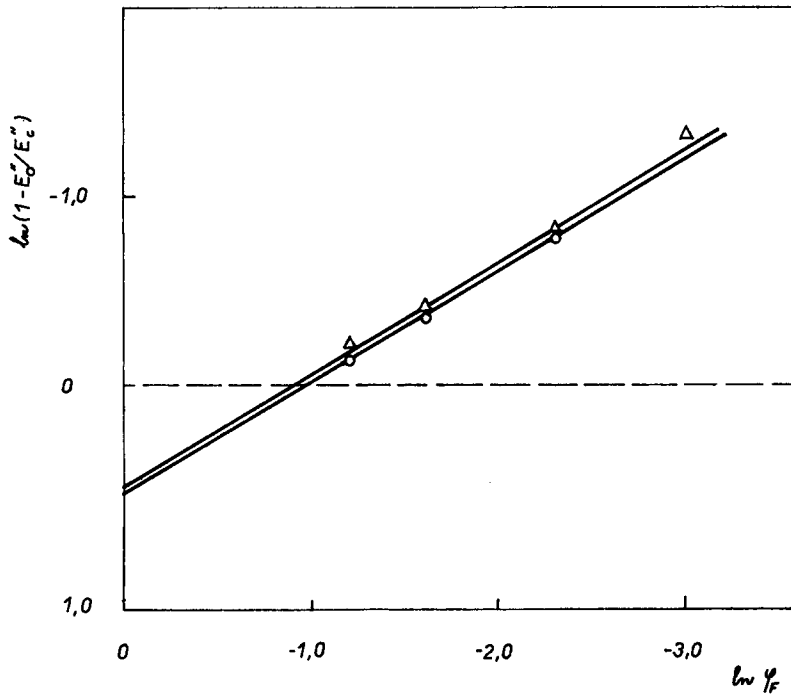Fig. 10. Plot of logarithm of eq (7): Nordel with (●) microbeads and (□) HiSil.

Fig. 11. Plot of logarithm of eq. (7): Neoprene with (△) Bayrites and (○) micro-beads.

volume fraction term. Using this empirical equation, good agreement in B values is obtained with those derived from the modified Kerner equation.

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