

Modulus Evaluation of Particulate Composites Using Generalized Viscosity Model for Solutions with Suspended Particles

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SYNOPSIS

The theoretical relationship between the shear modulus of a particulate reinforced composite and the viscosity of a solution with suspended particles was first proposed by Goodier. Since that time several partially successful attempts have been made in the literature to derive equations to describe the available relative shear modulus–particulate concentration data. Recently a new generalized suspension viscosity equation appeared in the literature which for the first time addresses the detailed effects of particle size, particle size distribution, and packing fraction. This new viscosity equation was applied to available modulus literature on particulate composites in this study. Four significant particulate composite modulus derivations in the literature were all shown in this study to yield the same theoretical “intrinsic modulus” of a particulate composite. The generalized viscosity–modulus equation yielded an excellent fit of the shear modulus–particulate concentration data of both Smallwood and Nielsen using a variable intrinsic modulus. Some fillers predicted the Einstein limiting value of the intrinsic modulus while other fillers yielded intrinsic modulus values that were either larger or smaller than this value. The intrinsic modulus for carbon black in rubber was much larger than Einstein’s predicted value. However, intrinsic modulus values smaller than Einstein’s prediction were obtained at temperatures below the glass transition temperature of the matrix. Unfortunately, the previously obtained direct relationship between the particle interaction coefficient and particulate size for suspension viscosities with a constant intrinsic viscosity was not obtained for shear modulus–particulate concentration data using a variable intrinsic modulus. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The theoretical relationship between the shear modulus of a particulate reinforced composite and the viscosity of a solution with suspended particles was first proposed by Goodier.¹ Smallwood² and Guth³ extended these initial theoretical considerations to justify the relative equality $G_r = \eta_r$ with $G_r = G_c/G_0$ and $\eta_r = \eta_c/\eta_0$, where G is the shear modulus, η is viscosity, and r indicates the relative value, c the composite or suspension, and 0 the matrix of the suspending fluid at zero (0%) volume percent

particles. The theoretical considerations of Goodier,¹ Smallwood,² and Guth³ each addressed the reinforcement of a rubberlike material in which stresses about a filler particle were analyzed to deduce the effect of filler concentration on the modulus. Because of the great similarity between the field equations of the theory of elasticity and those of hydrodynamics, this approach was substantially the same as that employed by Einstein^{4,5} to derive the increase in viscosity caused by spherical particles in a liquid suspension.

Several significant attempts have been made in the literature to derive equations to describe the relative shear modulus of particulate-filled systems.^{2,3,6–10} These equations were derived using the measurable physical properties of the composite such as the modulus of the filler, modulus of the matrix, and Poisson’s ratio of the matrix. Unfortunately, these

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equations have had only limited success in fitting the available modulus-particulate concentration data. Schwarzl et al.¹¹ point out that a major limitation of these mechanical property modulus derivations is that they do not include effects for particle size, particle size distribution, or a maximum packing fraction. In addition, no adjustable parameters have been included in these mechanical property modulus derivations to account for process variations.

In several instances investigators^{6,12-14} have found that available suspension viscosity equations were effective in describing shear modulus of particulate-reinforced composites as a function of concentration. The concept of a maximum packing fraction introduced in the viscosity equations was found to be useful in describing the modulus of particulate composites as a function of concentration. Schwarzl et al.¹⁵ had some partial success in describing the effects of particle size distribution in particulate composites using an empirical modification of the Eilers-van Dijk¹⁶ equation developed for suspension viscosities. Schwarzl¹⁵ generated two forms of the Eilers-van

Dijk equation and then combined these two equations to generate an effect indicative of particle size distribution.

Several attempts^{12,13,17-20} have been made to modify the original mechanical property modulus derivations to introduce both a maximum packing fraction and one or more adjustable parameters to better fit the data. Some success has been achieved by empirically modifying these equations to account for the maximum packing fraction. However, the effects of particle size and particle size distribution have remained elusive of adequate description.

Recent articles²¹⁻²³ indicate that the interest in the mechanical properties of particulate-filled composites remains high.

A series of articles²⁴⁻²⁷ that describe the derivation of a new generalized equation that addresses the viscosity of suspensions has recently appeared in the literature. This new generalized equation for the first time addresses the detailed effects of particle size, particles size distribution, and packing fraction. This suspension viscosity equation has not yet been applied to the evaluation of particulate composites.

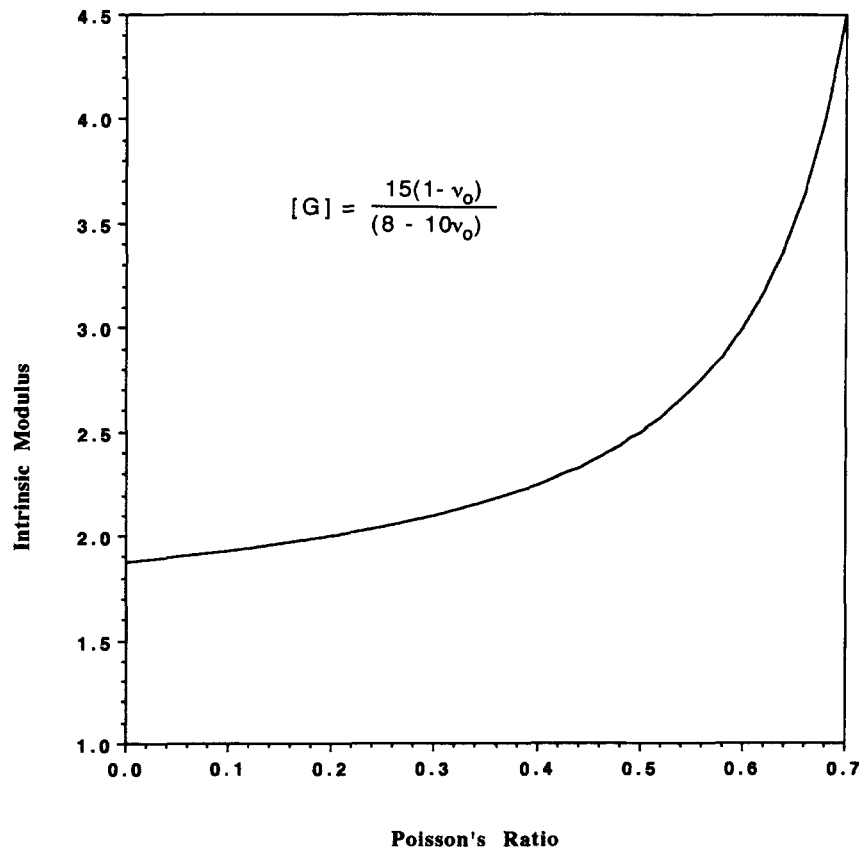


Figure 1 Calculated intrinsic modulus vs. Poisson's ratio for modulus ratios $\gg 1$.

The objective of this work was to apply this new equation to available literature on particulate composites to evaluate how adequately it predicts the modulus data. Available equations derived to describe the modulus of particulate composites will be shown to be very useful in predicting the “intrinsic modulus” of a particulate composite.

DESCRIPTION OF A NEW GENERALIZED SUSPENSION VISCOSITY EQUATION

In an earlier study²⁴ this author showed that the primary equations identified by Rutgers^{28,29} could be reduced to the following generalized equation to describe the viscosity-concentration relationships of suspensions:

$$\ln \frac{\eta}{\eta_0} = \frac{[\eta] \varphi_n}{\sigma - 1} \left[\left(\frac{\varphi_n - \varphi}{\varphi_n} \right)^{1-\sigma} - 1 \right] \text{ for } \sigma \neq 1 \quad (1)$$

For the case where $\sigma = 1$, the resulting equation can be written as

$$\ln \frac{\eta}{\eta_0} = -[\eta] \varphi_n \ln \frac{\varphi_n - \varphi}{\varphi_n} \quad (2)$$

or

$$\eta = \eta_0 \left(\frac{\varphi_n - \varphi}{\varphi_n} \right)^{-[\eta] \varphi_n} \quad (3)$$

where

- η = suspension viscosity
- η_0 = viscosity of suspending medium
- $[\eta]$ = intrinsic viscosity
- σ = particle interaction coefficient
- φ = suspension particle volume concentration
- φ_n = particle packing fraction

The particle packing fraction φ_n can be evaluated

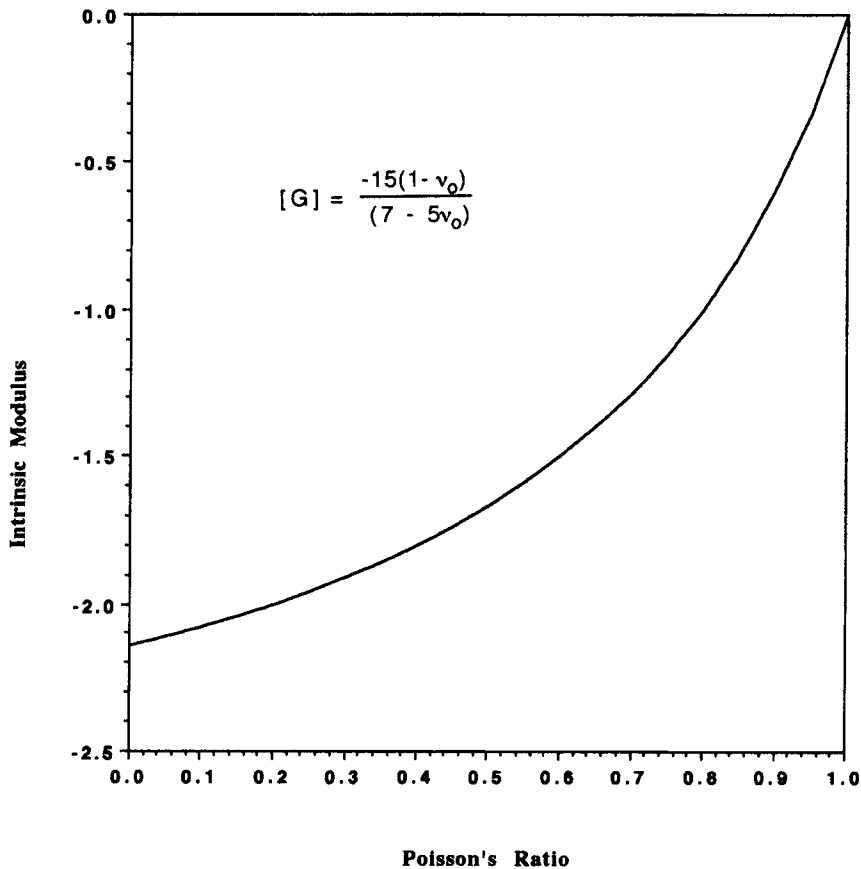


Figure 2 Calculated intrinsic modulus vs. Poisson's ratio for modulus ratios $\ll 1$.

from the particle size distribution²⁵ from the following equations:

$$\varphi_n = \phi_{n,ult} - (\varphi_{n,ult} - \varphi_m)e^{\alpha[1-(D_5/D_1)]} \quad (4)$$

$$\varphi_{n,ult} = 1 - (1 - \varphi_m)^n \quad (5)$$

$$D_5 = \frac{\sum_{i=1}^n N_i \mathcal{D}_i^5}{\sum_{i=1}^n N_i \mathcal{D}_i^4} \quad (6)$$

$$D_1 = \frac{\sum_{i=1}^n N_i \mathcal{D}_i}{\sum_{i=1}^n N_i} \quad (7)$$

where

- D_x = Xth average particle diameter (i.e., $x = 5, 1$)
- n = number of different particle diameters in batch combination
- N_i = number of particles of i th particle diameter
- \mathcal{D}_i = diameter of i th particle size
- $\alpha = \text{const} = 0.268$

- φ_n = packing fraction
- $\varphi_{n,ult}$ = ultimate packing fraction for specific number of particle sizes
- φ_m = monodisperse packing fraction

If an adequate description of the particle size distribution is available, the D_5 and D_1 particle size averages described by Eqs. (6) and (7) can be replaced with more convenient equations for the evaluation of particle blends that have been developed elsewhere.^{25,26}

In the original derivation of the generalized viscosity equation²⁴ it was found that the particle interaction coefficient σ can be described in general as

$$\sigma = \sigma_S + \sigma_P \quad (8)$$

where

- σ = particle interaction coefficient
- σ_S = solvent contribution to particle interaction coefficient
- σ_P = summation of all individual particle contributions to particle interaction coefficient

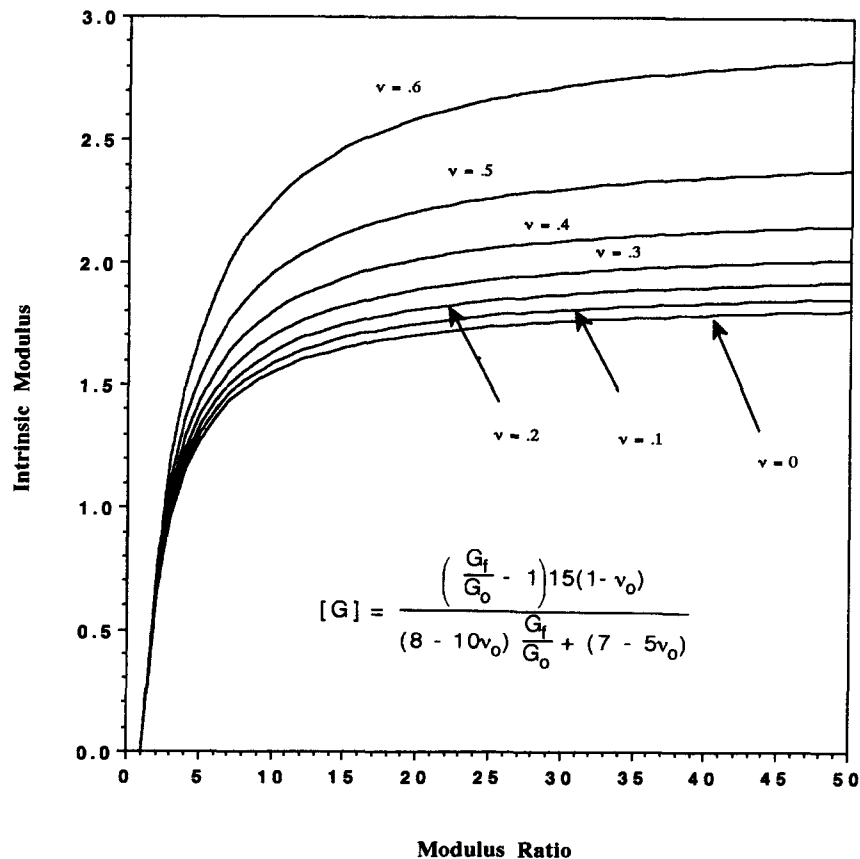


Figure 3 Calculated intrinsic modulus vs. modulus ratio and Poisson's ratio.

Further development of this analysis²⁴ showed that the summation of all of the individual particle contributions to the particle interaction coefficient σ_P should be inversely related to the number average particle size such that:

$$\sigma = \frac{\sigma_{PC}}{D_1} + \sigma_S \tag{9}$$

where σ_{PC} is the particle contribution constant assumed to be identical for all particles in a suspension. This analysis was confirmed in a later study²⁶ when the blends of suspensions were evaluated. For these suspension blends it was found that the particle interaction coefficient can be very adequately described as a linear function of the inverse of the number average particle size D_1 .

Note that the number average particle size diameter D_1 generally gives greater weightage to smaller particles than to larger particles. This means that the particle interaction coefficient would be expected to increase as the number of smaller particles in the suspension mixture increases.

As previously described,²⁴ this generalized sus-

pension viscosity equation predicts the form of many suspension equations that have previously appeared in the literature. For example, by varying the particle interaction coefficient σ , the Arrhenius equation^{30,31} results when $\sigma = 0$, the Kreiger-Dougherty equation³² results when $\sigma = 1$, and when $\sigma = 2$ the Mooney equation³³ results. Fractional values for the particle interaction coefficient were also found²⁴ to be useful and perfectly acceptable when optimizing the empirical fit of the literature data of Vand³⁴ and Eiler.³⁵

Further insight into the characteristics of the interaction parameter σ and the packing fraction ϕ_n can be obtained from the series expansion of the generalized suspension equation. Using a MacLaurin series expansion for Eq. (1) gives

$$\eta = \eta_0 \left[1 + [\eta]\phi + \frac{[\eta]}{2} \left([\eta] + \frac{\sigma}{\phi_n} \right) \phi^2 + \frac{[\eta]}{6} \left([\eta]^2 + 3 \frac{\sigma}{\eta_n} [\eta] + \frac{\sigma}{\eta_n} \frac{\sigma + 1}{\eta_n} \right) \phi^3 + \dots \right] \tag{10}$$

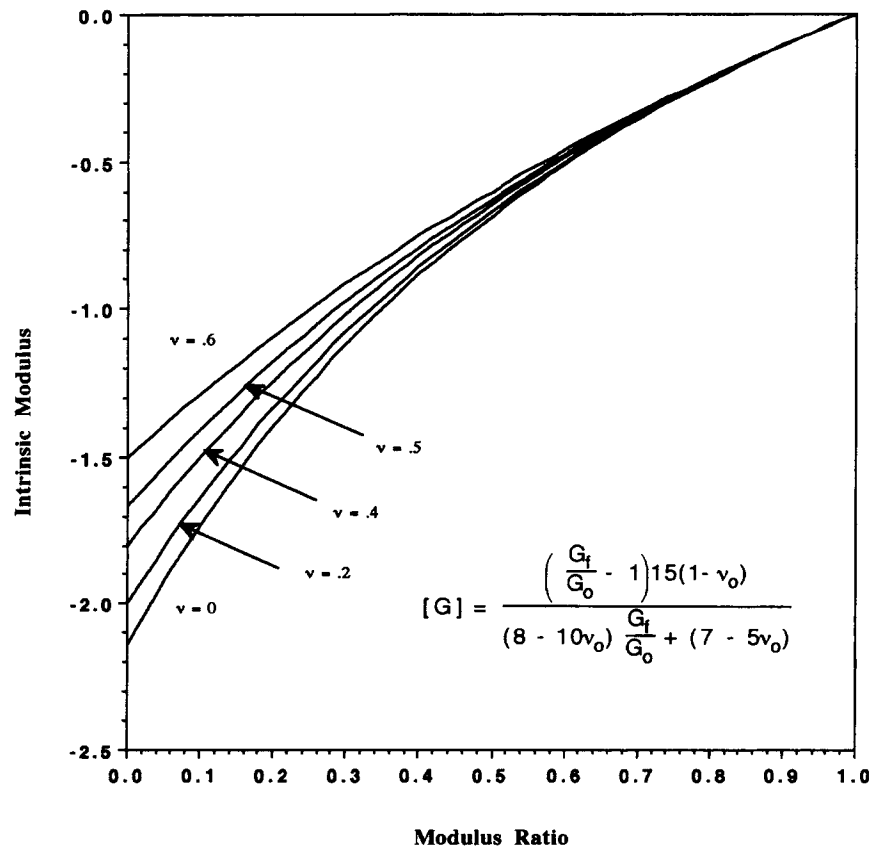


Figure 4 Calculated intrinsic modulus vs. modulus ratio and Poisson's ratio.

It is apparent that the first two terms are the Einstein^{4,5} limiting terms for all possible values for the particle interaction coefficient σ and the packing fraction φ_n when $[\eta] = 2.5$. It has also been found that σ and φ_n always occur as a paired ratio for second-order and higher expansion terms. Since these two parameters are paired in second-order and higher terms, if $\sigma = 0.0$, then the packing fraction does not enter into the viscosity calculation. This suggests that when the particle interaction coefficient is zero, particle packing is not important and particles have minimum interference with each other.

However, when σ increases, it is easy to see that the viscosity η will increase. Likewise, if the packing fraction φ_n increases, then the viscosity will decrease for the same particle interaction coefficient σ .

GENERATION OF EINSTEIN'S INTRINSIC VISCOSITY

The evaluation of the intrinsic viscosity $[\eta]$ of a general viscosity equation function $F(\varphi)$ describing

the viscosity of a suspension is in general evaluated from the second term of a MacLaurin series expansion for a viscosity function as

$$F(\varphi) = F(0) + F'(0)\varphi + \frac{F''(0)}{2!}\varphi^2 + \frac{F'''(0)}{3!}\varphi^3 + \frac{F''''(0)}{4!}\varphi^4 + \dots \quad (11)$$

This approach can be illustrated using the following equation developed by Einstein^{4,5}:

$$\eta = \eta_0 \frac{1 + \varphi/2}{1 - 2\varphi} \quad (12)$$

Einstein^{4,5} simplified this formulation using a MacLaurin series to give the more familiar equation

$$\frac{\eta}{\eta_0} = 1 + 2.5\varphi + 5\varphi^2 + 10\varphi^3 + \dots \quad (13)$$

It is apparent that only the first two terms of this

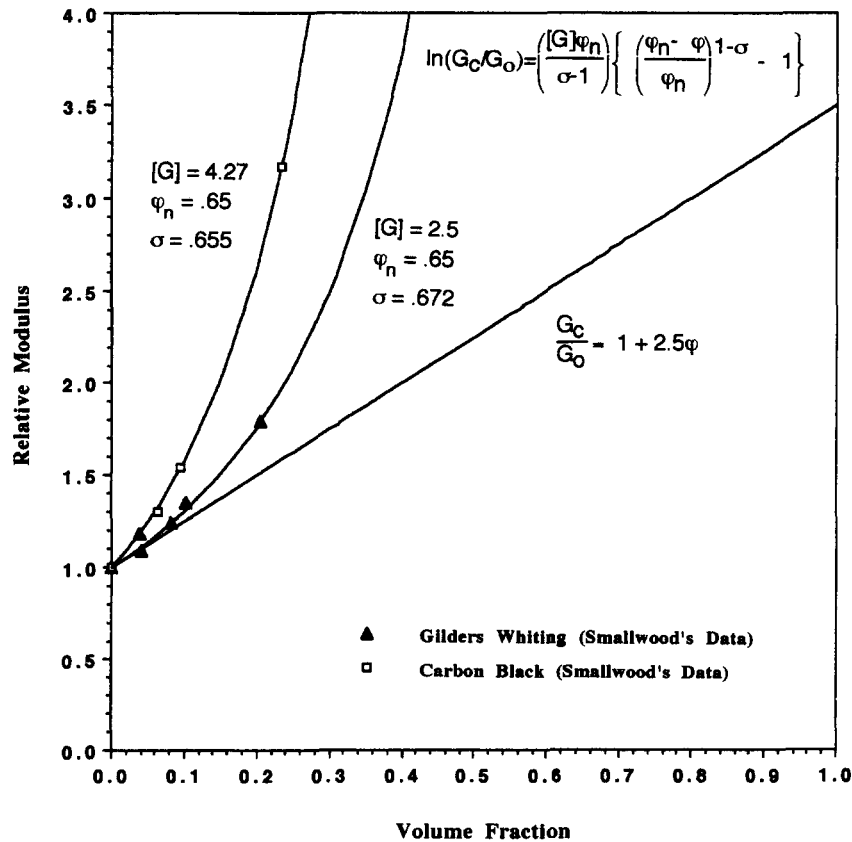


Figure 5 Smallwood's relative modulus vs. volume fraction data and generalized modulus equation predicted curves.

series are normally reported as Einstein's familiar equation.

The first derivative used to generate the intrinsic viscosity of Einstein's equation (12) is

$$\frac{d\eta}{d\phi} = \eta_0 \frac{2.5}{(1 - 2\phi)^2} \tag{14}$$

It is interesting to compare this first derivative with the first derivative of the generalized viscosity equation (1), which gives

$$\frac{d\eta}{d\phi} = \eta \frac{[\eta]}{(1 - \phi/\phi_n)^\sigma} \tag{15}$$

The similarity of these equations becomes apparent if

$$[\eta] = 2.5 \quad \sigma = 2 \quad \phi_n = \frac{1}{2} \quad \eta_0 = \eta$$

Theoretical discussions describing some justification for these relationships has been presented else-

where.²⁴ It has also been shown that the generalized suspension viscosity equation is applicable²⁴⁻²⁶ to fit most of the viscosity-vs.-concentration data in the literature. However, it is not yet clear what changes or additional assumptions would be required to make the generalized viscosity equation applicable to a modification of Einstein's original viscosity equation derivation.

GENERATION OF AN INTRINSIC MODULUS FOR PARTICULATE COMPOSITE MATERIALS

Goodier,¹ Smallwood,² and Guth³ justified the theoretical relationship between the shear modulus of a particulate reinforced composite, $G_r = G_c/G_0$, and the viscosity of a solution with suspended particles, $\eta_r = \eta_c/\eta_0$. This leads to the relative equality $G_r = \eta_r$, where G is the shear modulus, η is viscosity, and r indicates relative value, c the composite or suspension, and 0 the matrix or the suspending fluid

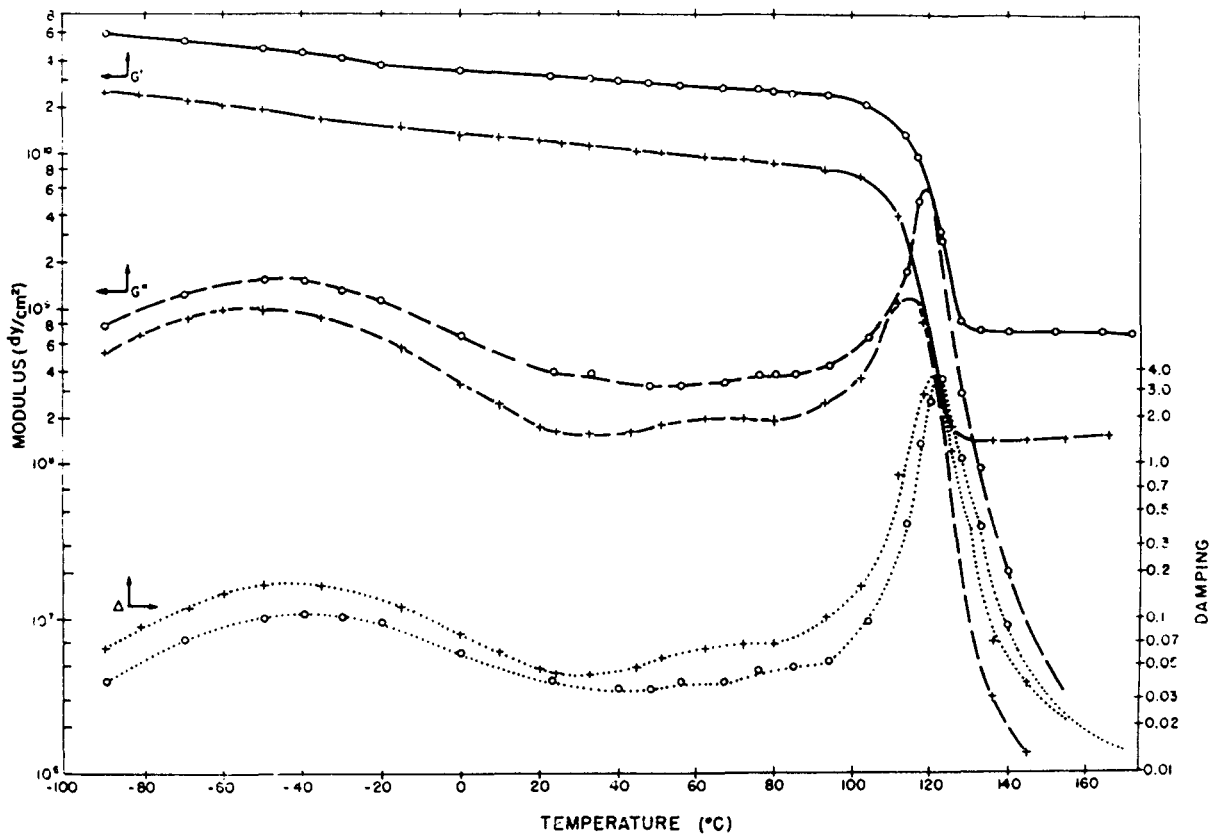


Figure 6 (—) Shear modulus, (---) loss modulus, and (----) damping vs. temperature for (+) unfilled epoxy and (O) epoxy with 0.41 volume fraction spheres of diameter 10–20 μm. (Reproduced from Ref. 17 with permission.)

at zero (0%) volume percent particles. Because of the great similarity between the field equations of the theory of elasticity and those of hydrodynamics, this approach was substantially the same as that employed by Einstein^{4,5} in deriving the increase in viscosity caused by spherical particles in a liquid suspension.

Since the evaluation of the intrinsic viscosity for suspensions required the evaluation of the first derivative of the viscosity function, it is expected that the evaluation of the "intrinsic modulus" for particulate composites would require the evaluation of the first derivative of the shear modulus function. Again the relative equality of the intrinsic viscosity $[\eta]$ and the "intrinsic modulus" $[G]$ would be expected as

$$[\eta] = [G] \quad (16)$$

Several significant attempts have been made in the literature to derive equations to describe the relative modulus of particulate-filled systems.^{2,3,6-10} These equations were derived using the measurable physical properties of the composite such as the modulus of the filler, modulus of the matrix, and Poisson's ratio of the matrix.

One of the more significant particulate composite modulus equations was developed separately by both Kerner⁷ and Hashin and Shtrikman,⁸ Lewis and Nielsen¹⁷ showed that Kerner's equation can be conveniently written as

$$G_c = G_0 \frac{1 + AB\phi}{1 - B\phi} \quad (17)$$

such that

$$A = \frac{7 - 5\nu_0}{8 - 10\nu_0} \quad (18)$$

and

$$B = \frac{G_f/G_0 - 1}{G_f/G_0 + A} \quad (19)$$

where

G_f = shear modulus of filler

G_0 = shear modulus of matrix material

ν_0 = Poisson's ratio of matrix

ϕ = volume fraction of filler in matrix

Table I. Lewis and Nielsen Data for Relative Modulus at $T - T_g$.

Diameter, μm	Volume Fraction, ϕ	Relative Modulus at $T - T_g$						
		-100°C	-80°C	-60°C	-40°C	-20°C	+20°C	+40°C
10-20	0.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	0.10	1.20	1.19	1.22	1.22	1.28	1.28	1.28
	0.19	1.52	1.51	1.51	1.51	1.57	1.96	1.90
	0.30	1.93	1.97	2.00	2.06	2.04	2.72	2.63
	0.41	2.63	2.75	2.84	2.97	3.03	4.90	4.74
30-40	0.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	0.10	1.18	1.19	1.20	1.22	1.23	1.23	1.23
	0.23	1.56	1.57	1.58	1.61	1.62	1.62	1.62
	0.30	1.89	1.97	2.04	2.08	1.96	1.96	1.96
	0.40	2.41	2.50	2.60	2.64	2.49	2.49	2.49
75-90	0.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	0.02	1.03	1.03	1.02	1.00	1.00	1.00	1.00
	0.05	1.10	1.12	1.10	1.10	1.10	1.10	1.10
	0.10	1.23	1.21	1.20	1.17	1.19	1.19	1.19
	0.15	1.27	1.29	1.29	1.29	1.30	1.30	1.30
	0.19	1.49	1.49	1.46	1.46	1.49	1.49	1.49
	0.24	1.66	1.66	1.64	1.64	1.66	1.66	1.66
	0.31	1.94	1.91	1.91	1.91	1.91	1.91	1.91
	0.32	1.94	1.95	1.96	1.98	1.96	1.96	1.96
0.38	2.32	2.34	2.38	2.44	2.41	2.41	2.41	

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Note the similarity between this equation and the Einstein equation (12). The first derivative of the Kerner equation (17) is then

$$\frac{dG_c}{d\phi} = G_0 \frac{B + AB}{(1 - B\phi)^2} \quad (20)$$

Again note the similarity between this first derivative with that of the Einstein equation (14) and that of the generalized suspension equation (15). The intrinsic modulus would then be defined as

$$[G] = B(1 + A) \quad (21)$$

Substituting gives

$$[G] = \frac{(G_f/G_0 - 1)15(1 - \nu_0)}{(8 - 10\nu_0)(G_f/G_0) + (7 - 5\nu_0)} \quad (21a)$$

Another approach addressing the theoretical prediction of the modulus of a composite particulate

composite was initially developed by van der Poel⁶ and modified by Smith.¹⁰ Smith's modified van der Poel equation was described as

$$AX^2 + BX + C = 0 \quad (22)$$

where

$$\begin{aligned} A &= [4P(7 - 10\nu_0) - Sa^7][Q - (8 - 10\nu_0)(M - 1)a^3] - 126P(M - 1)a^3(1 - a^2)^2 \\ B &= 35(1 - \nu_0)P[Q - (8 - 10\nu_0)(M - 1)a^3] - 15(1 - \nu_0)[4P(7 - 10\nu_0) - Sa^7](M - 1)a^3 \\ C &= -525P(1 - \nu_0)^2(M - 1)a^3 \end{aligned}$$

and the quantities *P*, *Q*, and *S* are defined as

$$\begin{aligned} P &= (7 + 5\nu_f)M + 4(7 - 10\nu_f) \\ Q &= (8 - 10\nu_0)M + (7 - 5\nu_0) \\ S &= 35(7 + 5\nu_f)M(1 - \nu_0) + 4(7 + 5\nu_0) \end{aligned}$$

Here *M* is the ratio *G_f/G₀* and the quantity *X* = *G_c/*

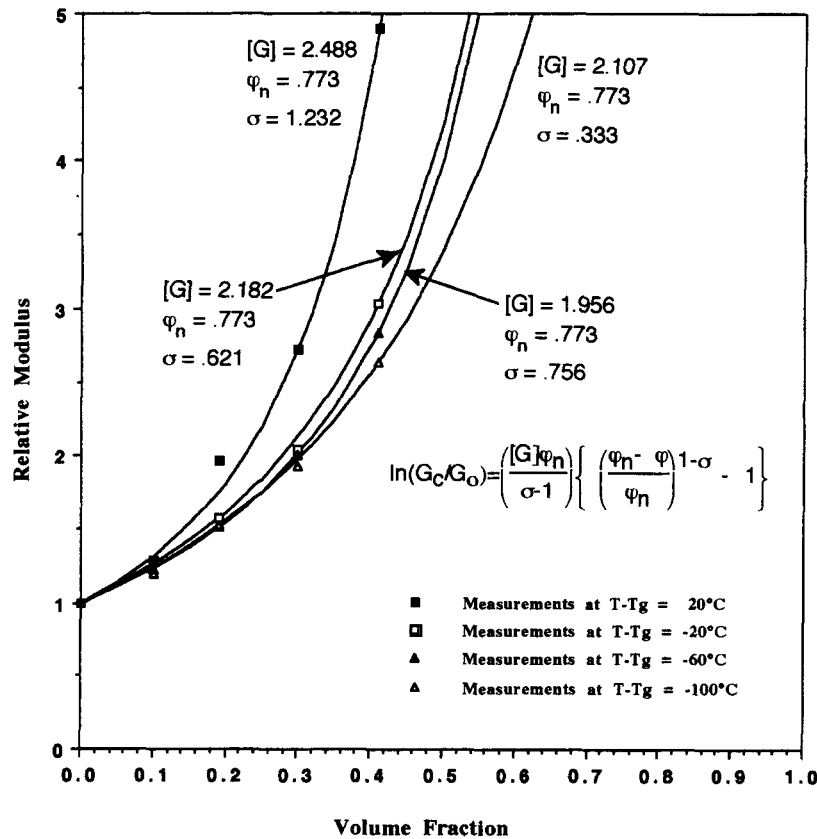


Figure 7 Lewis and Nielsen relative modulus vs. volume fraction data for 10–20-μm particles and generalized modulus equation predicted values using a variable intrinsic modulus.

$G_0 - 1$; G is the shear modulus; ν is Poisson's ratio; and $a^3 = \varphi$, the volume fraction of the dispersed phase. Subscript c denotes a property of the composite; 0 of the matrix, and f of the dispersed phase.

When the volume fraction $\varphi = a^3$ of the filler spheres is small, terms of higher order than a^3 can be neglected. Smith¹⁰ showed that with this assumption equation (22) reduces to

$$\frac{G_c}{G_0} = 1 + F\varphi \tag{23}$$

where

$$F = \frac{(G_f/G_0 - 1)15(1 - \nu_0)}{(8 - 10\nu_0)(G_f/G_0) + (7 - 5\nu_0)} \tag{23a}$$

It is apparent that Eq. (23) is really the first two terms of the MacLauren series for Eq. (22). The term F is effectively the intrinsic modulus $[G]$. Note that the intrinsic modulus from the Smith-van der

Poel equation is the same as that obtained for the Kerner equation.

A third approach to the modulus prediction of a particulate composite was generated by Budiansky,⁹ who generated an equation that Smith¹⁰ showed could be written in the form

$$\frac{G_c - G_0}{G_f - G_0} = \frac{(8 - 10\nu_c)G_c + (7 - 5\nu_c)G_c}{(8 - 10\nu_c)G_f + (7 - 5\nu_c)G_c} \varphi \tag{24}$$

This equation again results in a quadratic equation for the shear modulus of the particulate composite, G_c . It can be shown that the first derivative of this equation can be described as

$$\frac{dG_c}{d\varphi} = \frac{(G_f - G_0)15(1 - \nu_c)}{(7 - 5\nu_c) + (8 - 10\nu_c)(G_f G_0 / G_c^2)} + \frac{5(G_c - G_0) + 10G_f(1 - G_0/G_c) - 15(G_f - G_0)\varphi}{\partial\varphi(7 - 5\nu_c) + (8 - 10\nu_c)(G_f G_0 / G_c^2)} \tag{25}$$

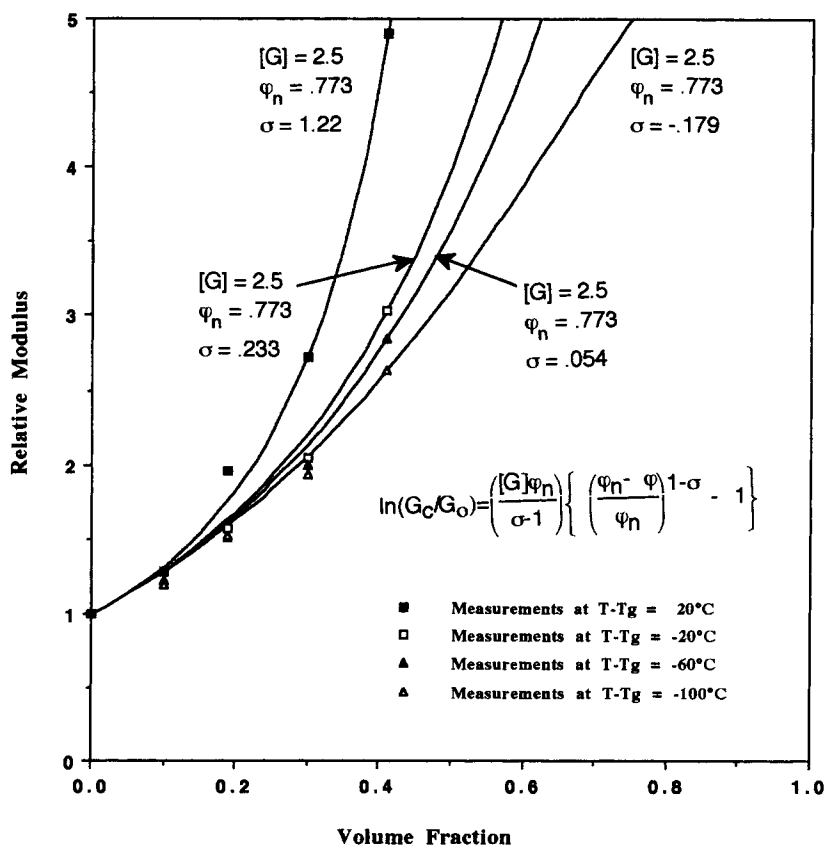


Figure 8 Lewis and Nielsen relative modulus vs. volume fraction data for 10–20- μm particles and generalized modulus equation predicted values using a constant intrinsic modulus.

This derivative can be evaluated by noting that when $\varphi = 0$, then

$$G_c = G_0 \quad \nu_c = \nu_0$$

Making these substitutions, the derivative $dG_c/d\varphi$ for Budiansky's⁹ equation at $\varphi = 0$ gives

$$\frac{dG_c}{d\varphi} = \frac{G_0(G_f/G_0 - 1)15(1 - \nu_0)}{(7 - 5\nu_0) + (8 - 10\nu_0)(G_f/G_0)} \quad (26)$$

It is apparent that this yields the same intrinsic modulus $[G]$ previously obtained [Eq. (21a)] for both the Kerner and the van der Poel-Smith equations:

$$[G] = \frac{(G_f/G_0 - 1)15(1 - \nu_0)}{(8 - 10\nu_0)(G_f/G_0) + (7 - 5\nu_0)}$$

Hence all four of the significant derivations dealing with the prediction of a shear modulus of a particulate composite yield the same formulation for the intrinsic modulus.

ELUCIDATION OF LIMITS OF INTRINSIC MODULUS

When the modulus of the filler material, G_f , is significantly greater than the modulus of the matrix, G_0 , such that $G_f \gg G_0$, the intrinsic modulus defined by Eq. (21a) reduces to

$$[G] = \frac{15(1 - \nu_0)}{8 - 10\nu_0} \quad (27)$$

In general, it can be shown³⁶ that the volume change of a homogeneous material is related to Poisson's ratio as

$$\frac{\Delta V}{V} = \frac{(1 - 2\nu_0)}{E} 3\sigma_m \quad (28)$$

where

- ΔV = change in volume
- V = original volume
- E = Young's modulus

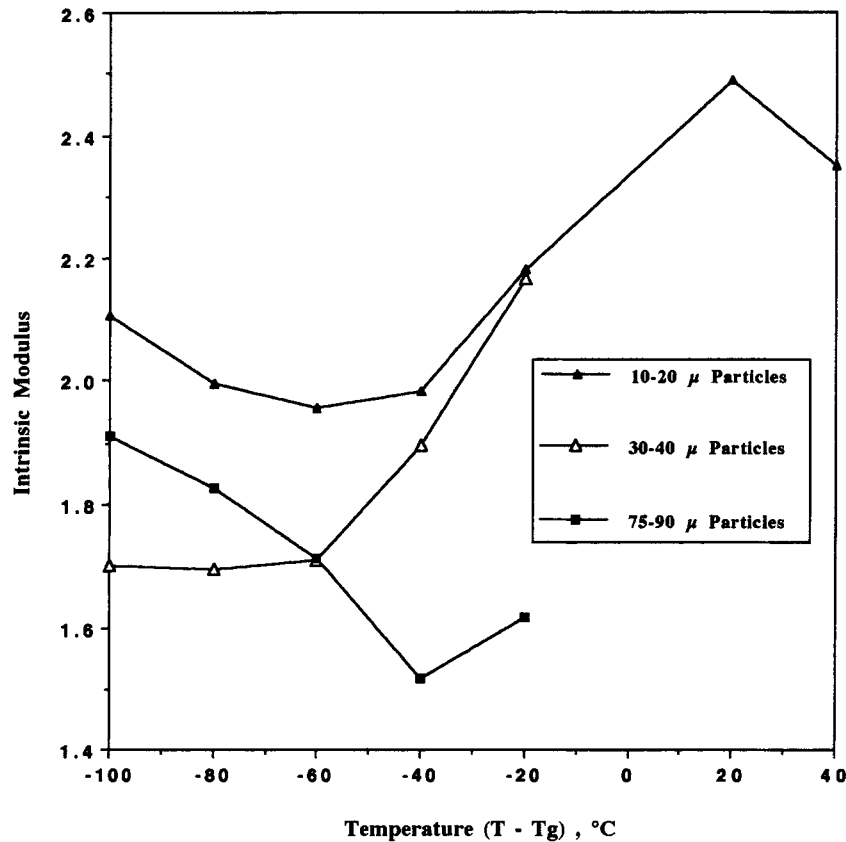


Figure 9 Calculated intrinsic modulus values at $T - T_g$ for Lewis and Nielsen data.

σ_m = uniform three-dimensional stress
 ν_0 = Poisson's ratio

It is apparent from Eq. (28) that a material will have a negligible volume change and be incompressible if the Poisson ratio is approximately 0.5. If the assumption is made that a particulate composite is incompressible such that Poisson's ratio $\nu_0 = 0.5$, then the intrinsic modulus defined by Eq. (27) reduces to

$$[G] = 2.5 \tag{29}$$

This is also the familiar result obtained by Einstein as the intrinsic viscosity $[\eta]$ of a liquid suspension. The assumptions required to reduce the intrinsic modulus to $[G] = 2.5$ were also the same ones specified by Einstein. The upper limit of the intrinsic modulus $[G]$ as described by Eq. (27) is shown in Figure 1 for values of Poisson's ratio ν_0 ranging from 0 to 0.7. As indicated in this figure, the upper limit of the intrinsic modulus ranges only from 1.88 to 3

when Poisson's ratio ranges from 0 to 0.6. Above a Poisson's ratio of 0.6 the intrinsic modulus increases more rapidly.

The second limit of the generalized intrinsic modulus occurs when the modulus of the filler G_f is essentially zero such that $G_f \ll G_0$. This condition would apply, for example, if the particles were voids with essentially no mass or strength. For this case the intrinsic modulus reduces to

$$[G] = \frac{-15(1 - \nu_0)}{7 - 5\nu_0} \tag{30}$$

The lower limit of the intrinsic modulus $[G]$ as described by Eq. (30) is shown in Figure 2 for values of Poisson's ratio ν_0 ranging from 0 to 0.7. It is interesting that the lower limit of the intrinsic modulus is negative when Poisson's ratio ranges from $0 \leq \nu_0 < 1$.

The limits defined by Eq. (27) and (30) represent the extremes of the intrinsic modulus. Between these extremes there is one range of values where the in-

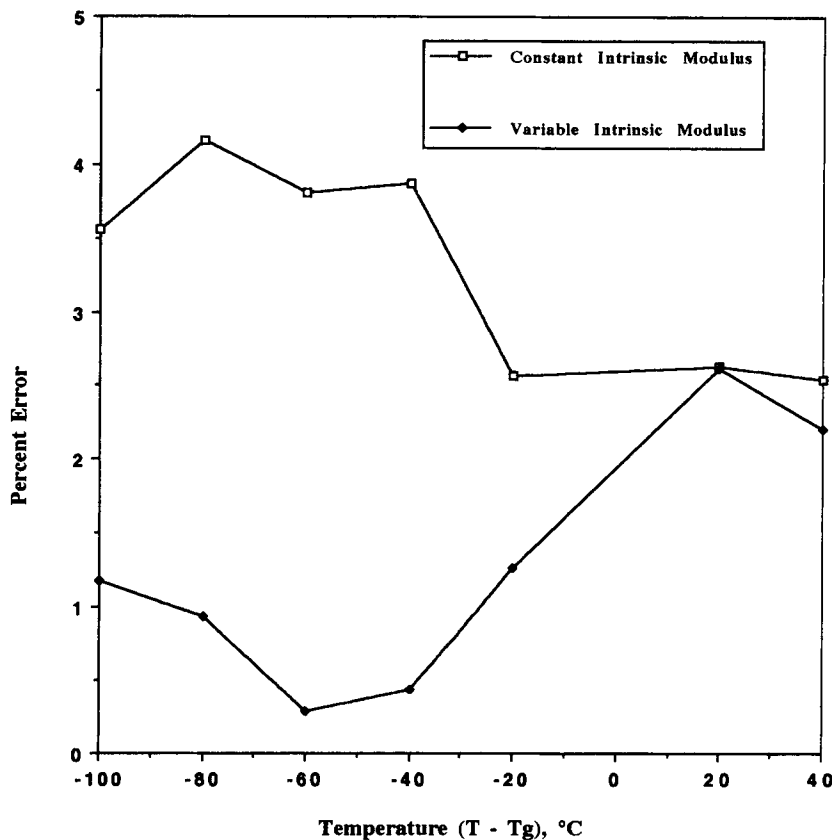


Figure 10 Calculated average percent error in fitting generalized modulus equation vs. temperature ($T - T_g$) for 10-20- μ m particles using Lewis and Nielsen data.

trinsic modulus is positive and a second range where the intrinsic modulus is negative. In general these ranges for the intrinsic modulus are

$$[G] \geq 0 \quad \text{when } 1 \leq \frac{G_f}{G_0} \leq \infty \quad (31)$$

and

$$[G] \geq 0 \quad \text{when } 0 \leq \frac{G_f}{G_0} \leq 1 \quad (32)$$

The effect of Poisson's ratio ν_0 on the intrinsic modulus $[G]$ when the modulus ratio ranges from $1 \leq G_f/G_0 \leq 50$ is shown in Figure 3. This figure indicates that the upper limit of the intrinsic modulus is nearly reached for most values of Poisson's ratio at relatively low values of the filler to the matrix modulus ratio G_f/G_0 .

Figure 4 shows the effect of Poisson's ratio ν_0 on the intrinsic modulus $[G]$ when the modulus ratio ranges from $0 \leq G_f/G_0 \leq 1$. For modulus ratios rang-

ing from 0.5 to 1.0 the lower limit of the intrinsic modulus is nearly independent of Poisson's ratio.

APPLICATION OF GENERALIZED VISCOSITY EQUATION TO SMALLWOOD'S PARTICULATE COMPOSITE MODULUS VS. VOLUME FRACTION DATA

Smallwood² evaluated Young's modulus of compounded natural rubber using several fillers in a rubber matrix. Young's modulus E , the shear modulus G , and Poisson's ratio ν_0 , are related through the following formulation³⁷:

$$G = \frac{E}{2(1 + \nu_0)} \quad (33)$$

Since the shear modulus and Young's modulus are directly related, Smallwood evaluated Young's modulus in place of the shear modulus in his rubber

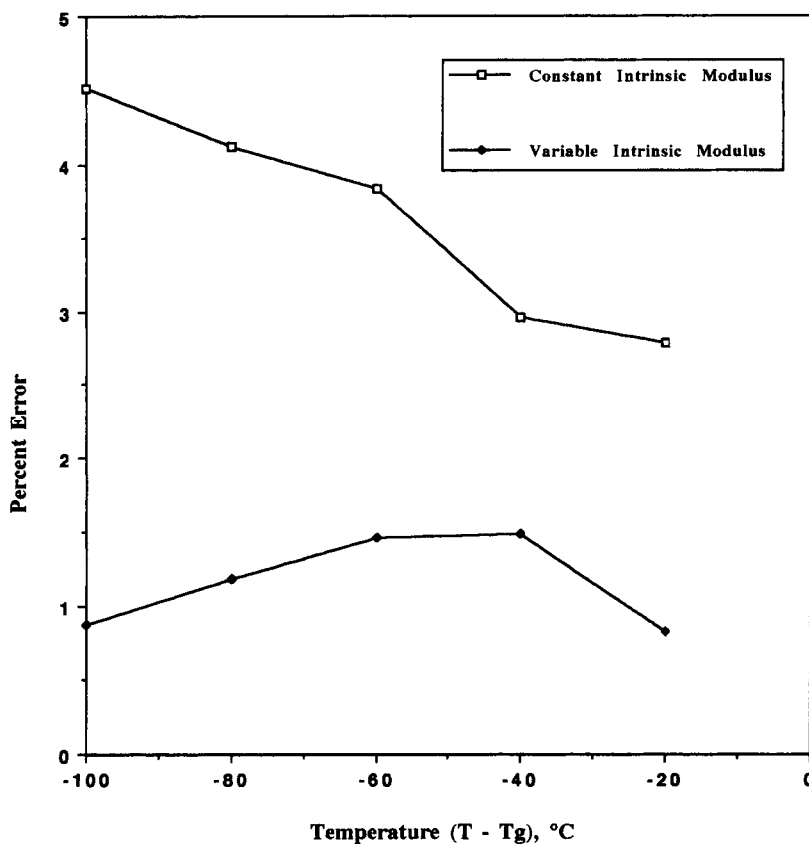


Figure 11 Calculated average percent error in fitting generalized modulus equation vs. temperature ($T - T_g$) for 30-40- μ m particles using Lewis and Nielsen data.

formulations. The modulus results for two filler materials measured by Smallwood are shown in Figure 5 at several concentration levels. The theoretical curves included in this figure for each filler series were generated using the generalized viscosity equation (1) modified for shear modulus as

$$\ln \frac{G_c}{G_0} = \frac{[G]\varphi_n}{\sigma - 1} \left\{ \left(\frac{\varphi_n - \varphi}{\varphi_n} \right)^{1-\sigma} - 1 \right\} \text{ for } \sigma \neq 1 \quad (34)$$

$$[G] = \frac{(G_f/G_0 - 1)15(1 - \nu_0)}{(8 - 10\nu_0)(G_f/G_0) + (7 - 5\nu_0)} \quad (35)$$

For the case where $\sigma = 1$, the resulting equation can be written as

$$\ln \frac{G_c}{G_0} = [G]\varphi_n \ln \frac{\varphi_n - \varphi}{\varphi_n} \quad (36)$$

or

$$G_c = G_0 \left(\frac{\varphi_n - \varphi}{\varphi_n} \right)^{-[G]\varphi_n} \quad (37)$$

where

- G_c = composite shear modulus
- G_f = shear modulus of filler
- G_0 = shear modulus of matrix
- $[G]$ = intrinsic modulus
- ν_0 = Poisson's ratio
- σ = particle interaction coefficient
- φ = particle volume concentration in matrix
- φ_n = particle packing fraction

The other equations [(4)–(10)] associated with the generalized viscosity equation should apply equally well to the shear modulus modified version.

In the absence of particle size distribution data the packing fraction for the two filler materials in Figure 5 were assumed to be approximately $\varphi_n = 0.65$. A packing fraction of 0.64 was found by Lee³⁸ to be the average of several reported literature values for dense random packing of spherical particles. With this assumption it was found that an intrinsic modulus of $[G] = 2.5$ successfully predicted the experimental results for the Gilders whitening filler material. However, it was found that an intrinsic mod-

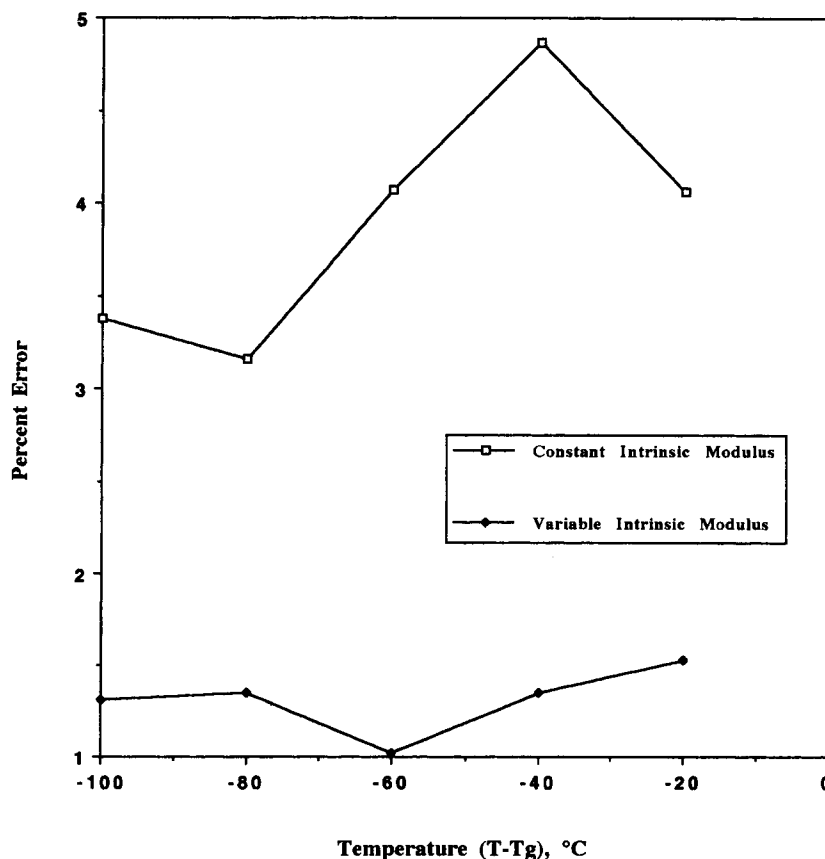


Figure 12 Calculated average percent error in fitting generalized modulus equation vs. temperature ($T - T_g$) for 75–90- μm particles using Lewis and Nielsen data.

ulus of $[G] = 4.27$ was required to minimize the error in the prediction of the Smallwood carbon black data. Based on the assumptions used in this evaluation the particle interaction coefficients were nearly the same for both filler materials. The minimum error in fitting the carbon black data was obtained when the particle interaction coefficient was $\sigma = 0.655$. For the Gilders whitening data the optimized particle interaction coefficient was $\sigma = 0.672$.

In general, the generalized viscosity/modulus equation was shown to fit Smallwood's data very well for these two filler materials. However, it is not yet clear why the intrinsic modulus calculated to fit the data for the carbon black filler material was so much larger than Einstein's predicted value, which worked well for the Gilders whitening filler. This is particularly true since the intrinsic modulus is theoretically predictable solely from the properties of the matrix material and both filler materials had the same rubber matrix.

It is possible that the intrinsic modulus developed from Budiansky's modulus derivation for a particulate composite, as indicated in Eq. (25), may be more appropriate for some materials. For these cases the intrinsic modulus may not be able to be estimated from the pure matrix properties. However, it is not yet clear how to estimate the influence of composite properties on the intrinsic modulus for these materials. At this time, the influence of composite properties on the intrinsic modulus can best be estimated from experimental evaluations of the intrinsic modulus.

The first two terms of the MacLauren series for Eq. (34) reduce to the straight-line equation shown in Figure 5 when $G_f \gg G_0$ and the Poisson ratio $\nu_0 = 0.5$. Smallwood² was the first to show that this equation, which was originally derived by Einstein for the viscosity of a liquid suspension, could also be derived for the modulus of a particulate composite. However, it is apparent that this equation was only applicable at very low concentration levels for the Gilders whitening filler whereas the generalized modulus equation successfully predicts the whole concentration curve for both fillers.

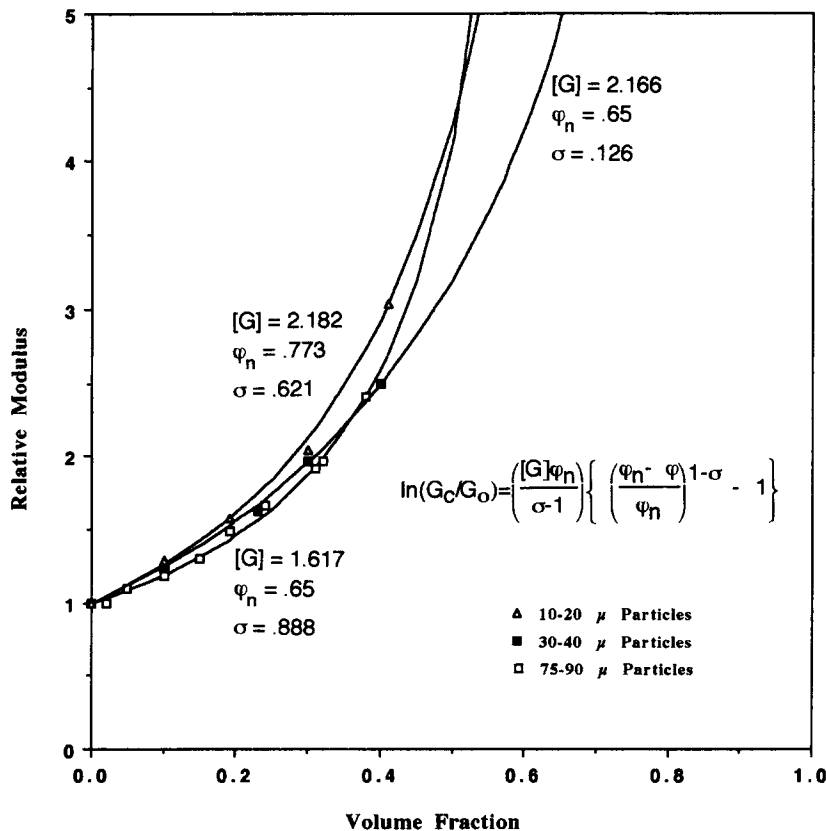


Figure 13 Lewis and Nielsen relative modulus vs. volume fraction data for $T - T_g = -20^\circ\text{C}$ and generalized modulus equation predicted values using a variable intrinsic modulus.

APPLICATION OF GENERALIZED VISCOSITY EQUATION TO LEWIS AND NIELSEN'S PARTICULATE COMPOSITE MODULUS VS. VOLUME FRACTION DATA

Lewis and Nielsen¹⁷ measured the shear modulus for composites with glass spheres dispersed in an epoxy matrix as a function of temperature for several values of volume fraction and particle size filler. Representative data from the study by Lewis and Nielsen¹⁷ are shown in Figure 6 for shear modulus G' , logarithmic decrement or damping Δ , and calculated loss modulus G'' versus temperature for samples of pure matrix and a high volume fraction of spheres. For this study Lewis and Nielsen defined the glass transition temperature T_g as the maximum in the dampening curve between the glass and rubbery regions.

Selected data from Lewis and Nielsen¹⁷ have been summarized in Table I to illustrate the effectiveness of the generalized viscosity/modulus equation evaluated in this study. Lewis and Nielsen's data in Table I include three different particle size ranges for

measurements within 100°C of T_g . Unfortunately, the particle size distribution of these particle ranges was not available.

Using the generalized viscosity/modulus equation, it was possible to generate a reasonable packing fraction of $\varphi_n = 0.773$ for particles ranging from 10 to 20 μm from an optimization of data at $T - T_g = +20^\circ\text{C}$. This packing fraction was then assumed to be appropriate for all the other temperatures for this particle size range.

A reasonable estimate of the maximum packing fraction was not obtainable from an optimization of the data for the other two particle size ranges. For these cases the maximum packing fraction was assumed to be approximately $\varphi_n = 0.65$, as was done for Smallwood's data.

The generalized viscosity equation modified for shear modulus as described by Eqs.(34)–(37) was used to characterize the shear modulus data in Table I. These data were analyzed using both a variable intrinsic modulus and a constant intrinsic modulus. A comparison of Figures 7 and 8 indicates that a variable intrinsic modulus allows a better fit of the

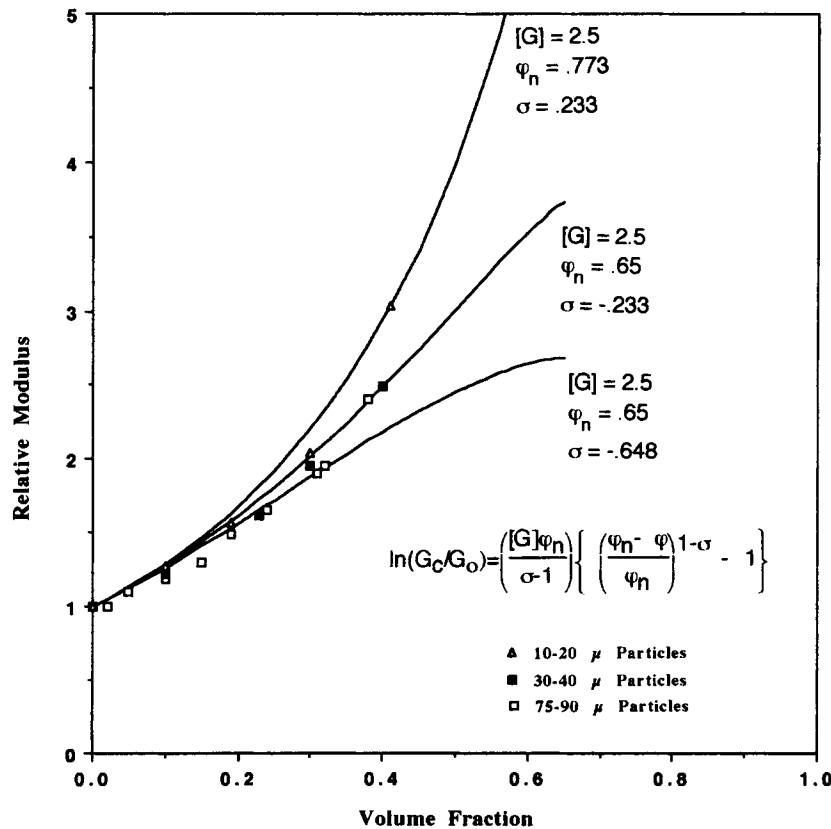


Figure 14 Lewis and Nielsen relative modulus vs. volume fraction data for $T - T_g = -20^\circ\text{C}$ and generalized modulus equation predicted values using a constant intrinsic modulus.

10–20 μm particle size data in Table I. The intrinsic moduli that gave the best fit of the data are shown in Figure 9. Note in this figure that the intrinsic modulus for both the 10–20- and 30–40- μm particle ranges approach 2.5 at or above the T_g but decreases significantly below T_g .

It can easily be shown that the observed results in Figure 9 are consistent with the predicted results for the intrinsic modulus as indicated by Eq. (35) and Figure 3. As the glass transition is approached with a lowering of temperature, the modulus of the epoxy matrix will increase and tend to approach the modulus of the glass sphere filler material, resulting in a decrease in the filler-to-matrix modulus ratio. As indicated by Eq. (35) and Figure 3, a decrease in the modulus ratio will cause the intrinsic modulus to decrease if Poisson's ratio is held nearly constant.

As indicated in Figures 10–12, the percent error in the fit of the data significantly decreases when the intrinsic modulus is allowed to vary. Since the intrinsic modulus is approximately 2.5 at $T - T_g = 20^\circ\text{C}$ and above for the 10–20- μm particle range, the difference between the variable and the constant

intrinsic modulus was negligible in this temperature range. However, below T_g a variable intrinsic modulus allows a significant decrease in the error in fitting the data.

It is not yet clear in Figure 9 why the intrinsic modulus increased with a decrease in temperature below $T = -40^\circ\text{C}$ for the particle size range 75–90 μm and below -60°C for the 10–20- μm particle size range. It also appears that there could be an unexplainable minimum in the intrinsic modulus for each particle size range in Figure 9. It is interesting, however, that this minimum, if real, does appear to correlate with particle size. The location of this minimum could also be related to particle size distribution in some way not yet understood. Additional data are needed to answer these questions.

As illustrated in Figures 13 and 14, a significant improvement in the fit of the data occurred when the intrinsic modulus was allowed to be a variable. Unfortunately, there was not an obvious trend of the particle interaction coefficient with particle size for these data with a variable intrinsic modulus, as indicated in Figure 15.

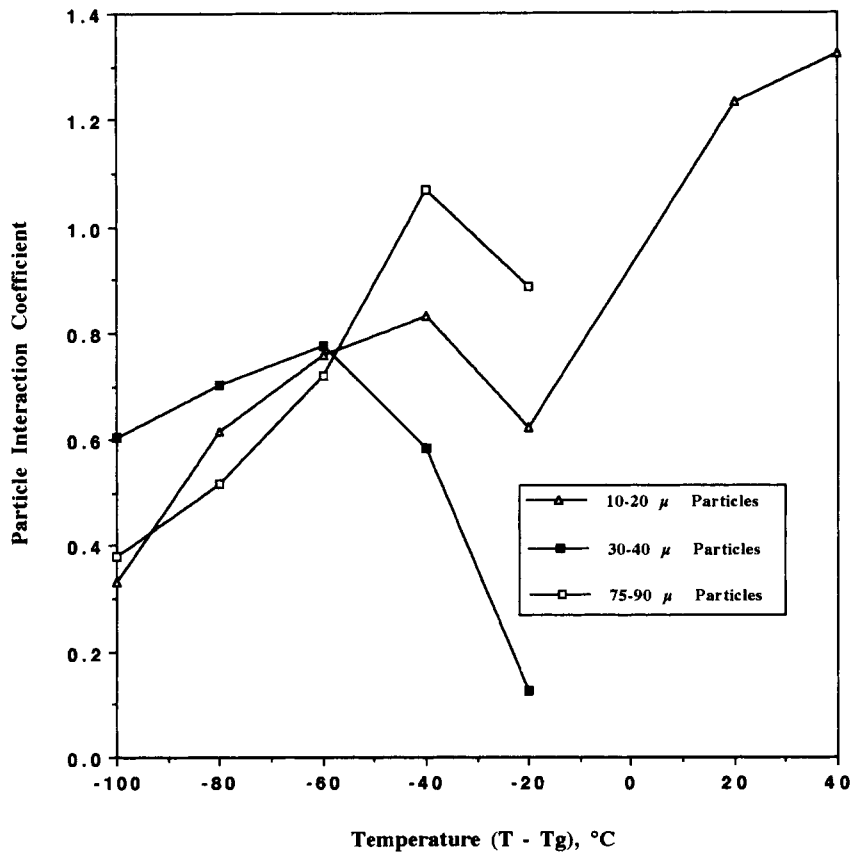


Figure 15 Calculated particle interaction coefficients at $T - T_g$ using a variable intrinsic modulus for Lewis and Nielsen data.

However, when the intrinsic modulus remained a constant at $[G] = 2.5$ there was a definite trend in the particle interaction coefficient as a function of particle size, as indicated in Figure 16. As indicated in Figure 17, the particle interaction coefficient was nearly linear with the mean particle size for these three particle ranges at a constant intrinsic modulus. However, with no information on the particle size distribution the number average of the particle size ranges could not be determined. This latter result was consistent with that found in an earlier evaluation²⁶ for the relationship of the particle interaction coefficient with latex particle size for the viscosity of suspension blends. Of course, for liquid suspensions the intrinsic viscosity was expected to be a constant at $[\eta] = 2.5$.

It is not clear from the Lewis and Nielsen data how to best represent the effect of particle size in particulate composites. It is hoped, however, that this problem can be remedied with more detailed information on the particle size distribution in future solid particulate composite studies.

CONCLUDING REMARKS

Several significant attempts have been made in the literature to derive equations to describe the relative shear modulus of particulate-filled systems.^{2,3,6-10} Unfortunately, these equations have had only limited success in fitting the available modulus-particulate concentration data.

A series of articles²⁴⁻²⁷ that describe the derivation of a new generalized equation that addresses the viscosity of suspensions has recently appeared in the literature. This new generalized equation, which for the first time addresses the detailed effects of particle size, particles size distribution, and packing fraction, was applied to the available literature on particulate composites. Since the evaluation of the intrinsic viscosity for suspensions required the evaluation of the first derivative of the viscosity function, the evaluation of the intrinsic modulus for particulate composites required the evaluation of the first derivative of the shear modulus function. The relative equality of the intrinsic viscosity $[\eta]$ and the

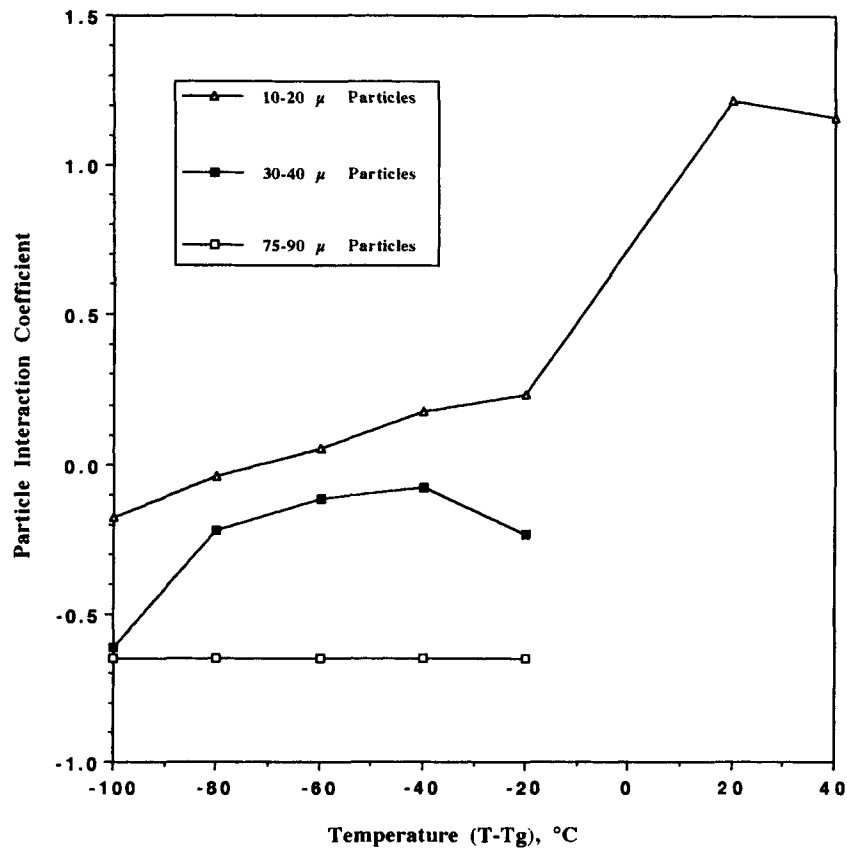


Figure 16 Calculated particle interaction coefficients at $T - T_g$ using a constant intrinsic modulus for Lewis and Nielsen data.

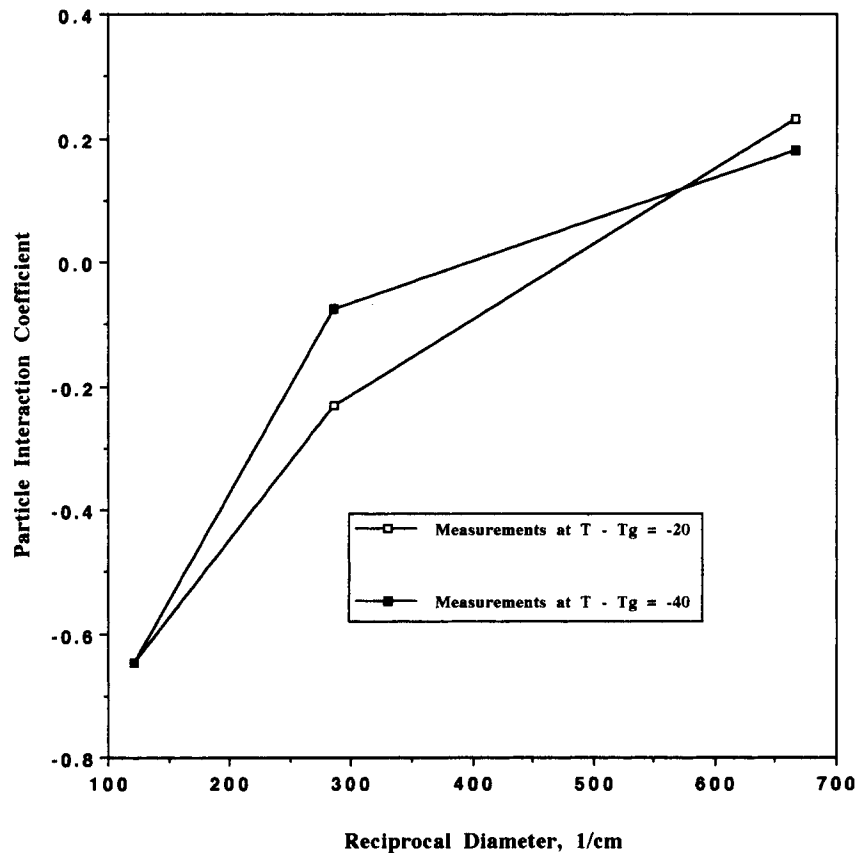


Figure 17 Calculated particle interaction coefficients using a constant intrinsic modulus vs. reciprocal average particle diameter for Lewis and Nielsen data.

intrinsic modulus [G] was assumed from the analysis. Available equations derived by Kerner,⁷ Hashin and Shtrikman,⁸ van der Poel⁶ and Smith,¹⁰ and Budiansky⁹ to describe the modulus of particulate composites were shown to all yield the same intrinsic modulus of a particulate composite.

In general the intrinsic modulus was shown to be positive when the filler to the matrix modulus ratio G_f/G_0 was $1 \leq G_f/G_0 \leq \infty$ and the intrinsic modulus was shown to be negative when $0 \leq G_f/G_0 \leq 1$. If the filler to the matrix modulus ratio is large and the particulate composite is incompressible such that Poisson's ratio $\nu_0 = 0.5$, then the intrinsic modulus reduces to Einstein's value of [G] = 2.5.

In general, the generalized viscosity/modulus equation was shown to fit Smallwood's data very well for the two filler materials evaluated. However, it is not yet clear why the intrinsic modulus calculated to fit the data for the carbon black filler material was so much larger than Einstein's predicted value, which worked well for the Gilders whiting filler. This is particularly true since the intrinsic modulus is theoretically predictable solely from the

properties of the matrix material and both filler materials had the same rubber matrix. It is possible that the intrinsic modulus developed from Budiansky's modulus derivation for a particulate composite may be more appropriate for some materials. At this time, the influence of composite properties on the intrinsic modulus can best be estimated from experimental evaluations of the intrinsic modulus.

The generalized viscosity/modulus equation was used to characterize the Lewis and Nielsen shear modulus data. It was found that a variable intrinsic modulus allowed an excellent fit of the data. As the temperature was lowered below the glass transition temperature, the modulus of the epoxy matrix increased and tended to approach the modulus of the glass sphere filler material. This decrease in the modulus ratio of filler to matrix resulted in a decrease in the intrinsic modulus.

The percent error in the fit of the Lewis and Nielsen data significantly decreased when the intrinsic modulus was allowed to vary. Above the glass transition temperature the difference between the variable and the constant intrinsic modulus was nearly

negligible. Below T_g a variable intrinsic modulus allowed a significant decrease in the error in fitting the data.

It is not yet clear why the intrinsic modulus increased with a decrease in temperature below $T = -40^\circ\text{C}$ for the particle size range 75–90 μm and below -60°C for the 10–20- μm particle size range. It also appears that there could be an as-yet unexplainable minimum in the intrinsic modulus for each particle size range used in this study. If this minimum is real, it does appear to correlate with particle size. The location of this minimum could also be related to particle size distribution in some way not yet understood. Additional data are needed to answer these questions.

While there was a significant improvement in the fit of the data when the intrinsic modulus was allowed to be a variable, there was not an obvious trend in the variation of the particle interaction coefficient with particle size for these data. However, when the intrinsic modulus remained a constant at $[G] = 2.5$, there was a definite trend in the particle interaction coefficient as a function of particle size. This latter result was consistent with that found in an earlier evaluation²³ for the variation of the particle interaction coefficient with latex particle size for the viscosity of suspension blends. Of course, for liquid suspensions the intrinsic viscosity was expected to be a constant at $[\eta] = 2.5$.

It was not clear from the Lewis and Nielsen data how to best represent the effect of particle size in particulate composites. It is hoped, however, that this problem can be remedied with more detailed information on the particle size distribution in future solid particulate composite studies.

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