

Characteristics of the Intrinsic Modulus as Applied to Particulate Composites with Both Soft and Hard Particulates Utilizing the Generalized Viscosity/Modulus Equation

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ABSTRACT: Recently, four significantly different particulate composite modulus derivations from the literature were found to yield the same theoretical “intrinsic modulus” for a particulate composite. In this article, this new intrinsic modulus was successfully combined with the generalized viscosity/modulus equation to yield a good fit of the shear modulus–particulate concentration data of both Smallwood and Nielsen using a variable intrinsic modulus. Some fillers yielded an intrinsic modulus that was close to the Einstein limiting value ($[G] = [\eta] = 2.5$), while other fillers yielded intrinsic moduli that were either somewhat larger or somewhat smaller than this value. The intrinsic modulus for carbon black in rubber was much larger than was Einstein’s predicted value. However, intrinsic modulus values for Nielsen’s data for particulate composites were smaller than were Einstein’s prediction at temperatures below the glass transition temperature of the matrix. The explanation for this phenomenon can easily be understood from a review of the properties of the intrinsic modulus. Likewise, the generalized viscosity/modulus equation was also successfully applied to available modulus literature for ceramics where voids were the particulate phase. When applied to Wang’s data, the intrinsic modulus was found to be negative when describing the compaction of voids in the hot isostatic pressing of a ceramic. For this application, the modulus of a particulate composite as a function of the volume fraction of particles was modified to describe the modulus as a function of porosity. For the sets of data analyzed, values of the interaction coefficient and the packing fraction were not necessarily unique if the data sets were limited to the lower particulate volume fractions. For applications where a minimum amount of data was found to be available, a new approach was introduced to address a relative measure of the compatibility of the particle and the matrix using a new definition for Kraemer’s constant. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1954–1963, 2000

Key words: particulate composites; intrinsic modulus; glass transition temperature

INTRODUCTION

Several significant attempts have been made in the literature to derive equations to describe the

relative shear modulus of particulate-filled systems as a function of particulate concentration.^{1–7} 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 equations have had only limited success in fitting the available modulus–particulate concentration data. Schwarzl et al.⁸ pointed out that a major limitation of these mechanical property

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Journal of Applied Polymer Science, Vol. 77, 1954–1963 (2000)
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modulus derivations is that they did not include effects for particle size, particle-size distribution, or a maximum packing fraction. In addition, no adjustable parameters were included in these mechanical property modulus derivations to account for process variations.

Some relatively recent articles^{9–11} have indicated that interest in the mechanical properties of particulate-filled composites remains high. A series of articles^{12–16} that described the derivation and development of a new generalized equation that addresses the viscosity of suspensions as a function of concentration has recently appeared in the literature. This new model for the first time addresses the detailed effects of particle size, particle-size distribution, and packing fraction on viscosity. In addition, it has been shown that the modulus of particulate composites^{17,18} can also be effectively predicted as a function of concentration using this new model. In applying this new equation to particulate composites, a new term described as the “intrinsic modulus” was introduced.

This article shows that the intrinsic modulus can be either positive or negative depending on the modulus of the particulate relative to that of the matrix. In addition, it was also found that values for the interaction coefficient, σ , and the packing fraction, ϕ_n , as predicted from this generalized viscosity/modulus model are not always unique. This is particularly true if the data are restricted to only the lower concentrations.

SELECTED APPLICATIONS FOR THE GENERALIZED SUSPENSION VISCOSITY/MODULUS EQUATION

The generalized equation describing the viscosity–concentration relationship for suspensions was initially introduced by Sudduth¹² in the following format:

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

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

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

where η is the suspension viscosity; η_0 , the viscosity of the suspending medium; $[\eta]$, the intrinsic viscosity; σ , the particle interaction coefficient; ϕ , the suspension particle volume concentration; and ϕ_n , the particle packing fraction.

Smallwood¹ and Guth² showed that the relative ratios of the viscosity are equivalent to the relative ratios of the shear modulus. Consequently, the above equations were also found to be directly applicable to the evaluation of modulus¹⁷ in particulate composites. In addition, Sudduth¹⁷ also introduced the intrinsic modulus that was initially derived to apply primarily to particulate composites. The intrinsic modulus was defined as

$$[G] = \frac{\left(\frac{G_f}{G_0} - 1\right)15(1 - \nu_0)}{(8 - 10\nu_0)\frac{G_f}{G_0} + (7 - 5\nu_0)} \quad (3)$$

Sudduth¹⁷ also showed that the intrinsic modulus, $[G]$, should be essentially equivalent to the intrinsic viscosity, $[\eta]$, as

$$[G] = [\eta] \quad (4)$$

As expected, the intrinsic modulus reduces to the Einstein^{19,20} value of $[G] = 2.5$ when the Einstein assumptions are applied. These assumptions specify both an incompressible particulate composite such that Poisson’s ratio is $\nu_0 = 0.5$ and a spherical filler material modulus, G_f , that is significantly greater than is the modulus of the matrix, G_0 , such that $G_f \gg G_0$.

Also note that the intrinsic modulus can be negative if the modulus of the filler, G_f , is less than the modulus of the matrix, G_0 . Thus, the Einstein intrinsic viscosity, $[\eta]$, can be negative if the shear modulus of the solute (or particle) is less than the shear modulus of the solvent (or matrix).

The suspension viscosity data of Vand²¹ as indicated in Figure 1 is an example of data that has been found to yield an intrinsic viscosity of approximately 2.5. For reference, a plot of the computer-generated locus of points characterizing the minimum errors in fitting Vand’s data for each possible packing fraction is indicated in Figure 2. For all the data analyzed in this study including Vand’s data, the following error function, E , was minimized for each packing fraction:

$$E^2 = \left(\frac{1}{n}\right) \sum_{i=1}^n \left(\frac{\eta_i - \eta_{iM}}{\eta_{iM}}\right)^2 \quad (5)$$

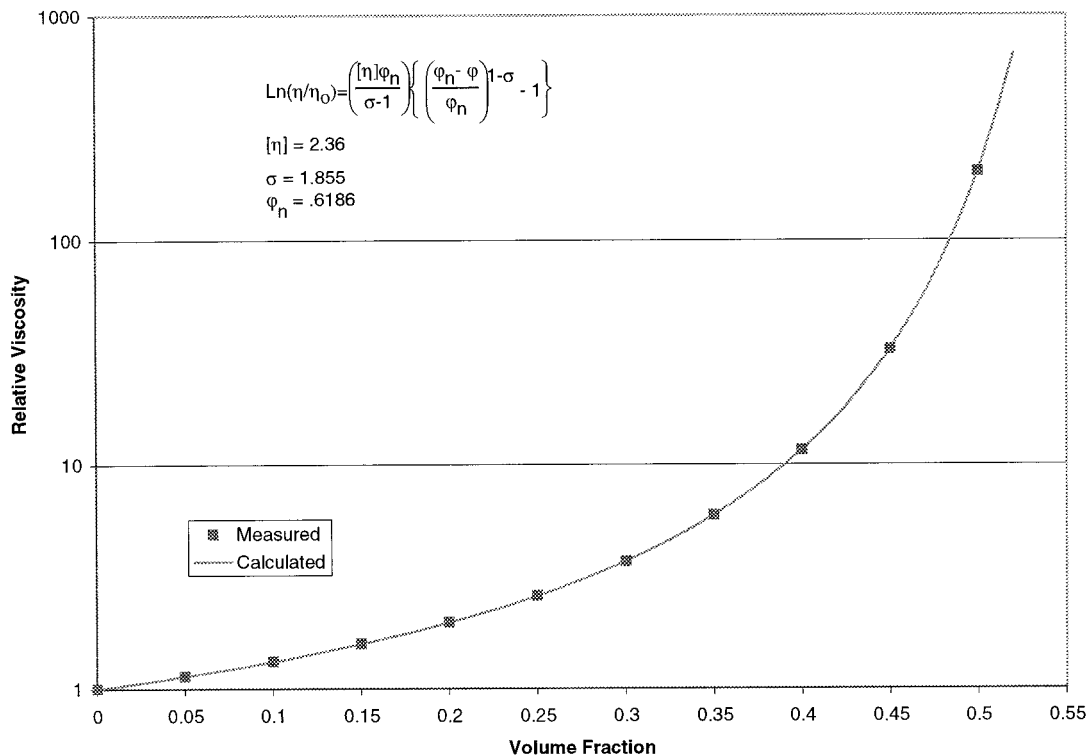


Figure 1 Vand's measured and calculated relative viscosity data versus volume fraction.

where n is the number of data points; η_i , the viscosity/modulus from eq. (1); and η_{iM} , the measured viscosity/modulus. Note that a clear minimum error, E , is indicated for Vand's data in Figure 2, which, consequently, yielded a unique value for the intrinsic viscosity, $[\eta]$, the packing fraction, ϕ_n , and the interaction coefficient, σ . Further details describing the computer program used to calculate these constants will be addressed in a later publication.

The dynamic shear modulus data of Lewis and Nielsen²² were evaluated as a function of the temperature and the results are summarized in Figures 3 and 4. As indicated in Figures 3 and 4, it was found that the intrinsic modulus rose to a value of approximately 2.8 when the modulus measurements were made at temperatures above the T_g of the resin. The particulate composites evaluated by Nielsen were prepared with glass spheres in an epoxy matrix. As illustrated in Figure 4, when the measurement temperature decreased below the T_g of the resin, the modulus of the resin apparently increased and began to approach the modulus of the particulate filler. The reduction in the ratio of the modulus of the particulate to the modulus of the matrix satisfactorily

explains the reduction in the intrinsic modulus.

It was also found that the intrinsic modulus can be negative as indicated in Figure 5 for the experimental data of Wang²³ where the particulate is the voids being compacted in an alumina ceramic. For this case, the voids as a particulate would have had a much smaller modulus than that of the matrix that was, in this instance, alumina. Ironically, the alumina matrix material started this compaction process as spherical ceramic particles with a void content as the particulate phase. In addition, the void content would be at its maximum at the beginning of the compaction process.

For the data of Smallwood¹ summarized in Figure 6, an intrinsic modulus of approximately 4.1 was indicated for a carbon black filler in rubber. However, for the Smallwood data, a minimum error in fitting the data is not clearly indicated in Figure 7. Therefore, a unique value for the interaction coefficient, σ , and the packing fraction, ϕ_n , was not clearly identified for Smallwood's data for carbon black in rubber. The packing fraction chosen for calculation purposes in Figure 6 was a value of $\phi_n = .64$, which Lee²⁴ indicated is the

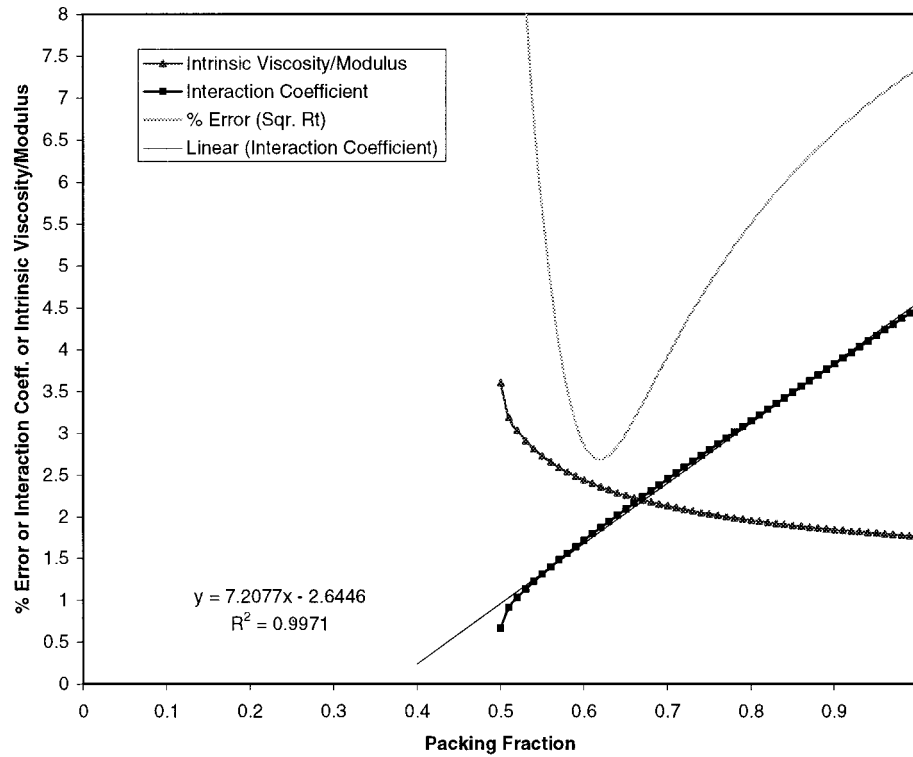


Figure 2 Percent error and associated analysis constants involved in fitting Vand's data to the generalized viscosity/modulus equation.

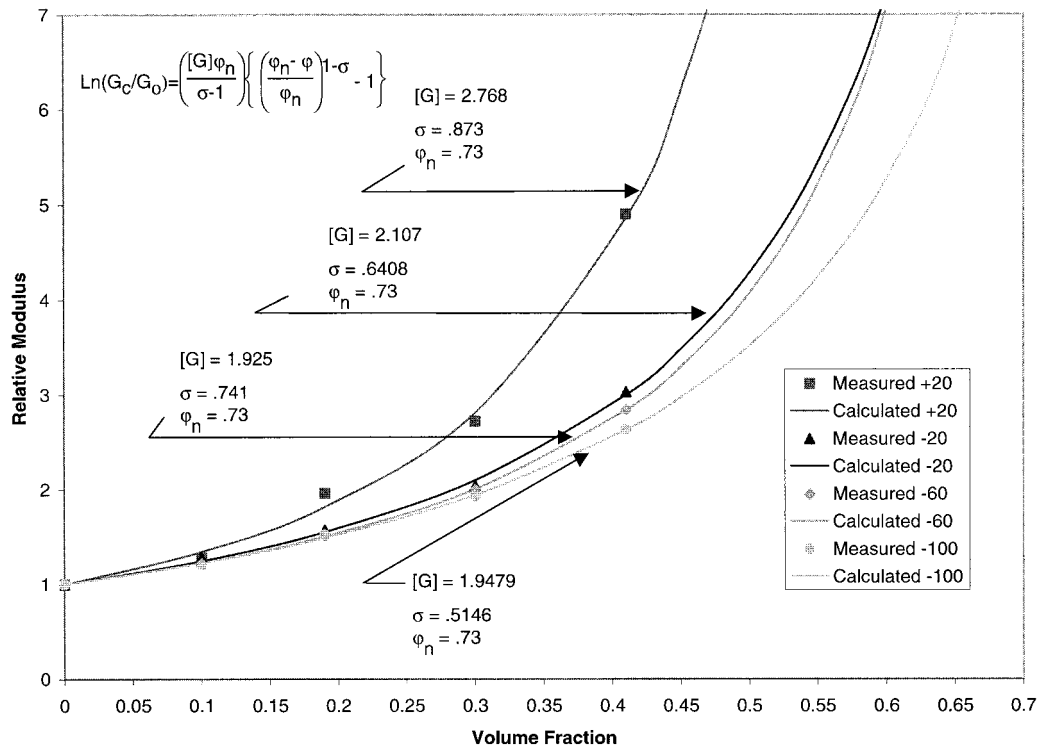


Figure 3 Nielsen's measured and calculated relative modulus data versus volume fraction for 10-20-micron particles.

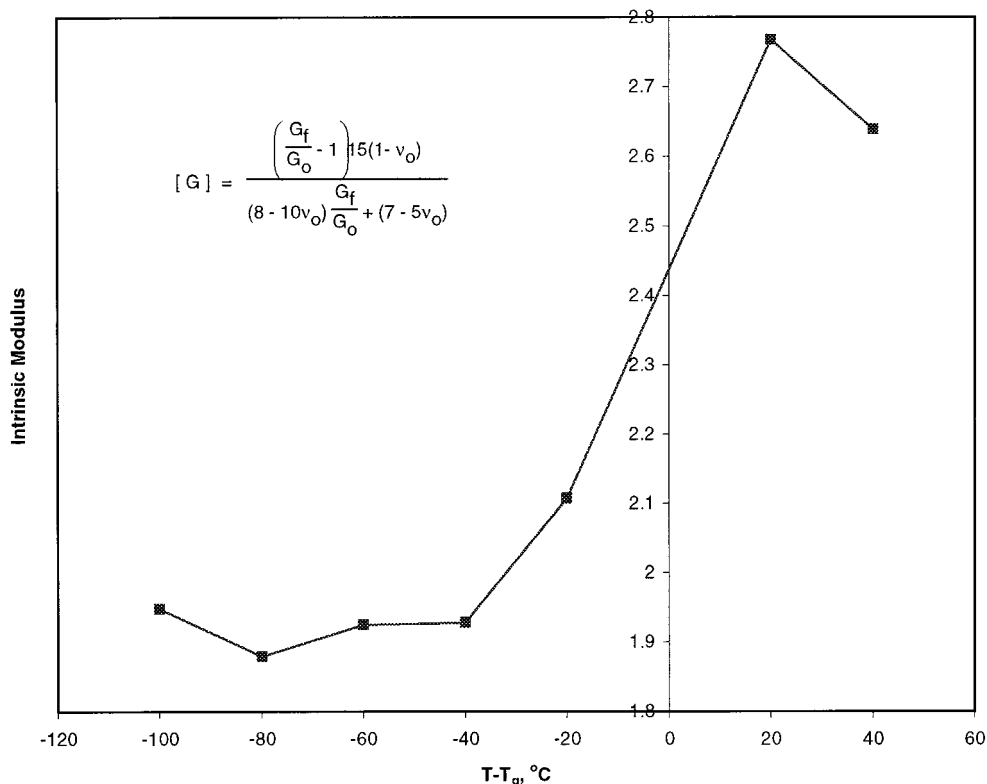


Figure 4 Intrinsic modulus values versus $T - T_g$ for Nielsen's data using 10–20-micron glass spheres in epoxy matrix at $\phi_n = 0.73$.

packing fraction for dense random packing of spherical particles.

The apparent reason for this lack of fit for Smallwood's data can be partially indicated in the expansion of eq. (1) using a McLaurin series to give

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

It is apparent that the first two terms are the Einstein^{19,20} limiting terms for all possible values for the particle interaction coefficient, σ , and the packing fraction, ϕ_n . It was also found that σ and ϕ_n always occur as a paired ratio for second-order and higher expansion terms. This persistent ratio of σ/ϕ_n means that these two variables are hard to define with unique values if only the first few terms of eq. (6) adequately define the available data. Sudduth¹⁶ showed that the first few terms of eq. (6) can be written in the more common Huggins' form as

$$\left(\frac{\eta_{sp}}{\phi}\right) = [\eta] + [\eta]^2 \left\{ \left(\frac{1}{2}\right) + K \right\} \phi = [\eta] + [\eta]^2 K' \phi \quad (7)$$

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} \quad (8)$$

$$K = \left(\frac{1}{2}\right) \left(\frac{\sigma}{[\eta]\phi_n}\right) \quad (9)$$

where η_{sp} is the specific viscosity; K , the Kraemer constant; and K' , the Huggins constant = $(1/2) + K$. Similarly, Sudduth¹⁶ showed that a MacLaurin series expansion of eq. (1) can also be written in the Kraemer form as

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

The first few terms of eq. (10) can then be written as

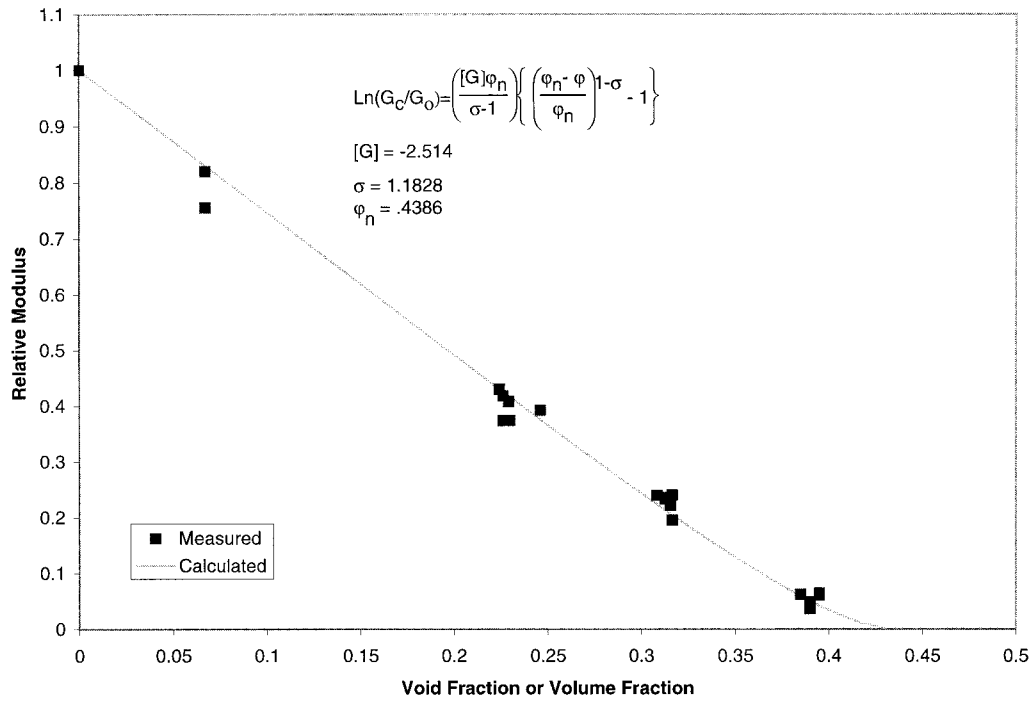


Figure 5 Wang's measured and calculated relative modulus for ceramic compaction versus void fraction or volume fraction or using the generalized modulus/viscosity equation.

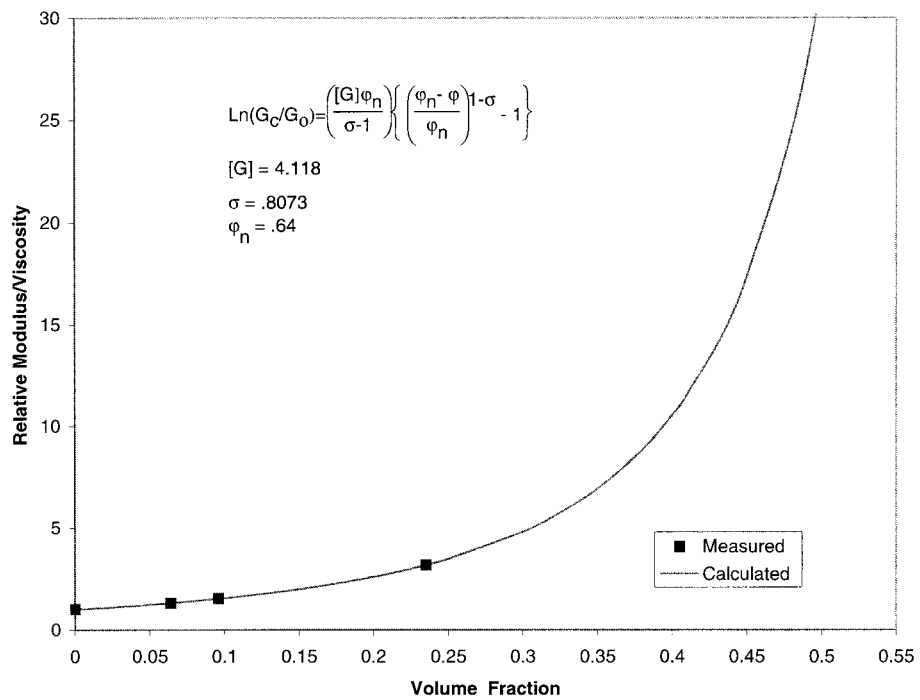


Figure 6 Smallwood's measured and calculated relative modulus/viscosity for carbon black in rubber versus volume fraction using the generalized modulus/viscosity equation.

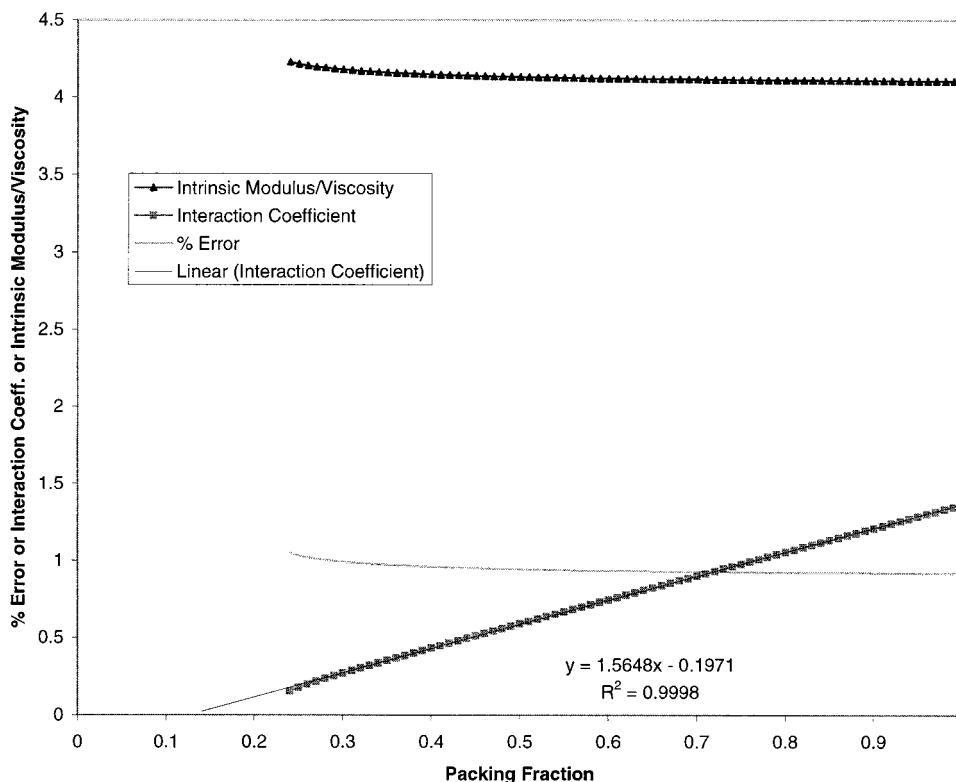


Figure 7 Percent error and associated analysis constants involved in fitting Smallwood's modulus data for carbon black in rubber.

$$\left(\frac{\ln(\eta/\eta_0)}{\phi}\right) = [\eta] + [\eta]^2 \left\{ \left(\frac{1}{2}\right) \left(\frac{\sigma}{[\eta]\phi_n}\right) \right\}$$

$$\phi = [\eta] + [\eta]^2 \{K\} \phi \quad (11)$$

If either a Huggins' plot of $[(\eta_{sp}/\phi)$ versus $\phi]$ or a Kraemer's plot of $\{[\ln(\eta/\eta_0)/\phi]$ versus $\phi\}$ is essentially linear over the available data set, then the data may be inadequate to generate unique values of the interaction coefficient, σ , and the maximum packing fraction, ϕ_n . For this type of data limitation, then the error in fitting the data to eq. (1) should be nearly identical for a significant range of values for the packing fraction, ϕ_n . This is clearly indicated in Figure 7 for the Smallwood carbon black rubber data. For these results, the locus of points forming the minimum errors evaluated for each packing fraction in fitting the data yields an amazingly linear relationship between the interaction coefficient, σ , and the packing fraction, ϕ_n .

For reference, both Huggins- and Kraemer-type plots for Vand's data are indicated in Figure 8. For this data set, neither the Huggins- nor the Kraemer-type plots were linear over the whole

concentration data range available. This then suggested that the probability of finding a unique value of both σ and ϕ_n was high. As previously indicated in Figure 2, it was, in fact, found that a unique value of the interaction coefficient, σ , and the packing fraction, ϕ_n , were obtained for Vand's data.

However, independent of whether a unique value can be obtained for σ and ϕ_n , a unique value can always be found for the intrinsic viscosity, $[\eta]$, as the volume fraction of particulate/solute approaches 0 or as $\phi \rightarrow 0$. This result is clearly indicated in eqs. (7) and (11) as $\phi \rightarrow 0$.

It is well known that Huggins' constant and Kraemer's constant are related as

$$K' = \left(\frac{1}{2}\right) + K \quad (12)$$

Sudduth¹⁶ also reviewed available experimental Huggins-type constants from the literature and found that they typically fall well within the range of $0 \leq K' \leq 1$. This range for the Huggins constant would correspond to a range for a Kraemer constant of $-0.5 \leq K \leq 0.5$.

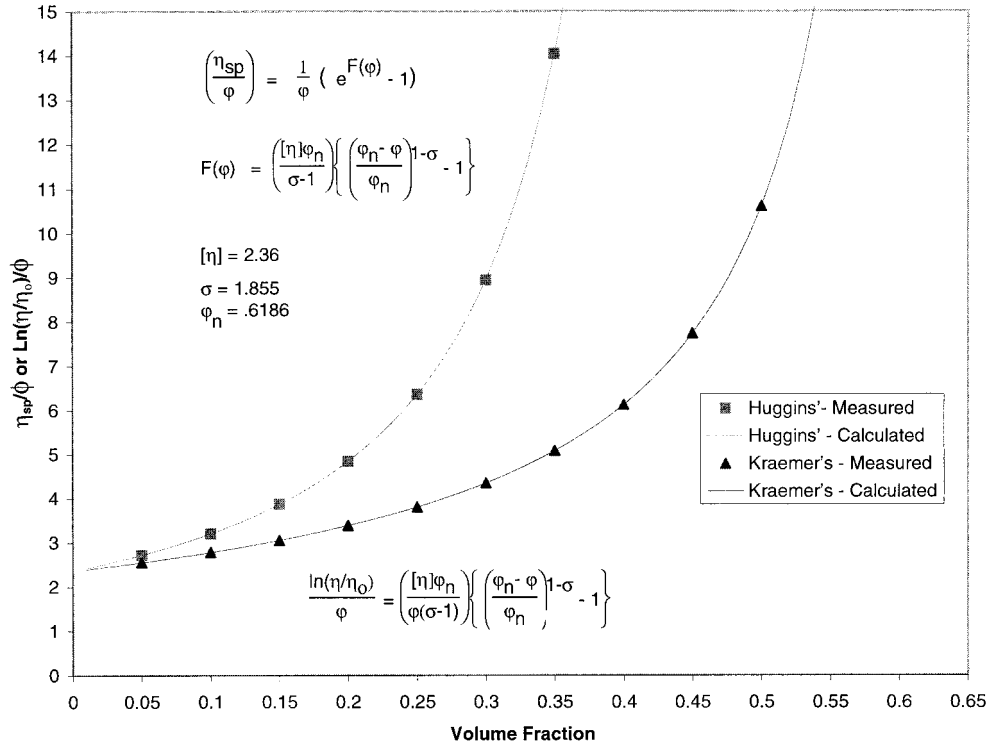


Figure 8 Huggins- and Kraemer-type plots of Vand's data.

If a good solvent requires a Huggins' constant of less than 0.5, then a negative Kraemer's constant would appear to be required. If Kraemer's constant must be negative for good-to-excellent solute/solvent systems, then at least one of the constants in eq. (9) must be negative. Since the packing fraction ranges from $0 \leq \phi_n \leq 1$ and cannot be negative by definition, then either the interaction coefficient, $[\sigma]$, must be negative or the Einstein intrinsic viscosity, $[\eta]$, must be negative.

As discussed earlier, the intrinsic modulus can be negative if the modulus of the filler, G_f is less than the modulus of the matrix, G_0 . Similarly, it would be expected that the Einstein intrinsic viscosity, $[\eta]$, can be negative if the shear modulus of the solute (or particle) is less than the shear modulus of the solvent (or matrix). However, since the intrinsic viscosity, $[\eta]$, for most polymer solutions and suspensions is predominantly positive, the obvious conclusion is that for polymer solutes or for particles the interaction coefficient, σ , must be negative to yield a Huggins' constant of less than 0.5. Thus, for good-to-excellent solutions, it would be expected that the interaction coefficient, σ , would be negative.

It is also important to note that Kraemer's constant contains all three of the primary vari-

ables in eq. (1). In addition, Kraemer's constant has been shown to be a direct measure of the solubility of the solute or particle in a solution or a composite. Therefore, a plot of Kraemer's constant for the locus of points of the solutions to eq. (1) should be a direct measure of the compatibility of the solute or particle in a solvent or matrix.

For reference, the locus of points representing the minimum data-fitting errors for the data of Vand, Nielsen, and Smallwood are summarized in Figure 9. Note that each of these sets of data represents Kraemer's constants that are positive over the whole range of the locus of points representing these error minimums. Since Vand's data represents a known suspension, it would be expected that the locus of points for Kraemer's constants in Figure 9 would be large and predominantly positive.

It is interesting that Kraemer's constants for Nielsen's data are more positive at the higher temperatures. Interestingly, as the temperature is reduced, these Kraemer's constants tended to be reduced, suggesting that the glass particles and the epoxy matrix start to improve compatibility as the temperature is reduced. Note, however, that there is a minimum in these data just below the T_g . It is not yet clear why Kraemer's constant for Nielsen's data would increase again

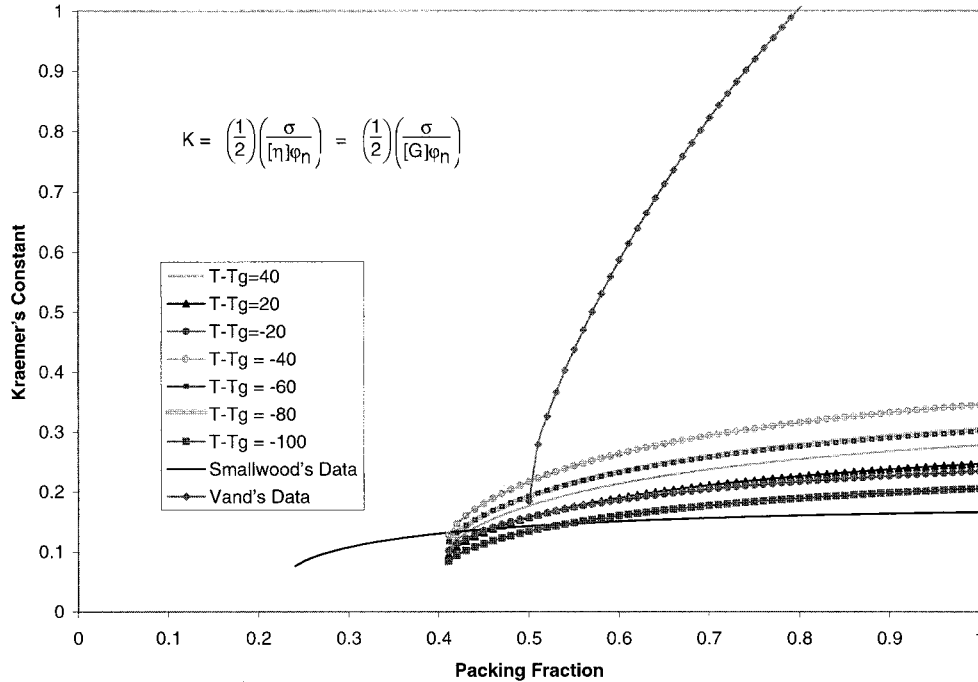


Figure 9 Kraemer's constants for Nielsen's Smallwood's, and Vand's data analysis.

after reaching a minimum below the T_g . The final decrease in the Kraemer constant after this increase would again appear to be related to an increase in the compatibility between the matrix and the particulate.

Finally, Kraemer's constants for Smallwood's data are lower than for either of the other two sets of data in Figure 9, suggesting that these carbon particles and rubber develop a better compatibility than for the materials associated with the

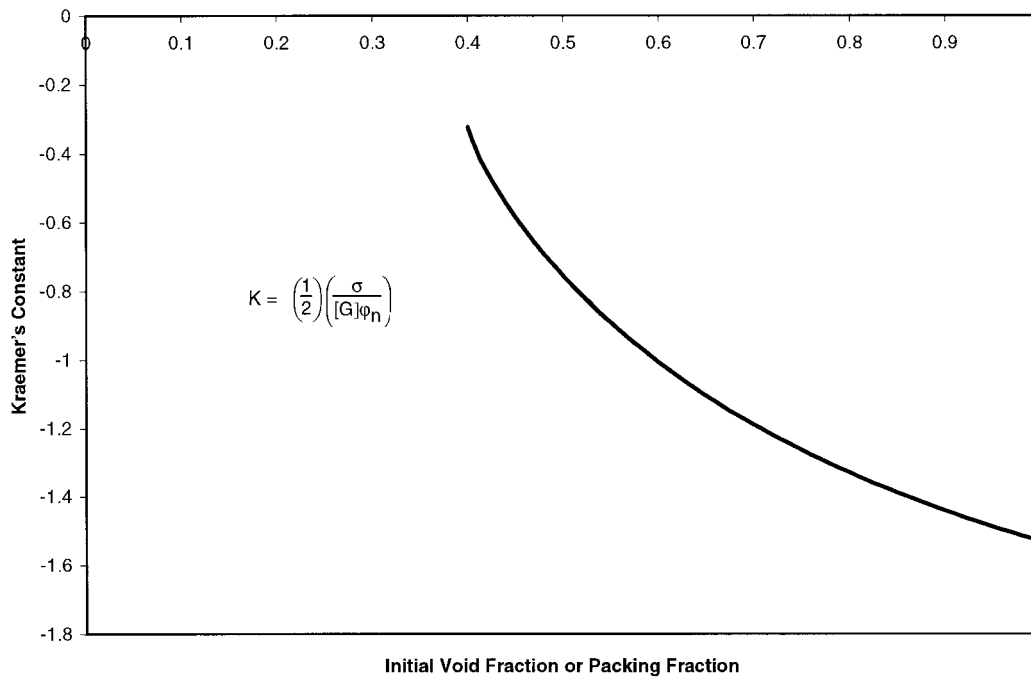


Figure 10 Kraemer's constants for Wang's ceramic compaction data analysis.

other sets of data. For reference, Kraemer's constants for the locus of points for Wang's data are also indicated in Figure 10. However, for this set of data, the interaction coefficient is positive and the intrinsic viscosity is negative. Since the interaction coefficient does not dominate the sign of Kraemer's constant for this case, it is not yet clear that the negative Kraemer constant is a direct indication that the voids form a solution in the alumina matrix during compaction.

CONCLUSIONS

It was shown that the intrinsic modulus can be effectively used in support of the generalized viscosity model. Even though the intrinsic modulus was found to encompass a wide range of potential positive values, it can also approach the Einstein value of 2.5 for spherical particles under specific conditions. It was also shown that the intrinsic modulus can be negative as was found for the Wang void compaction data.

For the sets of data analyzed, it was found that values of the interaction coefficient and the packing fraction were not necessarily unique if the data sets are limited to the lower particulate volume fractions. For those cases where a minimum amount of data is available, a new approach was introduced to address a relative measure of the compatibility of the particle and the matrix using Kraemer's constant.

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