

Model for Prediction of the Elastic Response of Reinforced Materials over Wide Ranges of Concentration

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Synopsis

A model for the prediction of the elastic response of reinforced materials over wide ranges of concentration is presented. The method is based on the mathematical analogy between the motion of particles suspended in viscous media and the elastic deformation of solids. The system is locally described by linearized forms of the elastic moduli. The validity of these relations is then extended to all concentrations under the assumption that any new portion of filler "sees" the existing structure as a noninteracting homogeneous matrix. The method predicts the behavior of reinforced materials with solid spherical inclusions and foams over wide ranges of concentration. The model, free from adjustable parameters, shows excellent agreement with existing experimental data. The extension of the method to other inclusion geometries is straightforward.

INTRODUCTION

In the search of a mathematical model for the mechanical behavior of heterogeneous systems, a complete analogy is found between the basic equations for elasticity theory and those for the motion of suspended particles in viscous media. The analogy can be easily proved by writing the equations of motion for an incompressible material in terms of displacements (Christensen¹):

$$-p_{,i} + Gu_{i,jj} + F_i = \rho \frac{\partial^2 u_i}{\partial t^2} \quad (1)$$

where G is the shear modulus, u_i is the displacement, F_i is the body force, p is the reactive pressure, and ρ is the density.

For comparison, the Navier–Stokes equations for an incompressible Newtonian fluid are

$$-p_{,i} + \eta v_{i,jj} + \rho F_i = \rho \left(\frac{\partial v_i}{\partial t} + v_j v_{i,j} \right) \quad (2)$$

where η is the viscosity, v the velocity, and F the body force per unit mass. Equations (1) and (2) have a term by term equivalence, with the exception of the nonlinear component $v_j v_{i,j}$ representing a convective acceleration. Under creeping flow conditions, acceleration terms become irrelevant, and a complete analogy can then be established. Given a certain geometry, the theoretical equations for a viscous flow problem and those for the elastic deformation of a

TABLE I
Models for Viscosity of Suspensions

Methodology		
Geometric model specified	Linearized solutions at ∞ dilution (Einstein ²)	Extension to high conc (Mooney, ³ Roscoe, ⁴ Brinkman, ⁵ Farris ⁶)
Additional information on random geometry of suspension, particle shape, etc.		Weissberg and Prager ⁷
Determination of bounds	Minimum entropy production	Hashin, ⁸ Prager ⁹

TABLE II
Models for the Prediction of the Elastic Response of Reinforced Materials

Methodology		
Geometric model specified	Linearized solutions at ∞ dilution (Dewey ¹⁰)	Extension to high conc. (Kerner, ¹¹ Van der Poel, ¹² Budiansky, ¹³ Roscoe ¹⁴)
Additional information on packing arrangements		Hashin ¹⁵
Determination of bounds for elastic moduli	Energy theorems Variational methods	Voigt ¹⁶ Paul ¹⁷ Hashin and Shtrikman ¹⁸

solid are of the same form; e.g., shear rate:viscosity; shear strain:shear modulus. For a suspension of rigid particles in an incompressible matrix, there is a simple relationship between relative viscosities and relative shear moduli (relative to the unfilled matrix):

$$\eta/\eta_m = G/G_m$$

Thus, if a theory for the viscosity of a filled system or suspension is available, it can be used to estimate the shear modulus of an elastic system.

A second analogy can also be found in relation to the methods used in the solution of both problems, as indicated in Tables I and II. In very general terms, it is found that there is an important group of contributions based on the establishment of an idealized geometry and packing arrangement (top of Tables I and II). A second group is based on the determination of bounds, which avoids (or reduces) the idealization problem by use of energy and

variational techniques (bottom of Tables I and II). Typical limitations of geometric models and bound methods gave origin to a third group of contributions containing elements of both techniques (middle of Tables I and II).

With regard to the problem of predicting the elastic performance of reinforced materials (Table II), most of the models deal with specific idealized geometries and packing arrangements. These theories provide relations between any two independent elastic constants among a shear modulus (G), a bulk modulus (K) and a Young's modulus (E):

$$K = K(G_m, K_m, G_i, K_i, c)$$

$$G = G(G_m, K_m, G_i, K_i, c)$$

where subindices m and i refer to the matrix and the inclusion and c is the volume fraction of the inclusion. Smith¹⁹ noted that through algebraic manipulation, most of these theories can be displayed in the form of a generalized "rule of mixtures":

$$G = G_m + (G_i - G_m)\Phi = (1 - \Phi)G_m + \Phi G_i$$

where Φ takes different functional forms. According to the most familiar contributions,

$$\Phi = \frac{(8 - 10\nu_m)G_m + (7 - 5\nu_m)G_m}{(8 - 10\nu_m)G_i + (7 - 5\nu_m)G_m} c \quad (\text{approximate Van der Poel}^{12,19})$$

$$\Phi = \frac{(8 - 10\nu_m)G + (7 - 5\nu_m)G_m}{(8 - 10\nu_m)G_i + (7 - 5\nu_m)G_m} c \quad (\text{Kerner}^{11})$$

$$\Phi = \frac{(8 - 10\nu)G + (7 - 5\nu)G}{(8 - 10\nu)G_i + (7 - 5\nu)G} c \quad (\text{Budiansky}^{13})$$

where G and ν are the shear modulus and Poisson's ratio of the composite.

All of the previous models developed by elastic analysis, i.e., deformation of the matrix and inclusion, have a common feature: A specific idealized geometry and packing arrangement has to be assumed. In many reinforced materials, this regularity in geometry does not exist, and the material cannot be identified with any particular arrangement or ensemble valid throughout the whole structure. Thus, the previous treatments, in the strictest sense, do not truly represent a real reinforced system. One way to avoid this idealization problem is through the use of variational techniques, which do not need to use a precise geometric model.

The most elementary type of bounds can be calculated through the formalism of the complementary energy and strain energy theorems (Voigt¹⁶ and Paul¹⁷). However, the resulting bounds are often too far apart to be useful.

In order to improve these bounds, Hashin and Shtrikman¹⁸ formulated new variational theorems on the basis of polarization tensors. However, limitations in the applicability of bounds still persist. In general, it is not known if the

calculated bounds are indeed the most restrictive, and the problem becomes a trade-off between the amount of information introduced in the formulation, and the resulting contiguity of the bounds.

As a rule, it may be said that the usefulness of bounds is restricted to systems where the properties of the phases are similar, i.e., metal alloys. In polymer reinforcement, however, the differences between matrix and inclusion may be considerable. As a consequence, the upper and lower bounds tend to separate, making this technique inadequate for any predictive purpose.

PROCEDURE

As indicated earlier, a basic problem in the theory of viscosity of suspensions is the determination of correlations useful at high concentrations. Most of the contributions are based on extensions of Einstein's law of viscosity at infinite dilution.

The analogous problem of correlating the elastic properties of heterogeneous systems over wide ranges of concentration has not been successfully solved. As will be discussed later, predictions according to different theories show a considerable lack of agreement.

The proposed model is based on a differential scheme similar to that used by Brinkman⁵ and Roscoe⁴ for the prediction of the viscosity of suspensions at high concentrations. In a later publication, Roscoe¹⁴ tried to extend the method to the prediction of elastic properties of reinforced materials. McLaughlin²⁰ presented a similar differential scheme and evaluated its estimates in relation to the Hashin-Shtrikman bounds.

The present model is based on the calculation by elastic analysis of any two independent parameters for the filled system, namely, the shear modulus, the bulk modulus, or the Young's modulus. Calculations may proceed as follows¹:

1. describe the deformation state (simple shear, etc.),
2. choose adequate coordinates for a given geometry,
3. state the deformation equations for matrix and inclusion,
4. state continuity of stress at the interface,
5. reduce volume integrals to surface integrals by Eshelby's formula,¹
6. integrate.

For spherical inclusions and dilute conditions, the shear modulus takes the form

$$\frac{G}{G_m} = 1 - \frac{15(1 - \nu_m)(1 - (G_i/G_m))}{7 - 5\nu_m + 2(4 - 5\nu_m)G_i/G_m} c = 1 + fc \quad (3)$$

and the bulk modulus is

$$\frac{K}{K_m} = 1 + \frac{(1/K_m)(K_i - K_m)}{1 + [(K_i - K_m)/(K_m + (4/3)G_m)]} c = 1 + gc \quad (4)$$

where c denotes the volume fraction and the subindices m and i refer to the matrix and the inclusion.

For an infinitely rigid inclusion ($G_i \rightarrow \infty$) in an incompressible matrix ($\nu_m = 0.5$), eq. (3) results in a relation similar to Einstein's law of viscosity:

$$\frac{\eta}{\eta_m} \approx \frac{G}{G_m} = 1 + 2.5c \quad (5)$$

Consider a suspension containing a small concentration (volume) c_1 of spheres into which is placed a small concentration c_2 of spheres, and into this again a small concentration c_3 of spheres, and so on, up to n sets of spheres, and let the total concentration be c . Then on adding another set of spheres of concentration (volume fraction) c_{n+1} , the new total concentration (volume fraction) is

$$c(1 - c_{n+1}) + c_{n+1} \quad (6)$$

So the increase in concentration is

$$\Delta c = c_{\text{final}} - c_{\text{initial}} = c_{n+1}(1 - c) \quad (7)$$

If the original suspension is considered a homogeneous medium (matrix) around the new spheres which are in small concentrations, it is possible to express the increment in shear modulus according to eq. (3) as

$$\frac{G_{n+1}}{G_n} = 1 + f c_{n+1} \quad (8)$$

Defining

$$\Delta G = G_{n+1} - G_n$$

and replacing c_{n+1} according to eq. (7),

$$\Delta G/G = f c_{n+1} = f \Delta c / (1 - c)$$

For infinitely small increments in concentration,

$$\Delta c \rightarrow dc$$

$$\Delta G \rightarrow dG$$

and

$$\frac{dG}{dc} = \frac{Gf}{(1 - c)} \quad (9)$$

This differential expression for the increment in concentration can now be used in eq. (3). After following a similar reasoning for the bulk modulus K ,

eqs. (3) and (4) become

$$\frac{dG}{dc} = \frac{G15(1-\nu)(1-G_i/G)}{[7-5\nu+2(4-5\nu)G_i/G](1-c)} \quad (10)$$

$$\frac{dK}{dc} = \frac{(K_i - K)}{(1 + \{(K_i - K)/[K + (4/3)G]\}) (1 - c)} \quad (11)$$

where $\nu = (3K - 2G)/2(3K + G)$ is the Poisson's ratio.

Equations (10) and (11) constitute a coupled system to be numerically integrated with the following boundary conditions:

$$\begin{aligned} c=0, \quad G &= G_m \quad (\text{matrix properties}) \\ K &= K_m \\ c=1, \quad G &= G_i \quad (\text{inclusion properties}) \\ K &= K_i \end{aligned} \quad (12)$$

RESULTS

Solid Inclusions

Smith⁹ compared the behavior of well-known models for the prediction of the mechanical response of reinforced materials, i.e., Van der Poel,¹² Kerner,¹¹

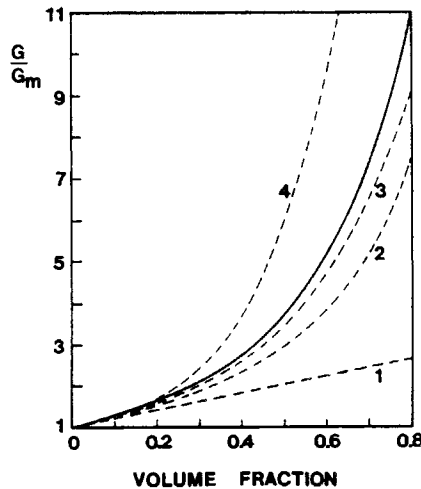


Fig. 1(a). Relative shear modulus vs. volume fraction of filler for $G_i/G_m = 30$, $\nu_i = 0.25$, $\nu_m = 0.4$ (from Smith⁹): (—) model performance; (---) predictions with different models: (1) approximate Van der Poel¹²; (2) Kerner or Hashin and Shtrikman highest lower bound¹⁸; (3) corrected Van der Poel¹²; (4) Budiansky.¹³

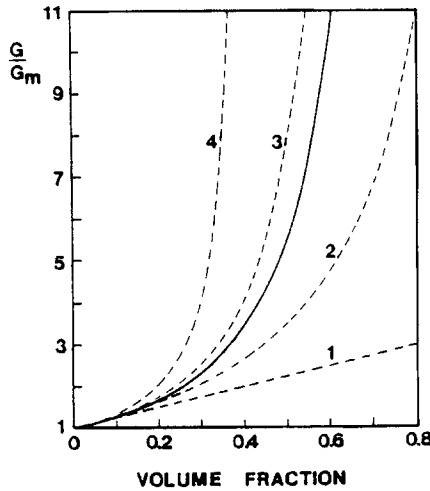


Fig. 1(b). Relative shear modulus versus volume fraction of filler for $G_i/G_m = 70,000$, $\nu_i = 0.25$, $\nu_m = 0.5$ from Smith¹⁹: (—) model performance; (---) predictions with different models: (1) approximate Van der Poel¹²; (2) Hashin and Shtrikman highest lower bound¹⁸; (3) corrected Van der Poel¹²; (4) Budiansky.¹³

Budiansky,¹³ etc. In order to test the performance of the present model, the same parameter values were used in the simulation. Data in Figure 1(a) have been calculated with a shear modulus ratio $G_i/G_m = 30$ and Poisson's ratios $\nu_i = 0.25$ and $\nu_m = 0.40$, representing the case of glass spheres embedded in an epoxy matrix.

Figure 1(b) has been calculated with $G_i/G_m = 70,000$, $\nu_i = 0.25$, $\nu_m = 0.5$, representing the expected shear properties of glass spheres embedded in a lightly vulcanized matrix of natural rubber.

In both cases, a considerable discrepancy among the different models is observed. The inconvenience of bounds calculated according to Hashin and Shtrikman¹⁸ is also stressed. The predictions of the present simulation are close to those of Van der Poel.¹²

Richard²¹ presented experimental data for elastic modulus and Poisson's ratio of a polyester matrix reinforced with glass spheres ($G_m = 5.94 \times 10^8$ Pa, $\nu_m = 0.45$, $G_i = 2.90 \times 10^{10}$ Pa, $\nu_i = 0.21$). This author compared his experiments with the predictions of several theories. Figure 2 indicates the excellent prediction of the present model, while theories by Kerner¹¹ and Hill^{22,23} only perform well at filler concentrations below 20 vol %.

Richard's data²¹ were also used by Smith¹⁹ for comparison with other theoretical contributions as indicated in Figure 3(a) for relative moduli, and Figure 3(b) for Poisson's ratio. Calculations were performed with $G_m = 5.84 \times 10^8$ Pa, $\nu_m = 0.44$, $G_i = 2.90 \times 10^{10}$ Pa, and $\nu_i = 0.21$.

Smith²⁴ compared his own experimental findings on epoxy resin-glass spheres systems with several theoretical predictions. The properties of matrix and inclusion are $E_m = 2.68 \times 10^9$ Pa, $\nu_m = 0.394$, $E_i = 7.6 \times 10^{10}$ Pa, $\nu_i =$

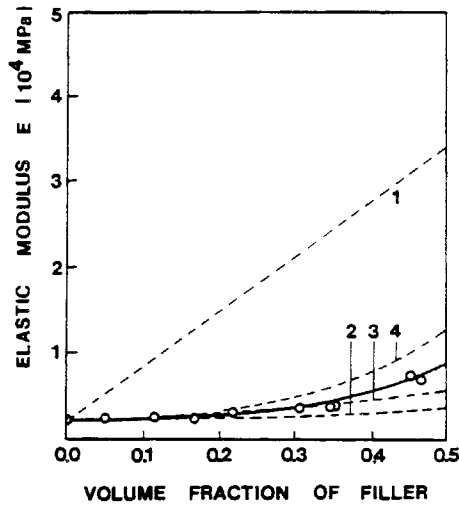


Fig. 2. Elastic modulus vs. volume fraction of filler for the case of glass beads in a polyester matrix. Experimental data from Richard²¹; (—) model performance; (---) predictions according to: (1) isostrain; (2) isostress; (3) Kerner¹¹; (4) Hill.^{22,23}

0.23. Results from those predictions are plotted and compared to the present model in Figure 4.

Foams

Equations (10) and (11) have been integrated for the case of a foam by assuming negligible moduli for the inclusion,

$$G_i \rightarrow 0$$

$$K_i \rightarrow 0$$

The simulation was compared with the experimental results of Gent and Thomas²⁵ for a vulcanized rubber foam ($E_m = 2.59 \times 10^6$ Pa, $\nu_m = 0.49$). Figure 5 shows excellent agreement in the prediction of relative modulus vs. relative density δ ,

$$\delta = \delta_{\text{foam}}/\delta_{\text{rubber}} \approx 1 - c \quad (13)$$

where c is, as before, the volume fraction of the inclusion.

The performance of the model in the prediction of foam properties was also tested with the experimental work of Moore et al.²⁶ for a variety of foamed thermoplastics (PVC, polypropylene copolymer, styrene-acrylonitrile copolymer, etc.). These authors observed that plots of relative modulus (relative to the solid matrix) vs. relative densities (δ) could be correlated with a single curve in shear, tension, and compression according to

$$\frac{E_{\text{foam}}}{E_{\text{solid}}} = \left[\frac{\text{density of foam}}{\text{density of solid}} \right]^2 = (\delta)^2 = (1 - c)^2 \quad (14)$$

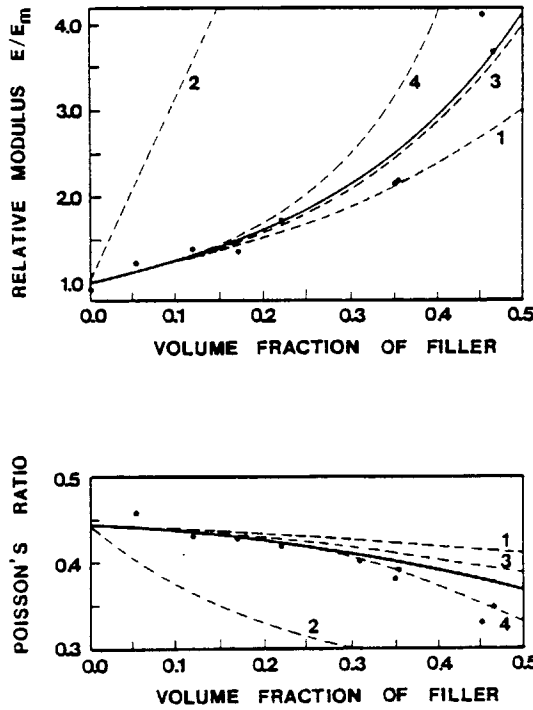


Fig. 3. Relative Young's modulus E/E_m (3a) and Poisson's ratio (3b) vs. volume fraction of filler for the case of glass beads in a polyester matrix. Experimental data from Richard²¹; (—) model performance; (---) predictions with different models: (1) Hashin and Shtrikman highest lower bound¹⁸; (2) Hashin and Shtrikman least upper bound¹⁸; (3) Van der Poel¹²; (4) Budiansky.¹³

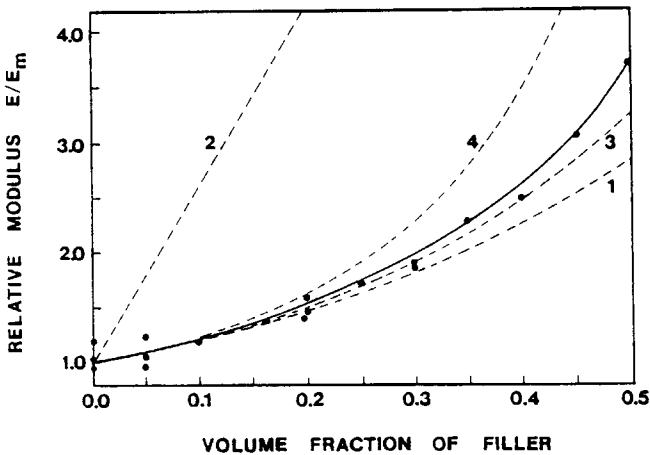


Fig. 4. Relative Young's modulus E/E_m vs. volume fraction of filler for the case of glass spheres in an epoxy matrix. Experimental data by Smith²⁴; (—) model performance; (---) predictions with models by: (1) Hashin and Shtrikman highest lower bound¹⁸; (2) Hashin and Shtrikman least upper bound¹⁸; (3) Van der Poel¹²; (4) Budiansky.¹³

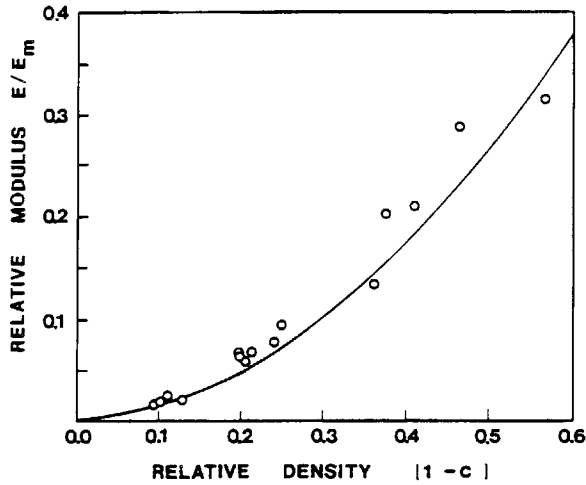


Fig. 5. Young's modulus of a highly vulcanized rubber foam E_f relative to the solid rubber E_m vs. volume fraction of rubber in the foam: (—) model performance. Experimental points were determined by Gent and Thomas.²⁵

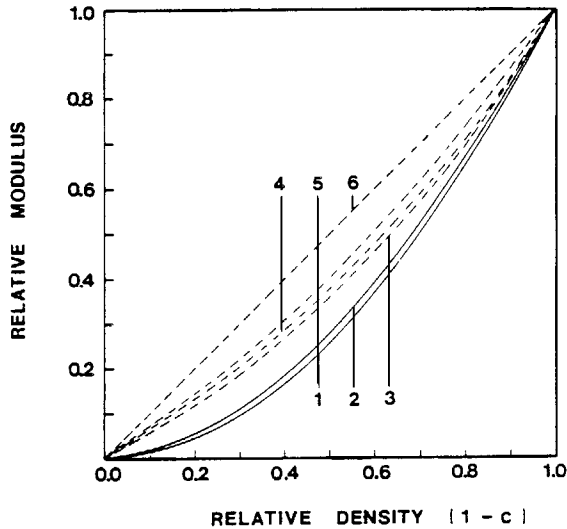


Fig. 6. Relative moduli of foams vs. relative densities. Calculations here have been performed for the thermoplastics described by Moore et al.²⁶: (—) model performance for: (1) Young's modulus; (2) shear modulus; (---) predictions according to different models: (3) Kerner¹¹; (4) square-in-square model²⁷; (5) cube-in-cube model²⁷; (6) law of mixtures. Moore et al.²⁶ correlated experimental moduli with a square law which results coincident with curve 1 (model prediction).

Figure 6 compares the predictions of several theories with the empirical findings of Moore et al.²⁶ and the results of the present model. Simulations were performed for a polypropylene copolymer characterized by $E_m = 1.13$ GPa, $\nu_m = 0.41$. Again, the proposed method shows total agreement with the experimental values.

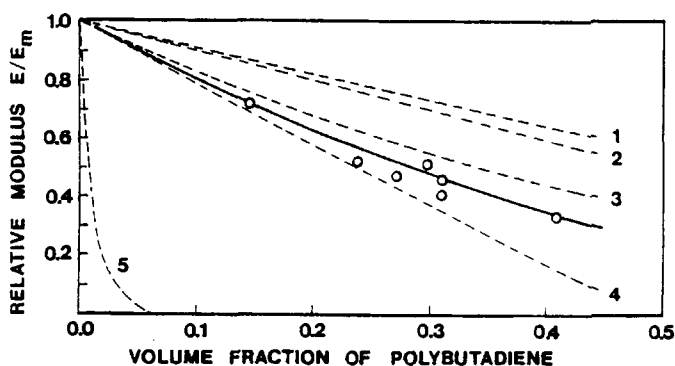


Fig. 7. Relative modulus of acrylonitrile-butadiene-styrene (ABS) copolymer vs. volume fraction of polybutadiene. Experimental data by Holliday and Mann²⁸; (—) model performance; (---) predictions with different models: (1) Van der Poel¹²; (2) parallel; (3) Kerner¹¹; (4) Reiner-Haashin²⁹; (5) series.

Low Modulus Incompressible Inclusions (Rubbers)

For the limiting case of an incompressible matrix ($\nu_m = 0.5$) with $G_i = 0$, eq. (10) admits an analytical solution as

$$G/G_m = (1 - c)^{5/3} \quad (15)$$

which represents the behavior of rubber modified polymers.

Holliday and Mann²⁸ compared several theories for a case representing soft spheres in a rigid matrix (Fig. 7). The experimental data correspond to acrylonitrile-butadiene-styrene (ABS) polymers, which consist of a dispersion of soft polybutadiene rubber spheres in a styrene-acrylonitrile (SAN) copolymer matrix, which has a relatively high modulus.

The different available theories examined are not in good agreement, as compared in Figure 7. The proposed model was tested with typical values for styrene-acrylonitrile copolymer (SAN) ($E_m = 3.1 \times 10^{-3}$ MPa, $\nu_m = 0.38$),³⁰ and $E_i/E_m = 0$. Results presented in Figure 7 indicate good prediction of the experiments.

CONCLUSIONS

Despite many contributions, the problem of predicting the elastic behavior of reinforced materials over wide ranges of concentration has not been satisfactorily solved.

Different theories based on well-defined geometric models present a considerable divergence of results. The use of bound methods has been proven inadequate for problems in polymer reinforcement, where solutions become a trade-off between the contiguity of the bounds and the amount of information (complexity) introduced in the model.

In the present work, a correct linearized relation for the elastic deformation of matrix and inclusion is assumed at each concentration. This relation, which is valid locally, can then be extended to all concentrations under the assump-

tion that any new portion of filler "sees" the existing structure as a noninteracting homogeneous matrix.

The model, presenting no adjustable parameters, accurately represents available experimental data on solid spherical inclusions and foams. The method can be readily extended to other geometries for the inclusion.

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