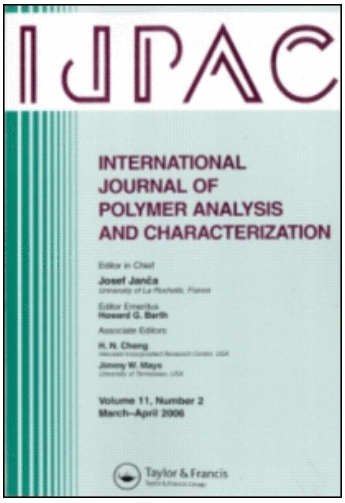

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Ultrasonic Measurements of Longitudinal and Shear Moduli in Loaded Epoxy Networks

T. N. Nguyen; M. Lethiecq[a]; F. Levassort[a]; F. Patat[a]
[a] G.I.P. ULTRASONS—Fac, Médecine—LBM, TOURS cedex, FRANCE

To cite this Article Nguyen, T. N. , Lethiecq, M. , Levassort, F. and Patat, F.(1995) 'Ultrasonic Measurements of Longitudinal and Shear Moduli in Loaded Epoxy Networks', International Journal of Polymer Analysis and Characterization, 1: 4, 277 — 287
To link to this Article: DOI: 10.1080/10236669508233881
URL: http://dx.doi.org/10.1080/10236669508233881

Int. J. Polymer Analysis & Characterization
1995, Vol. 1, pp. 277–287
Reprints available directly from the publisher
Photocopying permitted by license only

Ultrasonic Measurements of Longitudinal and Shear Moduli in Loaded Epoxy Networks

T. N. NGUYEN,* M. LETHIECQ, F. LEVASSORT, and F. PATAT

G.I.P. ULTRASONS—Fac. Médecine—LBM, 2 bis boulevard Tonnellé BP 3223—37032 TOURS cedex (FRANCE)

(Received July 8, 1994; in final form February 15, 1995)

The purpose of this study is to use an ultrasonic method to characterize the longitudinal (Young) and shear moduli of (0–3) composites made from novolac-epoxy/anhydride loaded with tungsten particles. The experimental results obtained for different volume fractions of filler and different particle sizes are compared to the predictions of different models based on scattering theories.[1-3] Scanning electron microscopy is used to determine size and shape of the tungsten particles and the microstructure of the composites. Good agreement between experiments and the predictions based on multiple scattering theories is obtained when the particle shape is almost spherical. The results also show that the particle size has no effect on the mechanical properties as long as the particles are much smaller than the ultrasonic wavelength.

KEY WORDS Ultrasonic characterization, composite, epoxy, mechanical properties, filler, scattering theory

INTRODUCTION

A (0–3) composite is a mixture of two materials, one of them in the form of inclusions (or filler) and the other in the form of a matrix. The "0" is the connectivity of the filler which is not self connected in any dimension and the "3" is the connectivity of the matrix which is interconnected in all three dimensions.[4] The (0–3) polymer composites are widely used and it is well known that the incorporation of a filler in a polymer can improve the physical and mechanical properties of the material. The addition of a filler in the polymer can change various properties, such as electric and thermal conductivity, volume contraction during the curing process, elastic constants or thermal degradation of the material.

In this paper, we are interested in the mechanical changes in the polymer accompanying filler incorporation. We use an ultrasonic method for measuring the moduli of composites and the measurements are compared to the theoretical values given by different models using elastic wave scattering theory.

*Correspondence to: Dr. Ngoc Tuan Nguyen, G.I.P. Ultrasons, Faculty Medicine, LBM, 2 bis boulevard Tonnellé BP 3223-37032 TOURS cedex (FRANCE) Fax 33-47366120

ULTRASONIC TECHNIQUE

The characterization of materials using ultrasonic waves has become a standard method mainly because it is nondestructive and simple to use. It consists in measuring the velocities of ultrasonic waves travelling in the material under test. The types of waves generally used in ultrasonic testing are compressional and shear waves. In a compressional wave, the direction of particle motion and of wave motion are the same. In the case of a shear wave, the particle motion is perpendicular to the direction in which the wave travels. By measuring the longitudinal velocity v_L of the compressional wave and the shear velocity v_S of the shear wave, we can calculate the bulk modulus K the shear modulus G and the longitudinal (Young) modulus E by using the following equations:

Stand

$$G = \rho v_S^2 \tag{2}$$

$$E = \frac{9KG}{3K + G} \tag{3}$$

where ρ is the density of the composite which is simply the average density:[5]

$$\rho = \rho_1 v_1 + \rho_2 v_2 \tag{4}$$

v_1, ρ_1, v_2, ρ_2 are the volume fractions and the densities of the matrix and fillers, respectively.

The longitudinal velocity was measured by transmission in water at 22 ± 1°C (Fig. 1). Two transducers (ISL 0104 GP at 1 MHz, ISL 0303 HR at 3.5 MHz and ISL 1002 HR at

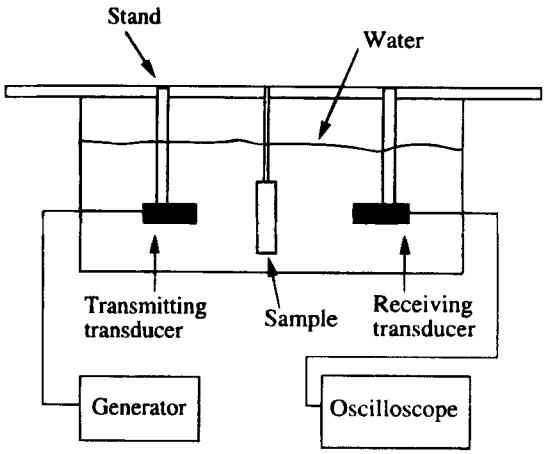

FIGURE 1 Longitudinal velocity measurement scheme.

10 MHz, Technisonic Research Inc., Fairfield, Connecticut) are placed on each side of the sample under test and the velocity is derived from the difference in time of flight between the two transducers with and without the sample. A Hewlett Packard signal generator (HP 3314A) was used to generate bursts of 10 cycles at frequencies between 1 and 10 MHz with 0.5 MHz steps. The transmitted signals were directly sent to a digital scope (HP 54504A).

The shear velocity was determined by a contact method where the sample is sandwiched between two shear wave transducers (V154 at 2.25 MHz, Panametrics Inc., Waltham, Massachusetts). Honey was used for acoustic coupling. An Accutron 1035PR was used to generate a pulse and to amplify the signals transmitted through the sample before they were sent to the oscilloscope.

Measurements were performed at frequencies between 1 and 10Mhz. In this frequency domain, the influence of viscoelasticity is negligible and the wavelengths are much larger than the inclusion size, so we can consider that the materials are purely elastic and not dispersive.

MATERIALS AND PREPARATION

Materials

The (0–3) composite were obtained by mixing epoxy resin and tungsten particles. The epoxy resin (Novolac epoxy and anhydride) was supplied by Cotronics Corporation (Brooklyn, New York). The filler was commercial tungsten powders with several particle sizes. Particle size measurements of these powders were carried out on a Malvern MSE analyser (Malvern Instruments, Orsay, France). This instrument uses the principle of Fraunhofer diffraction where a parallel, monochromatic beam of laser (red light $\lambda = 633$ nm) illuminates the suspension of particles in deionized water. The light diffracted by the particles gives a diffraction pattern which allows to measure the average particle size and particle size distribution.[6] These measurements are listed in Table I.

The shape of the particles was studied by scanning electron microscopy (SEM). Values of the density and elastic constants for each constituent of the composite are given in Table II. The values for the epoxy resin were measured while those concerning tungsten powder were taken from ref.[7]

TABLE I

Average particle size and particle size distribution of different tungsten powders

Average particle size (μm)	Particle size distribution (μm)
0.5	0.1 to 0.6
1	0.5 to 5
5	3 to 10
10	2 to 29
14	7 to 25

TABLE II

Density and elastic moduli of epoxy resin and tungsten

Constituent	Density *(g/cm³)*	Longitudinal Modulus *(GPa)*	Shear Modulus *(GPa)*
Epoxy resin	1.26	4.5	1.6
Tungsten	19.3	414	162

Manufacture of (0–3) composites

The filler powder and the epoxy resin were mixed and warm pressed under 200 bars and at 100°C for 2 h. Samples were then heated in an oven at 175°C for 4 h to complete polymerization of the resin. The samples had a thickness of approximately 5mm and a diameter of 40mm. The different composites were made with the same polymer phase but with different tungsten particle sizes. Volume fractions of filler varied between 0.02 and 0.6.

THEORETICAL MODELS

The methods for calculating macro-constants of heterogeneous media have a long history. Many theories have been proposed, the most simple models being those of Reuss[8] and Voigt.[9] Reuss assumes constant stress throughout the solid and Voigt assumes constant strain. These two models lead to extreme upper and lower limits. More restrictive limits are obtained by Hashin-Shtrikman whose analysis is based on energetic considerations[10]. Empirical curve fitting methods have also been proposed,[11,12] but an arbitrary parameter is left unspecified.

Recently, new methods have been proposed using scattering approximations for estimating elastic properties of composite materials: the average T-matrix approximation (ATA), the coherent potential approximation (CPA), and the differential effective medium (DEM).[2] Devaney and Levine[3] have proposed another model based on a self-consistent formulation of multiple-scattering theory. These different approaches assume that the inclusions are spherical and that they all have the same radius. These models also involve the assumption that the wavelengths of the incident wave and the scattered waves are much longer than the size of the inclusions. The homogeneous medium (the matrix) has a bulk modulus K_1 and a shear modulus G_1. The spherical inclusions have a bulk modulus K_2 and a shear modulus G_2. The parameters K and G are the moduli of the effective composite medium. We will examine these models in the case where there is only one type of filler.

Average T-matrix Approximation (ATA)

The problem is formulated in terms of scattering phenomena for long wavelengths. The displacement fields for waves scattered by an effective composite medium and individual inclusions are equated.[5] This approach is a single-scattering approximation, it neglects the multiple-scattering contributions. ATA model gives the following equations:

$$\begin{cases} \dfrac{1}{K+\frac{4}{3}G_1} = \dfrac{v_1}{K+\frac{4}{3}G_1} + \dfrac{v_2}{K+\frac{4}{3}G_1} \\ \dfrac{1}{G+F_1} = \dfrac{v_1}{G_1+F_1} + \dfrac{v_2}{G_2+F_1} \end{cases} \tag{5}$$

where

$$F_1 = \frac{G_1}{6}\left(\frac{9K_1+8G_1}{K_1+2G_1}\right) \tag{6}$$

Coherent Potential Approximation (CPA)

The coherent potential approximation is determined by requiring that the single-scattering contributions from all the inclusions equal zero[1] (the multiple-scattering effects are not taken into account). The equations are:

$$\begin{cases} \dfrac{1}{K+\frac{4}{3}G} = \dfrac{v_1}{K_1+\frac{4}{3}G} + \dfrac{v_2}{K_2+\frac{4}{3}G} \\ \dfrac{1}{G+F} = \dfrac{v_1}{G_1+F} + \dfrac{v_2}{G_2+F} \end{cases} \tag{7}$$

where

$$F = \frac{G}{6}\left(\frac{9K+8G}{K+2G}\right) \tag{8}$$

Differential Effective Medium (DEM)

The differential effective medium theory is defined by homogenization. The volume fractions of the two constituents are $x = v_1$ and $y = v_2 = (1 - v_1)$. Starting with pure material 1, an infinitesimal dy amount of material 2 is added. The mixture is then homogenized and the process repeated until the volume fraction of constituent 2 in the composite equals v_2.[13] The equations are:

$$\begin{cases} (1-y)\dfrac{d}{dy}[K(y)] = \dfrac{K_2-K(y)}{K_2+\frac{4}{3}G(y)}\left[K(y)+\frac{4}{3}G(y)\right] \\ (1-y)\dfrac{d}{dy}[G(y)] = \dfrac{G_2-G(y)}{G_2+F(y)}[G(y)+F(y)] \end{cases} \tag{9}$$

with the boundary conditions $K(y=0) = K_1$
$G(y=0) = G_1$

where F is given by Equation (8)

Devaney model

The Devaney model is based on a self-consistent formulation of multiple-scattering theory[3]. In the particular case where the wavelengths are much larger than the particle size, and the concentration of inclusions is low, this model is reduced to the coherent potential

approximation (CPA). However, when the multiple-scattering effects are not negligible (i.e., when the concentration of inclusions is important), the Devaney model differs markedly from the CPA model. According to this model, the bulk modulus and the shear modulus of the composite are given by:

$$\begin{cases} K = K_1 + v_2 \dfrac{(3K + 4G)(K_2 - K_1)}{3K + 4G + 3(K_2 - K_1)} \\ G = G_1 + v_2 \dfrac{5(3K + 4G)\,G(G_2 - G_1)}{(15K + 20G)\,G + 6(K - 2G)(G_2 - G_1)} \end{cases} \tag{10}$$

The elastic bulk modulus K, the shear modulus G and the longitudinal modulus E were calculated using the different relations given previously in Equations (3),(5),(7),(9) and (10). These equations were solved numerically by iteration. We then compared the calculate values and the experimental values.

RESULTS AND DISCUSSION

The theoretical limits and experimental values are shown in Figures 2 and 3 for five different tungsten particle sizes (0.5, 1, 5, 10, and 14 μm). For small particle sizes as 0.5 μm for example, the specific area is large, so it is not possible to reach volume fractions over 0.3 because at higher volume fractions, the resin does not wet all the particles. However, for large particle sizes, for example 14 μm, the filler tends to form a sediment during the curing when the volume fraction is lower than 0.35. The SEM photographs verify that the tungsten particle distribution in the matrix is homogeneous as shown in Figures 4 for 5 μm size particles and a volume fraction of 0.37.

The upper limit is the Voigt model, the lower limit the Reuss model, and the Hashin-Shtrikman limits are situated between these two models. The longitudinal and shear moduli of composites seem independent of the particle size. It can be noted that for very low concentrations of inclusions ($v_2 < 0.1$), the measured values are close to the lower limit of Hashin-Shtrikman. In this interval the Reuss model also produces very close values. When v_2 is greater than 0.1, the experimental results deviate from theoretical curves. We also noticed that in this domain of frequency between 1 and 10 MHz, the moduli are independent of the frequency.

The ATA, CPA, DEM, and Devaney models are shown in Figures 5 and 6. The ATA model produces the same values as the Hashin-Shtrikman lower limit. The DEM model is slightly closer to the experimental results than the ATA model. The CPA shows a good agreement with experimental values. Up to volume fractions of 0.4, the Devaney model is the only model which shows good agreement with all our experiments.

A closer look at these different tungsten powders reveals two extreme cases: on the one hand, the composites with 5-μm particles for which modulus values are very close to theoretical data, and on the other hand, the 0.5-μm powder for which modulus values appear to deviate from theoretical values (Figs. 7 and 8). Our suggestion for an explanation of these results is that the particle size is not taken into account in the Devaney model, the shape of the particle is supposedly spherical. It has been observed[14, 15] that the particle shape has a considerable influence on the elastic constants. The SEM pho-

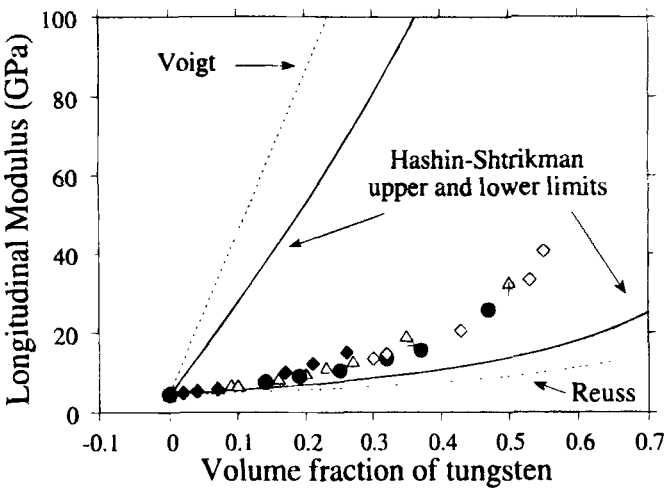

FIGURE 2 Voigt-Reuss and Hashin-Shtrikman limits for epoxy-tungsten composite system with experimental values (average particle sizes: ◆ 0.5 μm, △ 1 μm, ● 5 μm, ◇ 10 μm, + 14 μm).

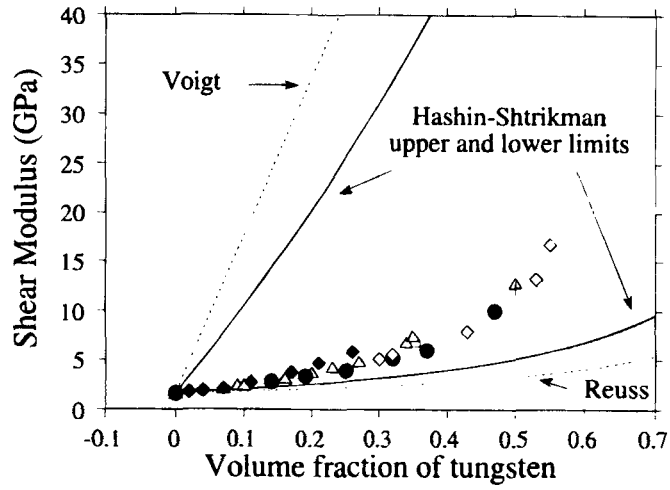

FIGURE 3 Voigt-Reuss and Hashin-Shtrikman limits for epoxy-tungsten composite system with experimental values (average particle sizes: ◆ 0.5 μm, △ 1 μm, ● 5 μm, ◇ 10 μm, + 14 μm).

tographs (Figs. 9 and 10) show that the particles are not always spheres. The particles of the 5-μm powder have a shape which is similar to a sphere (Fig. 9). However, the 0.5-μm powder consists of a mixture of spherical grains and needle-shaped grains (Fig. 10). In our opinion, this is the reason why in the case of 0.5-μm powder, the Devaney model is less valid. For all the other powders (1 μm, 10 μm and 14 μm), the shape of the particles appeared to be essentially spherical and the agreement between theory and experiment is good.

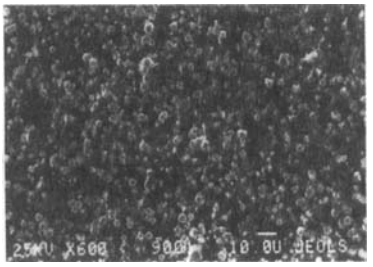

FIGURE 4 SEM micrograph of composite made with 5 μm tungsten particles in a volume fraction of 0.37. The magnification is x600.

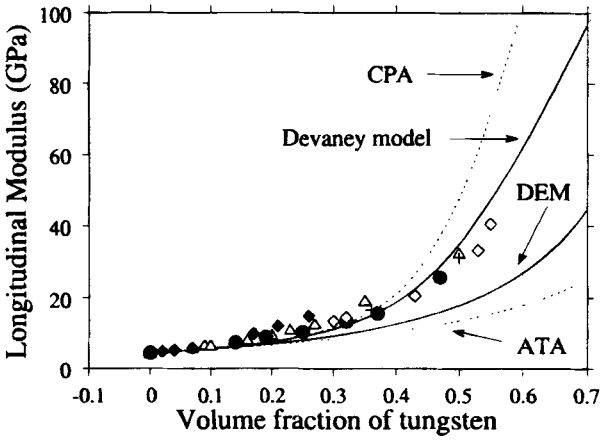

FIGURE 5 CPA, DEM, ATA and Devaney models for epoxy-tungsten composite system with experimental values (average particle sizes: ◆ 0.5 μm, △ 1 μm, ● 5 μm, ◇ 10 μm, + 14 μm).

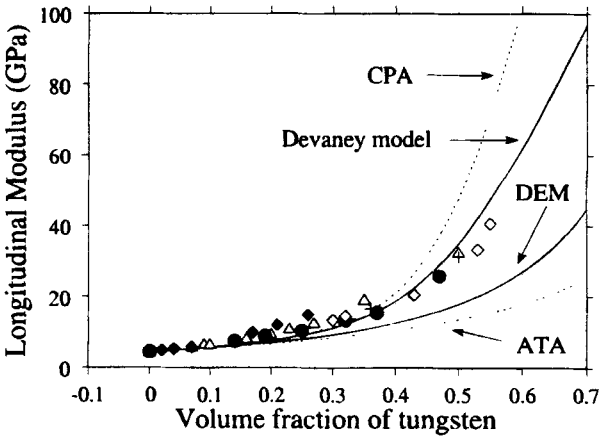

FIGURE 6 CPA, DEM, ATA and Devaney models for epoxy-tungsten composite system with experimental values (average particle sizes: ◆ 0.5 μm, △ 1 μm, ● 5 μm, ◇ 10 μm, + 14 μm).

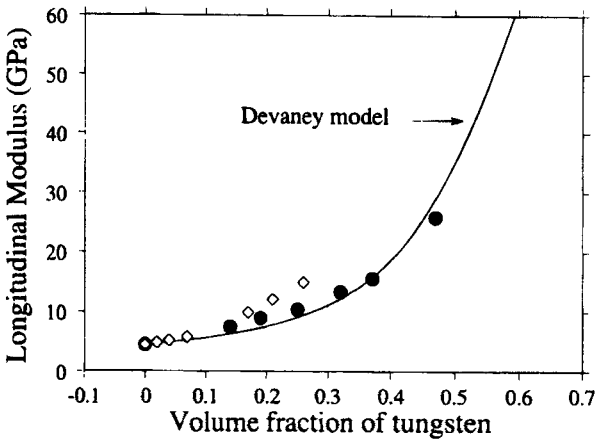

FIGURE 7 Longitudinal modulus as a function of the volume fraction of filler. Devaney model with experimentally determined values (average tungsten particle sizes: ● 5 μm, ◇ 0.5 μm).

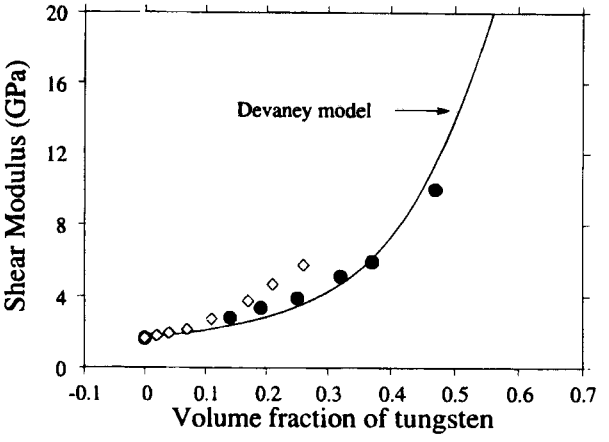

FIGURE 8 Shear modulus as a function of the volume fraction of filler. Devaney model with experimentally determined values (average tungsten particle sizes: ● 5 μm, ◇ 0.5 μm).

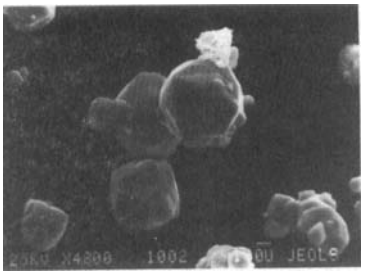

FIGURE 9 SEM photograph of sample of 5-μm tungsten powder. The magnification is 4800x.

FIGURE 10 SEM photograph of sample of 0.5-μm tungsten powder. The magnification is 22000x.

None of theses models take into account the particle size distribution. However, it has been shown by Farris[16] that at very high concentrations of filler, the elastic moduli of composites are influenced by the particle size distribution. He has demontrated that it is possible to decrease the elastic moduli, for a highly concentrated composite containing coarse particles (volume fraction of particle > 0.6), by adding fine particles. Our experimental values of moduli seem to be independent of the particle size distribution. This result is probably due to the moderate concentrations of filler in our composites which remain lower than 0.55. Nevertheless, for a large size distribution, such as that of the 10-μm tungsten powder for example, it is possible to increase the limiting concentration compared to the other powders. Indeed geometrically, it is easy to see that the fine particles allow to fill the voids situated between the large particles.

CONCLUSION

The longitudinal and shear moduli of epoxy resin filled with different volume fractions and different grain sizes of tungsten powders have been measured by an ultrasonic technique. Results show that the classical models (Reuss, Voigt and Hashin-Shtrikman) do not accurately predict the elastic constants of composites. The coherent potential approximation (CPA) model gives a fair estimate for the composites with volume fractions of filler under 0.4. For higher volume fractions, it appears that the multiple-scattering effects cannot be neglected. In this case the Denaney model is the only one which is close to experiments. One can note that for volume fractions lower than 0.3, the CPA and the Devaney models give the same results and are in agreement with experiments.

It appears that the shape of the filler particles is of importance. However, the particle size and the size distribution do not contribute significantly to composite moduli when the particles are much smaller than the wavelength and the volume fraction of filler is lower than 0.55.

References

1. J. G. Berryman, *Appl. Phys. Lett.*, **35**, 856 (1979).
2. J. G. Berryman, *J. Acoust. Soc. Am.*, **91**, 551 (1992).
3. A. J. Devaney and H. Levine, *Appl. Phys. Lett.*, **37**, 377 (1980).
4. R. E. Newnham, *Ferroelectrics*, **68**, 1 (1986).
5. G. T. Kuster and M. N. Toksöz, *Geophysics*, **39**, 587 (1974).
6. M. Hennock, R. R. Rahalkar and P. Richmond, *J. Food Sci.*, **49**, 1291 (1984).
7. *Handbook of Chemistry and Physics*, CRC: Florida, 1988; 68th ed.
8. A. Reuss, Z. *Angew. Math. Mech.*, **9**, 49 (1929).
9. W. Voigt, *Lehrbuch der Kristallphysik*, Teubuer: Leipzig, 1928.
10. Z. Hashin and S. Shtrikman, *J. Mech. Phys. Solids*, **11**, 127 (1963).
11. J. C. Halpin and S. W. Tsai, *Air Force Materials Laboratory, Technical Report AFML-TR-67-423*, 1967.
12. T. T. Wu, *J. Appl. Mech.*, **32E**, 211 (1965).
13. R. McLaughlin, *Int. J. Eng. Sci.*, **15**, 237 (1977).
14. L. Piche and A. Hamel, *Polym. Compos.*, **7**, 355 (1986).
15. L. Piche and A. Hamel, *Polym. Compos.*, **8**, 22 (1987).
16. Farris R. J., *Trans. Soc. Rheol.*, **12**, 303 (1968).