

On the Compressive Elasticity of Epoxy Resins Filled with Hollow Glass Microspheres

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SYNOPSIS

The mechanical properties of a hollow glass microsphere-filled epoxy resin composite system were investigated in air as a function of the weight content of particles ranging from 0 to 15.38% (wt/wt). The analysis based on necessarily modified classical models together with structural observations enabled explanation of the composition dependencies of elastic moduli of the blends studied. It was found that, together with a presumption of no interfacial adhesion between the filler and matrix, an interlayer of immobilized matrix with changed mechanical properties compared to the formal matrix seems to strongly affect the mechanical behavior of the composite. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

One of the most prominent peculiarities of polymers is the possibility to change the inherent physical and mechanical properties by chemical or physical modifications.¹ The simplest way of physical modifications of common polymers is their compounding with particulate fillers. Organic fillers are mostly used to increase toughness while inorganic rigid fillers are mostly used for rigidity improvement, creep compliance, and price/volume ratio reduction.²⁻⁴ Interest has also been shown in the use of hollow microspheres as fillers (syntactic foams) for polymeric composites due to their unusual and useful characteristics, including low density, high stiffness compared to normal foams (especially in compression), low thermal conductivity, and interesting electrical properties.⁵

A variety of approaches has been proposed to develop relationships to predict the thermomechanical properties of particulate-filled materials in terms of the properties and concentration of the polymeric and filler components. These approaches range from empirical curve-fitting techniques to sophisticated analytical treatments.⁶ Very little work has been

published on the strength of hollow-sphere filled polymers.

Taking into account the above arguments our contribution pursues the following aims:

1. To determine and to explain the effects of the filler particle shape on the elastic moduli of epoxy resins filled with hollow glass microspheres, and
2. To investigate the applicability of existing models on the blends studied.

EXPERIMENTAL

Materials

The materials used in the present study were an epoxy resin (DOW DER 334: $\rho = 1.14\text{--}1.16\text{ g/cm}^3$) hardened with tetraethylene pentamine (TEPA: $\rho = 0.94\text{ g/cm}^3$; 50% of the weight of the resin) and a reactive diluent (1,4-butanedioldiglycidyl ether: $\rho = 1.01\text{ g/cm}^3$; 15% of the weight of the resin) which lowered the viscosity of the mixture in the uncured state. The glass microspheres used (3M Scotchlite type B37/2000: $\rho_f = 0.37\text{ g/cm}^3$, $\rho_{f,\text{bulk}} = 2.4\text{ g/cm}^3$) had a wall thickness between 1 and 3 μm with particle diameters ranging from 50 to 70 μm . They were given no special surface treatment but were cleaned with isopropanol and dried at 130°C *in vacuo* (10^{-3}

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bar for 12 h) before molding to remove any contaminants.

Molding and Characterization

The epoxy resin mixture was degassed at room temperature and measured quantities of glass particles were added. The mixtures were gently stirred at the same temperature for a further period of time (2 h) to allow air bubbles generated during mixing to escape and then poured under vacuum into the mold. The composites were cured at room temperature for at least 24 h, eventually post-cured at 70°C for 24 h, and then machined into cylinders with smooth parallel ends.

The moldings were carefully characterized to ensure that the volume fractions of particles and void content were known accurately. The densities of samples from each molding were determined by weighing in air and dioxane. Samples were also ashed to determine the mass of the resin and glass. Since the densities of the matrix ($\rho_{\text{measured}} = 1.11 \text{ g/cm}^3$; $\rho_{\text{calculated}} = 1.06 \text{ g/cm}^3$) and the glass are known, the volume fraction of particles and voids could be determined. It may be seen from Table I that the theoretical air volume content always exceeds the air volume content. This may be due to the mechanical destruction of filler particles during the composite preparation or to residual thermal stresses as a consequence of different coefficients of thermal expansion.

Another problem that can be encountered with these composites is local variation in the particle distribution due to settlement or aggregation. This was routinely checked with density measurements

and the distributions were found to be fairly uniform. Figure 1 shows a section from a typical uncured molding containing 15.38% of particles by weight; apparently, the particles are evenly distributed without aggregations or settlements.

The specimens were compressed axially to failure by means of a servohydraulic machine (Instron 500 KN). Figure 2 shows typical variations in the uniaxial compression strengths of the composites with different matrix composition and porosity.

Increasing the porosity of the composites by incorporating untreated glass microspheres produced a rapid decrease in strength. A typical fracture surface morphology as observed with untreated filler particles (15.38% wt/wt) shows fracture within the resin and extensive debonding (see Fig. 3) between the filler particles and the resin. The extent of exposure of fractured microspheres on the fracture surfaces suggest that by acting as regions of local weakness and stress concentration their function is more important than simply that of reducing the proportion of resin in the composite.

RESULTS AND DISCUSSION

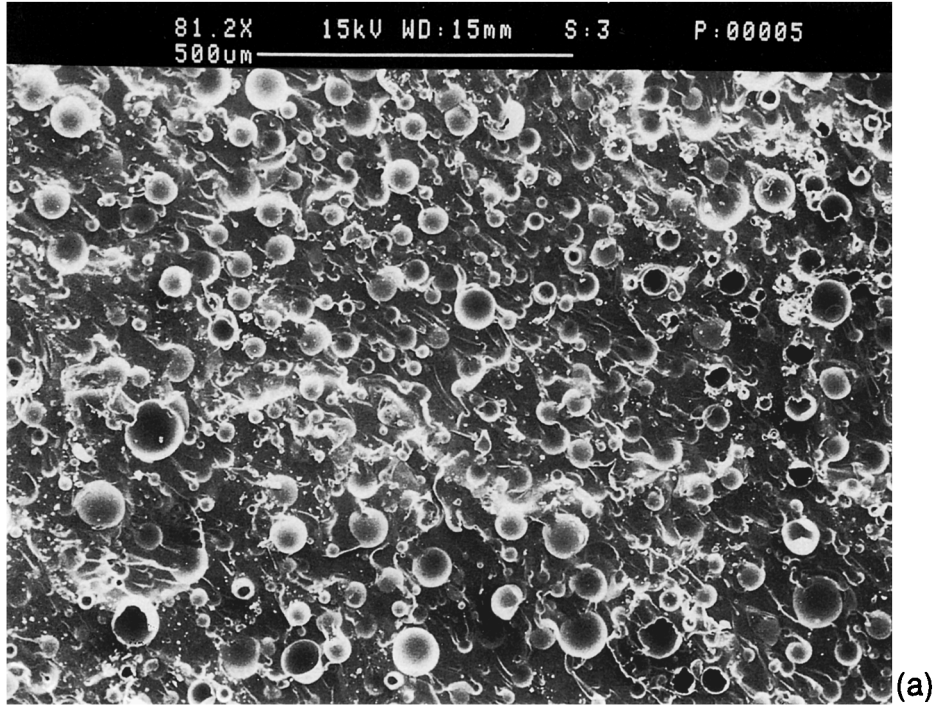
Apparently, no study dealing with the composition dependencies of elastic moduli of syntactic foams⁷ has so far been published. For a preliminary analysis of the composition dependence of the composites' elastic moduli, we used one of the most versatile and elaborate equations due to Kerner⁸:

$$\frac{E_c}{E_m} = \frac{1 + AB\phi_f}{1 - B\phi_f} \quad (1)$$

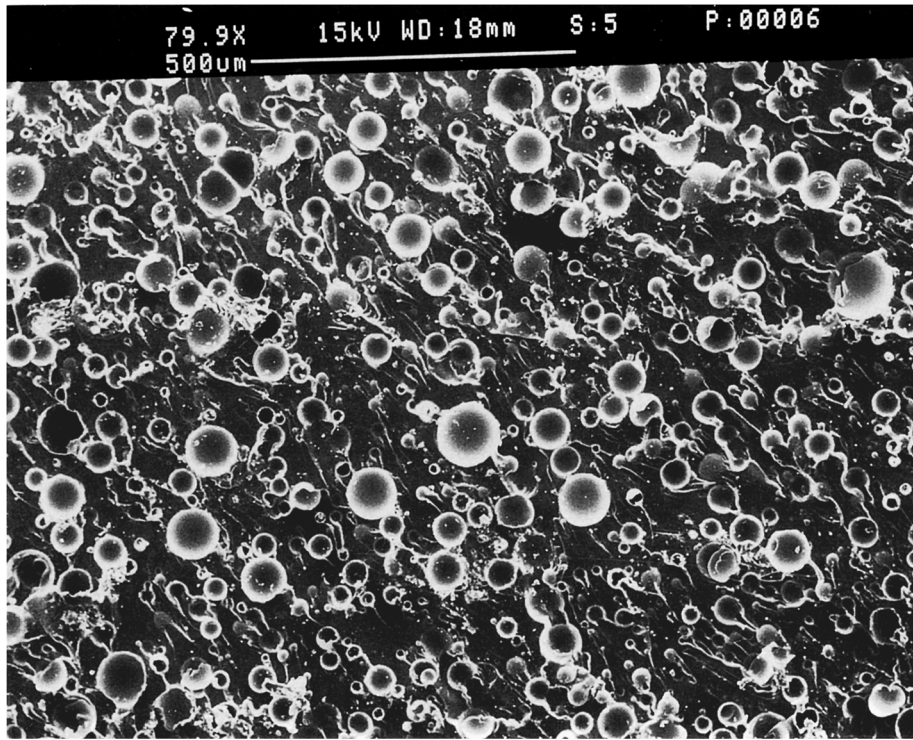
Table I Volume Content of Voids

	Filler (% wt/wt)	Filler (g/g _{comp.})	V_{air} (mL/g comp) (I)	V'_{air} (mL/g comp) (II)	e (%) (III)	ϕ'_f (% vol/vol) (IV)	ϕ_f (% vol/vol) (IV)
Uncured	5.71	0.057	0.116	0.130	11.44	0.154	0.136
	10.81	0.108	0.238	0.247	3.70	0.267	0.257
	15.38	0.154	0.335	0.352	4.66	0.353	0.337
After curing 24 h 70°C	5.71	0.057	0.113	0.130	13.49	0.154	0.133
	10.81	0.108	0.213	0.247	13.90	0.267	0.230
	15.38	0.154	0.330	0.352	6.17	0.353	0.332

(I) The measured air volume content is obtained as follows: $V_{\text{air}} = (m_c/\rho_c) - (m_m/\rho_m) - (m_f/\rho_{f,\text{bulk}})$, where the densities of the composite (ρ_c) and of the matrix (ρ_m) have been experimentally determined. (II) The theoretical air volume content is obtained as follows: $V'_{\text{air}} = (m_f/\rho_f) - (m_f/\rho_{f,\text{bulk}})$ under the hypothesis that the air content is due only to the presence of hollow microspheres. (III) The error "e" is defined as follows: $e = [(V_{\text{air}} - V'_{\text{air}})/V_{\text{air}}] \cdot 100$. (IV) ϕ'_f and ϕ_f are the theoretical and corrected values of the filler fraction volume: $\phi_f = [(100 - e)/100]\phi'_f$.



(a)



(b)

Figure 1 Scanning electron micrograph of a (a) higher or (b) lower section of a typical molding (filler fraction: 15.38% wt/wt).

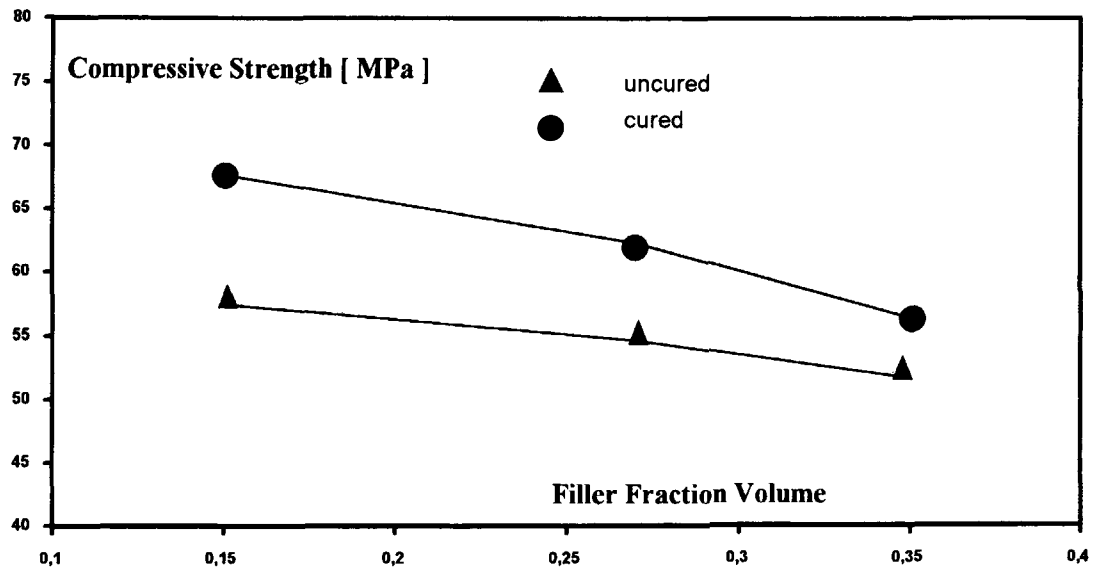


Figure 2 Dependence of uniaxial compressive strengths of the composites on the fraction volume of the filler.

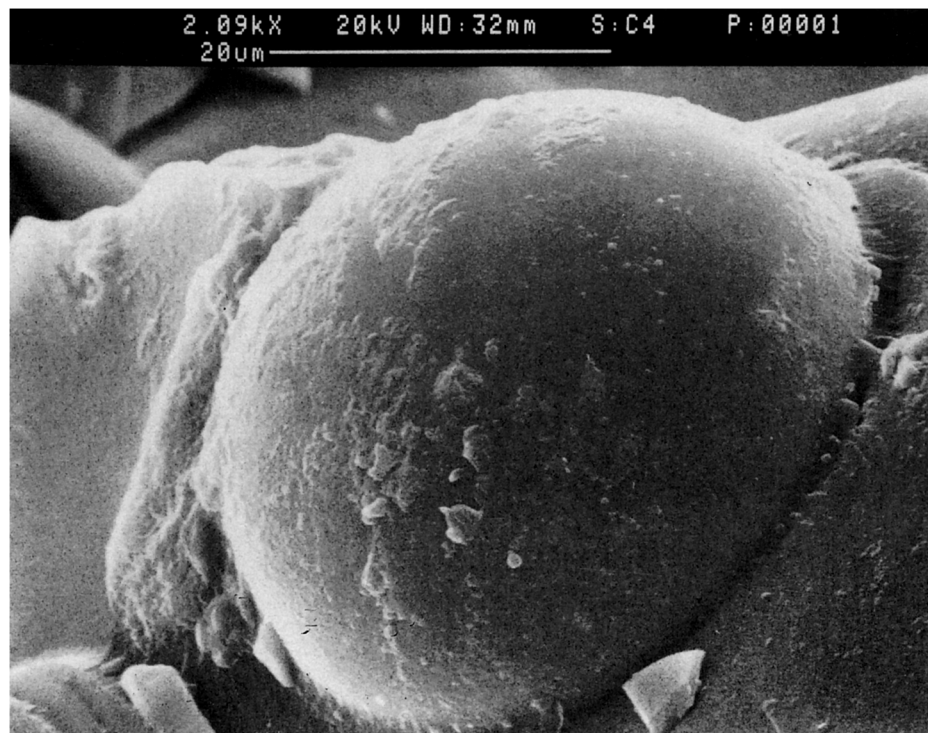


Figure 3 Scanning electron micrograph of a typical fracture surface morphology showing extensive debonding.

In this equation, E_c and E_m are the elastic moduli of the composite and matrix, respectively, ϕ_f is the volume fraction of filler phase, while A and B are constants which take into account the relative moduli of filler and matrix phases:

$$B = \frac{(E_f/E_m) - 1}{(E_f/E_m) + A} \quad (2)$$

Lewis and Nielsen⁸ modified eq. (1) as follows:

$$\frac{E_c}{E_m} = \frac{1 + AB\phi_f}{1 - B\Psi\phi_f} \quad (3)$$

with a semiempirical modifying function Ψ in the form

$$\Psi = 1 + [(1 - \phi_f^{\max})/(\phi_f^{\max})^2]\phi_f \quad (4)$$

where ϕ_f^{\max} is the maximum volumetric packing fraction.

The dependence of Young's modulus on the volume fraction of particles as computed from eqs. (1) and (3) is shown in Figure 4, where it may be seen that the predictions from selected models seriously

overestimate Young's modulus at volume fractions of filler greater than ≈ 0.1 . It should be emphasized that eqs. (1) and (3) both refer to solid microspheres.

If one can estimate the apparent modulus of the hollow spheres in terms of their inner and outer radii, then from the theory of Kodama⁹ or from equations listed by Roark,¹⁰ the apparent modulus of the hollow sphere can be related to the cubes of the outer and inner radii as follows:

$$\frac{G_H}{G_S} = \frac{1 - (a/b)^3}{1 + (a/b)^3} \quad (5)$$

where G_H is the apparent shear modulus of a hollow sphere; G_S , the shear modulus of a solid sphere; b , the outer radius of the hollow sphere; and a , the inner radius of the hollow sphere. G_H can now be substituted as the modulus of the filler phase in known equations for the modulus of filled systems. The Young's modulus E may be calculated instead of the shear modulus by means of the well-known equation

$$E = 2G(1 + \nu) \quad (6)$$

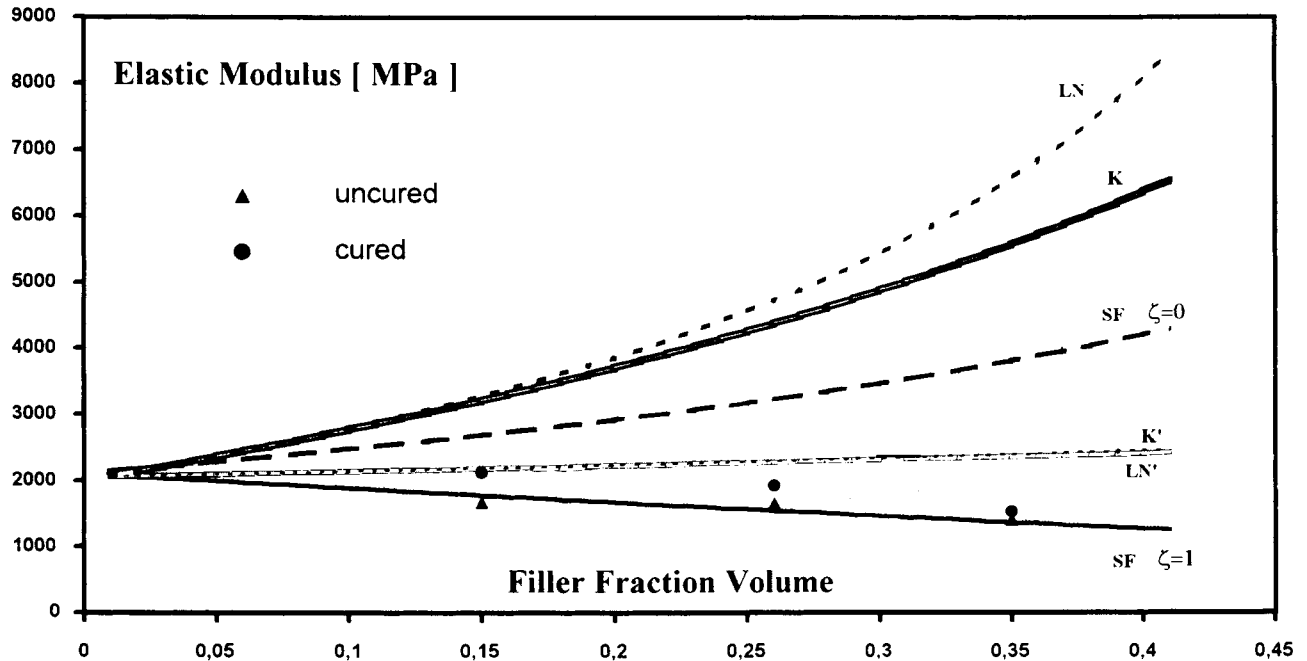


Figure 4 Comparison of the predictions for the Young's modulus E as a function of volume fraction filler, from theoretical models: Kerner (K), eq. (1); Lewis-Nielsen (LN), eq. (3); Kerner (K'), eq. (1) modified with eqs. (5) and (6) using the upper limit data (U_i) of Table II; Lewis-Nielsen (LN'), eq. (3) modified with eqs. (5) and (6) using the upper limit data (U_i) of Table II; Sato-Furukawa (SF), eq. (7), under the hypothesis of perfect ($\zeta = 0$) and no ($\zeta = 1$) adhesion.

Table II Hollow Microspheres: Limits of Some Physical Parameters

	U_l (Upper Limit)	L_l (Lower Limit)
b (μm)	35	25
a (μm)	34	22
G_H/G_S	0.0434	0.189
G_H (MPa)	1260	5493
E_H (MPa)	3024	13,184

where ν is the Poisson's ratio of the filled system; we assumed that $\nu_H \approx \nu_S$.⁷

Under the following conditions (Table II), the accordance between theoretical (best fitting) and experimental values of elastic moduli (see Fig. 4) is still unsatisfactory, since for volume fractions of filler less than 0.1, the models tend to coalesce, while for volume fractions of filler in excess of 0.2, they progressively overestimate the Young's modulus. The latter effect can be partially attributed to the rising number of voids which exist on the glass-epoxy interface. Indeed, a closer theoretical approximation of experimental data of Young's moduli over the whole concentration region studied has been

reached (see Fig. 4: Sato-Furukawa [SF, $\zeta = 1$]) by using the Sato-Furukawa equation¹¹ which assumes that the unbounded filler particles act as holes (vacuoles) and therefore predicts a decrease in modulus with increasing filler content.¹²

The equation of Sato-Furukawa is

$$\frac{E_c}{E_m} = \left\{ 1 + \left[\frac{y^2}{2(1-y)} \right] \right\} (1 - \psi\zeta) - \left[\frac{y^2\psi\zeta}{(1-y)y^3} \right] \quad (7)$$

where $\phi_F = y^3$, $\psi = \frac{(y^3/3)(1+y-y^2)}{(1-y+y^2)}$, and ζ is the adhesion parameter ($\zeta = 0$ for perfect adhesion and $\zeta = 1$ for no adhesion).

Rather than a presumption of no adhesion which seems to hardly justify the trend observed in Figure 5, we feel that there are at least two mechanisms of void formation which cause the discrepancies between the observed theoretical and experimental composition dependencies of the elastic moduli.

A first simpler mechanism may be attributed to mechanical destruction of filler particles which occur in the course of the composite preparation or may be due to residual thermal stresses around the glass sphere as a consequence of the inevitable mismatch between coefficients of thermal expansion. Indeed,

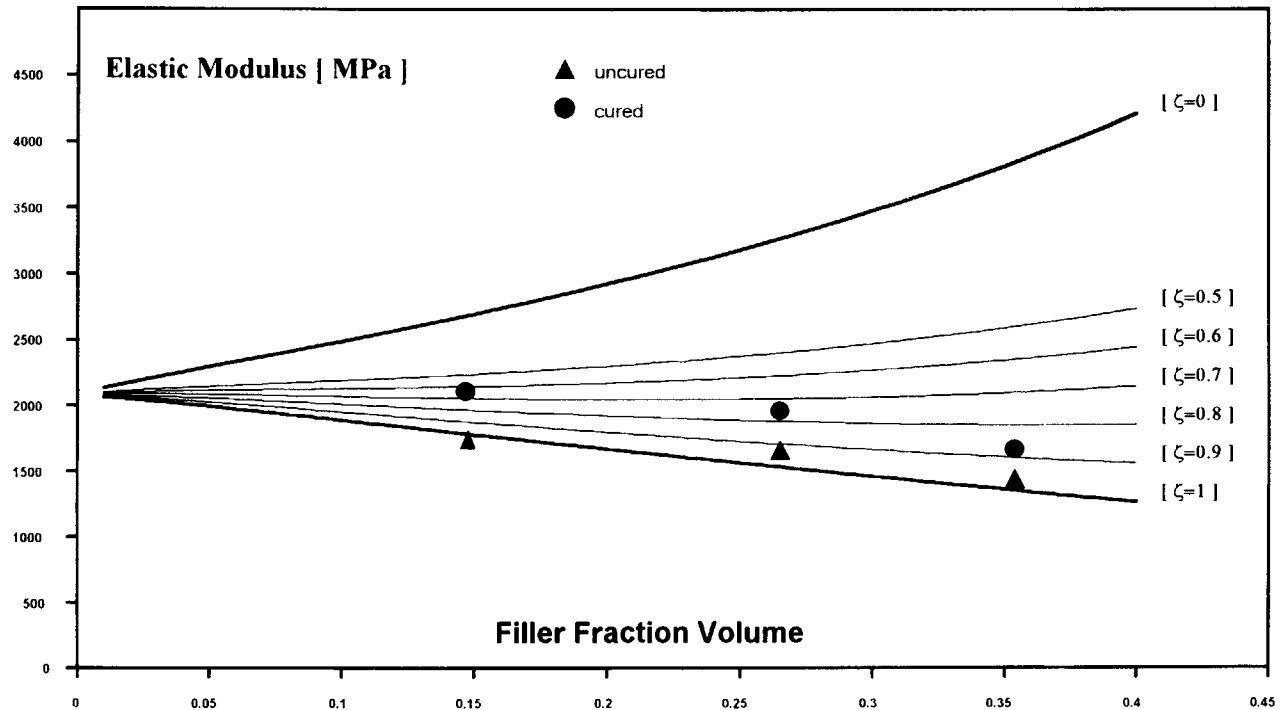


Figure 5 Comparison of theoretical predictions based on the Sato-Furukawa model (SF), eq. (7), under the hypothesis: $0 \leq \zeta \leq 1$.

on a macroscopic level, it has been found that (Table I) the number of voids and other defects of phase geometry increases with the volume fraction of the filler as demonstrated by the density measurements.

A second mechanism of void formation may be attributed to matrix immobilization¹³⁻¹⁵ in the resin filler interlayer, which, in creating clusters of filler particles, accounts for a matrix volume insufficiency in the bulk. The term "interlayer"^{13,16,†} is assumed to create a dispersed phase around the filler particles with changed morphology and physical properties and with an appreciable influence on the deformation response of composites.¹⁷ The origination of an infinite agglomerate with the interlayer as a "bounding agent" can give rise to a new hyperstructure, i.e., the formation of a physical network. In this regard, a similarity may be drawn with a physically bound space arrangement of filler particles¹⁸ as clusters effectively bounded by weak physical forms.

The interlayer, or intermediate phase, may be assumed to have a different modulus (E_i) than the two other moduli which characterize the matrix (E_m) and the filler (E_f).¹⁹ If the modulus of the composite material has the form

$$E = E_f\phi_f(1 - \zeta) + E_m\phi_m + E_i\phi_i, \quad (8)$$

then ϕ_i may be obtained as follows²⁰:

$$\phi_i = \phi_f\hat{s}\delta \quad (9)$$

where \hat{s} is the specific surface area of filler and δ is the thickness of the interlayer.

Under our experimental conditions, no reliable assumptions can yet be made when all of the polymer phase is exposed to the influence of the filler:

$$\phi_{f,crit.} = \frac{1}{1 + \hat{s}\delta} \quad (10)$$

† See Figure 3: specifically, the interlayer between the matrix and the debonded microsphere.

Further work is in progress in order to evaluate $\phi_{f,crit.}$ experimentally.

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