

Thermal and Mechanical Properties of Aluminum Powder-Filled High-Density Polyethylene Composites

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SYNOPSIS

Thermal conductivity and mechanical properties such as tensile strength, elongation at break, and modulus of elasticity of aluminum powder-filled high-density polyethylene composites are investigated experimentally in the range of filler content 0–33% by volume for thermal conductivity and 0–50% by volume for mechanical properties. Experimental results from thermal conductivity measurements show a region of low particle content, 0–12% by volume, where the particles are distributed homogeneously in the polymer matrix and are not interacting with each other; in this region most of the thermal conductivity models for two-phase systems are applicable. At higher particle content, the filler tends to form agglomerates and conductive chains resulting in a rapid increase in thermal conductivity. The model developed by Agari and Uno estimates the thermal conductivity in this region. Tensile strength and elongation at break decreased with increasing aluminum particles content, which is attributed to the introduction of discontinuities in the structure. Modulus of elasticity increased up to around 12% volume content of aluminum particles. Einstein's equation, which assumes perfect adhesion between the filler particles and the matrix, explains the experimental results in this region quite well. For particle content higher than 30%, a decrease in the modulus of elasticity is observed which may be attributed to the formation of cavities around filler particles during stretching in tensile tests. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The use of metal powder as filler in polymers relates chiefly to applications requiring a certain degree of electrical conductivity, magnetic permeability, sound absorption, and improved thermal conductivity. The composite material is more rigid than pure polymer and the addition of metal particles to polymer during injection has the effect of reducing internal stresses in injection-molded parts. Metal-filled polymers are used widely for electromagnetic interference shields; they have the advantages of being less costly and of lighter weight than the metals. Metal-filled polymers find outlets in other specific applications such as discharging static electricity, heat conduction, electrical heating, and converting mechanical signals to electrical signals. To make adequate use of metal powder-filled polymers, the variation of physical

properties with the kind and percentage of filler materials must be known.

Extensive studies have been carried out with metal-filled thermosets, but corresponding reports on their thermoplastic counterparts are rather scanty. Among those, studies carried out by Agari and Uno¹ on thermal and electrical conductivities of polyethylene filled with copper particles and of polymethyl methacrylate filled with aluminum particles may be cited. More recently, studies on thermal, rheological, and mechanical behavior of aluminum- and nickel-filled polypropylene have been reported by Maiti and Mahapatro.^{2–5}

THEORY

Thermal Conductivities

There is no single model which predicts effective thermal conductivity of two-phase materials for all

possible combinations of materials and for all filler concentrations. Reviews of many of these models are given by Progelhof, Throne, and Ruetsch,⁶ Cheng and Vachon,⁷ Godbee and Ziegler,⁸ and Agari and Uno.⁹ Some of the most frequently used models are explained with the conditions of applicability.

Using potential theory, Maxwell¹⁰ obtained a simple relationship for the conductivity of randomly distributed and noninteracting homogeneous spheres in a homogeneous medium:

$$k_e = k_p \frac{k_m + 2 \cdot k_p + 2 \cdot \phi \cdot (k_m - k_p)}{k_m + 2 \cdot k_p - \phi \cdot (k_m - k_p)} \quad (1)$$

Where k_e , k_p , and k_m are, respectively, the thermal conductivities of the composite (metal particle-filled polymer), continuous phase (polymer), and discrete phase (metal particles), and ϕ is the volume fraction of filler (discrete phase). This model predicts fairly well the effective thermal conductivities at low filler concentrations, whereas for high filler concentrations, particles begin to touch each other and form conductive chains in the direction of heat flow, so this model underestimates the value of effective thermal conductivities in this region.

Starting with Tsao's probabilistic model,¹¹ Cheng and Vachon¹² assumed a parabolic distribution of the discontinuous phase. The constants of the parabolic distribution were evaluated as a function of the discontinuous phase volume fraction. The equivalent thermal conductivity of a unit cube of the mixture is derived in terms of the distribution function and the thermal conductivity of the constituents. The effective thermal conductivity is given for the case $k_m > k_p$

$$\frac{1}{k_e} = \frac{1}{\sqrt{C \cdot (k_p - k_m)(k_p + B \cdot (k_m - k_p))}} \times \ln \frac{\sqrt{k_p + B(k_m - k_p)} + B/2\sqrt{C \cdot (k_p - k_m)}}{\sqrt{k_p + B \cdot (k_m - k_p)} - B/2\sqrt{C \cdot (k_p - k_m)}} + \frac{1 - B}{k_p} \quad (2)$$

where $B = \sqrt{3 \cdot \phi/2}$, $C = -4 \cdot \sqrt{2/3 \cdot \phi}$.

For two-phase materials for which the thermal conductivity of the continuous phase is much smaller than the thermal conductivity of the discrete phase, $k_p \ll k_m$ or $k_m/k_p > 100$, as long as $\phi < 0.667$, effective thermal conductivity of the composite may be approximated by the second term of eq. (2)

$$k_e \approx \frac{k_p}{1 - B} \quad (3)$$

The semitheoretical model proposed by Lewis and Nielsen¹³ is derived by a modification of the Halpin-Tsai equation¹⁴ to include the effect of the shape of the particles and the orientation or type of packing for a two-phase system

$$k_e = k_p \frac{1 + A \cdot \beta \cdot \phi}{1 - \beta \cdot \phi \cdot \psi} \quad \beta = \frac{k_m/k_p - 1}{k_m/k_p + A} \quad \text{and} \quad \psi = 1 + \frac{1 - \phi_m}{\phi_m^2} \phi \quad (4)$$

The constant A is related to the generalized Einstein coefficient k_E ^{15,16}

$$A = k_E - 1 \quad (5)$$

The constant A depends upon the shape and orientation of the dispersed particles. ϕ_m is the maximum packing fraction of the dispersed particles, which is defined as the true volume of the particles divided by the volume they appear to occupy when packed to their maximum extent. The values of A and ϕ_m for many geometric shapes and orientation are given in tables.¹⁷ For randomly packed spherical particles, $A = 1.5$ and $\phi_m = 0.637$, whereas for randomly packed aggregates of spheres or for randomly packed, irregularly shaped particles, $A = 3$ and $\phi_m = 0.637$.

In the range of high volume content, the particles touch each other and form agglomerates and chains. Maxwell's equation is no more valid in the region where particles begin to touch each other. Agari and Uno¹ propose a new model for filled polymers, which takes into account the parallel and series conduction mechanisms. According to this model, the expression that governs the thermal conductivity of the composite is

$$\log k_e = \phi \cdot C_2 \cdot \log k_m + (1 - \phi) \cdot \log(C_1 \cdot k_p) \quad (6)$$

where C_1 , C_2 are experimentally determined constants of order unity. C_1 is a measure of the effect of the particles on the secondary structure of the polymer, like crystallinity and the crystal size of the polymer. C_2 measures the ease of the particles to form conductive chains, the more easily particles are gathered to form conductive chains, the more thermal conductivity of the particles contributes to change thermal conductivity of the composite, C_2 becomes closer to 1.

Mechanical Properties

In a two-phase composite made up of a continuous matrix and particle fillers, the type, the concentration, the size, the shape, and the orientation of the filler particles are important factors in determining the mechanical and physical properties. Among several other factors that can greatly affect the mechanical behavior of filled systems, the strength of the adhesive bond between different phases, the type of dispersion, and the amount of particle agglomeration are especially important. Unfortunately, these factors are often difficult to separate and to evaluate in a quantitative manner. Although there is no good general theory about the stress-strain behavior of filled systems, it is known from observations that generally fillers cause a large decrease in elongation to break and also fillers often decrease the tensile strength of a material. The simple model developed by Nielsen¹⁸ explains in a semiquantitative manner many of the stress-strain properties of filled systems. For the case of perfect adhesion, and for any kind of a stress-strain curve, the model predicts that the elongation to break of a system filled with particles (ϵ_c) of approximately spherical shape is:

$$\epsilon_c = \epsilon_p(1 - \phi^{1/3}) \quad (7)$$

where ϵ_p is the elongation at break of the unfilled polymer.

Because of large stresses and strains encountered during tensile tests, dewetting is often observed. Dewetting is the result of the formation of voids during the stretching of a specimen due to poor interfacial adhesion, or it can be due to the breaking up of aggregates of low strength. Tensile strength and modulus drastically decrease after dewetting takes place. As the concentration of the filler increases, the lower the elongation at which dewetting takes place. For the case of no adhesion between the filler and the matrix, the tensile strength of the composite (σ_c) may be expressed as¹⁹

$$\sigma_c = \sigma_p(1 - b \cdot \phi^{2/3}) \quad (8)$$

where σ_p is the tensile strength of the matrix polymer and b is a constant. The factor " b " accounts for the adhesion quality between the inclusion and the matrix. $b = 1.1$ describes dense hexagonal packing in the plane of highest density; $b = 1.21$ represents the extreme case of poor adhesion with spherical inclusions for the minimum cross section between spher-

ical beads. In general, the lower the value of " b " below 1.21, the better the adhesion.

Many equations have been developed for the elastic modulus of a material filled with spherical particles. The simplest theoretical equation is the Einstein's equation,²⁰ which is valid only at low concentrations of filler and which assumes perfect adhesion between the filler and the polymer matrix, as well as perfect dispersion of individual filler particles

$$E_c = E_p(1 + 2.5\phi) \quad (9)$$

where E_c and E_p are, respectively, the modulus of elasticity of the composite and the polymer matrix.

For the case where the polymer matrix slips by the spherical filler particles rather than adhering to them, Einstein worked out a theory where the modulus of the composite is given by the equation:

$$E_c = E_p(1 + \phi) \quad (10)$$

If the bond or adhesion between the filler and the polymer is weak, the bond may break when the load is applied. The polymer will then deform more than the filler so that elliptical cavities or voids develop around each filler particle. In this case a decrease in the modulus of elasticity is observed with increasing particle content.

In actual practice there may not be perfect adhesion, and the particles may be in the form of base aggregates rather than being individually surrounded by matrix. These are important factors that are often difficult to measure experimentally. For these reasons, there is a lot of scatter in experimental data on filled systems, and the agreement between theory and experiment is often not very good. Even for the case of perfect adhesion when high stresses are applied, the interfacial bond may break, and the adhesion is no longer perfect. Thus, the magnitude of the applied stresses often determines whether or not there is perfect adhesion.

EXPERIMENTAL

Sample Preparation

The matrix material is a commercial high-density polyethylene in powder form, with a density of 0.968 g/cm³ and a melt index of 5.8 g/10 min. The metallic filler is aluminum in the form of fine powder, with particles approximately spherical in shape and particle size in the range of 40–80 microns (Fig. 1). The

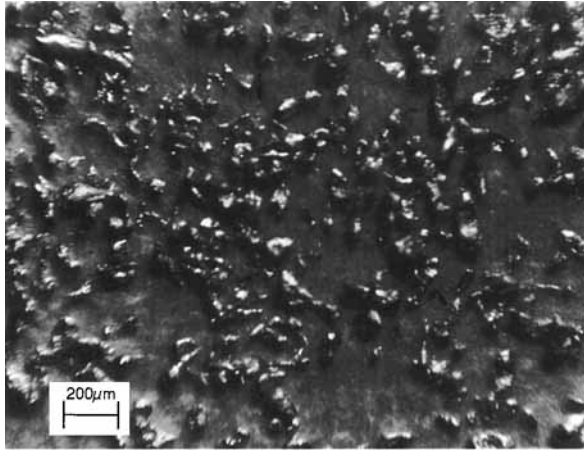


Figure 1 Microscopic photograph of the aluminum particles.

solid density of aluminum is 2.7 g/cm³ and its thermal conductivity 204 W/m · K.

Composite samples are prepared by the mold compression process. In order to obtain a homogeneous mixture, HDPE and aluminum powders are mixed at various volumetric concentrations in a tumble mixer for 20 min. The calculation of volumetric concentrations is based on solid densities of the constituents. The relationship between the volume fraction (ϕ) and the weight fraction (φ) of aluminum particles in the composite is given by

$$\phi = \frac{\varphi}{\varphi + (1 - \varphi) \cdot \frac{\rho_m}{\rho_p}} \quad (11)$$

where ρ_m and ρ_p are, respectively, the densities of the metal particles (Al particles) and of the polymer (HDPE). The mixed powder is then melted under pressure in a mold and solidified by air cooling. The process conditions are: molding temperature of 185°C, pressure of 4 MPa, heating residence time of 20 min for samples prepared for thermal conductivity measurements, and heating residence time of 10 min for samples prepared for tensile strength tests, cooling residence time of 50 min under pressure for both cases. The resulting samples for thermal conductivity measurements are rectangular in shape of 100 mm length, 50 mm width, and 17 mm thickness, whereas the standard samples for tensile strength tests are obtained from sheets of 2 mm thickness. Homogeneity of the samples is examined using a light microscope. Aluminum particles are found to be uniformly distributed in HDPE matrix with no voids in the structure.

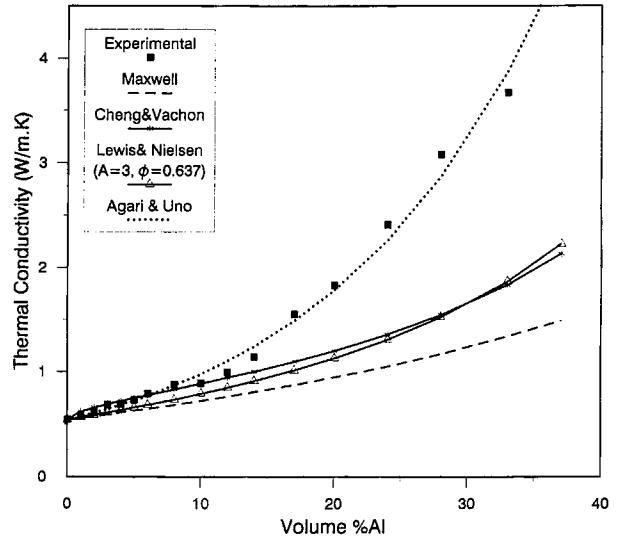


Figure 2 Predicted and experimental values of thermal conductivity of high-density polyethylene filled with aluminum particles.

Measurements

Thermal conductivity measurements are carried out in a Shotherm QTM thermal conductivity meter using the modified hot wire method. A thin straight wire through which a constant electric current is passed generating constant heat (Q) per unit length of wire, per unit time, is placed between two rectangular shaped materials, the first one is an insulating material of known thermal properties which is a part of the measuring probe and the second one is the sample for which the thermal conductivity has to

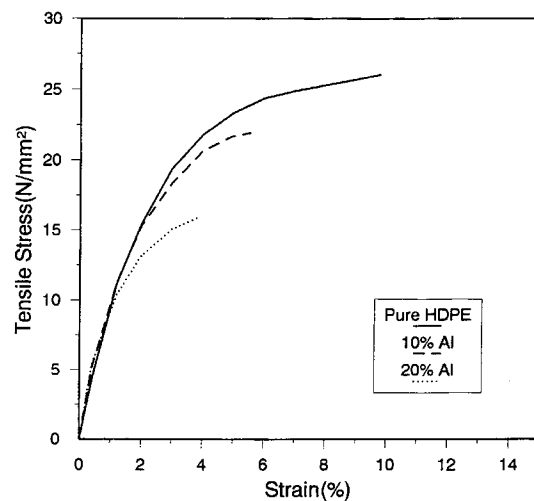


Figure 3 Stress-strain curves of pure HDPE and HDPE-Al composites with 10% and 20% of Al concentrations by volume.

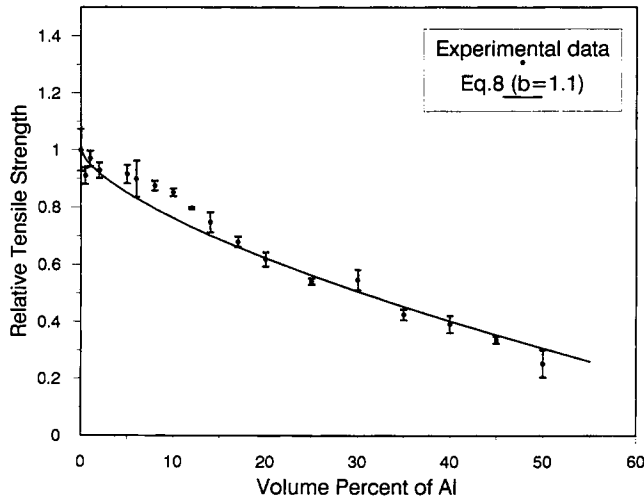


Figure 4 Relative tensile strength of HDPE-Al composite versus volume percent of Al.

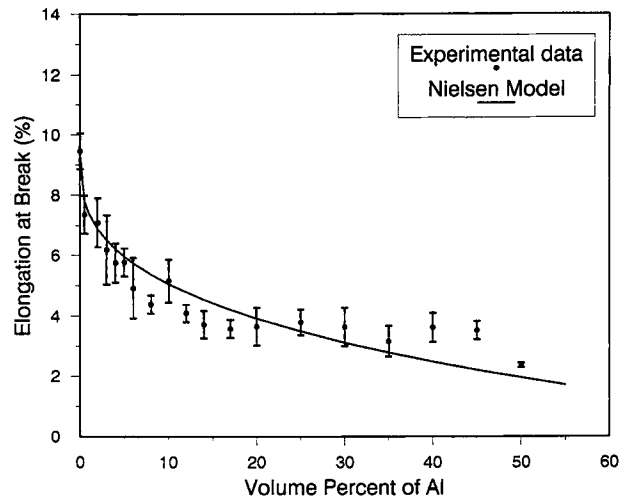


Figure 5 Elongation at break of HDPE-Al composite versus volume percent of Al.

be measured. A constant power is supplied to the heater element and the temperature rise ΔT of the heating wire is measured by a thermocouple and recorded with respect to time during a short heating interval. The thermal conductivity (k) of the sample is measured from the temperature-time (ΔT - Δt) record and power input (Q) according to the equation

$$k = F \cdot \frac{Q \cdot \ln(t_2/t_1)}{T_2 - T_1} - H \quad (12)$$

where F and H are specific constants of the probe to be determined with materials of known thermal conductivities. By using this method, the thermal conductivity is measured with an accuracy of $\pm 5\%$ and reproducibility of $\pm 2\%$. For each specimen the thermal conductivity is measured five times and the mean values are reported.

Tensile tests are performed at room temperature (20°C) with an Instron Universal Testing Machine (Model 1114), the strain rate being 1 mm/min, initial crosshead separation 5 cm. At least four specimens are tested in each case, the average value is reported and the standard deviation is shown in figures.

RESULTS AND DISCUSSION

Thermal Conductivities

Thermal conductivity measurements are performed on high-density polyethylene filled with aluminum particles up to a volumetric fraction of 33%. The experimental values of thermal conductivity are

compared with the calculated values of Maxwell, Cheng and Vachon, Lewis and Nielsen, and Agari and Uno models (Fig. 2). As aluminum particles form aggregates and their shapes are not perfectly spherical, the shape factor "A" in the Lewis and Nielsen model is taken equal to 3, and $\phi_m = 0.637$. At low particle content, $\phi < 12\%$, the increase in thermal conductivity with increasing volume content of aluminum filler is slow; for 12% Al content, the thermal conductivity is 1.8 times that of pure HDPE. Aluminum particles are dispersed in the polymer matrix and they are not interacting with each other; all the models, especially the Cheng and Vachon model, predict the thermal conductivity in this region well. For particle content greater than 12%, conductive

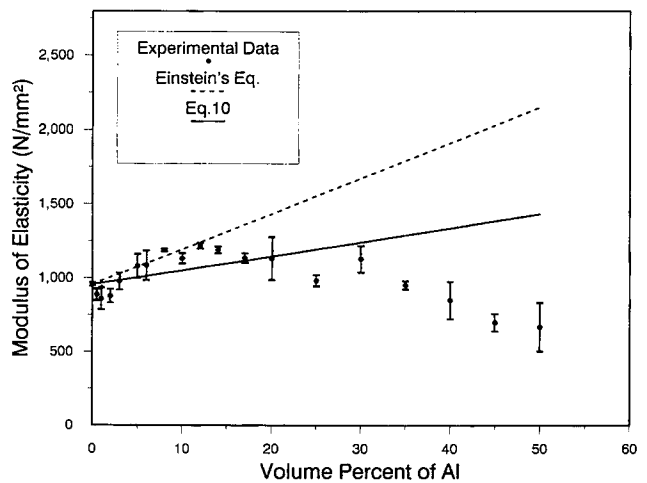
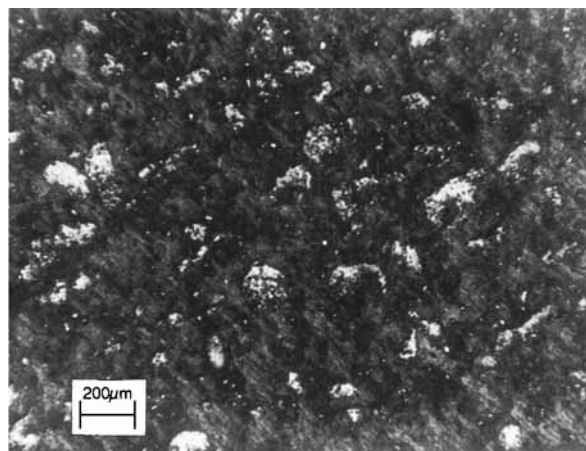
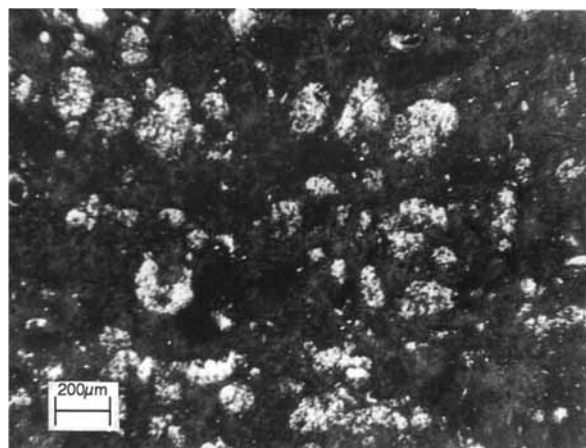


Figure 6 Modulus of elasticity of HDPE-Al composite versus volume percent of Al.



(a)



(b)

Figure 7 Microscopic photographs of aluminum powder-filled HDPE composites. (a) 20% volume fraction of Al particles, (b) 33% volume fraction of Al particles.

chains are exponentially formed by aluminum particles, causing a large increase in effective thermal conductivity of the composite. All the models, except Agari and Uno, fail to predict thermal conductivity in this region.

The Agari and Uno model predicts quite well the thermal conductivities of the composite in the whole range of aluminum particle content. In the case of the present study, values of the coefficients C_1 and C_2 are calculated by plotting the logarithm of the thermal conductivities of the experimental data against volume contents of the particles, $C_1 = 0.9923$ and $C_2 = 1.0076$. Since it uses the actual experimental data to fit a curve, it is natural that this model best predicts the effective thermal conductivities of filled systems in the whole range; the main

disadvantage associated with this method is that experimental data are needed to calculate C_1 and C_2 or there must be a list of values C_1 and C_2 available for each matrix material and filler.

Mechanical Properties

From the stress-strain curves, tensile strength, elongation at break, and modulus of elasticity are determined and are presented in Figures 4 through 6 as functions of volume fractions of aluminum powder. Figure 3 compares the stress-strain behavior for pure HDPE and for composites with 10% and with 20% aluminum powder fillers. Results of tensile strength versus volume fraction of Al are given in Figure 4. From this figure, it may be noticed that there is a gradual decrease in the relative tensile strength (σ_c/σ_p), as the volume fraction of filler increases; for 50% of aluminum filler, the tensile strength is 25% of the pure HDPE values, which is 25.685 N/mm². It may be seen from Figure 4 that the values predicted by eq. (8), with $b = 1.1$ corresponding to dense hexagonal packing of particles, follow the experimental results quite well.

Results of elongation at break versus volume fraction of aluminum are given in Figure 5, and the experimental values are compared with the results calculated from the model developed by Nielsen. It may be noticed from this figure that elongation at break decreases more rapidly than what may be predicted from the Nielsen model up to 20% Al content. Between 20% and 45% of Al content, the elongation at break is nearly constant.

Results of modulus of elasticity versus volume fraction of aluminum are given in Figure 6, the experimental results are compared with the values calculated from equations (9) and (10). For low-volume fraction of aluminum particles (up to about 12%), Einstein's equation, which assumes perfect adhesion between the particles and the polymer, matches quite well with the experimental results. For higher particle contents, up to 20% Al particles, eq. (10), which assumes that the polymer matrix slips by spherical particles, explains experimental results in this region. For particle content greater than 20%, filler particles begin to form aggregates, as also has been noticed from microscopic studies (Fig. 7). The bond between the filler particles is not as strong as that between the matrix and the particles; there may be voids forming with the application of a tensile load, which explains the decrease in the modulus of elasticity of high particle content.

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