

Hardness Evaluation of Epoxy Resin Filled with Mineral Waste

J. R. M. D'ALMEIDA, B. H. P. MANFREDINI

Materials Science and Metallurgy Department, Pontifícia Universidade Católica do Rio de Janeiro, Rua Marquês de São Vicente, 225-22453-900, Rio de Janeiro, RJ, Brazil

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ABSTRACT: The care of the world environment poses many challenges to the proper disposal of mineral wastes. Particulate wastes can be used to modify the properties or lower the cost of polymers. The influence of an iron–silica rich waste on the hardness of an epoxy resin is evaluated in this work. It is shown that the hardness values are polymer dominated for volume fractions of waste lower than 0.30, but for higher volume fractions a useful increase in the hardness numbers can be achieved. The coarser the particles are the more heterogeneous is the microstructure of the composite. Nevertheless, particulate rich layers increase the hardness of the material several times. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2178–2184, 2002

Key words: mineral waste; hardness; composite materials

INTRODUCTION

All over the world the plastic industry uses large amounts of minerals as extenders and fillers. The annual consumption of these materials is currently greater than 3 million tons and is continuously increasing.^{1,2} The main purposes for the use of minerals in the plastic industry are modification of the physical properties and cost reduction. The Young's modulus, density, dimensional stability, and resistance to abrasion are typical examples of properties that can be changed when a polymer is charged with a mineral.^{3,4} Calcium carbonate, titanium dioxide, and talc are the most used minerals and account for nearly 80% of the market.¹

A common characteristic of these and other minerals used as fillers in polymers is their particulate form. This is a very interesting characteristic because many wastes generated by min-

ing and metallurgical operations are obtained as particulate materials. Therefore, they could also potentially be used as fillers in polymers. This could be a very good perspective because many wastes from mineral extraction and metal refining represent serious environmental problems and the cost for their disposal can be extremely high.

In this work a study was undertaken to investigate the effect of a particulate waste, which was obtained at the final stage of a hydrometallurgical refining operation at a zinc plant, on the hardness of an epoxy resin. The zinc plant produces as much as 500 tons of waste a day and its disposal poses serious problems to the surrounding environment. The hardness test was used to perform this evaluation because of its simplicity and because it can provide information on the microstructure relationships of polymers and polymer composites,^{5–8} including biocomposites.^{9,10}

EXPERIMENTAL

The waste used as filler is mainly formed by rounded particles, as shown in Figure 1. Iron

Correspondence to: J. R. M. d'Almeida (dalmeida@dmm.puc-rio.br).

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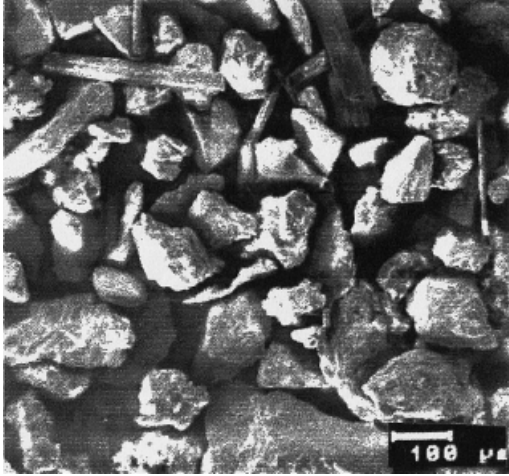


Figure 1 The overall aspect of the particulate waste material used as filler. The sample material retained at #200 mesh size.

oxide and silica are the main components of this waste^{11,12} and, because they are harder than epoxy resin,¹³ one could expect that they would cause an increase in the hardness of the filled polymer. This could be another relevant characteristic for this filled epoxy material, because an earlier investigation showed that the compressive Young's modulus and yield strength of this filled epoxy resin could be comparable to the values of the bare epoxy, provided the size and volume fraction of the particulate waste are conveniently controlled.¹¹ In fact, this result was very interesting, because the cost of the filled epoxy is expected to be lower than the cost of the unfilled resin. Nevertheless, one could take advantage of using a harder epoxy, for example, as coatings for the cement industry, where wearing of materials is a serious problem.

The difunctional liquid epoxy monomer diglycidyl ether of bisphenol A (DGEBA), cured with the hexafunctional aliphatic amine triethylene tetramine (TETA), was used as the basic polymer matrix. The epoxy monomer to hardener ratio was 100/13 by weight, which corresponds to the stoichiometric ratio of this epoxy system. The filled materials were fabricated by mixing together the proper quantities of filler and epoxy resin. This blending was done using an IKA mixer with variable adjustment of the velocity and torque. After thoroughly mixing the resin matrix and particles for at least 15 min, the slurry obtained was cast in bar-shaped open silicone rubber molds. The composite bars obtained were 200 mm long, 15 mm wide, and 25 mm deep. A mixing

time of at least 15 min was found to be an experimentally optimum time, because it is near the initiation of hardening for this epoxy system¹⁴ and the torque has stabilized. The cure was achieved at room temperature ($23 \pm 3^\circ\text{C}$). The composites were fabricated with a 0.10, 0.20, 0.30, 0.40, and 0.50 nominal volume fraction of filler (V_f) and with five different particle sizes per volume fraction. Table I shows the granulometry of the particles used. It is worth mentioning that, although the particle size distribution within each range was not determined, the observation of many samples by scanning electron microscopy showed that the particles have a rather uniform size distribution.

The nominal volume fraction of the filler for each composite was calculated using the following equations from the micromechanics of composite materials¹⁵:

$$\rho_c = \frac{1}{\frac{v_v}{m_c} + \frac{M_f}{\rho_f} + \frac{M_m}{\rho_m}} \quad (1)$$

where ρ_c , ρ_f , and ρ_m are the density of the composite, filler, and matrix, respectively; M_f and M_m are the mass fraction of the filler and the matrix, respectively; v_v is the volume of voids; and m_c is the mass of the composite. Supported by optical microscopy analysis (see Fig. 2 for an example), v_v was taken as zero. Therefore, and because the values of M_f , M_m , and ρ_c were experimentally measured and $\rho_m = 1.16 \text{ g/cm}^3$, eq. (1) could be solved for ρ_f . One can then calculate the volume fraction of filler using eq. (2):

$$V_f = \rho_c \frac{M_f}{\rho_f} \quad (2)$$

Cylindrical specimens ($20 \times 10 \text{ mm length} \times \text{diameter}$) were machined from the bars with their

Table I Size Distribution of Waste Used as Filler

Sieve (Mesh)	d (μm)
Under #400	$37 < d$
#400	$37 < d < 52$
#325	$52 < d < 73.5$
#270	$73.5 < d < 104$
#65	$d > 208$

d , Particle size.

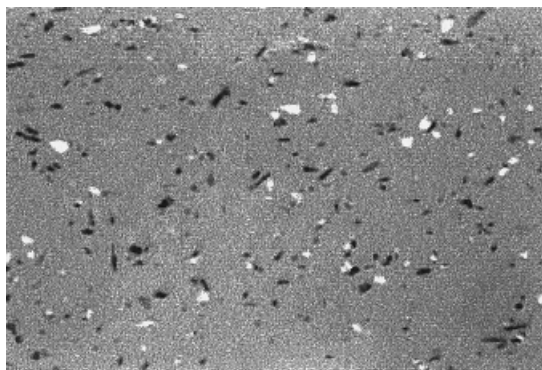


Figure 2 The common microstructure of the filled composites with a volume fraction of ≤ 0.30 . The optical micrography is taken from the composite with #325 mesh size and a 0.20 volume fraction.

axis along the depth of the composite bars. Therefore, any gradient of particles along the length of the test specimens could be analyzed and mapped if necessary. These specimens were used for mechanical measurements¹¹ and the hardness test. Before performing the hardness tests, the already flat and parallel bases of the specimens were polished with alumina powder ($d = 1 \mu\text{m}$) to obtain a completely smooth surface. The specimens were then mounted at the base of a microhardness HMV-2000 Shimadzu instrument and their Vickers hardness number was evaluated at room temperature ($23 \pm 3^\circ\text{C}$) and 65% relative humidity. Six to eight measurements were made for each of the materials analyzed. A load of 50 g was used and the indentation time was 15 s. These experimental conditions were strictly followed to avoid any effect of viscoelastic flow or even elastic relaxation on the measured hardness values.^{9,16,17} The bare epoxy resin was also prepared and tested using the same experimental procedure.

The material charged with #65 mesh particles was the only one that showed a strong variation in the spatial distribution of filler, and the particles agglomerated at the bottom of the fabricated bars (Fig. 3). Therefore, for these composites the hardness was evaluated on both bases of the specimens and a hardness profile was also determined for the composite with a volume fraction of 0.30.

RESULTS AND DISCUSSION

The experimental results obtained for the filled epoxy are shown in Table II. For the composites charged with #65 mesh particles, because of the

heterogeneous microstructure found for these composites (Fig. 3), the standard deviation was also reported only for the hardness measured at the upper, resin-rich face of the test specimens. For the lower, particulate-rich face the average value and the range of measured values were reported. Figure 4 depicts the hardness profile determined for one of these heterogeneous composites. One can see the strong gradient of hardness obtained because of the sedimentation of the coarse particles during setting of the resin matrix.

The figures quoted in Table II can be compared with the hardness value measured for the bare epoxy, which was 15.8 ± 0.4 , and it is in close agreement with the values reported by other authors.¹⁶

With the exception of the composites fabricated with the coarser material, which is the one with a particle size greater than $208 \mu\text{m}$ (i.e., #65), the experimental results follow a common trend for all the materials tested. Their experimental data are therefore discussed together. One can see that there is no noticeable increase in hardness for the filled polymers with a volume fraction of particles equal to or less than 0.30. In addition, one can infer that a homogeneous microstructure was obtained for these composites as revealed by the low standard deviations obtained, and the only exception found was for the material filled with #400 mesh particles and a 0.30 volume fraction. Figure 2 shows that a regular distribution of particles was in fact found for these composites. We must mention here that, although the hardness of the iron-silica rich filler is expected to be much larger than the hardness of the epoxy matrix, these low

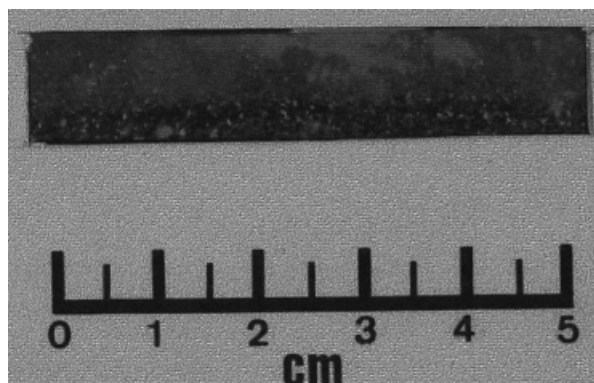


Figure 3 The composite charged with #65 mesh particles showing a heterogeneous microstructure and particles agglomerating at the bottom of the fabricated bars.

Table II Variation of Hardness of Filled Epoxy as Function of Volume Fraction and Mesh of Filler

Mesh Size for Filler Particles	Volume Fraction				
	0.10	0.20	0.30	0.40	0.50
Under 400	17.1 ± 0.8	14.3 ± 2.0	18.4 ± 1.6	21.6 ± 3.3	25.9 ± 5.6
#400	18.8 ± 1.5	16.6 ± 1.0	19.2 ± 6.1	25.0 ± 6.9	29.2 ± 6.4
#325	15.2 ± 1.0	15.9 ± 0.7	16.1 ± 0.6	17.7 ± 1.5	—
#270	15.2 ± 0.3	15.7 ± 2.2	16.5 ± 0.8	21.8 ± 2.4	27.1 ± 11.7
#65 UF	13.7 ± 0.4	14.5 ± 0.5	14.7 ± 0.5	14.0 ± 0.4	14.5 ± 0.5
#65 LF ^a	16.1	23.9	139.4	232.3	246.4
#65 LF range	15.0–17.3	15.1–61.9	14.2–745	14.7–677	16.6–802

UF, upper, resin-rich face; LF, lower, particulate-rich face.
^a Average value.

to medium charged polymers are matrix dominated. Therefore, only a secondary increase of the hardness values were obtained. Similar results were also found by other researchers.^{10,18}

However, the results obtained for these low to medium volume fraction filled polymers presented a dependence on the size of the particles. As is well established in the literature,¹⁹ if the volume fraction (V_f) is held constant, the average distance between particles is shortened with the decrease of the size of the particles, namely,

$$d = \frac{2D(1 - V_f)}{3V_f} \tag{3}$$

where d is the mean distance between particles and D is the size of the particle. Therefore, the hardness of the polymers filled with the smaller particles should be expected to be higher than that of the materials with larger particles because of the greater probability that at each hardness measurement the particles and matrix are being averaged. On the other hand, more matrix is

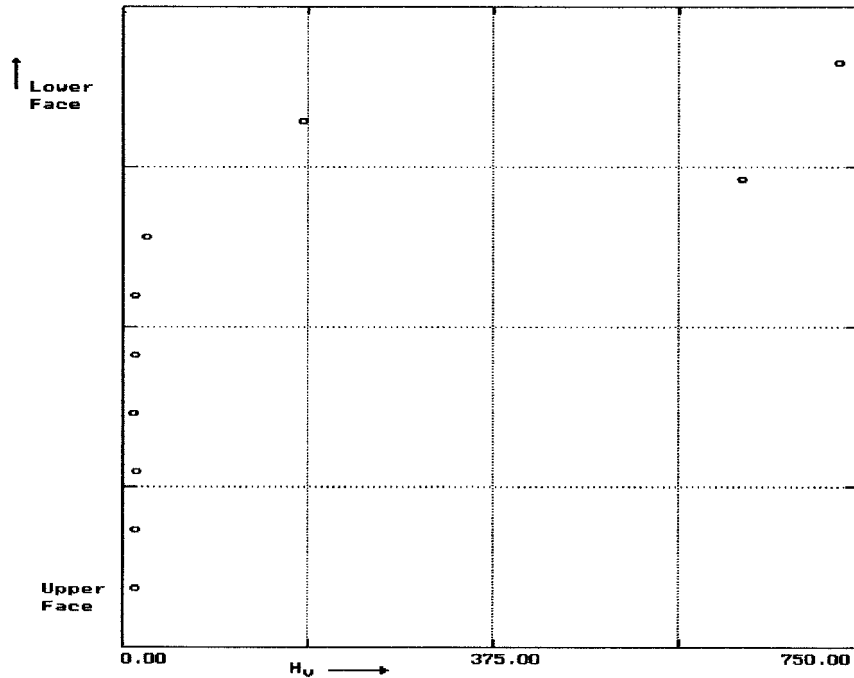


Figure 4 The hardness profile (H_v) of the composite with #65 mesh particles and a volume fraction of 0.30.

available to be under the hardness indenter for the material filled with the larger particles and therefore the average hardness decreases. This was indeed the behavior presented by the composites with a volume fraction of ≤ 0.30 , including the results found for the matrix dominated upper side of the composites filled with #65 mesh particles. For these composites the hardness of the resin-rich face was almost independent of the volume fraction, because of the larger distance between the particles, as shown in Table II.

The composites charged with the higher volume fractions (i.e., 0.40 and 0.50) showed higher hardness, as expected. With the exception of the one charged with #65 mesh particles that is discussed later, the average hardness value for these composites was 24.0, which is 52% higher than the hardness of the bare epoxy resin. This result also has a practical interest and one can envision the use of this charged polymer as a hardened surface layer for pavement coating. From the results shown in Table II one can also note that higher standard deviations were obtained for these materials. These figures are straightforwardly related to the presence of more filler particles and the difference of hardness between these particles and the soft matrix.

As shown in Figures 3 and 4, the heterogeneous particle distribution presented by the composites with the largest particles ($d > 208 \mu\text{m}$, #65 mesh screen) has a direct influence on the variation of the hardness of these composites. In fact, the upper face has the hardness values of a neat resin and the bottom face is harder. The consistently lower value of hardness obtained for all volume fractions for the upper face in relationship to the value of the bare resin could be attributable to an uneven setting of the resin matrix caused by the presence of the particles. In actuality, resin monomer-rich or hardener-rich areas could be present in a composite because of the higher or lower affinity of the reinforcement or filler by specific chemical groups present at the hardener molecule.²⁰

At the bottom face the experimental results obtained pointed to a phase-transition like behavior with a clear threshold point dividing the matrix dominated behavior from the particle dominated one. One can see from eq. (3) that with particles of constant size the increase of the volume fraction corresponds to a decrease of the mean particle distance.¹⁹ Therefore, the higher the volume fraction, the higher is the probability that the hardness number measured reflects the

contribution of the particles, whether by their intrinsic highest hardness or by the development of a frictional force due to the displacement of the particles in the matrix.^{9,10} The contribution of the filler size and morphology on the hardness of a resin matrix composite was indeed clearly shown for thermoplastic-based composites.¹⁰ However, if particles with large sizes are used, the average distance between them could be large enough even with higher volume fractions and a soft matrix dominated behavior could occur.

To see if the experimental results obtained for the bottom face of the #65 mesh particle filled composites have a definite threshold point, the data points were fitted by an S-shaped function. The S-shaped functions are rising-saturating functions that are governed by a nonlinear first-order differential equation and could represent processes that show sudden changes of behavior.²¹ The S-shaped function used was the logistic curve²¹:

$$f = k \frac{\exp(\gamma k(x - x_0))}{1 + \exp(\gamma k(x - x_0))} \quad (4)$$

where k is the saturation value, γ is the growth rate, and x_0 is the value of the controlling variable at which f reaches half its saturation value. For these functions x_0 corresponds to the point where a change in curvature occurs. This function was satisfactorily used to model the compressive and tensile behavior of the bare DGEBA/TETA epoxy system used here as the matrix, due to the variation of the epoxy to hardener ratio.^{22,23}

Figure 5 shows that the experimental results adhere very well to the S-shaped function. A saturation value of 234 H_v and an inflection point of 0.29 were obtained from the data fitting procedure. The correlation coefficient (r) found was 0.995. These results show that the composites with a volume fraction of filler higher than 0.29 in fact behave like functionally graded composites,¹⁸ which could be another relevant characteristic for these materials.

It is worthwhile to say here that the rule of mixtures has in some instances been successfully applied to model the variation of the hardness of composites with the variation of the volume fraction of filler,¹⁸ that is,

$$H_c = \sum_i^n H_i V_i \quad (5)$$

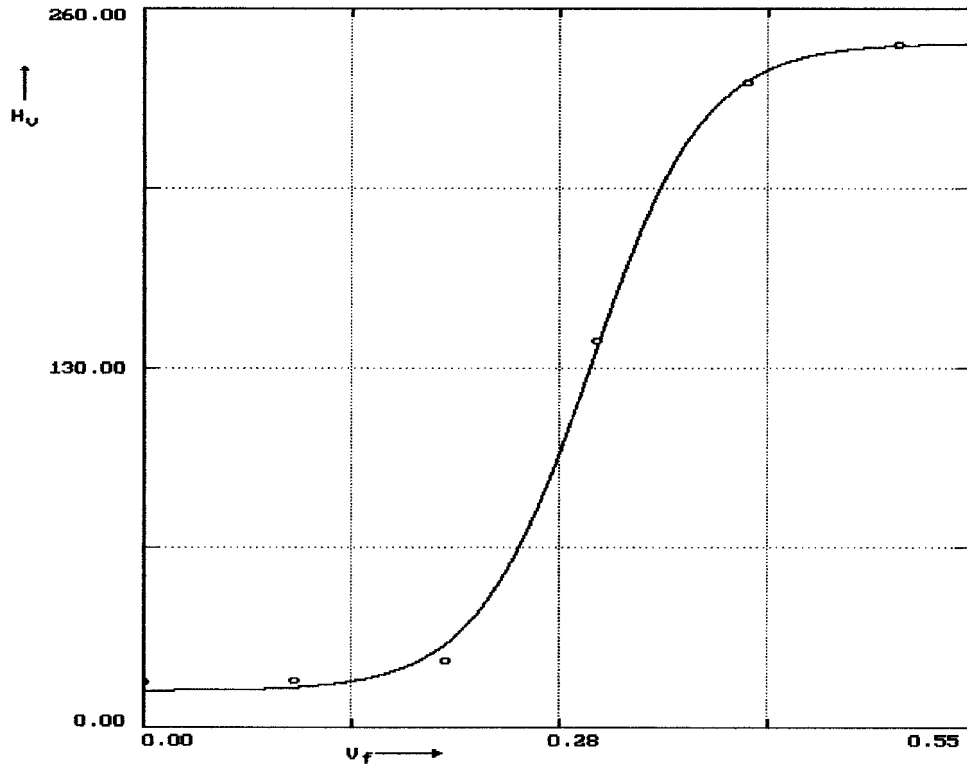


Figure 5 The variation of the hardness (H_v) as a function of the volume fraction (V_f) for the #65 mesh composites. The experimental values are modeled by the S-shaped function in eq. (4).

where H_i and V_i are the hardness and the volume fraction of the components, respectively. However, and as pointed out earlier, the size of the filler particle plays a definite and important role in the macromechanical behavior of these particulate composites. Krumova and coworkers¹⁸ found a very good linear relationship, but they work with particles with an average diameter of only $9 \mu\text{m}$ as compared with the large size ($d > 208 \mu\text{m}$) of the #65 screen particles used here. In addition, their equation does not match the real values of the bare resin and particles when $V_f \rightarrow 0$ or 1, respectively. Other authors^{9,10} found that a power law could model the relationship between the Vickers hardness number and the volume fraction of filler. The average size of the particles they used was also small ($< 10\text{--}45.7 \mu\text{m}$).^{9,10} Referring to eq. (3), it can be seen that the smaller the particle is, the smaller the distance between particles. For these low particle size reinforced composites, the hardness number does reflect a contribution of both the matrix and particles, even at low volume fractions of filler. For the #65 mesh, particle-rich lower face analyzed here the distance between particles is large

at low volume fraction and therefore a range of matrix dominated composites could exist. The modeling of the behavior of the particulate composites must take the characteristic size of the filler into account.

CONCLUSIONS

From the experimental results one can conclude that by proper tailoring of the volume fraction and particulate size, different microstructures and hardness behavior could be obtained using this iron-silica rich waste as filler. The composites with the smaller particles ($d < 208 \mu\text{m}$) have a homogeneous microstructure, and a volume fraction of the particulate waste greater than 0.30 must be used to obtain a useful increase in hardness.

For the composite fabricated with the coarser particles ($d > 208 \mu\text{m}$) a heterogeneous particle distribution was found. This produced a hardness gradient and a hardened surface 15 times harder than the bare resin matrix was obtained. The

data obtained for the harder surface were satisfactorily modeled by an S-shaped function. A threshold value of around 0.30 for the volume fraction was shown to divide the resin matrix dominated behavior from the particulate dominated one.

The results obtained open the prospect for a useful application of this waste, which is now very detrimental to the environment.

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