Analysis of the Use of an Industrial Waste as Reinforcement in Epoxy Composites

Marina Trindade Rödelheimer, José Roberto Moraes d'Almeida*

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

SUMMARY: A study was done to investigate the use of the waste generated at a hydrometallurgical zinc plant as filler in epoxy matrix composites. The waste was processed before its incorporation into the matrix and composites with volume fraction from 10 to 50% were fabricated with six different particle sizes. The results show that the mechanical properties increase with the decrease of the particle size until a threshold value is reached. Below this value the distance between particles became the controlling parameter. The results also show that this waste can be satisfactorily used as filler. Its advantages over commonly used fillers are its low cost and the environmental gain of its convenient disposal.

Introduction

Waste management poses many challenges to various industrial fields, particularly mining and metallurgical plants where large amounts of materials have to be disposed after mineral extraction and refining operations. If not suitably treated and/or disposed these materials can have a strong detrimental effect upon the environment. Some wastes, such as the slag from blast furnaces, have already useful applications. However, waste disposal is not a simple problem and special care has to be taken whenever heavy metals are concentrated as a result of ore processing. Many of the wastes generated by mining and metallurgical processing are, nevertheless, particulate materials that can be potentially used as filler in composite materials.

In this work it was investigated the use of the waste of a hydrometallurgical zinc plant as filler in an epoxy matrix composite. The volume fraction and particle size of the filler were varied and the composites were tested in uniaxial compression. The results were correlated with the average distance between the filler particles and with their surface to volume ratio.

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Experimental methods and materials

The filler used is a particulate powder obtained after drying the mud retained on the final sieving operation of a hydrometallurgical zinc plant. This plant produces as much as 500 tons of waste a day and the waste has an average cadmium content of 0.003%. Therefore, it has to be treated, or turned inert, before being disregarded to the environment. The dried mud forms a red brown agglomerate, as shown in Fig.1. This material was separated by size using a wet and dry sieving procedure. The complete description of the processing methods used to prepare the waste before its incorporation in the resin matrix is described elsewhere[1]. After sieving, particles with six different size distributions where obtained, as shown in Table I.

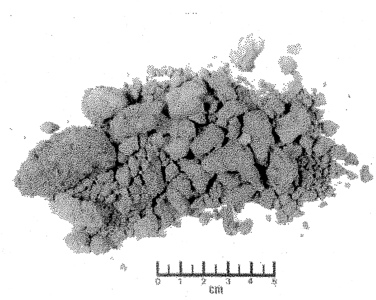

Figure 1 - The as-received red brown dried mud.

Sieves (mesh)	Size of the particles, ϕ (μm)
# 65	$\phi > 208$
# 200	$104 < \phi < 208$
# 270	$73.5 < \phi < 104$
# 325	$52 < \phi < 73.5$
# 400	$37 < \phi < 52$
under # 400	$37 < \phi$

Table I - Size distribution of the particles used as filler.

The morphology of the particles was analyzed by scanning electron microscopy (SEM) and their composition was determined by energy dispersive X-ray spectrometry (EDS). The particles were coated with a thin film of gold and the SEM analysis was performed with secondary and backscattered electrons and electron beam voltage of 15-20 kV.

The composites were fabricated by mixing together the proper quantities of filler and resin. The difunctional liquid epoxy monomer, diglycidyl ether of bisphenol-A, cured with the aliphatic amine, triethylene tetramine, was used as matrix. The epoxy to hardener ratio used was 100/13, in weight, what corresponds to the stoichiometric ratio[2]. The nominal volume fraction of filler was varied between 0.10 to 0.50. The real volume fractions were determined using automated image analysis. However, as under light microscopy the particles have different colors, that range from dark gray to bright white, a software was developed to account for that characteristic of the filler material. This procedure is described elsewhere[3].

After been thoroughly mixed, the particles and the resin formed a slurry that was cast in bar shaped silicone rubber molds. Fig.2 shows a common microstructure of the composites fabricated. Cylindrical specimens 20 mm in length and 10 mm diameter were machined from the bars and tested in a mechanically driven test machine. The test speed used was 1mm/min and 10 specimens were tested per each volume fraction and particle size.

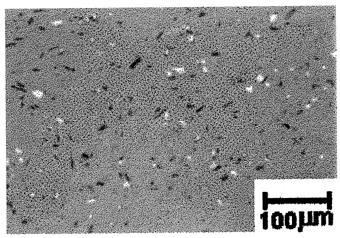

Figure 2 – Typical micrograph of the composites fabricated.

Experimental results and discussion

The common morphology of the particles retained by the several sieves are shown in Fig.3. One can see that as the particle size decreases, the fraction of needle like particles increases. These particles were identified as calcium sulfides, Fig.3d[4)], and their amount is relevant only for the material retained below #270 sieve. However, as shown in Table II, the properties measured were apparently not affected by the morphology of the particles.

The particle size, and the related mean distance between particles and interfacial surface area, was the main variable governing the mechanical performance of these composites. In fact, the experimental results show that the mechanical properties increase with the decrease of the mean particle size until a threshold value was reached. This result is in close agreement with many experimental data found in the literature[5)], and reflects, at a fixed volume fraction, the increase on the ratio between the surface area of the particles and their volume when the average size of the particles is reduced. Therefore, a higher interfacial contact area exists between the resin matrix and the particles and a more efficient stress transfer could take place between the phases of the composite. From the experimental results shown in Table II, one can see that a threshold value is attained for the material retained in the #400 sieve. The composites fabricated with this material showed the best mechanical performance.

Below the threshold value of the particle size, the average distance between the particles became the dominant parameter controlling the mechanical performance of the composites. In fact, as shown in equation 1, as the size of a particle, *D,* is reduced, the mean distance between particles, *d*, decreases[6]:

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

Equation 1 shows that only narrow channels will exist between the filler particles. For example, for a volume fraction of 0.10, the smaller one used, and taking from Table I, the value of 37 μm as an arbitrary mean particle size for the material under #400 sieve, the calculated mean distance between particles is only of 0.22 mm.

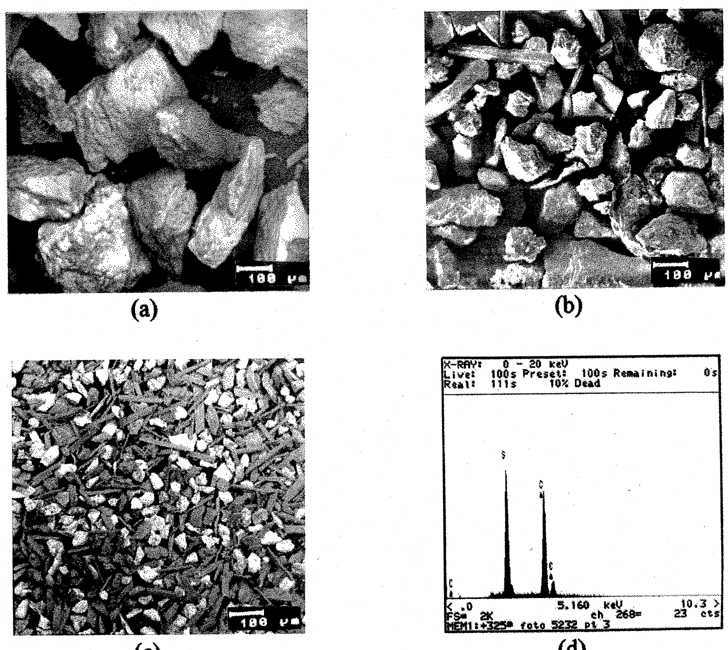

Figure 3 - Morphology of the particles after sieving. a) Rounded particles, common to the material retained in all sieves. Example taken from the material retained at #65. b) #200. c) #400. d) Energy dispersive x-ray spectrum of the needle like particles[4].

The effect of a small distance between particles on the wetting ability of the resin matrix can be inferred using the classic equations from fluid mechanics. The velocity of flow of a liquid filling the space between two parallel surfaces with a mean distance, *d*, is done by[7]:

$$\frac{d\ell}{dt} = \frac{K.d}{6.\eta.\ell} \quad (2)$$

where ℓ is the length of the space to be filled and η is the resin viscosity. $K = \gamma_{LV}.\cos\theta$, where γ_{LV} is the liquid-vapor surface tension and θ is the contact angle. Since d has small values, the rate of liquid resin flow between the filler particles is small from the very beginning of the fabrication procedure and the flow will be strongly reduced as the cure process proceeds, because the resin viscosity increases dramatically. Therefore, if the resin can not easily penetrate between the particles at the beginning of the cure process, when its viscosity is still small, it will not be able to completely wet the filler particles and the mechanical performance of the composites fabricated with the smaller particles will be affected. Besides of that, smaller particles have a higher tendency to agglomerate and this will also contribute for the lack of close contact between the resin matrix and all filler particles in these composites.

V_p, %	Under #400	#400	#325	#270	#200	#65
10	2.71 ± 0.14	2.14 ± 0.38	1.94 ± 0.16	1.93 ± 0.36	1.82 ± 0.40	1.32 ± 1.05
20	2.68 ± 0.19	2.96 ± 0.55	2.48 ± 0.12	2.49 ± 0.15	2.04 ± 0.55	1.33 ± 0.08
30	3.03 ± 0.60	3.01 ± 0.24	2.72 ± 0.13	2.88 ± 0.18	2.12 ± 0.59	1.23 ± 0.18
40	2.89 ± 0.27	3.66 ± 0.42	3.01 ± 0.42	2.85 ± 0.40	2.16 ± 0.57	1.58 ± 0.16
50	3.45 ± 0.48	4.44 ± 0.28	2.47 ± 0.78	3.13 ± 0.47	2.53 ± 0.77	-

(a)

V_p, %	Under #400	#400	#325	#270	#200	#65
10	105.5 ± 1.5	93.3 ± 1.7	89.6 ± 3.8	85.5 ± 2.1	83.4 ± 2.8	94.8 ± 1.4
20	94.3 ± 1.7	97.4 ± 2.2	86.9 ± 1.1	82.1 ± 2.7	89.4 ± 2.1	90.3 ± 2.6
30	88.9 ± 1.3	95.8 ± 1.1	86.9 ± 3.4	82.0 ± 2.0	85.5 ± 3.9	88.9 ± 4.0
40	83.1 ± 2.2	94.1 ± 2.7	80.5 ± 1.1	78.9 ± 1.5	83.3 ± 1.7	83.0 ± 3.6
50	84.9 ± 1.8	92.2 ± 1.3	54.9 ± 31.3	79.7 ± 5.1	79.8 ± 2.4	-

(b)

Table II – Experimental results for the mechanical properties as a function of the volume fraction of filler, V_p, and particle size. a) Elastic modulus, GPa b) Yield strength, MPa.

It is worth saying that the values determined for the elastic modulus of the composites, mainly those fabricated with the filler particles retained on sieves between #400 and #270, were close to, or higher than, the one presented by the bare epoxy resin, E = 2.55 ± 0.3 GPa[8)]. On the other hand, only composites fabricated with particles retained by #400 sieve showed values of yield strength close to that of the bare resin, σ_y = 97 ± 7 MPa[8)]. This is considered as an important result, as, in practice, materials are seldom used beyond their yield point. All other composites showed a worst performance in respect to the yield behavior of the bare epoxy resin, although for some of them the difference between the values was not high, Table II.

The experimental results obtained are, nevertheless, very promising since, even for volume fractions as high as 0.50, the mechanical performance of some composites is similar to that showed by the bare resin. Therefore, the waste analyzed can be very satisfactorily used as a filler for resin matrix composite materials. The advantages of its use over more common particulate fillers is its very low cost and the environmental gain of conveniently disposing an environmentally detrimental material. The use of this waste in thermoplastic resins and clay matrix composites is now being investigated.

Conclusions

The particulate material produced as waste on a hydrometallurgical zinc plant was shown to be useful as filler in epoxy matrix composites. With a filler content as high as 0.50 in volume, the composites fabricated with the material retained at #400 sieve have the same mechanical properties of the bare epoxy resin. The experimental results show that the mechanical performance of the composites was controlled by the size of the particles. Above a threshold value the surface area to volume ratio was the controlling parameter. Below the threshold value the mean distance between the particles play a more important role.

A reduction of the cost of parts or components fabricated with this waste is the first direct consequence of its use as filler in composites. Nevertheless, the main advantage of its incorporation in resin matrix composite materials is the environmental clean solution for what, nowadays, is considered as an harmful industrial waste.

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