Mechanical Properties and Thermal Stability of Rice Husk Ash Filled Epoxy Foams

P. M. Stefani,[1,2] V. Cyras,[1] A. Tejeira Barchi,[2] A. Vazquez[1]

[1]Institute of Material Science and Technology (INTEMA), University of Mar del Plata-National Research Council (CONICET), Av. Juan B. Justo 4302, (7600) Mar del Plata, Argentina
[2]Departamento de Ingeniería Civil, Facultad Regional Concepción del Uruguay, Universidad Tecnológica Nacional, Ingeniero Pereira 676, (E3264BTD) Concepción del Uruguay, Argentina

ABSTRACT: Mechanical properties and thermal stability of epoxy foams filled with white and black rice husk ash were studied. Epoxy foams were prepared from a commercial system and filled with different amounts of both the ashes (0, 6.8, 12.8, 18.0, and 22.7 wt %). The incorporation of both the ashes modified the final morphology of the foam, decreasing the average cell size and increasing the number of cells per volume unit. For all filler percentages used, the specific modulus and strength results showed that the white ash is more effective as reinforcing agent than the black ash. The initial degradation temperature was not affected by the content and type of ash used as the filler. The integral procedure decomposition temperature, weight loss, and char residue results were related to the ash type and atmosphere used in the thermogravimetric analysis. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2957–2965, 2006

Key words: epoxy foam; rice husk ash; mechanical properties; thermal stability; filler

INTRODUCTION

Epoxy foams have been developed because of their high mechanical properties, excellent adhesion to many materials, chemical, and good heat stability. They can be obtained by using physical or chemical blowing agents. In the physical foaming process, bubbles are generated from evaporation of low boiling liquid, such as freons, during the exothermic crosslinking reaction.[1] Another alternative is the use of microspheres where the gas containing particles are filled mechanically into the epoxy matrix (syntactic foams).[2] During the last years, industries have developed various epoxy foam systems where the blowing agent is chemically generated simultaneously with the crosslinking reaction. It is possible to produce foams with very different properties by changing the amount of chemical blowing agent or the curing conditions. During the foaming process, two parallel reactions occur in these systems: the reaction between epoxy and amine groups and the reaction between blowing agent with amino hardeners releasing a gas. The gas acts as expanding agent and the system foams out.[3]

This is an easy and economic method for the epoxy foam production. Some publications have shown that these foams can be used as matrices of composite materials and they have a good adhesion to most of the studied substrates.[4]

It is well known that the mechanical properties of epoxy matrix can be improved by the inclusion of fillers, as a second phase, to the resin batch. Silica (SiO_2) is one of the fillers mostly used in epoxy systems. Various publications have reported that silica filler improves the thermal stability, increases the modulus, and decreases the thermal expansion coefficient of epoxy matrix.[5–7] Rice husk is one of the main lignocellulosic residues of the agricultural industry and a natural source for silica production. World rice production in 2002/03 was ~582 million tons. As a consequence, 145 million tons of husk residues were produced. An increasing application of rice husk in rice producing countries, such as Brazil and Argentina, is as fuel in the heat generation for drying rice operations, due to its high calorific power. However, in the combustion process, only the organic part can be burned, giving silica-rich ash as the residue.

Rice husk contains a considerable amount of SiO_2 (~17 wt %), compared with other agricultural product.[8] However, because of the biological origin of rice husk, small variations in the silica content can be observed for different rice varieties. Mansaray and Ghaly[9,10] reported the char yield for different rice husk varieties obtained from pyrolisis in oxidative atmosphere at 700°C. Lemont, ROK 14, CP4, and Pa

Photo varieties showed char yield of 16.25, 17.06, 22.20, and 15.50 wt %, respectively.[9,10] These solid residues are formed mainly by SiO_2 (~95 wt %) and traces other oxides such as Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, and P_2O_5 in very small amounts.[11]

Depending on the burning conditions, silica content and unburned carbon amount, two ash types can be obtained: white rice husk ash (WRHA) and black rice husk ash (BRHA). The WRHA, mainly composed by amorphous silica, is obtained from the complete pyrolysis of rice husk in air up to a temperature of 700°C.[11–13] WRHA is mainly obtained in the upper layer of rice husk mound in direct contact with air during combustion. On the other hand, in the inner layer, where the atmosphere is poor in oxygen, incomplete combustion takes place, giving ash with a high percentage of carbon residues (BRHA). Normally, if both ash types are milled, they can be used as filler for different thermoset, thermoplastic, and elastomer polymers.[14–18]

In our previous article, a commercial epoxy foam system was characterized.[3] The optimum epoxy-amine relationship and the foaming agent amount effect on the final morphology, density, and mechanical properties were determined. However, the effect of filler addition on foaming process of epoxy systems has not been analyzed yet.

The aim of this work is to analyze the effect on foaming process, morphology, thermal stability, and mechanical properties of epoxy foams by incorporating rice husk ash as filler to a foaming epoxy system.

EXPERIMENTAL

Materials

The chemical system used in this work was kindly supplied by Ciba Geigy, Bassel. Epoxy resin (LY5054) was heated to 80°C and degassed by vacuum overnight before use. The siloxane (HY5054) and amine (DY5054) were used as received.

Rice husk (Don Juan INTA, variety) used in the present work was collected from the Cooperativa Arrocera Sarmiento, Concepción del Uruguay, Entre Ríos, Argentina.

Preparation of rice husk ash

White and black rice husk ashes (WRHA and BRHA) were obtained from combustion of rice husk in air and argon atmosphere, respectively, in a laboratory oven at a heating rate of 5°C/min from room temperature to 600°C. Each sample was held at 600°C for 2 h. The ashes were crushed using an analytic mill (IKA 50, Germany) for 20 min.

Preparation of epoxy foams

The chemical reactions during the foam formation are described in our previous article.[3] Basically, 100 weight part of epoxy resin, 35 weight part of amine, and 1 weight part of siloxane were placed in a plastic container. This system were mixed with 0, 10, 20, 30, and 40 weight part of rice husk ash for obtaining rice husk ash filled epoxy foams with different ash contents (0, 6.8, 12.8, 18.0, and 22.7 wt %). The reactive mixture was stirred for 10 min using a mechanical stirrer, and then it was placed in an oil bath at 50°C for the free foaming process. The $T = 50°C$ was selected because the foaming process occurs at slow rate and prevents the coalescence of bubbles during foaming process. The obtained foams were then transferred into an oven at 130°C for 3 h to ensure completion of the reaction.

Testing methods

X-ray scattering measurements were carried out with a Philips Model PW 1830 X-ray, operating at a Co Kα radiation and equipped with a rotative sample-holder device. Measurements were performed in an angular range of 5–70 2θ at room temperature and a scanning rate of 1°/min (RX).

Silica content in the rice husk ashes was determined gravimetrically: 1 g of ash was treated with 10 mL of concentrate HCl, followed by the addition of 10 mL of concentrate HNO_3. Then, the sample was boiled for a few minutes and treated with 25 mL of $HClO_4$. The sample was filtered off and washed repeatedly with HCl and water. The sample was burned until reaching constant weight.

Density of the WRHA and BRHA were determined by picnometry using water as solvent following the procedure described in the ASTM D792–87 norm.

The apparent density of the epoxy foams was determined using 20 mm × 20 mm (diameter and height, respectively) cylindrical specimens.

Compressive test was performed with a Shimadzu UH 100kNC machine following the test procedure ASTM D-1621–94. The samples test size was 20 mm × 20 mm (diameter and height, respectively). The displacement was calculated from the reading obtained with a linear variable differential transducer (LVDT) previously calibrated.

The SEM photographs of the polished surface of the different foams were taken with a scanning electron microscope Philips model SEM 505. Micrographs were magnified and regions containing about 100 bubbles were analyzed. This led to the determination of the size distribution, as n (number of bubbles) *versus* D (diameter) for each sample. The average diameter of the bubble (D_B) and void fraction (f_v) were calculated form eqs. (1) and (2), respectively.[19]

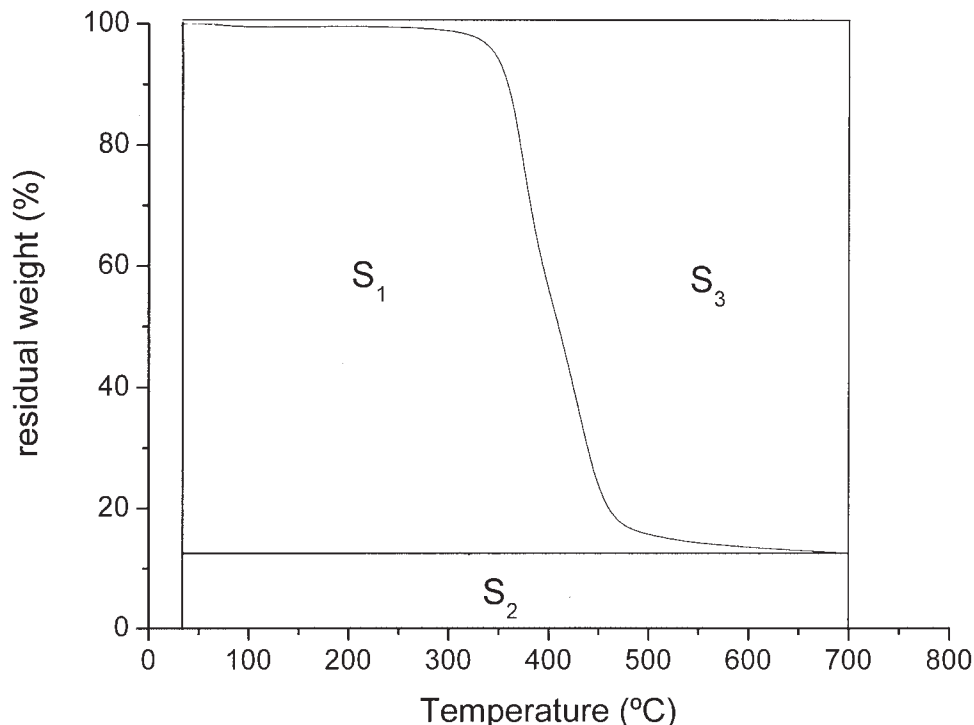$$D_b = \frac{\sum nD}{\sum n} \qquad (1)$$

Figure 1 Schematic representation of S_1, S_2, and S_3 for calculating $A*$ and $K*$.

$$f_v = (\pi/4)\frac{\sum nD^2}{A_T} \qquad (2)$$

where A_T is the total area of analysis.

Thermogravimetric analysis (TGA) was carried out using a Shimadzu thermal analyzer (Japan). Tests were performed in dynamic mode to cover a wide range of thermal conditions under nitrogen or air atmosphere (flow rate 200 mL/min). TGA tests were performed in alumina crucibles (5.9×4.7 mm^2) where samples were placed without any previous treatment and experiments were run immediately. The sample weight in all tests was approximately 7–10 mg. Temperature programs were run from 30 to 750°C at 20°C/min. Data obtained from TGA experiments were transformed in ASCII format and analyzed using a statistics computer program. The initial decomposition temperature (IDT) is the onset of weight loss taken at 1%. The integral procedure decomposition temperature (IPDT) was calculated from[20–22]:

$$IPDT(°C) = A*K*(T_F - T_I) + T_I \qquad (3)$$

$$A* = (S_1 + S_2)/(S_1 + S_2 + S_3) \qquad (4)$$

$$K* = (S_1 + S_2)/S_1 \qquad (5)$$

where $A*$ is the area ratio of total experimental curve divided by the total TGA thermogram; $K*$ is the coefficient of $A*$; T_I is the initial experimental temperature; and T_F is the final experimental temperature. A rep-

resentation of S_1, S_2, and S_3 for calculating $A*$ and $K*$ is shown in Figure 1.[20–22]

RESULTS AND DISCUSSION

Characterization of rice husk ashes

The densities of the WRHA and BRHA determined by picnometry were 2250 and 1650 kg/m^3, respectively. The normalized size distribution curves of WRHA and BRHA powder are shown in the Figure 2. The particles show an irregular form with a minimum size of ~110 nm and a maximum size of 8 μm. The particle average size of WRHA and BRHA were 2.5 and 2.9 μm, respectively.

Thermograms of the WRHA and BRHA in air are represented in Figure 3. The thermogram of WRHA did not show weight loss, because the combustion process for obtaining the ash was carried out in air atmosphere and the organic part was previously removed. However, even in air atmosphere, some carbon residue cannot be removed by oxidation because it is fixed with silica.[12] The BRHA sample shows an IDT of 245°C and a maximum weight loss of 49.6% (at 700°C), which represents the amount of total unfixed carbon in the sample.[11]

The SiO$_2$ contents obtained gravimetrically were 93.1 and 41.9 wt % for WRHA and BRHA, respectively. The differences between solid residues obtained by TGA and results of silica content determined gravimetrically indicate that approximately a 7 wt % of other oxides are present in both ashes, as aforementioned in this article.
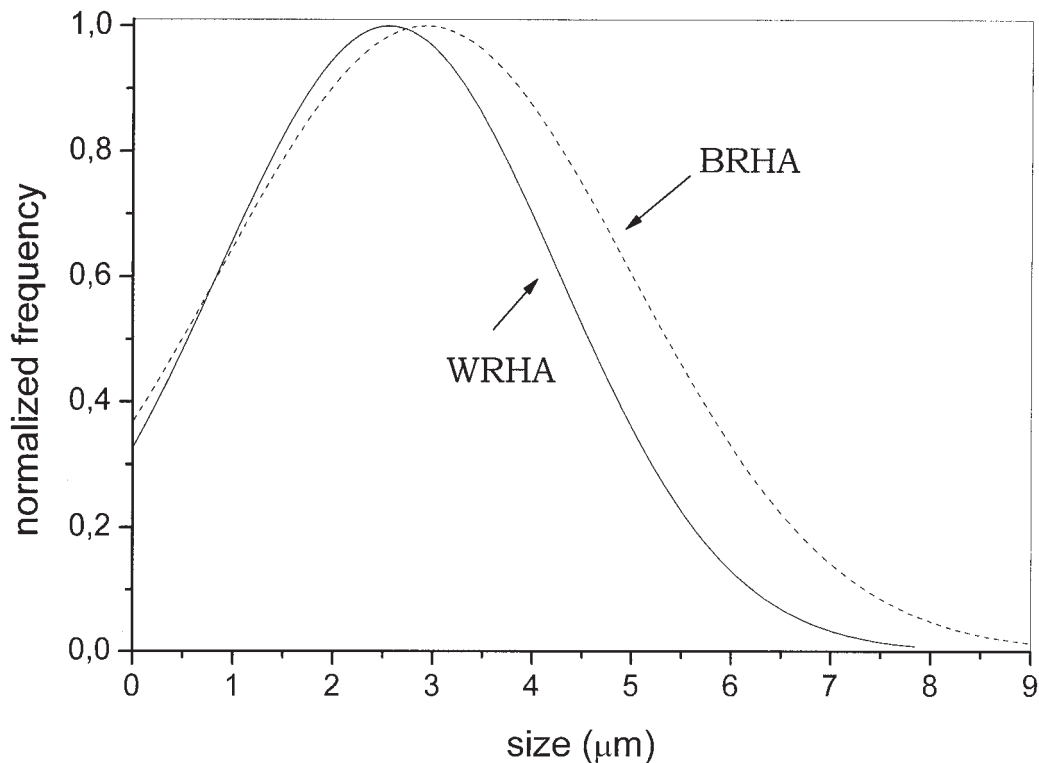
Figure 2 Size distribution of WRHA and BRHA.

Figure 4 shows the X-ray diffraction patterns of WRHA and BRHA. The pyrolysis conditions of rice husks (temperature, time, and atmosphere) are important to define whether silica remains essentially amorphous, as in the case of WRHA and BRHA used in this work. WRHA shows a peak at about $2\theta = 23°$, which indicates an incipient crystallization to crystobalite.[23] On the other hand, the peak at about $2\theta = 31°$ indi-
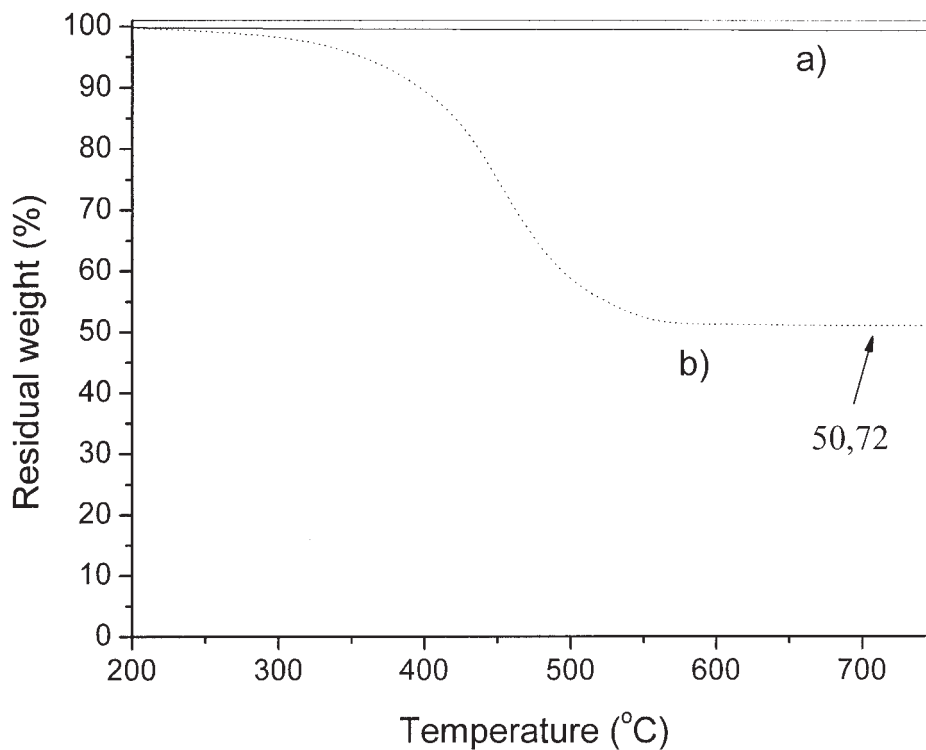

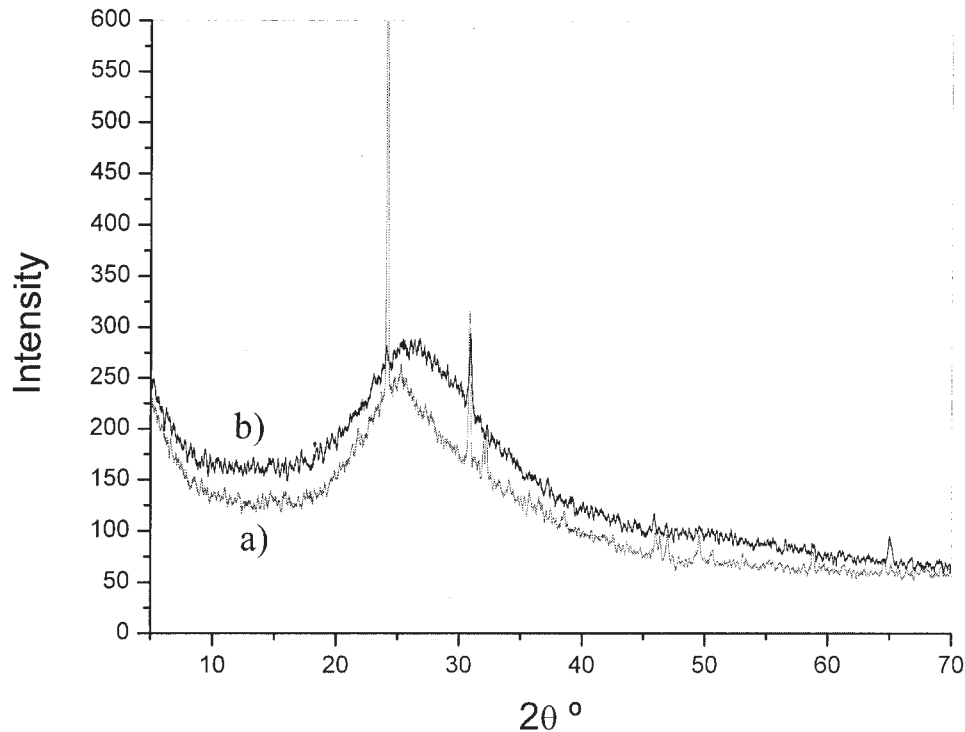**Figure 3** TGA curves for the ashes in air (a) WRHA and (b) BRHA.

Figure 4 X-ray diffraction patterns (a) WRHA and (b) BRHA.

cates the presence of unburned carbon.[24] Therefore, it will be necessary to heat at higher temperatures or to give any acid pretreatment to remove the unburned carbon.[12,25]

Morphology

Figure 5 shows the micrographs obtained by SEM of the pure and filled epoxy foams with different amounts of WRHA or BRHA. In all samples analyzed, bubbles are spherical with few contact points between them, as it is characteristic in high density foams. The variation in the bubble size distribution and average bubble size with the ash content is shown in Figures 6(a) and 6(b). The average bubble size decreases abruptly from 258 to 110 μm for the pure epoxy foam and the sample modified with 6.8 wt % of WRHA, respectively, remaining constant for higher percentages of WRHA [see Fig. 6(b)]. On the other hand, when BRHA is used, the average bubble size decreases smoothly up to 155 μm for 22.7 wt % of ash [see Fig. 6(b)]. The incorporation of rice husk ash into the basic system produces a nucleating effect during foaming process, increasing the number of bubbles per volume unit and decreasing its average size and the width of distribution.

Density and mechanical properties

Table I shows the mechanical properties in compression and density data for the pure and rice husk ash filled epoxy foams with different type and ash con-

tents. The density of the foams is a function of voids fraction and filler content.[3] As the ashes have a higher density than epoxy matrix, its incorporation should cause a density increase in the final foam. This increase is more notable in the foams filled with WRHA due to their higher density respect to BRHA. However, the increase in density due to the incorporation of ash may partially be compensated by an increase in the void fraction. As the results of Table I show, this compensation effect is observed in all foams, especially in the samples filled with 12.8 wt % of both ashes. It showed a minimum in density in agreement with the maximum void fraction determined.

To compare the effectiveness of filler on mechanical properties, the specific properties (property/density) were determined. As the results of Table I show, in the WRHA-filled samples the specific modulus and strength notably increase with filler content. On the other hand, when BRHA was used as filler, only a slight improvement in the specific strength was observed for the higher percentage analyzed. This different behavior can be explained by analyzing the variables that normally affect the modulus and compressive strength in filled foams: voids fraction, cell size, and filler content. The compression mechanical properties improve if the foams have a small cell size, low voids fraction, and high filler content.[2,3,6,26–28] Independently, the mechanical behavior of the foams improves when the ash content increases, and the foams filled with WRHA present a lower cell size and lower voids fraction than foams filled with BRHA, explaining their different behavior.
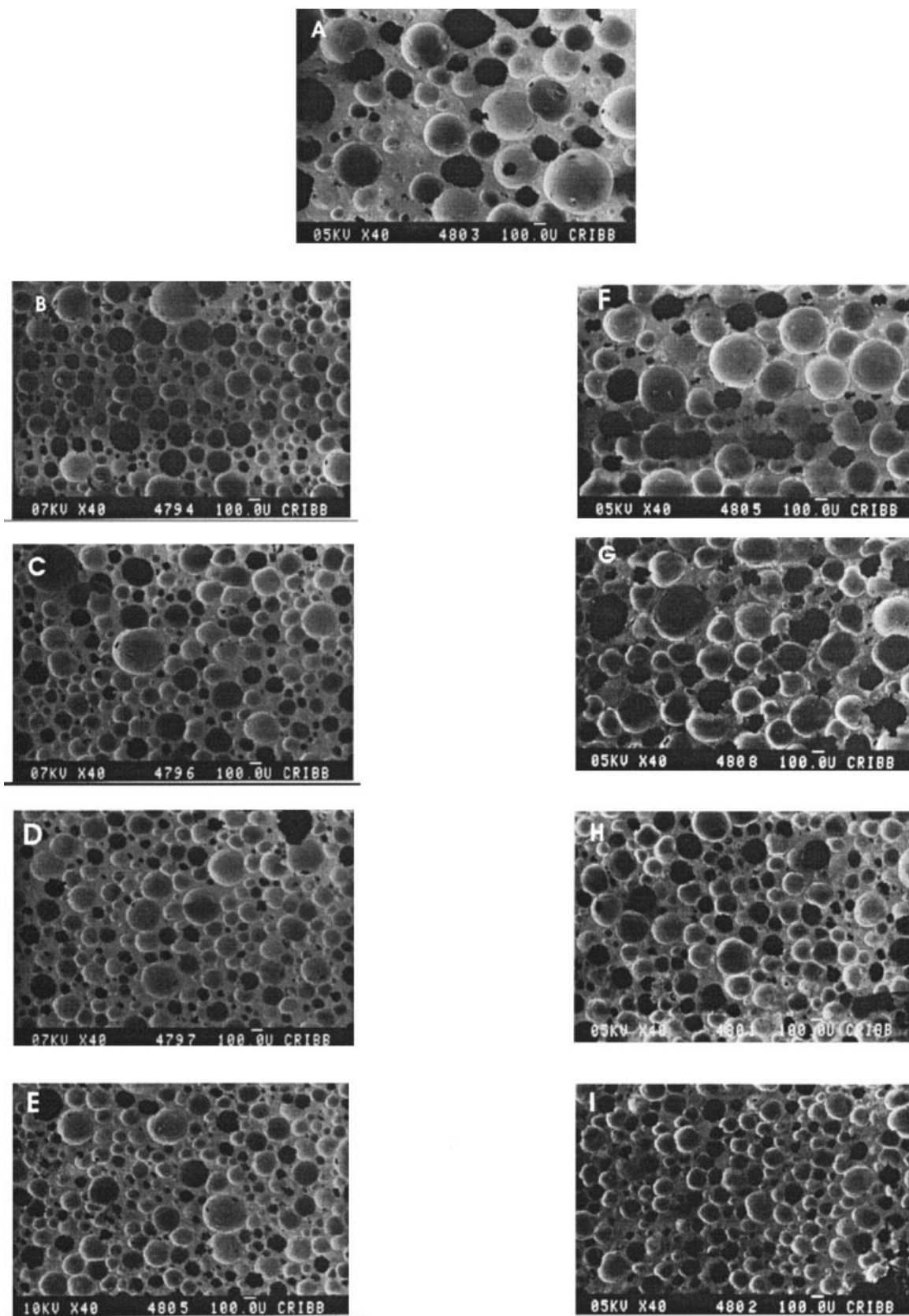
Figure 5 SEM microphotographies of epoxy foams with different ash contents (a) pure epoxy foam, (b) EF-WRHA10 (6.8 wt %), (c) EF-WRHA20 (12.8 wt %), (d) EF-WRHA30 (18 wt %), (e) EF-WRHA40 (22.7 wt %), (f) EF-BRHA10 (6.8 wt %), (g) EF-BRHA10 (12.8 wt %), (h) EF-BRHA30 (18 wt %), and (i) EF-BRHA10 (22.7 wt %).
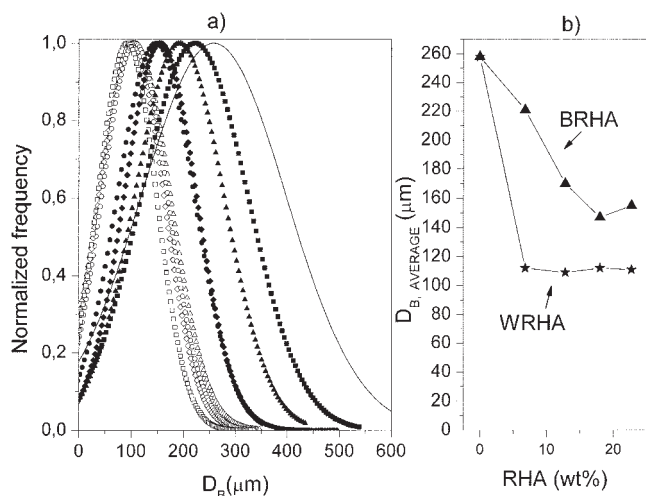
Figure 6 (a) Bubble size distribution of epoxy foams with different ash contents. (—-) pure epoxy foam, (■) EF-BRHA10 (6.8 wt %), (▲) EF-BRHA20 (12.8 wt %), (+) EF-BRHA30 (18 wt %), (♦) EF-BRHA40 (22.7 wt %), (△) EF-WRHA10 (6.8 wt %), (◇) EF-WRHA20 (12.8 wt %), (○) EF-WRHA30 (18 wt %), and (□) EF-WRHA40 (22.7 wt %). (b) Variation of average size of bubble for the foams filled with different ash contents (WRHA and BRHA).

Figure 7 Image of samples after compression test (a) pure epoxy foam, (b) BRHA filled epoxy foam, and (c) WRHA filled epoxy foam.

Figure 7 shows the final forms of the pure epoxy foam and filled with WRHA or BRHA after compression test. In all the tests, the load increases continuously even after the critical compressive strength (Sc) has been attained. At the same time, the crosssection of the sample increases and assumes a barrel-like shape up to failure is reached. The deformation at break values varied between 50 and 60% and did not show a tendency with the content and type of ash. In the pure epoxy foams, the barrel-like shape was maintained after testing and small cracks were observed in some cases. On the other hand, in agreement with the failure form described in the literature,[1] all samples filled with WRHA and BRHA showed a brittle failure involving cracking along the incline planes.

Thermal stability

Figures 8(a) and 8(b) show the typical dynamic TGA curves of pure epoxy foams and filled with 18 wt % of
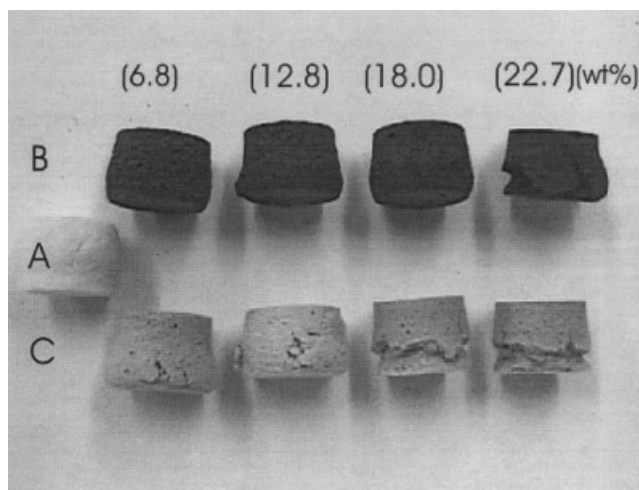
BRHA or WRHA in air and nitrogen atmosphere. The patterns of the thermogravimetric curves of the epoxy foam filled with WRHA and BRHA were similar to the patterns of the pure epoxy foams, showing that the thermal degradation of foamed epoxies consists in one or two independent stages under nitrogen or air atmosphere, respectively.[5,21,22] The thermal stability of pure and ash-filled epoxy foams were analyzed by determination of IDT, maximum weight loss temperature (T_{max}), and IPDT.

The thermal stability parameters of all the obtained foams are summarized in the Table II. IDT's results showed a difference between 60 and 66°C with atmosphere type (air or nitrogen), in agreement with other works reported in the literature.[29] The incorporation of WRHA or BRHA did not significantly alter IDT and T_{max} of the pure epoxy foams in nitrogen atmosphere. On the other hand, the IPDT increased with the ash content (WRHA or BRHA) because their volatile fraction is reduced. IDT results in air did not significantly change with the amount and type of ash. However, T_{max} in the first stage of BRHA-filled epoxy foams shifted toward lower temperatures, while in the foams filled with WRHA remained constant. As it was pre-

TABLE I
Mechanical Properties, Density, and Voids Fraction of the Pure and Filled Epoxy Foams

| Sample	RHA (wt %)	ρ (kg/m^3)	E (MPa)	Sc (MPa)	f_V	E/ρ (MPa m^3/kg)	Sc/ρ (MPa m^3/kg^{-1})
EF	0	320 ± 28	149.9 ± 33.1	5.14 ± 1.47	0.65 ± 0.1	0.469	0.0160
EF-WRHA10	6.8	313 ± 23	171.1 ± 11.6	5.30 ± 0.75	0.68 ± 0.2	0.547	0.0169
EF-WRHA20	12.8	310 ± 16	209.9 ± 10.7	5.32 ± 0.41	0.70 ± 0.2	0.677	0.0171
EF-WRHA30	18.0	339 ± 24	249.2 ± 24.6	6.28 ± 1.04	0.68 ± 0.1	0.735	0.0185
EF-WRHA40	22.7	367 ± 12	279.0 ± 27.2	7.38 ± 0.99	0.67 ± 0.1	0.760	0.0200
EF-BRHA10	6.8	302 ± 29	134.1 ± 32.7	5.10 ± 1.12	0.69 ± 0.2	0.444	0.0169
EF-BRHA20	12.8	285 ± 27	127.7 ± 25.1	4.71 ± 0.99	0.71 ± 0.3	0.448	0.0165
EF-BRHA30	18.0	313 ± 26	162.1 ± 28.3	5.48 ± 0.89	0.69 ± 0.1	0.518	0.0175
EF-BRHA40	22.7	320 ± 27	183.6 ± 28	5.56 ± 0.91	0.69 ± 0.1	0.574	0.0174
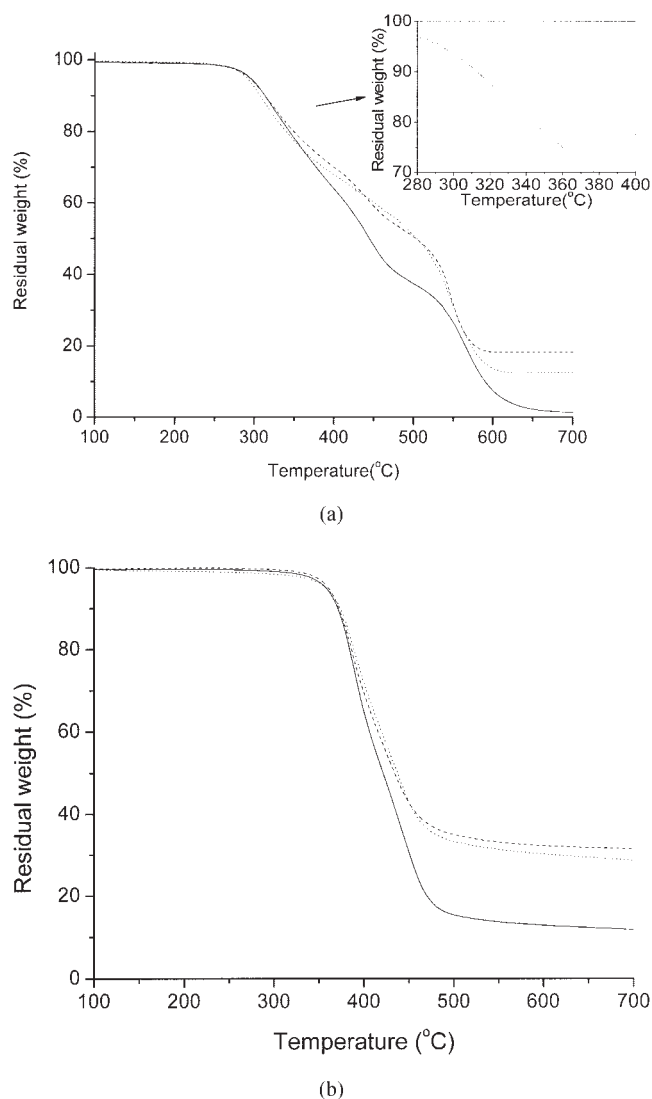
Figure 8 TGA curves of the epoxy foams. (—-) Pure epoxy foam, EF, (···), EF-WRHA30 (18 wt %), and (——) EF-BRHA30 (18 wt %). (a) In air and (b) in nitrogen.

viously indicated, Figure 8(a) shows in detail that the weight loss rate increases as a consequence of the thermal decomposition of BRHA inside this temperature range. In the second stage, the oxidation of the residue formed from the thermal decomposition of the matrix at 200–400°C occurs. Both ashes accelerate the thermal decomposition of the residue as shown by the lower values of T_{max} (see T_{max2} in Table II). IPDT results in air increased with the ash content (WRHA or BRHA) because their volatile fraction is reduced. The samples filled with WRHA showed a higher IPDT than samples filled with BRHA. This behavior is a result of higher silica content and consequently the higher thermal stability of WRHA. A similar effect was reported when other inert inorganic fillers were added to different polymers.[5]

The char yield of all the analyzed samples after reaching 700°C is shown in the Table II. Black and white chars were obtained under nitrogen and air

atmospheres, respectively. For the pure epoxy foam, a char yield of 1.5 wt % was produced in air atmosphere. This solid residue may be attributed the formation of SiO_2, from the oxidation of siloxane chain segments present in a low amount in the chemical structure of the polymeric network.[30] For the same sample, a char yield of 11.9 wt % was obtained under nitrogen atmosphere. In this case, the black color and the higher solid residue percentage are attributed to the formation of residual carbon.[30]

For the WRHA- or BRHA-filled epoxy foams, the char yield increased proportionally with the content of both ashes. On the other hand, under air atmosphere, lower char yields were obtained in the samples filled with BRHA. This difference is due to the higher content of carbon in the BRHA, which is removed in oxidative atmosphere.

The solid residues percentage after reaching 700°C in all the composites can be predicted by using a simple mixture rule from experimental values of char yield of pure component (ash and epoxy foam) obtained under the same conditions as follows.[31]

$$W_T = f_{RHA}W_{RHA} + f_{EF}W_{EF} \qquad (6)$$

where W_T is the predict weight residue percentage; W_{RHA} and W_{EF} are the weight percentage of rice husk and epoxy, respectively; and f_{RHA} and f_{EF} are the weight fraction of rice husk and epoxy, respectively. The experimental and predict char percentages were similar for all percentages analyzed, even while considering the experimental error of the measurements (Table II). These results suggest that in the residue the components behave as individual ones with no interaction between them.

CONCLUSIONS

The incorporation of two types of rice husk ashes to epoxy foams modify their final morphology, decreasing their average cell size and increasing the number of cells per volume unit. This indicates that rice husk ash particles act as a nucleating agent on foaming process.

The mechanical properties of the epoxy foams improve especially with the incorporation of WRHA. For example, the specific modulus increases from 0.469 to 0.760 MPa m³/kg for 0 and 22.7 wt % of WRHA. This improvement is not observed in the samples filled with BRHA.

The initial degradation temperature did not change with the incorporation of ash. However, BRHA accelerates the thermal decomposition during the initial stage in air atmosphere. In all the samples, the presence of inorganic and thermally stable filler reduces the amount of volatiles during the complete thermal degradation process, as shown by the higher IPDT results.

TABLE II
Thermal Stability Data from Thermogravimetric Analysis

Sample	RHA (wt %)	Atm.	IDT (°C)	T_{max1} (°C)	T_{max2} (°C)	IPDT (°C)	Exp. char at 700°C (wt %)	Predict char at 700°C (wt %)
EF	0	N_2	322	389		548	11.9	11.9
EF-WRHA10	6.8	N_2	322	389		640	18.6	18.7
EF-WRHA20	12.8	N_2	321	390		726	23.7	24.7
EF-WRHA30	18.0	N_2	323	390		879	31.4	29.9
EF-WRHA40	22.7	N_2	323	389		1072	35.9	34.6
EF-BRHA10	6.8	N_2	323	389		668	20.2	17.4
EF-BRHA20	12.8	N_2	324	388		737	24.4	22.3
EF-BRHA30	18.0	N_2	323	390		824	26.8	26.5
EF-BRHA40	22.7	N_2	325	390		889	33.8	34.6
EF	0	Air	255	324	567	464	1.5	1.5
EF-WRHA10	6.8	Air	257	325	560	511	8.4	8.3
EF-WRHA20	12.8	Air	256	324	549	613	13.7	14.3
EF-WRHA30	18.0	Air	257	326	548	684	18.4	19.5
EF-WRHA40	22.7	Air	258	329	545	768	23.3	24.2
EF-BRHA10	6.8	Air	257	321	565	504	4.5	4.8
EF-BRHA20	12.8	Air	256	313	546	534	7.7	7.8
EF-BRHA30	18.0	Air	256	314	545	595	12.3	10.4
EF-BRHA40	22.7	Air	255	312	544	614	12.9	12.7

The final conclusion of this study is the valid use of WRHA as reinforcing agent of epoxy foams. This means the increase of the added value for rice husk, currently considered a waste product with no industrial reuse possibilities.

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