

Microcellulose Fibers-Filled Epoxy Foams

P. M. Stefani, C. J. Perez, V. A. Alvarez, A. Vazquez

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

Received 28 August 2007; accepted 10 January 2008

DOI 10.1002/app.28162

Published online 11 April 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The dynamic-mechanical behavior of epoxy foams reinforced with microcellulose fibers was investigated. Microcellulose fibers were obtained from sisal fibers by a several step process which includes chlorination, alkaline extraction, and bleaching. To analyze the effect of cellular structure on DMA properties, unreinforced and reinforced unfoamed epoxy samples were also used. SEM experiments demonstrated that the addition of microfiber modified the final morphology, decreasing the average cell

size and increasing the number of cells per volume unit. The dynamic-mechanical behavior of the reinforced samples, unfoamed epoxy and foamed epoxy, showed improvements with respect to the unreinforced ones, but the effect was remarkable in the second case. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1009–1013, 2008

Key words: epoxy foam; sisal fiber; dynamical-mechanical properties; microcellulose

INTRODUCTION

Epoxy foams are cellular materials that display exceptional properties such as low shrinkage and moisture absorption, and excellent mechanical behavior.^{1,2} All of these properties make them very useful for several industries especially for transportation and construction.³ These materials have been extensively used since 1970 in the fabrication of naval vessels, military vehicles, aircraft, buildings, and offshore structures. In the last years, cellular materials have been reinforced with different fillers mainly particles and fibers.^{4–11} Whereas for pure foam the final properties depend on foam density and the geometrical structure of cells; in the case of reinforced foam; the particle source, size and content can also affect the cellular structure.

In two previous articles we have characterized a commercial epoxy foam system. The optimum epoxy-amine relationship and effect of foaming agent amount on the final morphology, density, and mechanical properties was determined.¹² After that, it was established that the addition of rice husk ashes to the same system¹¹ influenced the final morphology (average cell size decreased and the number of cells per volume unit increased) and improved the mechanical properties.

Natural fiber reinforced-foams have a significant implication on the reduction of density which is of crucial importance for construction and automobile

components. These materials exhibited high specific stiffness and tensile strength.¹³ Also, these fibers are very cheap driving to a material with very low cost/benefit relationship. However, the effect of this kind of reinforcements on the dynamic-mechanical properties of cellular materials has not been completely investigated.¹⁴ As it is known, the viscoelastic properties of a polymeric-based material in close relationship with time–temperature is a chief property for engineering applications that can be studied by means of the dynamic mechanical analysis (DMA). So, the study of DMA properties of these materials is really important for design purposes.

The aim of this work was to establish the effect of microcellulose fiber incorporation on the final morphology and dynamical-mechanical properties of epoxy foam. An unfoamed epoxy was used for comparison.

EXPERIMENTAL

Materials

Epoxy foams were formulated using a commercial system (Epoxy LY5054, amino hardener DY5054 and polydimethylsiloxane HY5054 as chemical foaming agent) supplied by Ciba-Geigy, Bassel. Epoxy resin was heated to 80°C and degassed by vacuum 24 h before use. The siloxane and amine were used as received. Sisal fibers from Brascorda, Brazil were used as raw material to prepare the microcellulose fiber.

Preparation of microcellulose fiber

Before microcellulose fiber (or microfiber) production a preconditioning of sisal fiber was carried out: first

Correspondence to: P. M. Stefani (pmstefan@fi.mdp.edu.ar).

Contract grant sponsor: CONICET, ANPCyT.

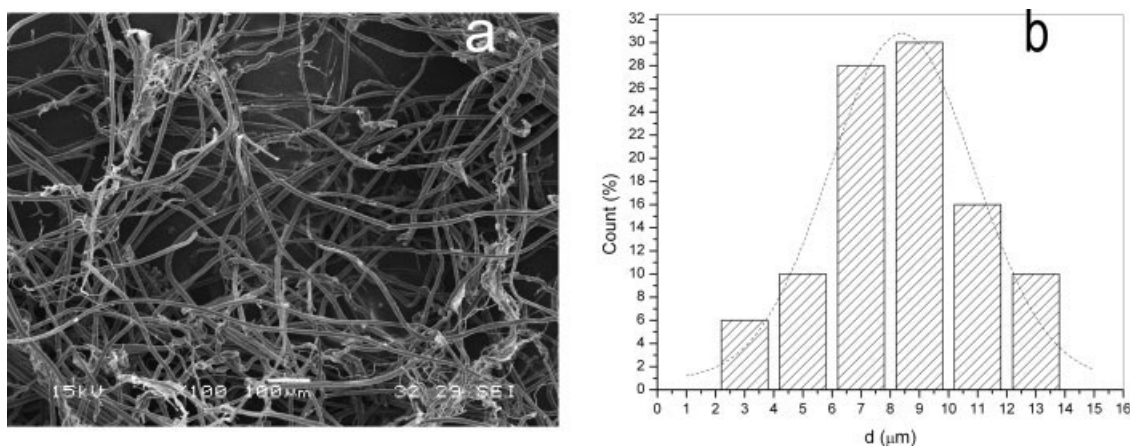


Figure 1 (a) SEM micrograph of microcellulose fibers obtained from sisal fibers; (b) Microfibers diameter distribution (histogram).

the fibers were washed with distilled water several times and dried in an oven at 80°C for 24 h. Then they were chopped to an approximate length of 5–10 mm. Finally the dewaxing of fiber was done by boiling them in a mixture toluene (Anedra)/ethanol (Anedra) (2 : 1 v/v) for 6 h. The dewaxed fibers were filtered, washed with ethanol for 30 min and drying to constant weight. After that, the following procedure was used: (i) holocellulose (α -cellulose + hemicellulose) was produced by the gradual removal of lignin: treatment with 0.7 wt/v % sodium chlorite (NaClO_2 ; PA Fluka Chemie) at pH 4 (buffer solution; Anedra) by boiling for 2 h using a fiber : liquor ratio of 1 : 50 and treated with sodium bisulphate (Barker) solution 5 wt/v %; (ii) treatment of holocellulose with 17.5 wt/v % NaOH (PA Anedra) solution; (iii) filtering, washing with distilled water, and dried at 60°C in a vacuum oven till constant weight.^{15,16}

Preparation of epoxy foams

The chemical reactions during the foam formation were described in our previous paper.¹² During the foaming process the amino hardener (amine) reacts with the blowing agent (siloxane) and the epoxy resin. In the first reaction, hydrogen gas is produced, leading to the formation of bubbles, which occurs simultaneously with the crosslinking of the amino hardener and the epoxy resin. The epoxy foam was synthesized with a ratio of epoxy : hardener : blowing agent of 100 : 35 : 1 (by weight), respectively. Different microfiber contents (0, 0.5, and 1 wt %, respect to total mass) were used to reinforce the epoxy foam. Initially, the microfibers were mixed with liquid epoxy resin using a mechanical stirrer for 3 h at 80°C. The mixture was degassed at 80°C, cooled at room temperature and finally the amine and siloxane were added. The reactive mixture was stirred for 10 min, and then it was placed in an oil bath at 50°C to allow the free

foaming process. The temperature of 50°C was selected because the foaming process occurs at slow rate and prevents the coalescence of bubbles.¹² The obtained foams were then placed into an oven at 130°C for 3 h to ensure completion of the reaction. All foams were manufactured to achieve a density of $350 \pm 10 \text{ kg/m}^3$. Unfoamed epoxy-amine samples were prepared in a similar way without using blowing agent.

Test methods

A dynamic mechanical analyzer (DMA 7, Perkin-Elmer) was used to determine the storage modulus (E') as a function of the temperature. Samples of 20 mm \times 6 mm \times 2.5 mm were tested in three-point bending mode from 20 to 160°C at 10°C/min and a fixed frequency of 1 Hz.

The morphological characterization of both, average diameter of microfiber and the cell size of epoxy foam, was performed with a scanning electron microscope (SEM, JEOL 505) and using the Image-Pro Plus software.

Micrographs of the foam were magnified, and regions containing approximately 50 bubbles were analyzed. This analysis led to the determination of the bubbles-size distribution, as n (number of bubbles) versus D (diameter) for each sample. The average diameter of the bubbles (D_b) and void fraction (f_v) were calculated from eqs. (1) and (2), respectively,¹⁷

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

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

where A_T is the total area of the sample and D is the diameter of each bubble. Equation (2) assumes that

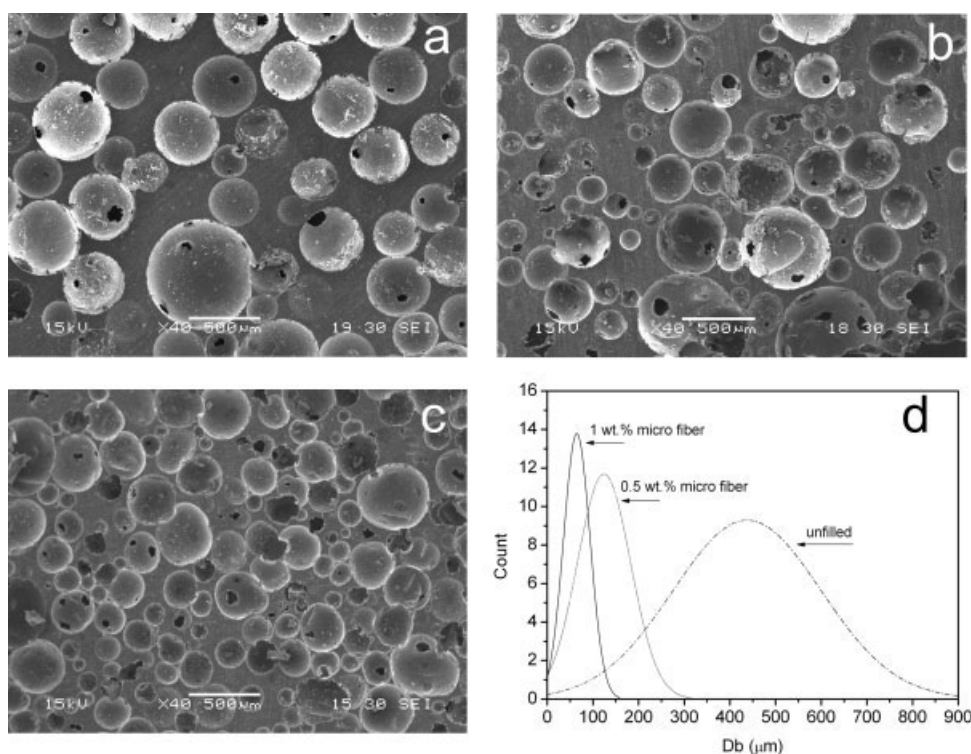


Figure 2 SEM micrographs of the pure and reinforced epoxy foams with different amounts of microfibers: (a) unfilled; (b) 0.5 wt % of microfiber and (c) 1 wt % of microfiber. (d) Bubbles diameter distribution for each sample.

the volume fraction is an isotropic property and so that, the values measured in the plane are the same as in the volume.¹⁷

RESULTS AND DISCUSSION

Figure 1(a) shows the microfibers obtained from sisal fibers. From this figure and by using adequate software (Image-Pro Plus), the average length and diameter of the microfibers were determined. Figure 1(b) shows the microfibers diameter distribution: the average diameter (d) of the fibers was $8.38 \pm 2.51 \mu\text{m}$ whereas the average length (L) was $2.07 \pm 0.785 \text{ mm}$ giving an aspect ratio (L/d) of around 232.3 ± 24.1 .

Figure 2(a-c) shows the SEM micrographs of the pure and reinforced epoxy foams. All the samples displayed spherical bubbles and the contact points were very low. Both characteristics are typical of high density foams. The variations of average bubble size and voids fraction with the microfiber content are summarized on Table I. Whereas the average bubble size decreased from 367 to 201 μm ; the number of bubbles per area unit increased three times with the addition of only 1 wt % of microcellulose fibers. Both results are related with the nucleating effect of microfiber during foaming process.^{18,19} Nevertheless, the void fraction (f_v) remains almost constant (around 55%) indicating that this parameter

depends only on the foaming agent content (the same in all samples).

Figure 3(a) shows a microfiber inside the epoxy foam matrix. It is clear from this figure, that microfiber is coated with epoxy matrix; this result indicates good fiber-matrix adhesion. On the other hand, as it is shown on Figure 3(b), microfibers are situated within the cell walls of the foam (intersection between bubbles). Both factors; fiber orientation and fiber-matrix adhesion, contribute to the improvement of the mechanical properties of the neat epoxy foam matrix.²⁰⁻²²

Figure 4(a) shows the effect of temperature and microfiber content on storage modulus of epoxy foams. As it can be observed, the microfiber did not affect the beginning of glass transition (around 92°C for all the samples). The same result was reported in our previous paper for pure epoxy foam.¹² As a general trend, the storage modulus was monotonically

TABLE I
Morphological Parameters of Microfiber Reinforced Epoxy Foam

Microfiber content (wt %)	D_b (μm)	f_v (%)	Number of bubbles for area unit (mm^{-2})
0.0	367	0.54	4.5
0.5	258	0.55	8.8
1.0	201	0.53	14.8

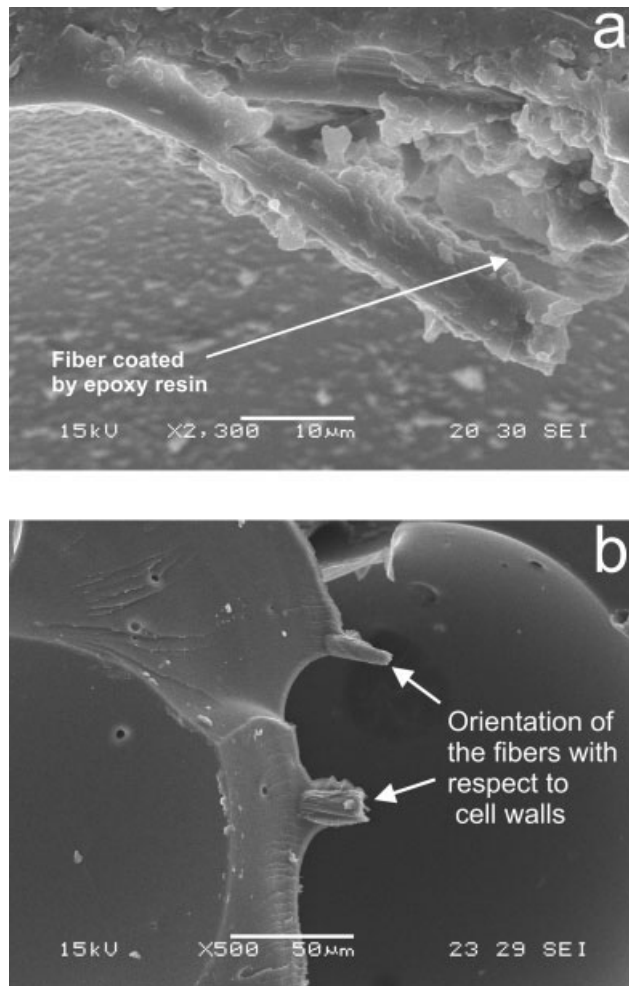


Figure 3 SEM micrographs of epoxy foam reinforced with 1 wt % of microfibers. (a) Fiber/epoxy foam adhesion; (b) position of the fibers with respect to the cell walls.

decreased with the temperature until the glass transition was reached. At the glass transition region the storage modulus drastically drops and foam reaches the rubber-like state. From Figure 4(a), it is clear that the storage modulus in both, the glassy and the rubber-like states, increased with microfiber content. These results are in agreement with previous studies on epoxy foams.^{8,11,13}

The mechanical behavior and durability of composite materials do not depend only on the properties of each component (matrix and fiber) but also on the fiber-matrix interfacial bonding that is related with the physical and chemical characteristics of fiber and matrix^{20,23,24} and on the fiber aspect ratio. In our case; the matrix and the microfiber are compatible [see Fig. 3(a)], because they are both hydrophilic in nature and the microfibers aspect ratio is very high.^{25,26} In addition, fiber orientation [Fig. 3(b)] has also a significant influence on the mechanical properties of the final composites because the strength is maximum along the microfiber axis.

Figure 4(b) shows the effect of temperature and microfiber incorporation on the storage modulus of unfoamed epoxy. Once again, the microfiber does not influence the glass transition temperature; the storage modulus decreases as a function of the temperature and this parameter clearly increased with the microcellulose in all the range of temperatures.

To compare the effects, Table II shows the change in storage modulus as a function of microfiber content for unfoamed and foamed epoxy in the glassy (T_{room}) and rubber like states ($T = 140^{\circ}\text{C}$) calculated as:

$$E'(\%) = \frac{E'_{\text{composite}} - E'_{\text{matrix}}}{E'_{\text{matrix}}} \times 100 \quad (3)$$

As it can be observed from this table, the storage modulus is really improved when microfibers are incorporated for the unfoamed as well as for the foamed epoxy and in both states (glassy and rubbery states) but the changes in the foams are higher prob-

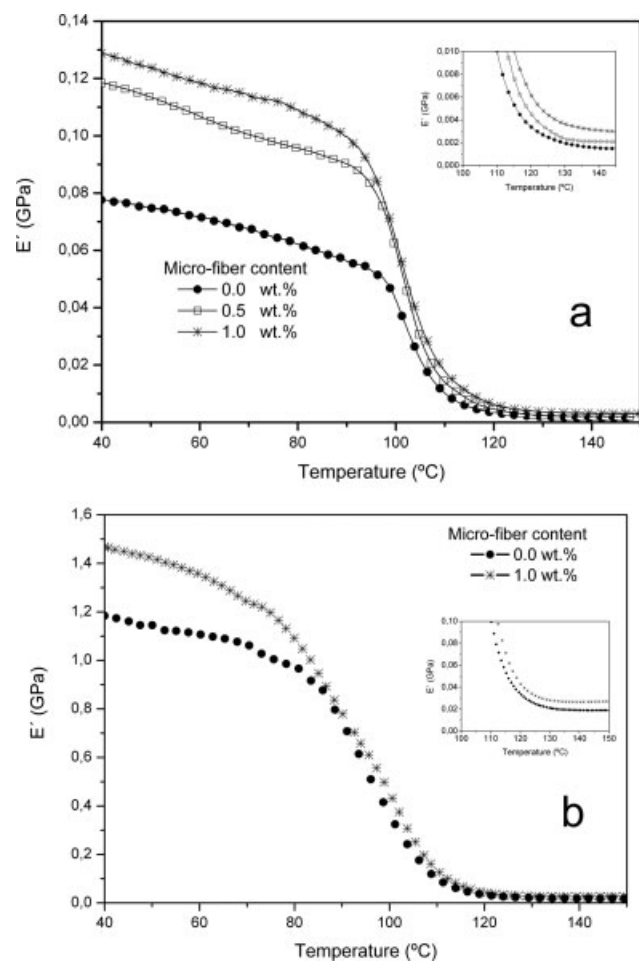


Figure 4 Storage modulus as a function of temperature for (a) pure epoxy foam and composites with 0.5 and 1 wt % of microfibers and (b) pure unfoamed epoxy and composite with 1 wt % of microfibers.

TABLE II
Change in Storage Modulus as a Function of Micro Fiber Content for Epoxy and Epoxy Foam in the Glassy and Rubber States

Material	E'_{Room} (MPa)	Increase (%)	$E'_{140^{\circ}\text{C}}$ (MPa)	Increase (%)
Epoxy	1210 ± 20	–	19 ± 2	–
Epoxy 1 wt % microfiber	1610 ± 10	32.9 ± 1.5	27 ± 2	39.5 ± 11.7
Epoxy foam	87 ± 2	–	1.5 ± 0.1	–
Epoxy foam 0.5 wt % microfiber	130 ± 4	50.2 ± 6.4	2.1 ± 0.2	36.6 ± 10.0
Epoxy foam 1 wt % microfiber	137 ± 6	57.6 ± 6.5	3.1 ± 0.2	102.0 ± 10.8

ably due to the fiber orientation because all the other factors are the same in both cases.

CONCLUSIONS

Epoxy foams reinforced with low cellulose microfiber content (0.5 and 1 wt %) obtained from sisal fibers with a constant density were fabricated. It was determined that these fibers have a nucleating effect on the foaming process.

From the DMA analysis it was demonstrated that microfibrils greatly improved the storage modulus in both the glassy and rubber-like states for unfoamed as well as for the foamed epoxy. The enhancement was related with the high fiber aspect ratio (determined from diameter and length analysis), the microfiber-matrix adhesion (observed by SEM) being both the same for unfoamed and foam epoxy and with the additional effect of the microfibrils orientation on the cell wall in the case of the foam. The microfiber content exhibited only a little additional contribution to storage modulus at room temperature.

Future works will be carried out to analyze the effect on the mechanical properties and foaming process by incorporating nano-cellulose fibers as reinforcing agent of epoxy foams.

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