Influence of Fiber Volume Fraction and Aspect Ratio in Resol–Sisal Composites

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ABSTRACT: Vegetable fibers are being used as reinforcements in polymeric matrices with a wide variety of applications. Among these fibers, sisal is of particular interest due to the high impact strength and moderate tensile and flexural properties of its derivated composites. Because of its low cost and affinity, a phenol–formaldehyde resin, resol, has been selected as the matrix to obtain resol–sisal composites. The influence of fiber length and volume fraction on flexural properties has been studied. An optimum for the fiber length as well as for the fiber volume fraction was found. The improvement of the properties occurred up to a length of about 23 mm. The use of longer fibers lead to reduced properties because they tended to curl and bend during processing. Besides, actual composite densities were lower than theoretical ones mainly due to the presence of voids. This undesirable porosity produced a reduction in flexural properties at high fiber contents. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2714–2722, 2003

Key words: composites; thermosets; mechanical properties; fibers

INTRODUCTION

The application of vegetable fibers as reinforcement in polymer composites has been continuously growing during the last years. Their low density values allow the production of composites that combine good mechanical properties with a low specific mass. The properties of composites depend on those of the individual components and on their interfacial compatibility. The influence of the interfacial region on the behavior of the final composite is significant. The absorption of moisture by natural fibers, poor wettability, and insufficient adhesion between polymer matrix and fibers lead to debonding and make their use in composites less attractive.[1] However, certain polymers such as phenol–formaldehyde resins, can generate chemical bonding with the lignocellulosic reinforcements, leading to strong forces between fiber and resin.[2] Thus, a high compatibility in the system vegetable fiber–polymer is achieved.

Because of the discontinuous nature of the vegetable fibers, it is necessary to consider that the tensile stress and stiffness of the composites are strongly influenced by the fiber length and its orientation. As the aspect ratio, AR ($AR = L/\phi$, where L and ϕ are fiber length and diameter, respectively), of the fibers decreases, the end effects become progressively more significant and the efficiency of the fibers in stiffening and reinforcing the matrix decreases. The effective modulus and strength of short fiber composites are, in general, lower than those of the continuous fiber composites, and in order to achieve the maximum level of stress in the fiber, the fiber length, L_f, must be at least equal to a critical value, L_c , known as the *critical fiber length.* L_c may be defined as the minimum fiber length required for the stress to reach the fracture stress of the fiber. Composites with $L_f < 5L_c$ have shown strength significantly lower than that of a continuous fiber composite with the same volume fraction (V_f) of fiber. However, the strength of a short fiber composite increases with the fiber length for a given V_f, and differences with continuous fiber composites become negligible if fibers are longer than 10 L_c.[3]

The effects of fiber lengths on the mechanical properties in different fiber–resin systems have been reported by various authors. Xian and coworkers[4] evaluated the mechanical properties for plastic composites prepared with bamboo fiber, varying its lengths, and they concluded that in terms of overall performance the composites would rank as follows: long bamboo fibers > short bamboo fibers > chopped bamboo fibers.

Paiva et al.[5] analyzed the impact behavior on composites from different phenolic resins and randomly oriented sisal fibers that were 1.5, 2, and 3 cm long. It was shown that the impact strength was higher as the fiber length increased.

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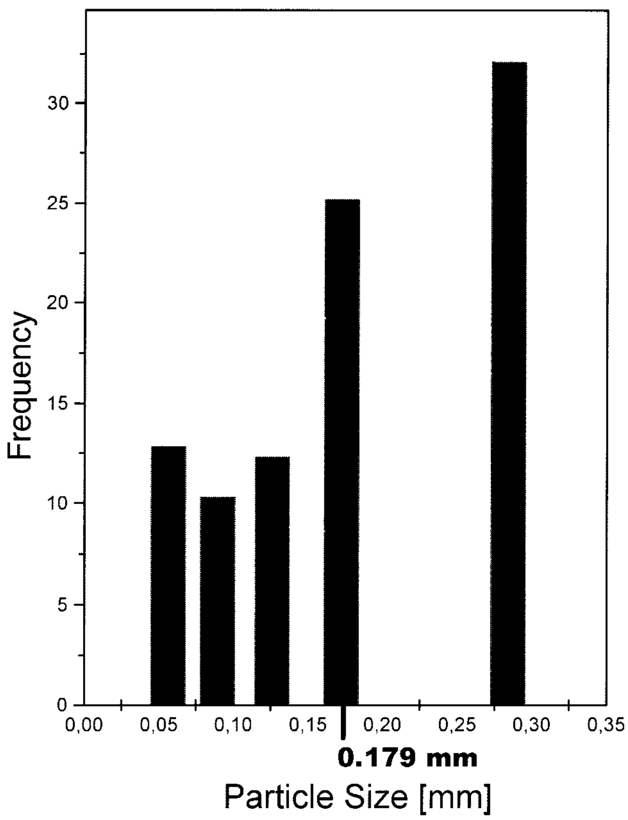

Figure 1 Particle size distribution of sisal powder.

Joseph et al.[6] studied composites from short sisal fibers and polyethylene, with fiber length from 2.1 to 9.2 mm. The strength and modulus of the composites showed an enhancement in their values by increasing the average fiber length from 2.1 to 5.8 mm followed by a decrease in the properties when a fiber length of 9.2 mm was employed. They attributed this reduction to the bending and curling of long fibers during the molding, causing a reduction in the effective length.

Similar results were found by Uma Devi et al.[7] They studied the tensile, flexural, and impact behavior of pineapple leaf fibers–reinforced polyester as a function of fiber loading, fiber length, and fiber surface modification. The mechanical properties were optimum for a fiber length of 30 mm.

In a previous work,[8] composites from resol–cotton, resol–sugar cane bagasse, as loose fibers, and resol–sisal fibers, as a mat, were analyzed. The results showed that the flexural properties for loose fiber composites presented a maximum for certain fiber volume fraction (V_f). At higher fiber loads these properties decreased. On the other hand, the modulus and strength of sisal composites always increased as V_f increased. The latter behavior was attributed to two causes, the arrangement of the fibers and the fiber length.

The objective of this work was to study the flexural properties of resol–sisal composites for several fiber lengths and fiber volume fractions as loose fibers and mat arrangements, to find the best fiber length range for this system and the existence of a maximum in the properties at an optimum fraction of loose fibers.

MATERIALS

The material used as matrix was a resol (R472; Atanor, Argentina), with 60.6% solids and a viscosity of 230 cp at 19°C. The sisal fibers (Indústria e Comercio Marques LTDA, Sao Paulo, Brazil) with a diameter (ϕ) of 0.19 ± 0.027 mm, were used as follows:

1. Nonwoven mats (S): fibers are in a needle punched web or continuous sheet, placed in a random manner and mechanically entangled (L = 43.6 mm; AR = 227.08).
2. Long loose fiber (FL): obtained by disentangling of the fibers from the mat (L = 43.6 mm; AR = 227.08).
3. Short loose fiber (FC): cutting the long loose fiber (L = 23.7 mm; AR = 123.44).
4. Extra short loose fiber (FCC): cutting the short loose fiber (L = 11.1 mm; AR = 57.81).
5. Sisal powder (PS_{ave} = 0.179 mm; AR = 0.93).

where PS_{ave} is the average particle size and is obtained after sieving the powder obtained in a mill IKA Labortechnick (Germany) 250 mL. Figure 1 shows the complete particle size distribution.

The properties of the sisal fibers and resol are given in Table I. The fiber mechanical properties were determined according to ASTM D3379 (single-filament tensile test). However, the flexural test (ASTM D790) was used for pure resol due to its inherent brittleness.

EXPERIMENTAL

All the fibers/particles were washed in distilled water and 2% detergent solution. They were water rinsed, dried in an oven, and cooled in a dessicator until achieving constant weight. The sisal mat was cut according to the mold dimensions. The loose fibers were arranged randomly to fit those dimensions.

Composites were prepared in an aluminum mold (ϕ = 145 mm and thickness = 3 mm) where the loose fibers or the fiber mats were placed. After that, the

TABLE I
Physical and Mechanical Properties of Raw Materials

Property	Resol	Sisal
Density, ρ (g/cm^3)	1.2433 ± 0.04	1.3624 ± 0.17
Strength, σ (MPa)	94 ± 10.5	420 ± 19
Elongation at break, ε (%)	0.03 ± 0.007	6.34 ± 0.38
Modulus, E (GPa)	2.58 ± 0.46	17.25 ± 1.2

resin was added and the mold closed. In the case of sisal powder composites (P), the powder and the resin were premixed and then introduced into the mold. The curing process was always performed under pressure (2.1 MPa), following the same thermal schedule: 60 min at 90°C, 90 min at 140°C, and 30 min at 175°C. Then, the composites were cooled down under pressure.

Finally, a theoretical value for the volume fraction of filler, V_f, was calculated as follows:

$$V_f = (W_f/\rho_f)/[(W_f/\rho_f) + (W_m/\rho_m)] \quad (1)$$

where W_i is the weight fraction, ρ_i is the density, and subscripts f and m denote fiber and matrix, respectively. The calculation of the volume fraction of natural fiber composites is difficult because of the inefficient penetration of the resin into the lumen of the fiber cells. This results in an underestimation of V_f in all the composites. However, differences in porosity of the composites were the result of different fiber arrangement and not of fiber chemistry, because all composites were prepared with the same sisal fibers.

The density of the composites, ρ_c, was measured by picnometry in distilled degassed water at 20°C. The void volume fraction, V_V, was calculated as follows:

$$V_v = (\rho_{\text{theoretical}} - \rho_{\text{experimental}})/\rho_{\text{theoretical}} \quad (2)$$

with

$$\rho_{\text{theoretical}} = \rho_f \times V_f + \rho_m \times (1 - V_f) \quad \text{(Rule of Mixture)} \quad (3)$$

Three point bending tests were performed using a Shimadzu Autograph S-500-C Universal testing machine (Kyoto, Japan), according to ASTM D790M. At least five specimens for each condition were tested. The fracture surfaces after flexural tests were analyzed through scanning electronic microscopy (SEM) using a Philips SEM 505 microscope (Eindhoven, The Netherlands).

RESULTS AND DISCUSSION

Density

The experimental densities of composites and the theoretical values calculated by the rule of mixture (ROM) are plotted as a function of V_f in Figure 2. The density of mat composite for $V_f \approx 0.66$ is the only value in agreement with the theoretical prediction. All the other composites have experimental densities below ROM estimation, indicating the presence of voids.

The experimental density values of loose fiber composites present a similar trend with increasing filler

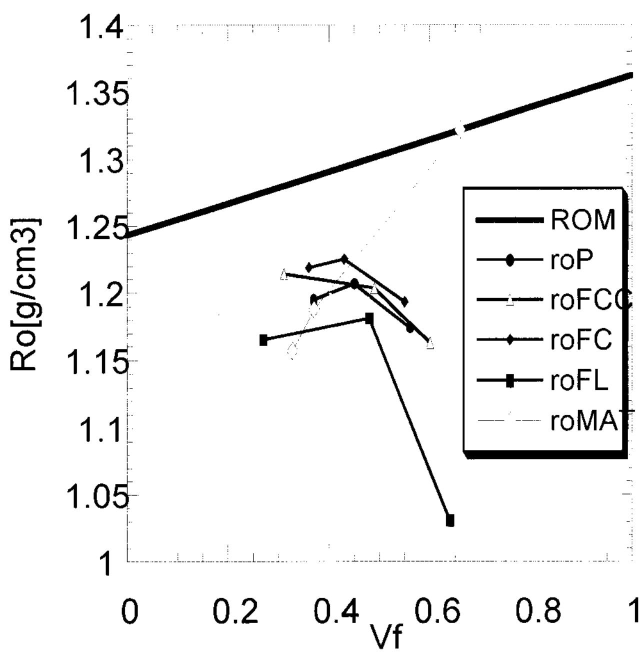

Figure 2 Density of composites as a function of V_f.

content (Fig. 2). The addition of the fibers produces an increment in the density of the composite. However, at high filler concentration, there is an important drop in the density of the composites due to the high volume content of these samples, as is discussed bellow. This drop is especially important in the sisal long loose fiber composites (FL), because the disarrangement of the long fibers increases the difficulty of wetting the sample. It is interesting that the sample prepared from sisal mats shows a different behavior, that is, the density of the composite continuously increases with V_f .

Figure 3 corresponds to the void volume fraction, V_V, as function of V_f. Almost all the composites show a porosity of 10% or less, except for the long loose fiber composites with high fiber content. This elevated value is detrimental for the composite performance, as the higher the porosity, the lower the mechanical properties.

The existence of voids can be attributed to two causes: (1) a deficient wetting of the fibers by the resin and (2) the generation of volatiles as by-products during the curing step. Figures 2 and 3 show the effect of increasing V_f on density and V_v, which leads to a higher void content (and consequently to a lower density), because of the difficulty to obtain good wetting as V_f increases. In the particular case of mat composites the more ordered arrangement of the fibers allows a better wetting, and then a higher density is attained.

Flexural properties

The values of flexural stress, σ_b, flexural modulus, E_b, and elongation at break, ϵ_u, for the composites at different V_f are given in Table II.

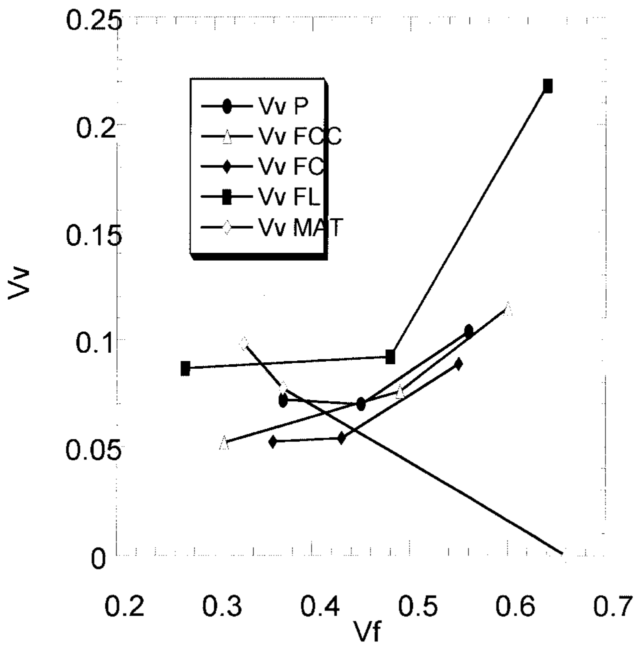

Figure 3 Voids volume fractions as function of V_f.

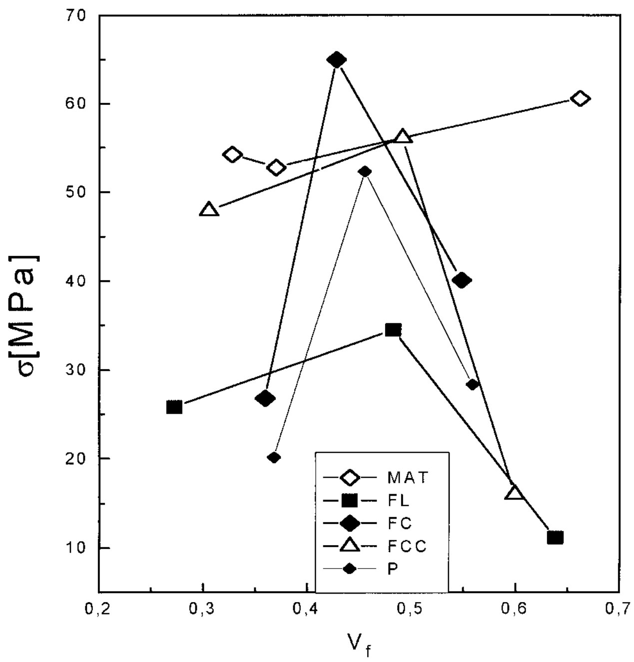

Figure 4 Flexural strength as a function of V_f.

Effect of fiber volume fraction

Figure 4 shows σ_b as a function of V_f for the five studied composites. The results could be unexpected if ROM is considered. According to that, as V_f increases, the mechanical properties should increase, but processing limitations are not taken into account in the theoretical analysis. Nevertheless, the results are consistent with the ones found in a previous work.[8] The loose fiber composites present a maximum in σ_b and E_b around $V_f = 0.5$, and at higher fiber contents these properties decrease. This behavior can be explained by the presence of voids. They act to weaken the composite and lead the materials to break at lower stresses. Areas rich in resin and areas rich in fibers appear due to the lack of good wetting, allowing the contact between fibers and producing a reduction in the composite adhesion.

The higher mechanical properties at higher V_f in mat composites are attributed to the minor percentage of voids and to the fiber mechanical entanglements present in the mat. The latter contributes to maintain the cohesion of the material.

TABLE II
Flexural Properties for Resol–Sisal Composites

Reinforcement	V_f	σ_b (MPa)	E_b (GPa)	ε_u (mm/mm)
S1	0.33	54.2 ± 2.4	2.41 ± 0.08	0.023
S2	0.37	52.8 ± 12.4	3.00 ± 0.99	0.019
S3	0.66	60.6 ± 6.2	3.27 ± 0.25	0.022
FL1	0.27	25.8 ± 5.6	1.78 ± 0.60	0.015
FL2	0.48	34.5 ± 12.0	2.03 ± 0.80	0.02
FL3	0.64	11.1 ± 2.5	0.33 ± 0.09	0.04
FC1	0.36	26.8 ± 14.0	1.34 ± 0.73	0.018
FC2	0.43	65.0 ± 15.7	3.31 ± 0.64	0.023
FC3	0.55	40.1 ± 11.2	2.55 ± 0.46	0.021
FCC1	0.31	47.9 ± 15.0	2.82 ± 0.55	0.016
FCC2	0.49	56.1 ± 11.4	3.02 ± 0.21	0.019
FCC3	0.60	16.0 ± 2.1	0.95 ± 0.26	0.012
P1	0.37	20.1 ± 4.4	1.65 ± 0.28	0.012
P2	0.46	52.3 ± 13.7	2.91 ± 0.52	0.015
P3	0.56	28.3 ± 10.6	2.88 ± 0.51	0.012

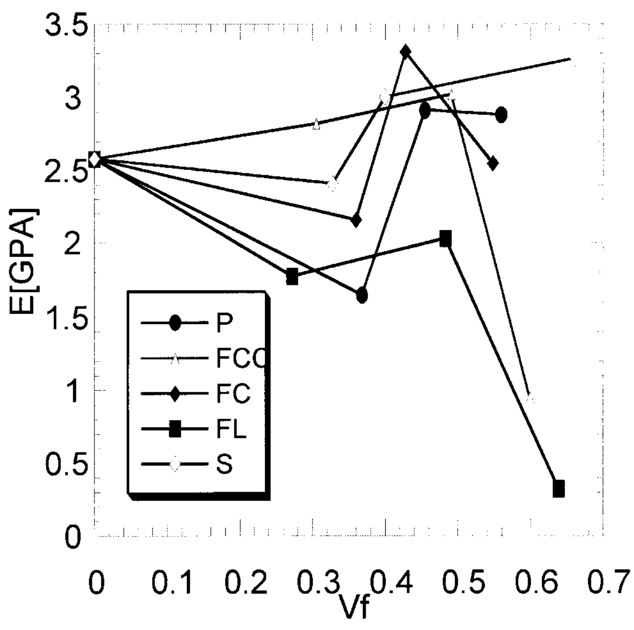

Figure 5 Flexural modulus for resol composites.

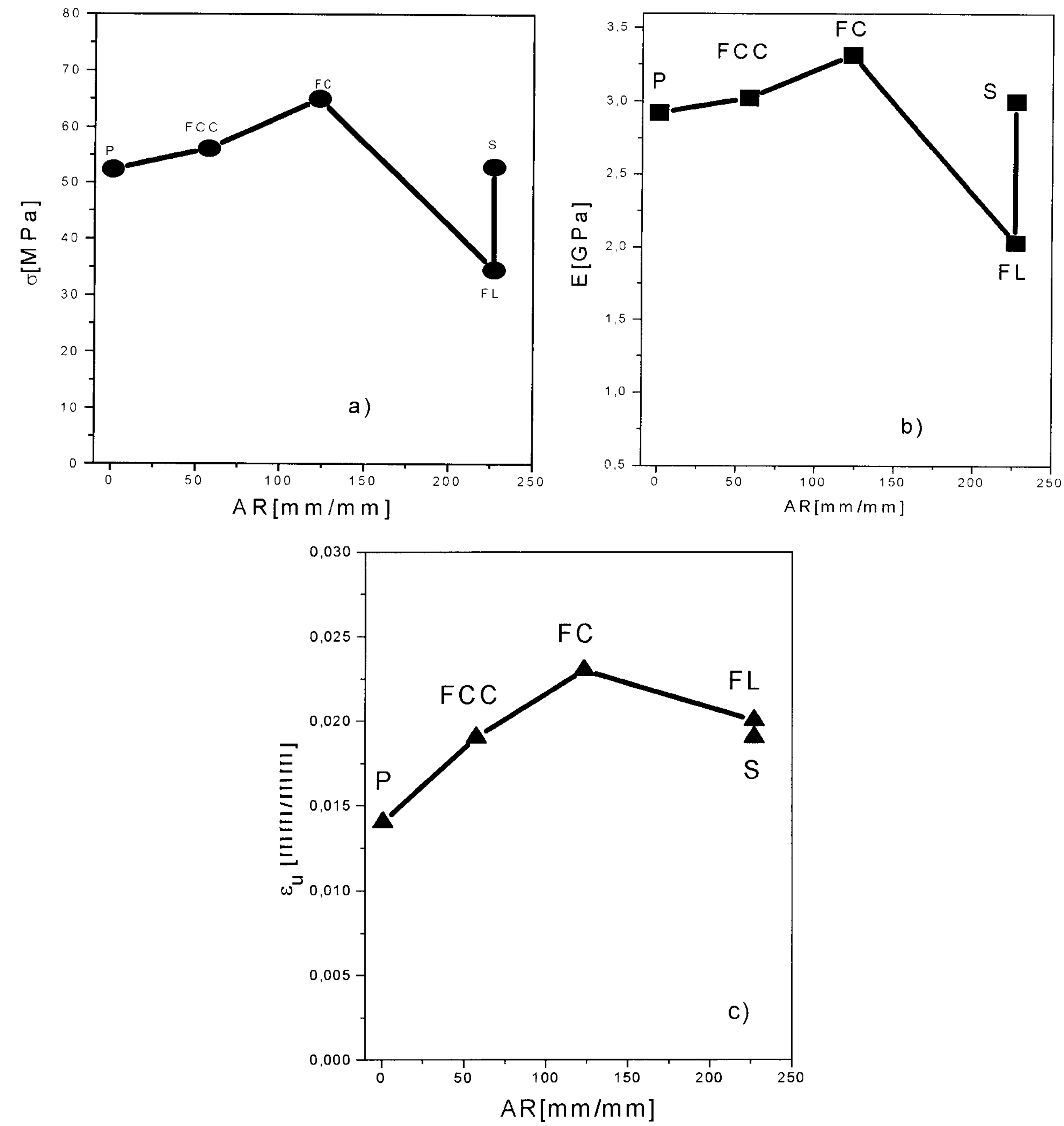

Figure 6 Mechanical properties as a function of AR for $0.4 \leq V_f \leq 0.55$. (a) Flexural strength. (b) Flexural modulus. (c) Ultimate deformation.

The effect of V_f in flexural modulus is plotted in Figure 5. The tendency for FL composites is in accordance to the porosity level found in these materials because voids act as defects lowering final properties.

The presence of an optimum concentration of fibers for flexural strength and modulus has been previously discussed in the literature, and similar trends for different short natural fiber reinforced thermosets have been found.[7,9,10]

Effect of the fiber AR (fiber length)

The influence of AR (AR = L/ϕ) on flexural properties is shown in Figure 6 for the optimum V_f corresponding to each composite. In this case it appears that for the maximum enhancement of properties, the AR should be between 100 and 150. Up to a fiber length of 23.7 mm (AR = 123.44), the flexural modulus and flexural stress of the composites increase as fiber length increases. Composites with very short fibers or particles show strengths significantly lower than that of continuous fiber composites with the same fiber volume fraction. As fiber length decreases, the end effects become progressively more significant, and the efficiency of the fibers in stiffening and reinforcing the matrix decreases.

However, the strength of a short fiber composite should increase with the fiber length for a given V_f, and, for a determined length (approximately 10 times the critical length), the difference between the strengths of the two composites (discontinuous and continuous, respectively) should become smaller. However, FL composites (longer fibers) show reduced properties. This performance is the result of two different features: (1) the high void content in these composites and (2) the fact that longer fibers tend to bend or curl during molding causing a reduction in the effective fiber length. Devi et al.[7] found a similar behavior for the composites with the longest fiber analyzed (L = 40 mm), attributing it only to the second reason. Nevertheless, both conditions contribute to the low properties obtained in FL composites. The elongation at break, ϵ_u, as function of AR follows the same pattern.

It is noted that sisal mat composites (S) show property values some place between sisal short loose fiber composite (FC) and sisal extra short loose fiber composite (FCC) values. Thus, it could be assessed that the effective fiber length in the mat is very different from the one measured, mainly due to mechanical entanglements present among the fibers in the mat.

The results indicate that there exists an optimum fiber length around 23.7 mm for the system resol–sisal loose fiber.

Figure 7 shows the stress–strain behavior of FC composites (23.7 mm). In the case of pure resol, the flexural stress increases linearly with strain. The sharp peak in the region of the maximal force indicates a brittle fracture process and a catastrophic failure. The flexural behavior of composites is nonlinear (stiffness varies with the strain up to the maximum in the strength, probably due to the presence of short fibers). The wide force maximum is due to a pseudo-yielding behavior so that a more ductile fracture is obtained. Besides, the composites present a controlled failure (it could be associated with the fibers pulling out). The simple observation of the curves indicates that the resistance of the material to breakage is improved as composites support higher final deformations.

Although the flexural strength values for the composites are always lower than the one for the neat resin, the controlled failure could allow for tougher materials. The work of fracture (toughness) in a flexural test can be estimated as the area under the stress–strain curve.[11] The results are 1.37, 0.51, 2.16, and 0.91

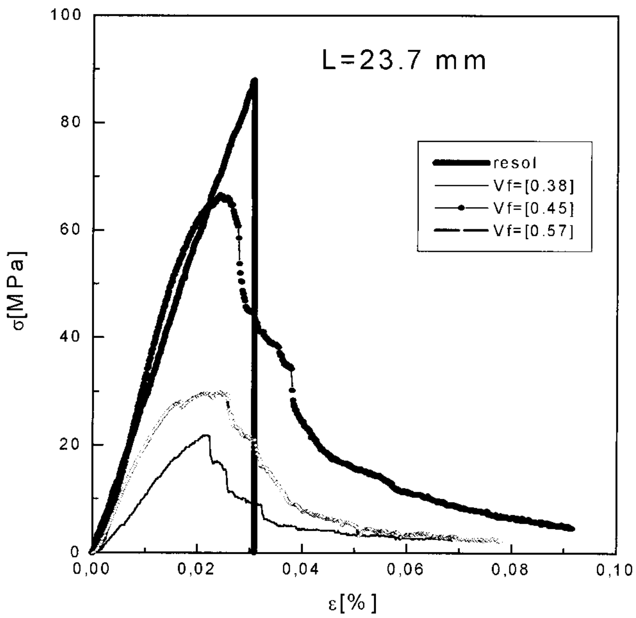

Figure 7 Flexural stress-strain curves of composites for L = 23.7 mm at different V_f.

MPa for resol, FC (V_f = 0.38), FC (V_f = 0.45), and FC (V_f = 0.57), respectively. These results indicate that the incorporation of short sisal fibers (L = 23.7 mm) to the resin increases the work of fracture for a V_f of 0.45.

Figure 8 shows typical bending σ-ϵ curves for pure resin, P, FCC, FC, FL, and S composites. The fiber composites exhibit a controlled fracture with a successive fiber pull out, preventing the catastrophic failure presented by the neat matrix [Fig. 8(a)]. Failure and fracture behavior of the sisal powder composites is intermediate behavior between fiber composites and pure matrix.

Fracture surfaces were observed by SEM. Figure 9 shows the micrographs for FL (V_f = 0.48) and Figure 10 for S (V_f = 0.37) composites. They both illustrate the matrix brittle fracture and the fiber pull-out that were pointed out in the discussion of the σ-ϵ curves from bending tests (Fig. 8). Figure 9(a) reveals the bending and curling of long loose sisal fibers. Figures 9(b) and 10(b) (SEM × 400) show the good fiber–matrix interfacial adhesion. Similar conditions were found in a previous work.[8]

CONCLUSIONS

1. Composite densities were lower than the theoretical ones due to the existence of voids. Their presence was attributed to a deficient wetting of fibers by the resin and to the volatile products that appear during the curing step. The void content could be diminished by optimizing and/or changing the method of preparation.

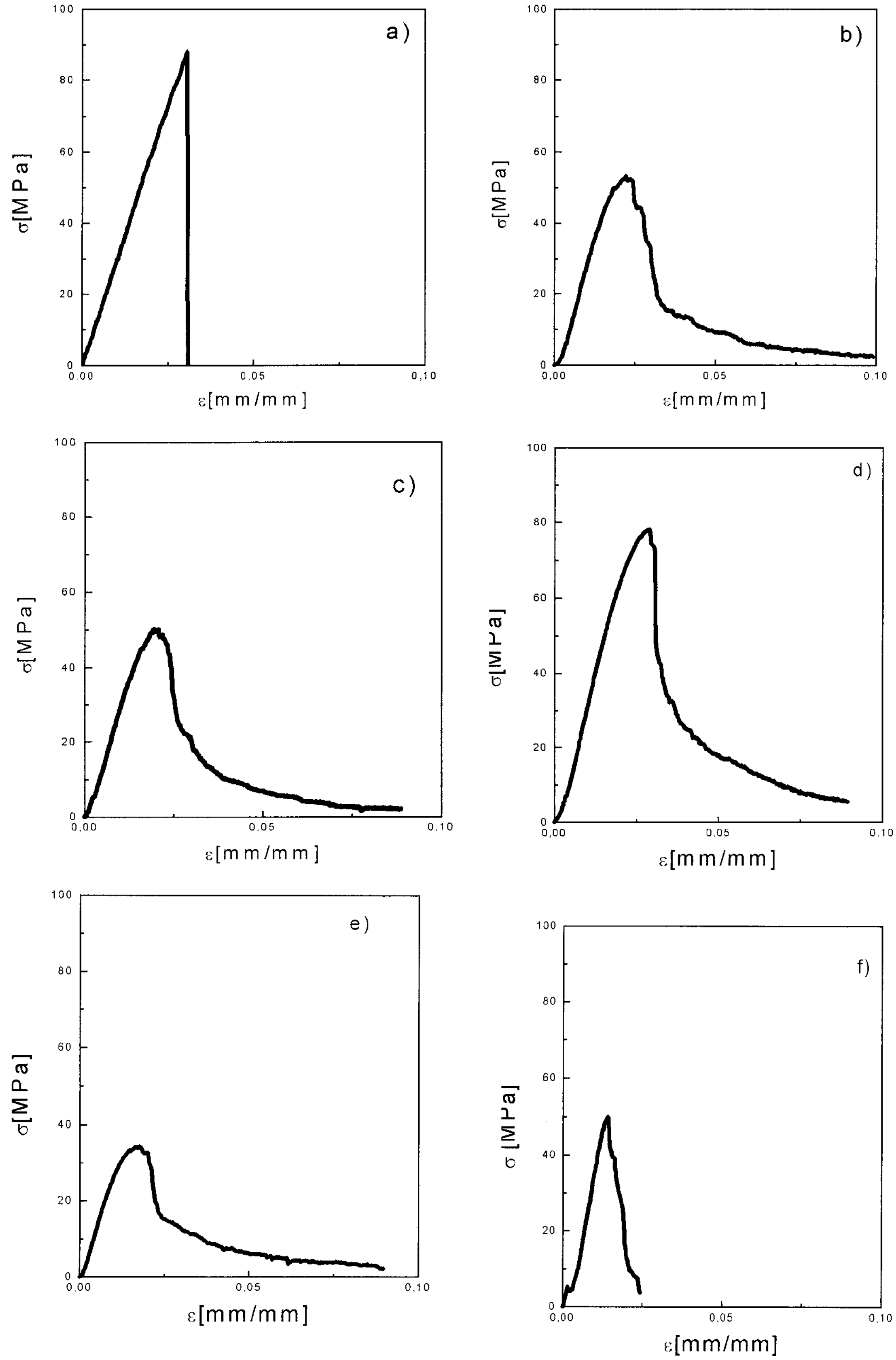

Figure 8 Flexural stress-strain curves for (a) pure resol, (b) resol–sisal mat composite, (c) resol–FL composite, (d) resol–FC composite, (e) resol–FCC composite, (f) resol–P composite.

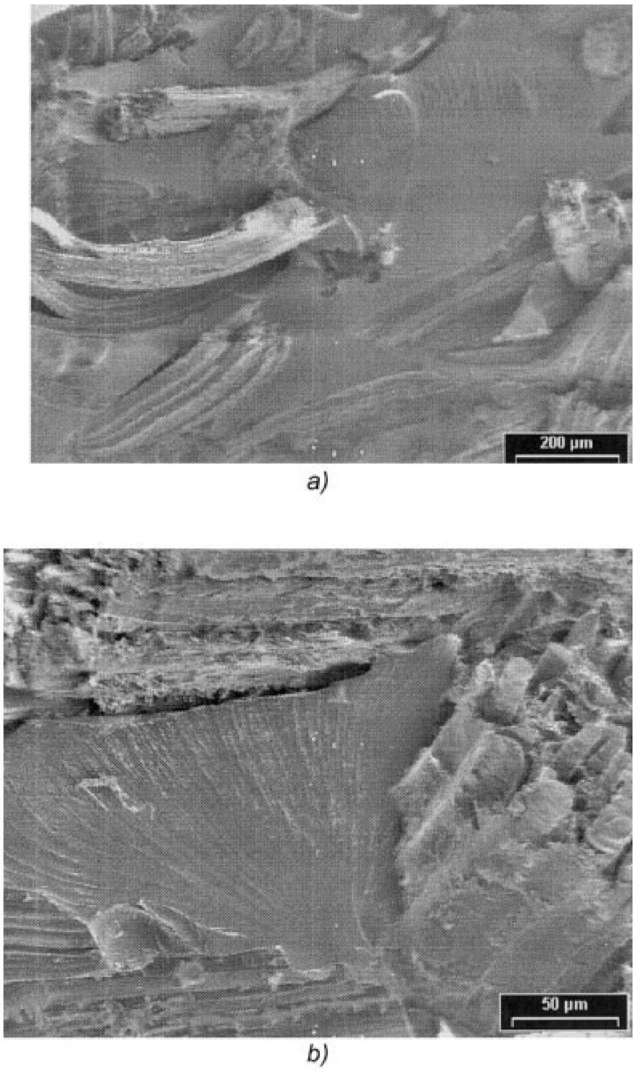

Figure 9 Cross section for FL3 composites. (a) SEM × 100, (b) SEM × 400.

2. The mechanical properties σ_b and E_b of resol–sisal composites are very influenced by both fiber volume fraction and fiber length.
   - 2a. For loose fiber composites (FL, FC, FCC, and P composites), σ_b and E_b increase as V_f increases, up to values of about 0.5. At higher loads, the properties decrease.
   - 2b. As the fiber length increases the properties also increase up to a fiber length of 23.7 mm. For longer loose fibers (FL composites), the properties decrease.
   - 2c. Both tendencies are attributed to the high void content and the bending and curling of long fibers. A great disorder in the composite appears when long loose fibers or high fiber content are used so that a perfect and total wetting of fibers is not accomplished.
3. In the case of mat composites, the lower content of voids and the mechanical entanglement between fibers in the mat lead to higher mechanical properties as V_f increases.
4. There is an optimum fiber length around 23.7 mm for the resol–loose-sisal- fiber composite.
5. The fibers in the mat act with an effective length smaller than the one measured.
6. The incorporation of fibers in a brittle matrix like resol leads to a controlled fracture with a successive fiber pull-out. They improve the mode of fracture, avoiding the catastrophic fracture typical of thermoset resins.
7. A good fiber–matrix adhesion is observed by SEM, mainly due to the chemical compatibility of the components.

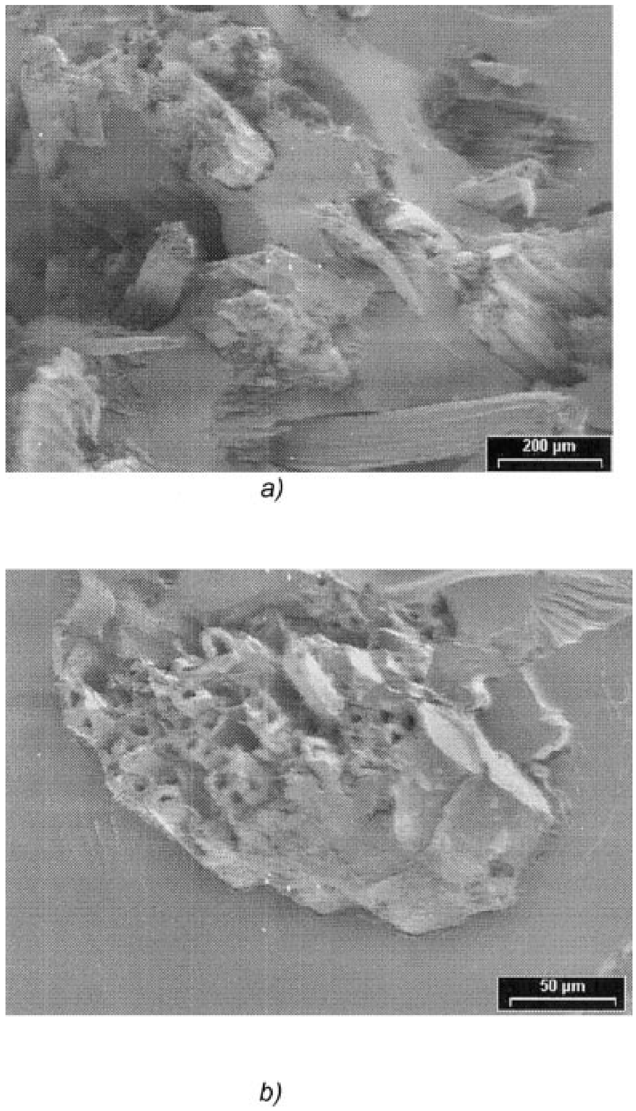

Figure 10 Cross section for S2 composites. (a) SEM × 100, (b) SEM × 400.

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