Resol –Vegetable Fibers Composites

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ABSTRACT: Vegetable fibers like cotton, sisal, and sugar cane bagasse have been used as reinforcement in a polymeric matrix. Because of its low cost and affinity with lignocellulosic fibers, a phenol-formaldehyde resin —resol— was selected as the matrix. Composites were prepared by compression molding. The influence of fiber volume fraction-V_f-in flexural properties and density of composites has been studied. Cotton and sugar cane bagasse composites present a V_f value at which flexural strength and modulus are maxima. However, sisal composites show a continuous rise in flexural strength and modulus as fiber volume fraction increases, up to 76%, which is the highest concentration studied. Composites made with raw cotton show the highest values of strength and stiffness. The actual density of composites is always lower than theoretical density, due to the presence of voids. Scanning Electron Microscopy reveals a good adhesion between fiber and matrix in the composites. In addition, the flexural properties were analyzed with an efficiency criterion, which relates strength and stiffness with density, and the values obtained were compared with those corresponding to typical structural materials. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1832–1840, 2000

Key words: resol composites; cotton fibers; sisal fibers; sugar cane bagasse

INTRODUCTION

A wide range of particulate and fibrous materials is commonly used to make polymeric composites. Besides, the need for new materials with specific properties has led to develop better and cheaper polymer composites. Today, the aircraft, automobile, leisure, electronic, and medical industries are quite dependent on fiber-reinforced plastics, and these composites are routinely designed, manufactured and used. Vegetable natural fibers are of particular interest, especially when weight considerations are fundamental in the design of material's characteristics, and strength and modulus are not a first priority.

The success of combining vegetable natural fibers with polymer matrices results from the improved mechanical properties of the composites compared with the matrix materials. These fillers are cheap and nontoxic, can be obtained from renewable resources, and are easily recyclable. Moreover, despite their low strength, they can lead to composites with high specific strengths because of their low density.

Textile vegetable fibers as cotton, sisal, flax, etc., have many of the requirements that might be expected from an ideal filler, but they are generally used for conventional applications as the production of yarns, fabrics, and clothes. However, in recent times, many of the uses of natural fibers have been threatened by synthetic fibers.

Bagasse is the remaining waste in the sugar cane process and is burnt to generate steam in the

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Table I Properties of Resol

Property	Value
Viscosity (cp) at T = 19°C)	330.17
Solid content [%]	64.32
Density (cured resin) (g/cm^3)	1.243
Tensile stress (MPa)	28[6]
Young modulus (GPa)	1.99[6]

sugar industries. Energy for such industries can be supplied using 50% of the bagasse's production.[1] The remaining 50% can be used in different applications. Hence, there is a need to develop new uses for these fibers.

Vegetable fibers are generally lignocellulosic, consisting of microfibrils with oriented cellulose macromolecules, in a hemicellulose and lignin matrix. The angle between the axis of the fiber and the microfibrils has an important effect on fiber mechanical properties. In general, the smaller this angle is, the smaller is the elongation at break and the higher are elastic modulus and resilience.

The final properties of composites are obviously controlled by the properties and quantities of the component materials and by the character of the interfacial region between matrix and reinforcement. Lack of good interfacial adhesion makes the use of cellulose fiber composites less attractive. But certain polymers, such as phenol-formaldehyde, generate chemical bonding with lignocellulosic reinforcements. Because of the high polarity of phenol-formaldehyde resins, very strong hydrogen bonds are formed with hydroxyl groups. Hence, strong dipole–dipole and van der Waals forces are developed and chemical reactions further occur between fiber components and the resin.[2]

Many researchers have studied different systems vegetable fiber–polymeric matrix. Bisanda et al.[3] studied the effect of silane treatment to improve adhesion between fiber and matrix of sisal–epoxy composites. They found that the flexural strength and stiffness were not affected by the silane; however, the relative density was affected by this treatment. Paiva et al.[4] analyzed the impact strength and hardness of sugar cane bagasse–resol composites, and showed that impact strength increased and hardness diminished as the fiber volume fraction increased. Moreover, phenolic resin composites with cotton fabric have been used in bearings as a substitute for phosphor bronze bearings, resulting in energy saving of up to 25%.[5] Kuruvilla et al.[6] reported that the tensile properties of sisal–polyethylene composites showed a gradual increase with the fiber content (up to 30 wt %).

The objective of this work is to study low-cost engineering materials made from a cheap polymeric resin and vegetable fibers, with similar properties to other structural materials. Thus, a commercially available phenol-formaldehyde resin was used as matrix and three different textile fibers and sugar cane bagasse were utilized as reinforcement. Because of the resin affinity with the reactive groups of vegetable fibers, a superficial treatment to the fibers was not necessary in order to improve adhesion.

The effect of fiber volume fraction on flexural properties and density were analyzed for three different textile fibers and compared with sugar cane bagasse –resol composites. The specific stiffness of the composites was calculated and compared with other typical structural materials.

EXPERIMENTAL

Materials

- The resol type phenol-formaldehyde resin used as matrix was RESOL 472, supplied by

Table II Properties of Fillers

Filler	ϕ (μm)	L (mm)	σ (Mpa)	E (Gpa)	ρ (g/cm^3)	AR[c] (L/ϕ)	U$S/*K*
RC	19.73	25.00	539[3]	8.8[3]	1.531	1267.2	1.29[8]
CC	18.9	24.92	539[3]	8.8[3]	1.411	1318.4	1.21[b]
S	197.21	43.58	548.2	15.9	1.362	221	0.36[9]
B		1.94[a]			1.330		0.16[b]

[a] Average size of particle. The size of 50% of all bagasse particles is between 0.34 cm and 2.16 mm, and the average size presents a large dispersion value.

[b] Price given by Matexsud and Papelera del Tucuman, respectively.

[c] AR = Aspect Ratio

Table III Flexural Properties for Resol–Vegetable Fiber Composites

Resol/Sisal								
V_f	0.33	0.48	0.52	0.57	0.62	0.70	0.76	
σ_b (Mpa)	28.4 ± 2.1	45.7 ± 4.1	45.1 ± 3.3	49.7 ± 3.4	51.4 ± 16.4	51.9 ± 3.4	65.6 ± 2.5	
E (Gpa)	2.7 ± 0.5	4.0 ± 0.4	3.8 ± 0.3	4.2 ± 0.3	3.9 ± 1.2	4.7 ± 0.6	4.7 ± 0.5	
Resol/Raw Cotton								
V_f	0.28	0.33	0.39	0.43	0.47	0.50	0.51	0.56
σ_b (Mpa)	51.4 ± 1.2	39.0 ± 15.0	53.8 ± 9.0	91.0 ± 24.9	81.1 ± 12.0	80.6 ± 18.0	52.7 ± 18.0	38.1 ± 12.0
E (Gpa)	3.1 ± 0.3	3.3 ± 0.9	5.3 ± 0.7	5.8 ± 1.1	4.6 ± 1.1	4.6 ± 0.9	3.7 ± 1.4	2.4 ± 0.7
Resol/Clean Cotton								
V_f	0.31	0.36	0.42	0.49	0.56	0.63	0.65	
σ_b (Mpa)	23.7 ± 1.8	25.3 ± 5.0	21.3 ± 12.3	52.0 ± 5.1	46.6 ± 8.1	34.3 ± 5.4	22.9 ± 9.6	
E (Gpa)	1.7 ± 0.4	2.0 ± 0.4	1.7 ± 0.8	3.0 ± 0.5	2.7 ± 0.4	3.3 ± 0.9	1.0 ± 0.4	
Resol/Sugar Cane Bagasse								
V_f	0.52	0.58	0.67	0.7	0.71	0.74	0.81	0.88
σ_b (Mpa)	46.4 ± 6.0	39.5 ± 7.9	40.6 ± 9.1	61.7 ± 5.5	52.2 ± 5.3	23.0 ± 2.8	28.5 ± 6.6	36.2 ± 11.1
E (Gpa)	3.7 ± 0.6	3.4 ± 1.1	2.9 ± 0.4	4.9 ± 0.2	4.1 ± 0.4	1.9 ± 0.3	3.2 ± 0.3	2.7 ± 0.9

Atanor Argentina. Its principal characteristics are shown in Table I. Low to medium viscosity is a relevant property for obtaining good wetting of the fibers and for producing good quality composite materials.

- Different fibers were selected in order to prepare the composites. Three textile fibers and one fibrous waste were used:

1. Loose raw cotton (RC) coming directly from the crop, without any treatment (Algodonera San Nicolás, Argentina).
2. Loose clean cotton (CC), which consists of mechanically clean fibers used generally for making nonwoven products, like blankets (Matexsud SA, Mar del Plata, Argentina).
3. Sisal (S) provided as a nonwoven mat (Incomar Industria e Comercio Marques LTDA, Sao Paulo, Brasil).
4. Sugar Cane Bagasse (B) supplied by Papelera del Tucumán, Tucumán, Argentina.

Their respective properties are listed in Table II. The diameters were determined by microscopy, lengths by direct measurements, and densities by picnometry. The average size of bagasse was obtained after sieving it.

Preparation of Composites

All the fillers were washed in distilled water and 2% detergent solution. They were rinsed, dried in an oven, and cooled in a dessicator. Cotton fiber mats were prepared and preformed with the humid fibers. Then, the mats were dried and stored in a dessicator. The sisal mat was cut following mold dimensions. It was impossible to obtain dried preformed mats from bagasse fibers, so they were randomly put into the mold before pouring the liquid resin.

Composites were prepared in an aluminum mold, (ϕ =145 mm and thickness = 3 mm) where the fibers or fiber mats were preplaced. After that, the resin was added and the mold closed. 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.

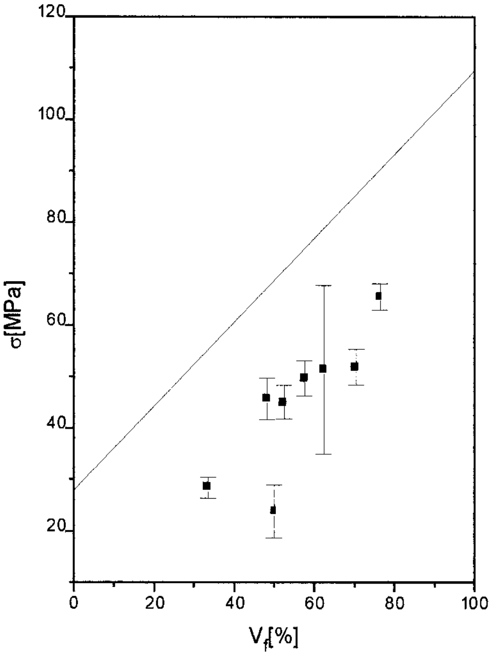

Figure 1 Flexural strength as a function of V_f for resol–sisal composites.

Finally, the fiber volume fraction V_f was calculated as follows:

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

where W_i weight fraction, ρ_i is the density, and subscripts f and m denote fiber and matrix, respectively.

Nevertheless, the calculation of volume fraction of natural fiber composites is difficult because of inefficient penetration of resin into the lumena of fiber cells. Thus, this results in an underestimation of V_f. However, the comparison is still valid since it considers only vegetable fibers.

Testing of Composites

Three-point flexural tests were performed on composites using a Shimadzu Autograph S-500-C Universal testing machine. Both sample size and flexural test conditions were selected according to American Society for Testing and Materials D 790M. Each value was obtained as the average of five specimens. A comparison of experimental and theoretically predicted values was further performed.

The strength and stiffness of composites can be calculated theoretically using a simple rule of mixture:

$$\sigma_c = \eta\sigma_f V_f + \sigma_m(1 - V_f) \qquad (2)$$

$$E_c = \eta E_f V_f + E_m(1 - V_f) \qquad (3)$$

where subscripts c, f, and m correspond to composite, fiber, and matrix, respectively. The η is Krenchel's efficiency factor and considers the orientation of reinforcement. For all cases presented in this work, $\eta = 1/5$ ([10] random distribution in three dimensions).

The density of the composites ρ_c was measured by the picnometry procedure.

The void volume fraction V_V was calculated as follows:

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

with

$$\rho_{\text{theoretical}} = \rho_f V_f + \rho_m(1 - V_f) \qquad (4)$$

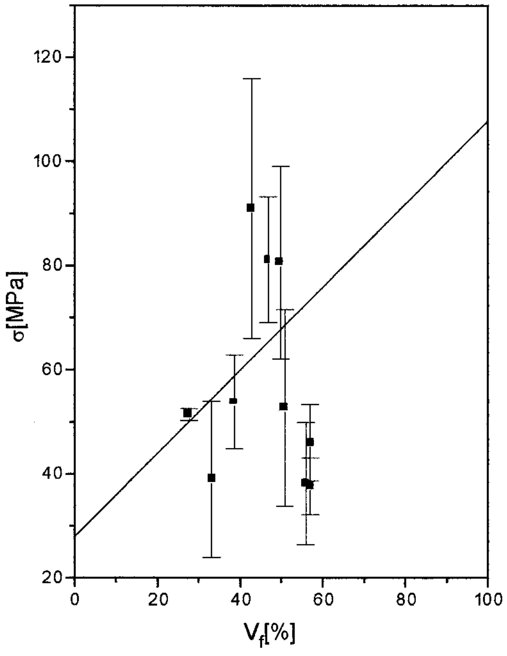

Figure 2 Flexural strength as a function of V_f for resol–raw cotton composites.

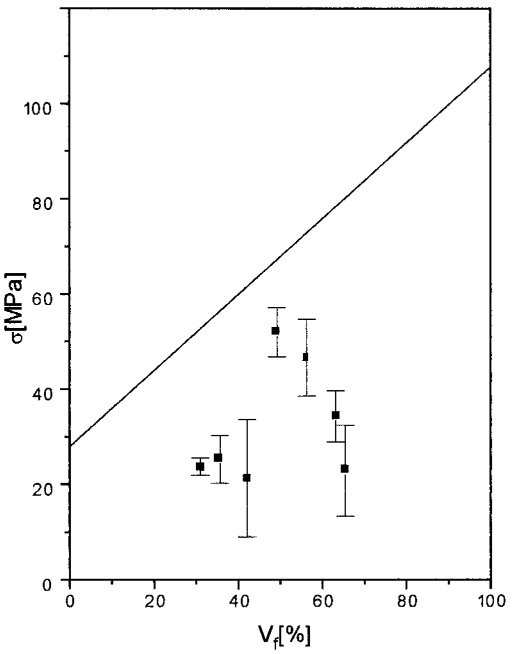

Figure 3 Flexural strength as a function of V_f for resol/clean cotton composites.

RESULTS AND DISCUSSION

Flexural Properties

Flexural moduli (E) and strengths (σ_b) were measured for all the composites for different fiber volume fractions, which were varied from 27 to almost 80%. Experimental results are shown in Table III.

In the case of cotton and sugar cane bagasse composites, the results showed that there is a V_f value at which flexural strength and modulus are maxima. At higher fiber contents, these properties decrease. These maxima values are found at fiber volume fraction in the range of 40–50%. The decrease in properties could be attributed to the incomplete wetting of fibers at higher loads because both, cotton fiber and bagasse, present a higher degree of disorder, generating a subsequent increase in void content and fiber–fiber contacts. These features favor the fracture of the composite at low strengths. Marcovich et al.[11] showed similar results for composites made with an unsaturated polyester resin reinforced with sawdust.

Sisal composites do not show this behavior: the values of σ_b and E always rise as the fiber fraction increases. This could be attributed to three causes: (1) the sisal fibers are longer than the other fibers and their effect can be considered similar to that of continuous fibers in polymer composites, (2) sisal fibers are provided in non woven mats, but where the fibers are highly entangled, and (3) the nonwoven mat presents the highest order arrangement of the fibers, leading to a better wetting . All these reasons contribute to maintain the cohesion of the material, even at high fiber fraction.

Figures 1–3 show the experimental results for σ_b compared to the theoretical values . It can be seen that the experimental values lie in almost all cases below the theoretical line, suggesting the presence of voids. However, all composites present higher σ_b and E than that of the neat polymer resin, with the exception of some of the composites made with a low fiber volume fraction of clean cotton, which could be attributed to an occasional and unwanted high percentage of voids.

Density

The experimental density of the composites is plotted vs V_f in Figures 4–7. Theoretical values given by the rule of mixture (Eq. 4) is shown as a straight line.

In all cases, the experimental composites are below the theoretical prediction, indicating the

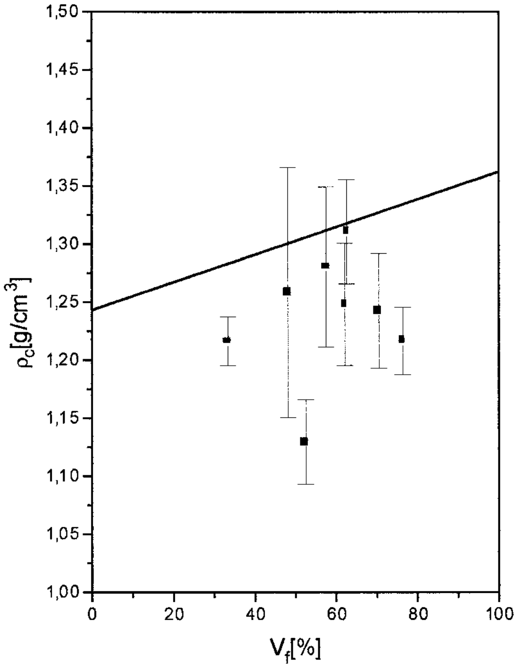

Figure 4 Density of resol–sisal composites.

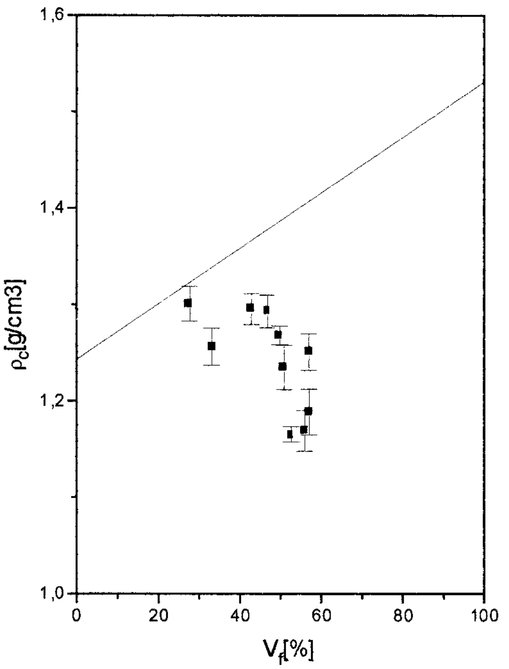

Figure 5 Density of resol–raw cotton composites.

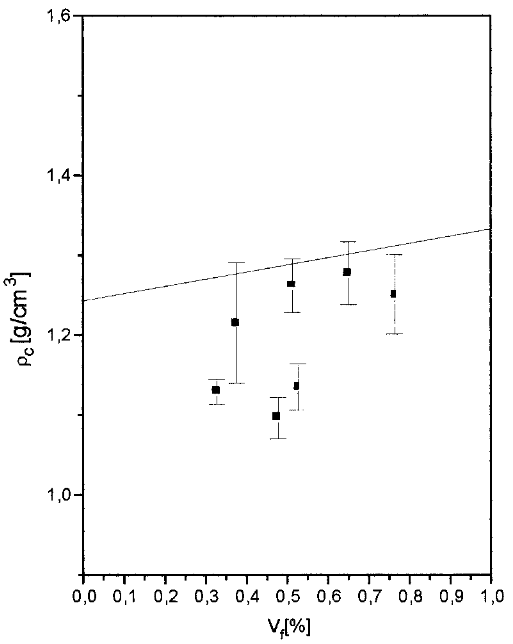

Figure 7 Density of resol–bagasse composites.

presence of voids. The porosity can be evaluated through the calculation of void volume fraction, which is shown in Figure 8 as a function of V_f, for resol–raw cotton composites. It can be seen that the void volume fraction increases as the fiber content increases, due to the incomplete wetting.

Figures 9 and 10 show the scanning electron micrographs (× 100) of the cross-section of resol–

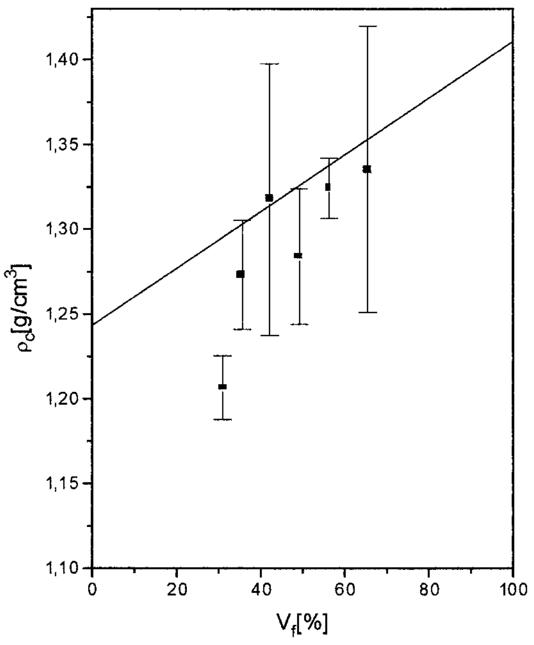

Figure 6 Density of resol–clean cotton composites.

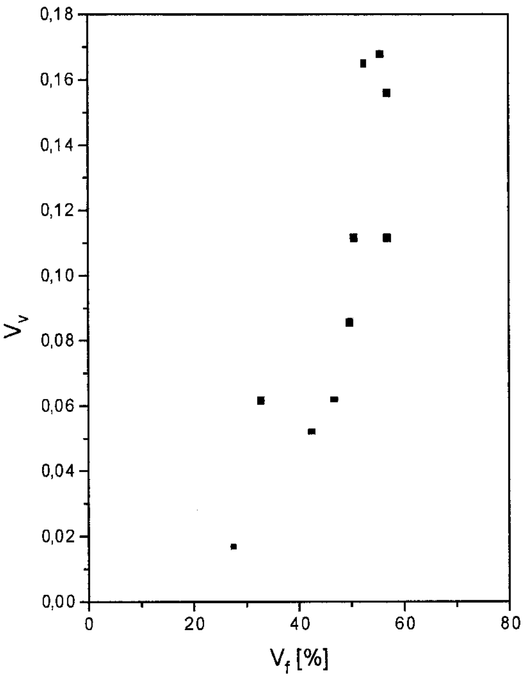

Figure 8 Void volume fraction for resol–raw cotton composites as a function of V_f.

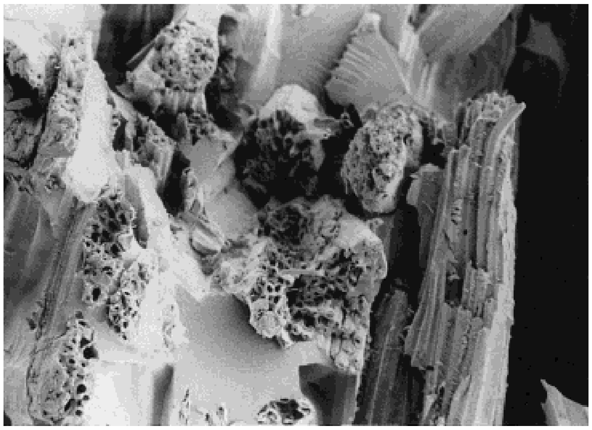

Figure 9 Cross section of resol/sisal composites for 50.4% V_f (SEM × 100).

sisal composites for 50.4 and 78% V_f, respectively. It can be observed for the 50.4% composite (Figure 9) the fibers embedded within the resin. Nevertheless, for 78% V_f, areas rich in resin and areas rich in fibers can be observed, indicating a deficient wetting of the fibers by the resin. This confirms the incomplete wetting at high reinforcement load.

Interfacial Adhesion

Figures 11–13 shows micrographs (SEM × 400, of the fracture surface for raw cotton, clean cotton, and bagasse composites respectively, with approximately 50% fiber volume fraction, as for sisal composites (Figure 9). A high percentage of well-adhered broken fibers can be noted, which indicates the existence of a good interfacial bond. This fact was anticipated because of the nature of matrix and reinforcement.

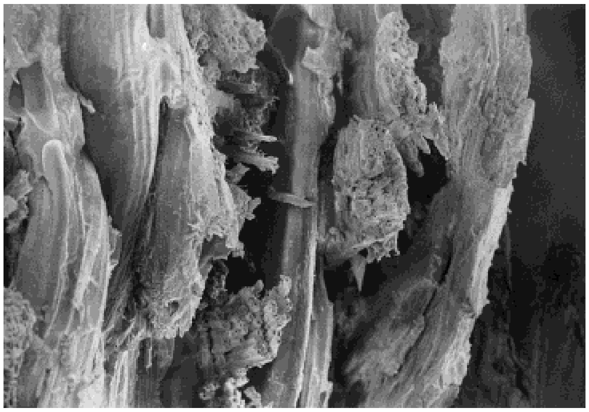

Figure 10 Cross section of resol/sisal composites for 78% V_f (SEM × 100).

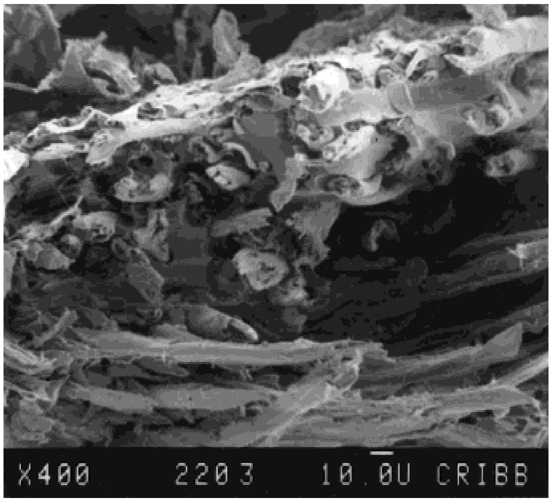

Figure 11 Cross section of resol/raw cotton composites for 47.95% V_f (SEM × 400).

However, micrographs of cotton composites show some holes, which may be due to the debonding of agglomerated fibers. In this case, the contact fiber-matrix is not as effective as for a single fiber and the "bundle" is pulled out from the resin more easily.

Optimal Stiffness

Generally, light materials have significant advantages. In many applications, requirement of low

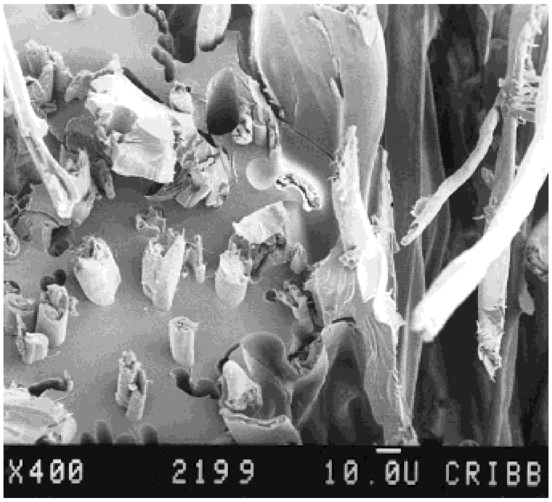

Figure 12 Cross section of resol/clean cotton composites for 45.28% V_f (SEM × 400).

density and high strength and stiffness should be combined, so that an efficient criterion of selection must be used. When materials have to resist bending or buckling, the most efficient material must have the largest value of $E^{1/3}/\rho$.[12] Table IV compares the values of $E^{1/3}/\rho$ for a number of structural materials with the experimental results obtained for the resol/vegetable fibers composites.

Clearly, the values obtained for the composites are higher than those for steel and polyethylene, and can compete with materials like aluminum and magnesium. Hence, these composites can be used in several applications when the parts have to resist bending and the weight is an important factor.

Table IV Stiffness–Density Parameters

Material	Density ρ (g/cm^3)	E (Gpa)	$E^{(1/3)}/\rho$
Aluminium[12]	2.7	71	1.53
Magnesium[12]	1.74	42	2.04
Polyethylene[12]	0.93	0.2	0.63
Steel[12]	7.87	212	0.76
Resol–raw cotton composites[a]	1.24	5.28	1.41
Resol–clean cotton composites[b]	1.28	3.04	1.13
Resol–sisal composites[c]	1.13	3.84	1.4
Resol–bagasse composites[d]	1.14	4.11	1.4

[a] Maximun value found for $V_f = 38.6\%$.
[b] Maximun value found for $V_f = 56.3\%$.
[c] Maximun value found for $V_f = 52.4\%$.
[d] Maximun value found for $V_f = 71.5\%$.

CONCLUSIONS

- Resol–natural fiber composites were prepared by compression molding. Sugar cane bagasse, clean cotton, and raw cotton composites always presented a maximum in both flexural properties (σ_b and E) at a certain fiber volume fraction. Sisal composites showed a linear rise in the same properties with the increase of fiber volume fraction, probably because of the length of the fibers and the macroscopic entanglement of the fibers in the mat. However, raw cotton composites showed the highest values of strength and stiffness.
- The void volume fraction increased as fiber volume fraction increased when the fibers were randomly distributed, leading to a considerable reduction in flexural properties. The actual density of composites was always lower than the theoretical density due to the presence of voids. Compression molding must be optimized in order to diminish void fraction at high percentage of fiber.
- With exception of the clean cotton composites at low fiber volume fraction, the flexural characteristics σ_b and E for the composites, are higher than that of the neat polymer resin.
- The incorporation of vegetable fibers in a resol matrix produces stiff structural composite materials that behave better than some of the typical structural materials (e.g., steel) when $E^{1/3}/\rho$ is considered. According to this parameter, composites made from resol and bagasse or raw cotton show the best behavior of the composites studied in this work. If σ_b is also important in the application, composites of resol–raw cotton should be preferred. However, bagasse is the cheapest fiber of those studied, and thus it will be preferred in applications with lower structural requirements.

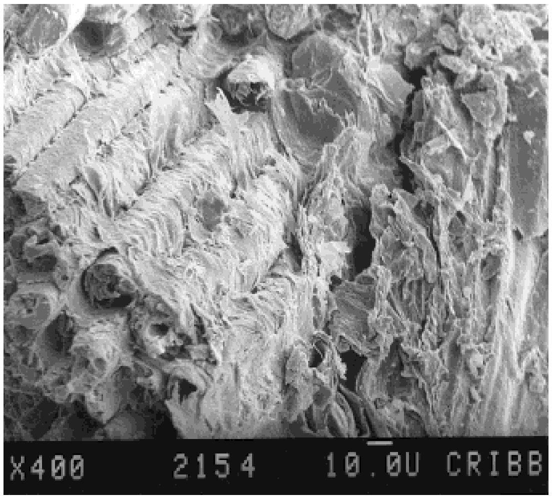

Figure 13 Cross section of resol/bagasse composites for 49.43% V_f (SEM × 400).

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