Thermal and Mechanical Properties of Woodflour/Tannin Adhesive Composites

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ABSTRACT: Composite materials formulated with a natural polyphenolic matrix (commercial tannin adhesive made from quebracho tannin extract), pine woodflour as reinforcing material, and hexamethylenetetramine as hardener were prepared and tested. Scanning electron microscopy of fractured samples was used to analyze the efficiency of the wetting and adhesion of the filler to the surrounding matrix. Thermogravimetric analysis was used in the thermal characterization of the woodflour and the tannin extract. Flexural, compression, and dynamic-mechanical tests were performed on composites to study the relationship of the filler content and particle size with the composite final properties. Moreover, the influence of the moisture content on the physical and mechanical properties of the different composites was analyzed. Results indicated that the mechanical properties were severely affected by the absorbed moisture. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3074–3082, 2004

Key words: tannin adhesives; woodflour composites; microstructure; thermal properties; mechanical properties

INTRODUCTION

In many countries, the development of new adhesives is driven by environmental considerations, which include the reduction of emissions of volatile organic compounds, such as phenol and formaldehyde. Most scientific studies and technological reports on the applications of tannin extracts are related to their use in the manufacture of adhesives for particleboards and plywood, as well as for laminated woods. On the other hand the use of woodflour as a reinforcing filler is an attractive commercial alternative because of its low cost and wide availability.

Polyflavonoid tannin extracts have been produced and used industrially in many applications since the end of the nineteenth century.[1] Among these uses, the major applications have been as tanning agents for the manufacture of leather and wood adhesives.[1,2] Polyflavonoid tannins are natural polyphenolic materials, composed mostly of flavan-3ol repeating units (Fig. 1) and smaller fractions of polysaccharides and sugars. These polyphenolic materials can be hardened by reaction with formaldehyde or hexamethylenetetramine (HEXA) crosslinking agents.[1,2]

The reaction of HEXA with tannin adhesives in aqueous solutions was studied by Pizzi,[3,4] who showed that HEXA is not a formaldehyde-yielding hardener and thus it leads to cured products with low formaldehyde emissions. The crosslinking reactions proceed by formation of reactive HEXA fragments or intermediates that react with the phenolic nuclei of the polyflavonoid tannins.

The most widely used industrial tannins are obtained from the wood of the quebracho tree (*Schinopsis balansae*, Argentine) and from the bark of mimosa (*Acacia mearnsii*, Brazil and South Africa). Most scientific studies and technological reports on the application of tannin extracts are related to their use in the manufacture of adhesives for particleboards and plywood, as well as for laminated woods.[1,2] Studies that report the behavior of these adhesives for the manufacture of molding powders or fiber composite materials are scarce in the open literature.[5]

Many authors have studied and reported information about the characterization of different tannin extracts and their reactions with several hardeners.[1,2,5–8] Nevertheless, analyses of the thermal and mechanical properties of these composite materials have not yet been published.

The focus of this work was on the analysis of the thermal and mechanical properties of composite materials formulated from a commercial quebracho tannin adhesive, pine woodflour, and HEXA as hardener: the effect of moisture on the final properties of these materials is also addressed.

Water absorption, flexural, compression, and dynamic-mechanical tests were performed on the composites and the relationship between the filler (concentration and particle size) and the measured properties was studied.
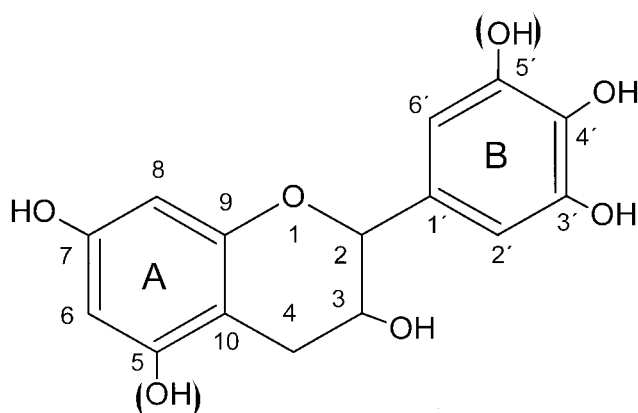
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Figure 1 Flavan-3ol repeating unit in polyflavonoid tannin.

EXPERIMENTAL

Materials

The matrix was obtained by crosslinking of a commercial quebracho tannin adhesive, Colatan GT100 (Unitan S.A.I.C., Argentine). This is a fine brown powder used as a 40% (by weight) aqueous solution in the preparation of specimens, according to the usual commercial practice. The hardener was hexamethylenetetramine (HEXA; Mallinckrodt, Argentine), used in a proportion of 10% with respect to the mass of dried adhesive.

The chosen filler was pine woodflour (J. Dos Santos Freire, Buenos Aires, Argentine). All the woodflour particles passed through a 40-mesh sieve (U.S. Standard) and were retained successively by 60-, 100-, and 200-mesh sieves corresponding to average particle sizes of 250 to 420, 150 to 250, and 75 to 150 μm, respectively.

Techniques and testing

Compounding and molding

The composite materials were prepared by mixing the filler and the 40 wt % tannin aqueous solution in an intensive mixer. Improved wetting of the particles was obtained by introducing the hardener (previously dissolved in water) at the end of the mixing step, given that the advance of the crosslinking reaction is minimized with this addition sequence. The resultant powderlike mixture was introduced into a metal mold to be cured under an applied pressure. Because of the initial condition of the mixture, the method used resembles the synthesizing technique of ceramics.

The mixture was cured in a metal mold (diameter: 145 mm; thickness: $\sim$ 3 mm) at 160°C and 4.2 MPa for 30 min. The mold was cylindrical, closed with a piston that applied the load of a heating hydraulic press to the sample. Water vapor as well as some ammonium-containing low molecular weight byproducts were evacuated from the mold, which was not hermetic, but that completely impeded the escape of the solids.

However, it was clear that a fraction of the products of low molecular weight produced in the condensation did not leave the mold and contributed to the formation of microvoids in this process. This "microfoaming," which was distributed throughout the sample, contributed to reduce the overall volumetric contraction and cracking was eliminated. Actually, this has been the goal of using fillers in thermosets for years.

According to the objective of this work, samples were prepared as follows:

1. By maintaining a fixed particle size (75–150 μm) and varying filler contents from 60 to 90% by weight with respect to total composite weight.
2. By maintaining a fixed filler content and varying particle size of the woodflour.

Because of the strong compatibility between the lignocellulosic materials and the chosen matrix, it was not necessary to use any compatibilizing or coupling agents.

Specimens of each sample were dried in a vacuum oven for 72 h at 60°C before testing.

Samples of the unfilled thermoset were prepared to obtain the value of the density of the cured matrix. Microvoiding occasioned by condensation byproducts was of more concern in these samples because contraction during curing was not alleviated by the presence of the woodflour. Thus, two different techniques were used to prepare the samples: (1) the tannin extract powder was mixed with 10% weight of HEXA (dry powders) to promote the condensation; (2) the tannin extract powder was molded to promote self-condensation. In both cases, the reaction was carried out under the same conditions as those used in the preparation of the composite materials. These samples were used only in the determination of the density of the unfilled thermoset of the composites' matrix. The higher value measured for the self-condensated tannin extract was preferred because, given that it produced less-gaseous byproducts, it led to a material without microvoiding.

Microscopy

The efficiency of dispersion during mixing was analyzed using optical microscopy. Scanning electron microscopy (SEM) was used to obtain microphotographs of the fracture surfaces of the wood pine composites (scanning electron microscope Model SEM 505; Philips, The Netherlands). The samples were previously coated with gold.

Thermogravimetric analysis

Thermogravimetric tests were performed using a TGA-50 thermogravimetric analyzer (Shimadzu, Kyoto, Japan) at a heating speed of 10°C/min under air atmosphere.

Dynamic-mechanical tests

Dynamic-mechanical tests were performed using a Perkin–Elmer dynamic mechanical analyzer (DMA 7e, length of specimen platform: 15 mm; Perkin Elmer Cetus Instruments, Norwalk, CT), under a nitrogen atmosphere. The dynamic and static stresses for the material composites were maintained at 400 and 800 kPa and those for the matrix at 200 and 400 kPa, respectively. The frequency of the forced oscillations was fixed at 1 Hz and the heating rate was 10°C/min. The specimens were cut to $20 \times 3 \times 2$ mm^3, and the linear dimensions were measured up to 0.01 mm. At least two replicate determinations were made for each sample to ensure the reproducibility of results.

Moisture sorption

Humid environments were prepared in hermetic containers maintained at 15 ± 2°C in equilibrium with aqueous solutions of sulfuric acid (18 and 35 wt %) to ensure 90 and 60% relative humidity (RH).

Specimens of each sample were dried to a constant weight, determined with an analytical balance (± 0.001 g), before exposure to humid environments.

The weight changes, attributed to moisture absorption, were recorded until no further change was detected. All the samples were maintained under these conditions for up to 100 days, a period of time that was sufficiently long enough to reach the equilibrium moisture content (EMC). The measurements were performed on at least four specimens for each sample.

The objective was to determine the percentage moisture content M (percentage weight gain), as manifested by the weight gain of the material as a function of time t:

$$M(t) = \frac{\text{Weight of wet material} - \text{weight of dry material}}{\text{Weight of dry material}} \times 100 \quad (1)$$

The EMC is the $M(t)$ value evaluated at the steady state, usually at the end of the test.

Compression tests

These tests were carried out on dry composites according to ASTM D 695-85. The specimens were cut from the molded plates in the form of prisms of 2.5 mm width and about 5 mm in height. An Instron 8501 universal testing machine (Instron, Canton, MA) was used, and all measurements were performed at a crosshead speed of 2 mm/min. The tests were performed on at least three specimens for each sample.

Flexural tests

Three-point bending tests were performed on wet and dry composites in accordance to ASTM D 790-93 standard (sample type 1) using an Instron 8501 Universal testing machine at a crosshead speed of 2 mm/min. The bending modulus (E_b), ultimate stress (σ_u), and ultimate deformation (r_u) were determined from the stress–strain curves. At least four specimens of each sample were tested.

Composite specimens of approximately $2.5 \times 10 \times 60$ mm^3 were cut from the molded plates for testing.

RESULTS AND DISCUSSION

Morphology analysis

Stiff gels are generally formed at room temperature, by mixing aqueous solutions of tannin adhesive and HEXA.[9] Figure 2(a) and (b) show the results of incorporating HEXA before and after dispersing the filler in the tannin aqueous solution. Incorporating the HEXA hardener before the filler leads to inhomogeneous materials, with gel-like lumps of resin, agglomerating a portion of the particles, while leaving other particles unwetted and generating empty zones (holes) in the material. The addition of HEXA after mixing the filler leads to better dispersion of the particles in the resin solution. Figure 2(b) shows that, in this case, most of the particles are coated by the tannin solution.

The cured material shows good bonding between the woodflour and the matrix. This adhesion could be observed by SEM and is illustrated in Figure 3, which shows the fracture surface of a sample tested in three-point bending. Fiber pull out is scarcely observed, whereas fiber breakage is the most common feature, indicating that there is a good adhesion between the matrix and the fiber.

The lumen of the wood cells appears partially unfilled with the resin because of the high filler concentrations used. The amount of matrix is insufficient to perfectly coat all the individual filler particles and so direct aggregation of wood particles can occur. The matrix presents a microfoamed structure that originated in the condensation reaction of the tannin adhesive with HEXA during the cure molding process. These features have an important effect on the density of the composites. The experimental values were in the range of 1–1.2 g/cm^3, which were lower than the densities predicted using the rule of mixtures as shown:
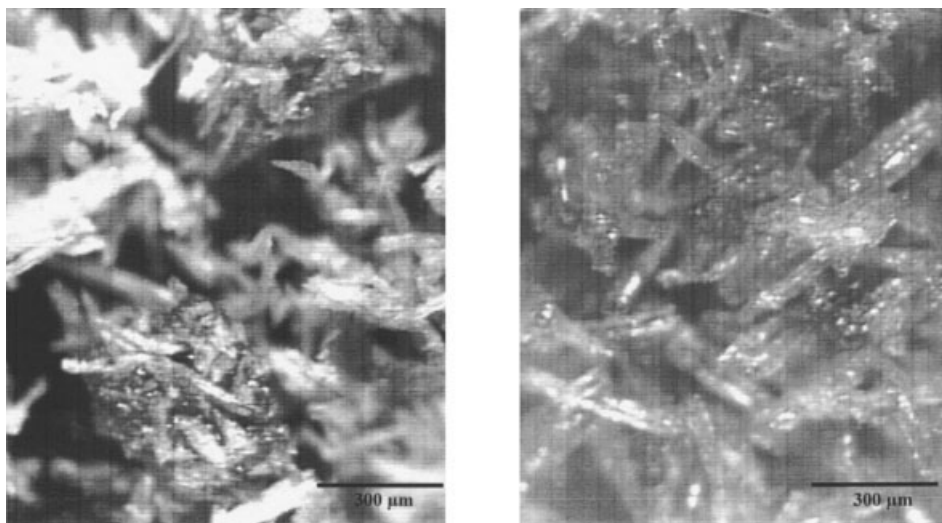
Figure 2 Different photographs showing the tannin/HEXA complex: (a) HEXA incorporated before filler dispersion; (b) HEXA incorporated after filler dispersion.

$$\frac{1}{\rho_{\text{composite}}} = \frac{x_{\text{matrix}}}{\rho_{\text{matrix}}} + \frac{x_{\text{woodflour}}}{\rho_{\text{woodflour}}} \quad (2)$$

where ρ is the density and x is the weight fraction; ρ_{matrix} (1.375 g/cm^3) is the experimental value obtained for the tannin self-condensed resin [this value was used instead of that corresponding to the hexa-crosslinked tannin, which produced a microfoamed matrix of lower density (voiding)]; and $\rho_{\text{woodflour}}$ (1.53 g/cm^3) is taken as the density of the cell wall.[10]

Nico[5] reported experimental density values close to the theoretical predictions for similar composites. However, to prepare these materials very high pressures were used during curing (200–400 bar), which are considerably higher than those used commercially.

Thermal characterization

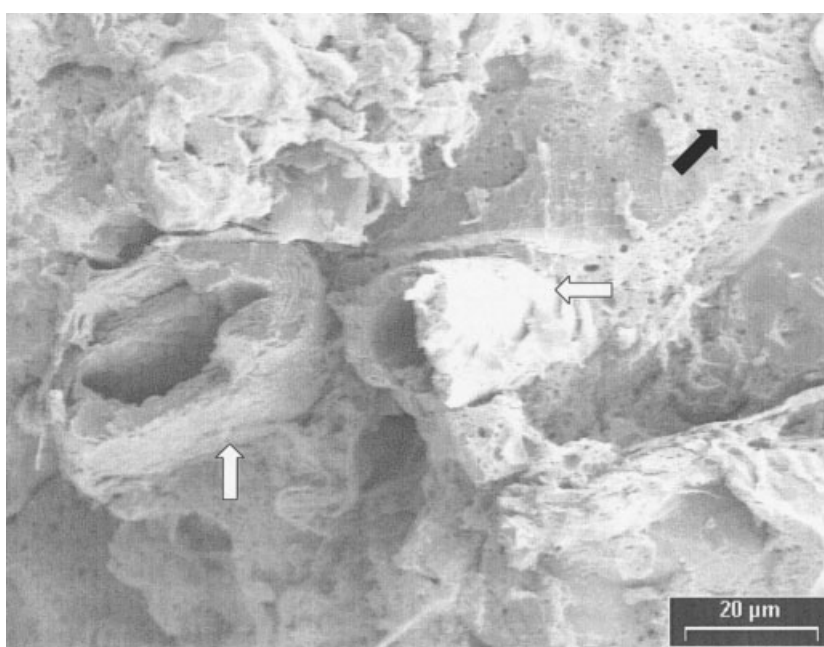These tests were carried out on samples of woodflour and tannin adhesive to study their degradation behav-

Figure 3 SEM micrographs of the composites (×1000) showing surface fractures from flexural tests. Matrix microvoiding and interphase adhesion are indicated with arrows (black and white, respectively).
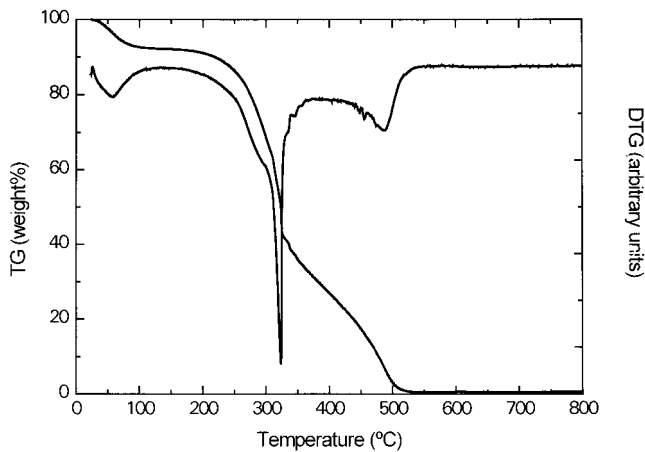
Figure 4 TG (percentage of remaining weight) and DTG (derivative signal) versus temperature curves for woodflour.

Figure 5 TG (percentage of remaining weight) and DTG (derivative signal) versus temperature curves for tannin adhesive.

ior and to select an optimum molding temperature for curing the samples.

Figure 4 shows that thermal decomposition of woodflour occurs in three main steps: (1) below 100–120°C; (2) in the range of 120 to 350°C; and (3) above 350°C. Similar data were reported for lignocellulosic materials.[11]

The first step corresponds to the loss of absorbed moisture and does not involve degradation of the material. The mass lost (7.7%) is in the same range of the equilibrium moisture content observed in the moisture absorption tests. The second step shows a double peak with maxima at about 270 and 325°C. In this region chain scissions occur and also water molecules are lost as a result of the intramolecular condensation of hydroxyl groups. Finally, in the third step, pyrolitic degradation of the wood components occurs.[12,13]

Figure 5 shows the thermal degradation curve for the tannin adhesive. It is a quite complex curve that shows the initial water loss (9.4% of the original weight), followed by different degradation steps that begin around 200°C. The complex condensed aromatic structure of tannin leads to high thermal resistance. Although wood degradation is almost complete at 500°C, tannin adhesive shows a remaining weight (TG) of about 42%. Actually, the TG curve shows a plateau at about 30%, which extends from 550 to 720°C, where the final degradation step takes place. It is concluded that the tannin adhesive shows remarkable thermal resistance, as is common in phenolic resins.

The glass-transition temperature (T_g) of the tannin adhesive was located at 126°C by differential scanning calorimetry, the same region where T_g appears for pure tannin.[1]

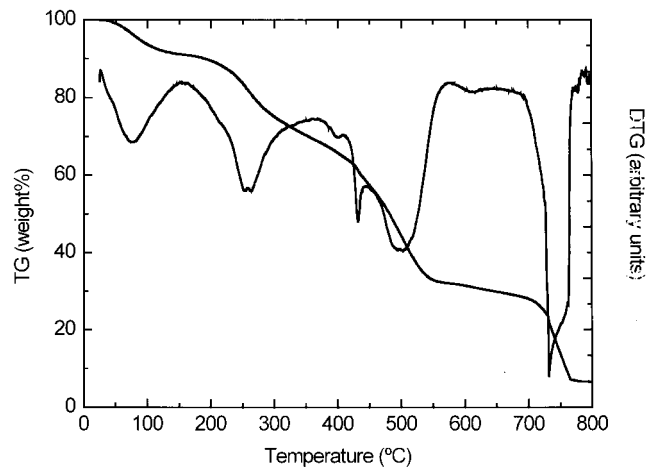According to the above results, a temperature of 160°C was selected for the curing step. In these con-

ditions the tannin adhesive is above its glass transition, whereas thermal degradation is negligible.

Dynamic mechanical tests

The dynamic mechanical behaviors of the pinewood, the HEXA-crosslinked tannin adhesive, and the composites were evaluated in the bending mode.

Figure 6 shows the storage modulus obtained from temperature scans for the different dry samples.

The dynamic modulus of the pinewood shows a very slight increase of the modulus from the beginning of the test to about 120°C. This change is related to the loss of water, which acts as a plasticizer in wood (as discussed in the TGA analysis). The storage modulus E' remains constant from that region up to about
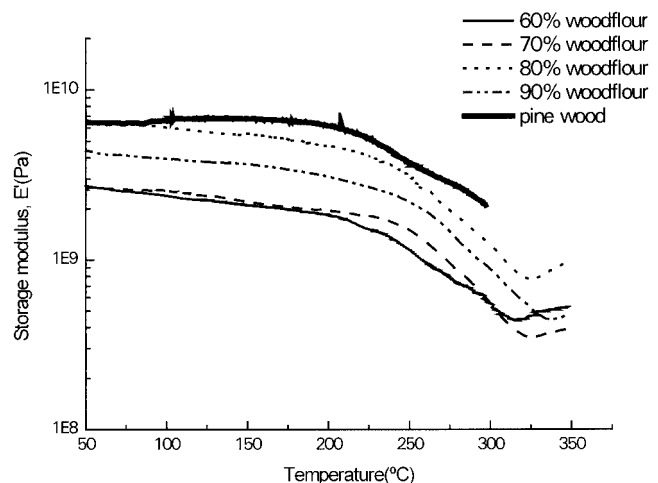

Figure 6 Storage modulus versus temperature for composites prepared with different percentages of filler and pine wood (frequency 1 Hz).
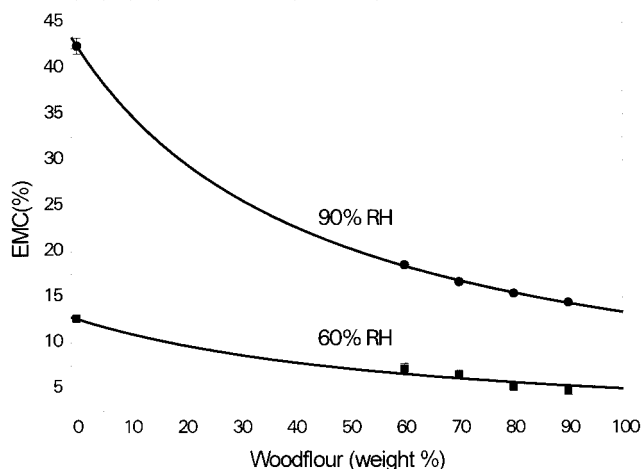
Figure 7 Final (equilibrium) moisture content (EMC) as a function of the wt % of filler at 60 and 90% RH.

Figure 8 Evolution of moisture content as a function of time at 90 RH for the material loaded with 70 wt % woodflour. Symbols correspond to four replicate samples.

200°C, and then a continuous decrease occurs coincident with the second degradation step in wood.

Because the percentage of wood filler added to the composites is relatively high, all of them show behavior comparable to that of the wood, with the main E' reduction beginning above 200–250°C.

The storage modulus of the composites at room temperature increases as the wood filler concentration is increased from 60 to 80% by weight. The 90% composite shows lower modulus than the 80% sample. The reason for this is the extremely high concentration of particles, which precludes complete particle wetting by the resin, so that the cohesion of the material is compromised. In general, at the concentrations used in this study, direct contact between filler particles is mostly responsible for the load transfer in the composites. Moreover, the particles introduce an elevated degree of mechanical restraint that reduces the mobility and deformability of the matrix.

Moisture absorption

Figure 7 shows the equilibrium moisture content (EMC) reached by the materials as a function of the filler content at 60 and 90% relative humidity. The results show an unexpected reduction of the EMC as more woodflour is added to the material. This unusual behavior is the result of the hygroscopic nature of the tannin matrix, which presents a high proportion of di- and tribenzylamine bridges.[9] These groups are highly polar and favor water absorption. Besides, the filler and the polymeric matrix have an abundance of hydroxyl groups that also contribute to the hygroscopicity.

Moreover, in the case of the tannin matrix, the SEM micrographs show a foamed morphology (Fig. 3),
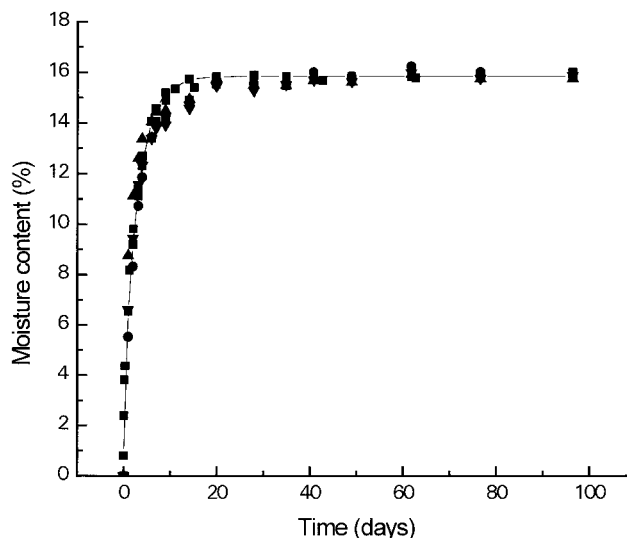
which also increases the capacity of water absorption by diffusion and capillarity effects.

As expected, the higher the ambient humidity, the higher the EMC, given that the driving force for water diffusion absorption increases. It can also be seen that the effect is more important for the unfilled material and becomes more moderate as the woodflour content increases.

The fitted curve was obtained using the following expression:

$$\frac{100}{\text{EMC \%}} = \frac{X_{\text{woodflour}}}{\text{EMC \%}_{\text{woodflour}}} + \frac{X_{\text{matrix}}}{\text{EMC \%}_{\text{matrix}}}$$

$$X_{\text{matrix}} = 1 - X_{\text{woodflour}} \tag{3}$$

where $X_{\text{woodflour}}$ and X_{matrix} are the wt % of woodflour and matrix, respectively.

The EMC of woodflour (EMC%$_{\text{woodflour}}$) was kept as a fitting parameter of the expression. The resulting values were 5.03 and 13.40 at 60 and 90% RH, respectively, which are in the same order of magnitude as for EMC values reported in the literature for other woodflours[15] and are in agreement with the previous discussion concerning TGA.

Figure 8 shows the typical evolution of the water absorption process as a function of elapsed time. All samples showed a very high initial rate of water absorption, which is revealed by the steep initial slope of the moisture content percentage versus time plots.

The rate of moisture absorption was modeled using not only the classical equations for unidirectional diffusion shown below, but also the diffusion coefficient D as a fitting parameter averaged over the whole curve.

TABLE I
Equilibrium Moisture Content for Pine Woodflour of Different Average Particle Sizes

Woodflour (average particle size, μm)	Equilibrium moisture content (%)	
	60 RH	90 RH
250–420	6.14 ± 0.22	15.89 ± 0.05
149–250	6.59 ± 0.31	15.85 ± 0.04
74–149	6.57 ± 0.12	16.71 ± 0.05

The total amount of diffusing substance entered into the sheet at time t (M_t) can be obtained from[16] the following equation:

$$\frac{M_t}{M_\infty} = 1 + \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[\frac{-D\pi^2}{(2l)^2}(2n+1)^2 t\right] \quad (4)$$

where D is the diffusion coefficient, $2l$ is the thickness of the sheet, and M_∞ is the total amount of diffusing substance that had entered into the sheet after an infinite time.

The repeatability of the test was very good as well as the resulting fitting but, because of the steep initial slope, the model has a very low sensitivity to variations in the D parameter. For this reason, although it was not possible to establish a functionality of D with woodflour content, it was possible to calculate a range of values for the diffusion coefficient of the samples between 2×10^{-8} and 9×10^{-8} cm^2/s. These values are of similar in magnitude to those usually reported for wood and similar composites.[15]

The effect of particle size on moisture absorption was initially investigated. Table I shows the results for a composite prepared with 70 wt % of woodflour. Although the average particle sizes used cover a relatively wide range, no significant differences were found in the results. This finding is understandable in view of the contribution of matrix and filler to moisture absorption. Because the matrix is responsible for the major part of the water absorbed in the composite,
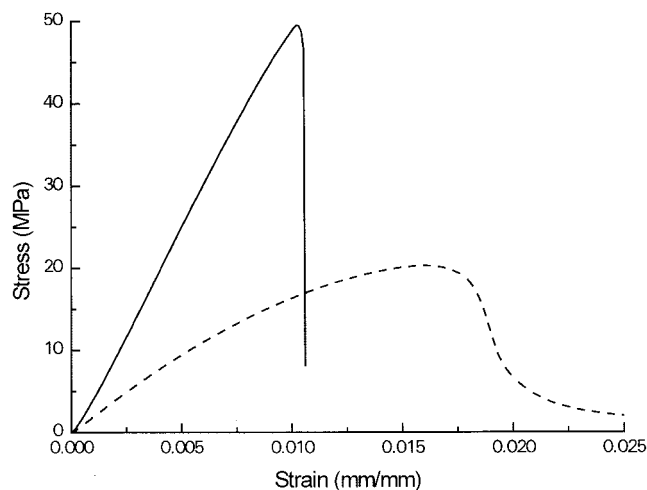

Figure 9 Stress–strain response of the dry (—) and wet (– – –) material with 80 wt % of filler.

details of the woodflour particles are not relevant to these results.

Flexural and compression tests

Effect of the filler content

The stress–strain response is linear up to the point of failure for all the dry composites, but shows some bending for the humid materials (Fig. 9). This observation is attributed to the plasticizing effect of water on wood cell wall components and the matrix.

Table II shows the bending modulus (E_b) of the composites as a function of the filler content. The elastic bending modulus increases with increasing woodflour concentration up to 80 wt % and then decreases. The behavior is analogous to that observed in dynamic mechanical tests. As mentioned before, this could be explained by the incomplete wetting of the particles, attributed to the high content of filler used. A similar tendency can be seen in this figure for the ultimate stress as a function of the concentration of woodflour.

TABLE II
Flexural (Bending Modulus, Ultimate Stress, and Ultimate Deformation) and Compressive Properties (Compressive Modulus and Ultimate Stress) as a Function of Neat Woodflour Content for Dry Samples

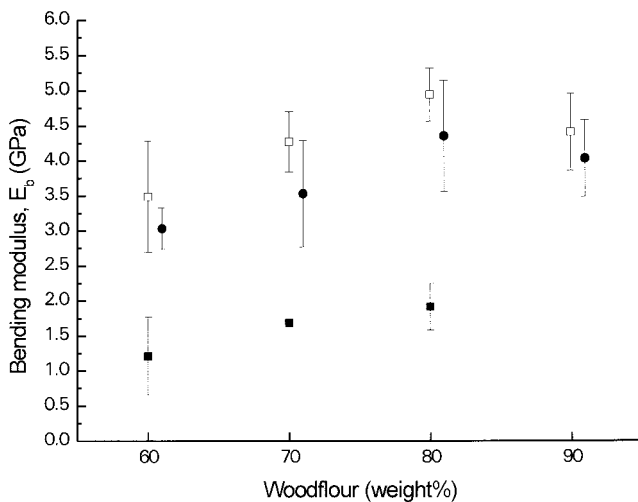| Woodflour (wt %)	Flexural properties			Compressive properties	
	Bending modulus, E_b (GPa)	Ultimate stress, σ_u (MPa)	Ultimate deformation, r_u (×1000)	Compressive modulus, E_c (GPa)	Ultimate stress, σ_u (MPa)
60	3.49 ± 0.79	31.10 ± 6.65	14.30 ± 4.10	0.91	0.14
70	4.27 ± 0.43	39.51 ± 4.77	10.74 ± 1.68	1.52	0.19
80	4.94 ± 0.37	48.24 ± 9.42	10.13 ± 0.68	2.03	0.48
90	4.41 ± 0.55	35.18 ± 7.32	8.99 ± 0.72	1.03	0.13

Figure 10 Comparison of flexural properties of dry (■), wet (●), and redried (□) samples for different filler weight percentages: (a) bending modulus (E_b); (b) ultimate stress (σ_u); (c) ultimate deformation (r_u).

As is usually the case, the elongation of the composites decreases with the increase of the filler content in the samples.

It is known that fillers with higher stiffness than that of the matrix can increase the modulus of composites, but generally cause a dramatic decrease in the elongation at break. Almost all the deformation occurs in the matrix, if the filler is more rigid than the matrix. On the other hand, if there is good adhesion between the two components, a decrease of the elongation at break of the composite can be expected.[17,18] In the present case, the mechanical response suggests good adhesion, in agreement with the SEM microscopic observations.

Similar behavior was found in compression tests (Table II). Material failure occurred in the linear part of the curve and no plastic deformation could be observed. This behavior is explained as being the result of combining a rigid matrix with a high concentration of rigid particles.

Figure 10 shows the comparison of the results obtained in three-point bending tests from dry, wet, and redried samples for different filler weight percentages. Regarding the properties of the wet samples at 90 RH (after 100 days), they exhibit an important reduction of the modulus attributed to moisture in the composites. The decrease in E_b for the humid materials can be attributed to two factors: changes in the wood cell wall and matrix plastification. The disruption of highly ordered hydrogen bonds in the wood structure, through formation of less-ordered water–water hydrogen bonds, weakens the resistance of wood to applied stress and thus results in the loss of strength and stiffness as the moisture content increases. It is important to notice that the materials recover, although not completely, after redrying, reaching property values close to those corresponding to the original dry materials.

Effect of the particle size

Figure 11 shows the dependency of the flexural mechanical properties with the particle size. The modulus and strength are lower for large size particles, probably because of larger dispersion problems and excessive direct particle–particle contacts. Large particle agglomerates are less effective in transfer load. Decreasing the woodflour particles below a 100-mesh sieve did not produce appreciable changes in the mea-
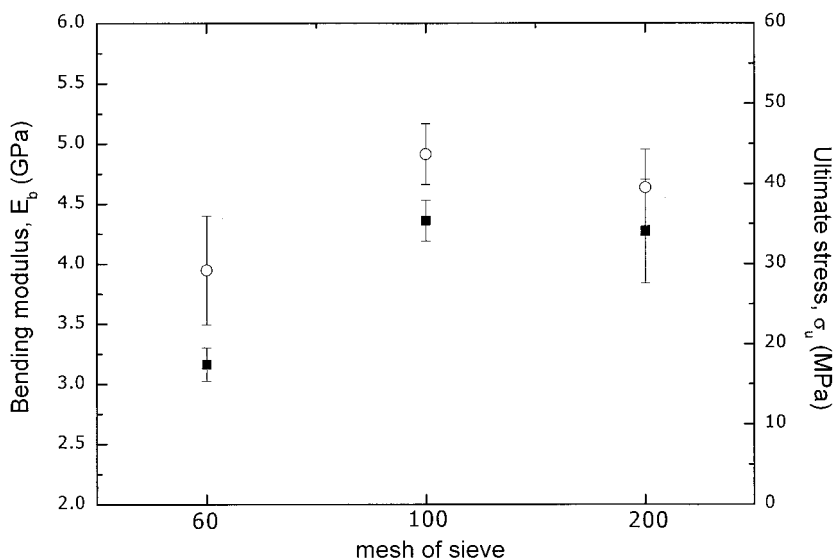

Figure 11 Dependency of the flexural mechanical properties as a function of the particle size. Bending modulus, E_b (■); ultimate stress, σ_u (○).

sured properties, indicating similar dispersion and load transfer characteristics.

Compression tests (not shown) showed identical trends.

CONCLUSIONS

The wetting behavior of woodflour by the aqueous tannin solutions is excellent, leading to very good matrix–fiber adhesion in the composite material.

Fracture surface morphologies show that the matrix, consisting of the cured tannin material, is partially foamed and the lumen of some wood particles is incompletely filled with the matrix material. These two features contribute to lower the experimental density from that corresponding to the compact material predicted by the rule of mixtures.

Flexural and compression mechanical properties reach a maximum at a woodflour concentration of 80%. Above that concentration, these properties diminish because the amount of tannin adhesive is insufficient to wet the fibers uniformly. At a fixed woodflour concentration, the flexural and compression modulus diminish when the size of woodflour particles increases.

The storage moduli of the composite materials have reasonable and constant values up to 200°C. Above this temperature, thermal degradation starts with the consequent deterioration of the properties.

The mechanical properties of the composites are significantly deteriorated because of water absorption. Results show that the cured tannin matrix is more hygroscopic than the woodflour fibers.

The water absorption rate is very high and practically independent of the concentration and size of the woodflour in the composites. This effect is associated with the high polarity of the composite components, matrix microporous structure, and partially empty lumen of fibers.

In the dried state, the thermal and mechanical properties of the investigated woodflour/tannin materials have values adequate for use in some industrial applications where high stiffness is an important requirement. On the other hand this study shows that their use in humid atmospheres must be avoided.

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