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Effect of Natural Rubber on Wood-Reinforced Tannin Composites

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AQ2

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ABSTRACT: Natural rubber latex was added to composite materials formulated from a quebracho tannin adhesive crosslinked with hexamethylenetetramine and wood flour as a reinforcing filler. The final microstructure of the thermoset modified by the addition of different concentrations of latex was observed by scanning electron microscopy. The flexural and impact behavior of the modified materials was analyzed and related to the final microstructure of the composites. The effect of exposing the materials to humid environments was also evaluated. The measurements indicated that the addition of latex did not significantly reduce water absorption. However, it facilitated the preparation

process of samples with low filler contents because of the increased viscosity of the mixture, which inhibited particle settling. On the other hand, the flexural properties increased with the addition of latex-containing proteins through a reaction similar to tanning in leathers. The impact properties presented a similar trend, with the largest change occurring between 0 and 5% natural rubber in the matrix formulation. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2007

Key words: composites; diffusion; elastomers; fillers; mechanical properties

INTRODUCTION

The development of phenolic polymeric materials based on renewable resources of wide availability and competitive prices (in contrast to petroleum-derived compounds) has experienced noticeable growth during the last years.^{1,2} Specifically, the study of tannin-based adhesives to replace standard phenolic polymers is important for achieving a reduction in the emissions of volatile organic compounds, such as phenol and formaldehyde, during the service life of the applications.³

F1 Polyflavonoid tannins are complex polyphenolic materials, and the chemical structure of the most common repeating unit is flavan-3-ol (Fig. 1).⁴ They have been used mainly in the leather industry because of their ability to interact strongly with carbohydrates and proteins, converting the skin in leather.⁵ More recently, attention has been paid to their use in the formulation of natural adhesives. The free C6 and/or C8 sites on the A-ring (Fig. 1) are reactive sites in crosslinking with hardeners, such as formaldehyde and hexamethylenetetramine

(HEXA).^{5–7} Many scientific studies and technological reports on the applications of tannin extracts are related to their use in particleboard, plywood, and laminated woods.^{6–8}

A recent publication has shown that the mechanical properties of composites obtained with tannin adhesives and wood flour as a filler have adequate values for their use in industrial applications, for which high stiffness is an important requirement. However, the humidity significantly degrades the mechanical performance (modulus and strength).⁹

During the condensation reaction, the high reactivity of the tannin molecules originates a high degree of crosslinking early in the cure reaction. Besides, it must be taken into account that tannin molecules are big and rigid and cannot rotate freely. All these effects are responsible for the residual active centers in the network becoming too far apart for hardener molecules to react and increase the extent of crosslinking.^{8,10} The resulting incomplete curing and the high number of inert hydroxyls and polar ammonia groups from the HEXA decomposition in the final material cause poor resistance to adverse humid environments.

The addition of natural rubber to tannin thermoset formulations was investigated. The idea was that the elastomeric component might act not only to improve the toughness of the material but also to reduce the water uptake because of its low polarity.

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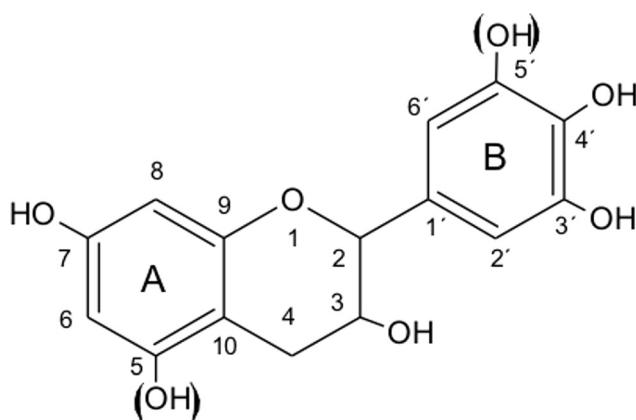


Figure 1 Flavan-3-ol repeating unit of the tannin extract.

The natural rubber obtained from the latex of *Hevea brasiliensis* (the rubber tree) is actually a latex mainly composed of *cis*-1,4-polyisoprene, but it also contains minor percentages of proteins and lipids.¹¹ These minor components are responsible for the colloidal stability of the latex^{11,12}; however, proteins are also responsible for the allergenic response of some persons using natural rubber products. Actually, this is an extended, well-known medical problem that affects people using natural rubber gloves which has not been solved yet.^{13–16}

On the contrary, in the case of composite materials, the presence of proteins in the natural rubber latex is an advantage because the nonrubber components can compatibilize the highly polar components, such as tannin-based thermosets and wood flour, with the nonpolar polyisoprene.

This article reports the effect of incorporating natural rubber latex into composite materials formulated with a commercial tannin adhesive, HEXA as a hardener, and wood flour as a filler. Scanning electron microscopy was used to analyze the matrix morphology of fractured samples. Flexural and impact tests were performed on composites with different contents of rubber. The effects of the filler content and moisture absorption on the final properties of the composites were also evaluated.

EXPERIMENTAL

Materials

AQ8 A commercial quebracho tannin adhesive, Colatan GT100 (Unitán S.A.I.C., Argentina), received as a fine, brown powder, was used to prepare a 40 wt % aqueous solution according to the usual commercial practice for adhesive manipulation. HEXA (Mallinckrodt, Argentina) was added to these solutions in a proportion of 10 wt % with respect to the mass of the dried adhesive. The natural rubber latex was used directly as extracted from the trees (*H. brasiliensis*).

Its solid content was 42%, which was determined by the drying of the emulsion in an air convection oven at 110°C for 12 h. The typical composition of the rubber phase in the latex was 96 wt % polyisoprene, 1 wt % proteins, and 3 wt % lipids, along with traces of magnesium, potassium, and phospholipids.¹¹

Pine wood flour (J. Dos Santos Freire, Buenos Aires, Argentina) was used as a filler. All the wood flour particles passed through #100 mesh (U.S. Standard) and were retained by a 200 sieve, corresponding to average particle sizes of 75–150 μm. AQ8

Compounding and molding

The composite materials were prepared by the mixing of the 40 wt % tannin aqueous solution, the natural rubber latex, and the HEXA with the pine wood flour in an intensive mixer. The addition of latex to the formulation permitted us to obtain a wider range of compositions of wood flour.

The macroscopically homogeneous paste formed by the mixture of the aqueous tannin solution, HEXA, and natural latex allowed us to obtain a good dispersion of the wood particles in the paste. With this proceeding, it was possible to easily prepare composite materials with less than 50 wt % wood flour.

The mixtures had different initial percentages of water depending on the formulation (tannin solution and rubber latex), but they were concentrated to equal water contents of 10 wt % by being allowed to dry at room temperature. This condition was selected to avoid high temperatures that could lead to undesirable premature crosslinking.

The resultant paste was introduced into a metal mold (145 mm in diameter and ca. 3 mm thick) to be cured at 160°C under an applied pressure of 4.2 MPa for 30 min. The mold was cylindrical and closed with a piston that applied the load of a heating hydraulic press to the sample. Water vapor and some low-molecular-weight byproducts containing ammonia compounds from the HEXA decomposition were evacuated from the mold, which was not hermetic but completely prevented the escape of the solids.

The samples were prepared as follows:

1. Maintaining a fixed natural rubber content of 0 or 5 wt % with respect to the total matrix weight and varying the wood flour filler content with respect to the total composite weight.
2. Maintaining a fixed filler content (50 wt %) and varying the percentages of the natural rubber from 0 to 20 wt % with respect to the total matrix weight.

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

Optical photography

AQ8 The macroscopic features of the broken impact specimens were analyzed from photographs taken with a JVC model G.R. DVF 31UM digital video camera.

Microscopy

AQ8 The fractured surfaces of the wood flour composites tested in three-point bending were studied by scanning electron microscopy with a Philips model SEM 505 scanning electron microscope. The samples were previously coated with gold.

Moisture sorption

Humid environments with 90% relative humidity (RH) were prepared with aqueous solutions of sulfuric acid (18 wt %) stored in hermetic containers maintained at $15 \pm 2^\circ\text{C}$.

Specimens of each composite sample were dried until a constant weight, which was determined with an analytical balance (± 0.001 g), before being exposed to humid environments.

Composite specimens were kept in the humid environments and were removed periodically to record the weight gain due to moisture sorption until the specimens reached the equilibrium values. All the samples were maintained under these conditions up to 100 days, which was found to be a period long enough to reach the equilibrium moisture content (EMC). The measurements were performed on at least four specimens for each sample.

The weight percentage change, M , as manifested by the weight gain of the material as a function of time t , was determined with the following equation:

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

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

The total amount of the diffusing substance that entered into the sheet at time t , M_t , could be calculated from the eq. (2),¹⁷ assuming Fickian diffusion as an approximation:

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

where D is the diffusion coefficient, $2l$ is the thickness of the sheet, and M_∞ is the total amount of the diffusing substance that entered into the sheet after an infinite time. This model considers unidirectional diffusion, and D is calculated as a fitting parameter averaged over the whole curve.

Flexural tests

AQ8 Three-point-bending tests were performed on wet and dry composites in accordance with ASTM Standard D 7771 with an Instron 8501 universal testing machine at a crosshead speed of 2 mm/min. The bending modulus, ultimate stress, and ultimate deformation were determined from the stress-strain curves. At least four specimens of each sample were tested. Composite specimens of approximately $3 \times 10 \times 60$ mm³ were cut from the molded plates for testing.

Instrumented falling weight impact testing

AQ8 Dart impact testing was performed with a Fractovision Ceast 6789 falling-weight-type instrumented machine. All the tests were carried out with a probe with a hemispherical tipped dart at an incident speed of 2 m/s. The incident energy was sufficient for ensuring that the impact test was performed to fracture. Sets of four discs 3 mm thick of each sample were tested. The impact test specimens were held in place on an annular stainless steel ring with an internal diameter of 40 mm. The impact force displacement trace was recorded to characterize the impact properties of the samples.

From these tests, the load-displacement curves were obtained, and the following properties were determined.

The impact strength (σ_d) related to crack initiation was computed with the following equation:

$$\sigma_d = 2.5 \frac{F_{\max}}{b^2} \quad (3)$$

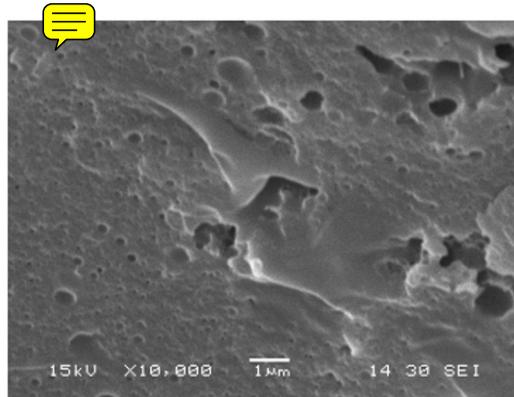
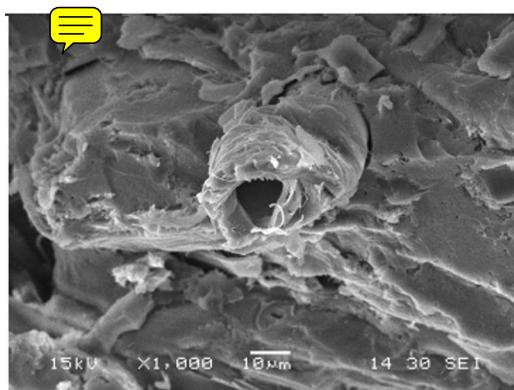
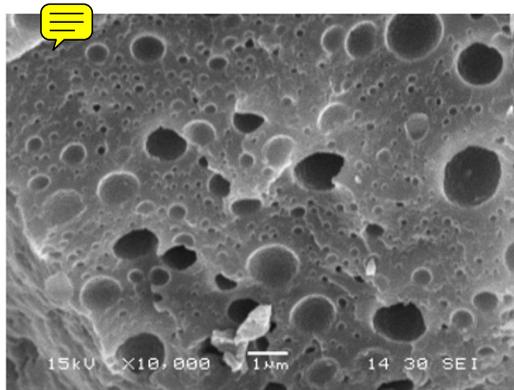
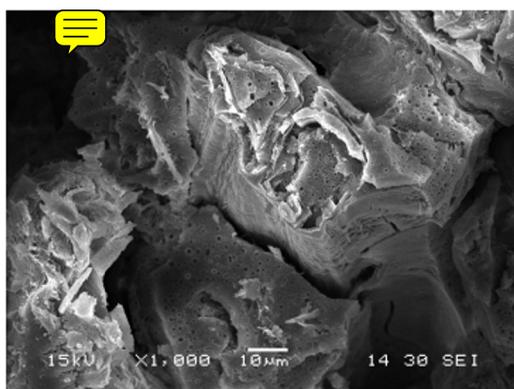
where F_{\max} is the maximum value of the recorded load and b is the thickness of the sample sheet.

The total energy required to completely penetrate the specimen (E_t) was calculated as the total area under the load-displacement curve normalized by the sample thickness:

$$E_t = \frac{1}{b} \int_0^{X_{\text{total}}} F dx \quad (4)$$

AQ3 where F is the load and x is the displacement. The energy at crack initiation (E_i) was calculated as the area under the load-displacement curve and up to the maximum load, normalized by the sample thickness:

$$E_i = \frac{1}{b} \int_0^{X_{\max}} F dx \quad (5)$$



AQ7 Figure 2 Fracture surface micrographs of samples with 50 wt % wood flour and 0 or 10 wt % rubber in the matrix: (a) 0 (1000×), (b) 0 (10,000×), (c) 10 (1000×), and (d) 10% (10,000×).

TABLE I
EMCs of Samples with 0 or 5 wt % Natural Rubber (with Respect to the Matrix Weight) Exposed to 90% RH

Wood flour (wt %)	EMC (%)	
	0 wt % rubber	5 wt % rubber
30	—	25.5 ± 0.1
40	—	23.5 ± 0.2
50	20.0 ± 0.5	20.2 ± 0.4
60	18.9 ± 0.1	16.6 ± 0.4
70	16.7 ± 0.0	17.0 ± 0.5
80	15.5 ± 0.2	15.7 ± 0.3
90	14.5 ± 0.2	14.3 ± 0.2

The propagation energy (E_p) is the energy required to complete disk penetration, and it was calculated as the area under the load-displacement curve after the maximum load, normalized by the sample thickness:

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$$E_p = \frac{1}{b} \int_{X_{max}}^{X_{total}} F dx \quad (6)$$

The ductility index (DI) was also calculated as the ratio of E_p to E_t :

$$DI = \frac{E_t - E_i}{E_t} = \frac{E_p}{E_t} \quad (7)$$

RESULTS AND DISCUSSION

Morphology analysis

Figure 2 shows the center of the fracture surface of samples tested in three-point bending and containing 50 wt % wood flour with 0 [Fig. 2(a,b)] or 10 wt % (with respect to the total matrix weight) natural rubber [Fig. 2(c,d)]. As observed in the materials without latex incorporation,⁹ a scanning electron microscopy analysis of the fracture surfaces indicated that the wood flour particles had fractured rather than pulled out. The wood cells appeared only partially filled with tannin because of the high filler percentages used. In a higher magnification (10,000×) of the bulk matrix region [Fig. 2(b,d)], a clear difference can be observed in the concentration

F2

TABLE II
EMCs of Samples with 50 wt % Wood Flour as a Function of the Weight Percentage of Natural Rubber (with Respect to the Matrix Weight) Exposed to 90% RH

Natural rubber (wt %)	EMC (%)
0	20.0 ± 0.5
5	20.2 ± 0.4
10	17.1 ± 0.5
15	18.0 ± 0.3
20	18.2 ± 0.3

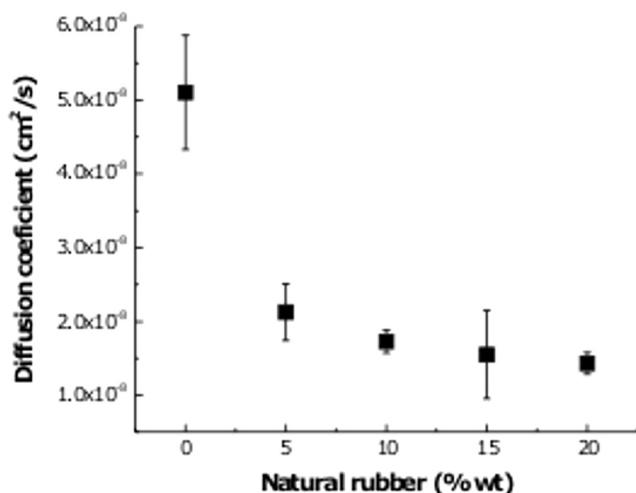


Figure 3 *D* as a function of the rubber content in the matrix for composite materials with 50 wt % wood flour.

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of microvoids, which seem to be lower and smaller in size in the composite containing natural rubber.

The interfacial quality between the tannin matrix and wood flour particles is good in these materials, as mentioned in a previous publication,⁹ and it does not deteriorate with the incorporation of latex. Fiber pullout is scarcely observed, whereas fiber breakage is the most common feature, indicating that there is a good adhesion between the matrix and the fiber. Composites formulated with the incorporation of rubber show these same characteristics just mentioned, indicating that the presence of rubber does not significantly change the quality of the fiber–matrix interface.

The presence of proteins and lipids at the surface of the rubber particles in the latex compatibilizes the polar matrix and wood flour with the natural rubber,

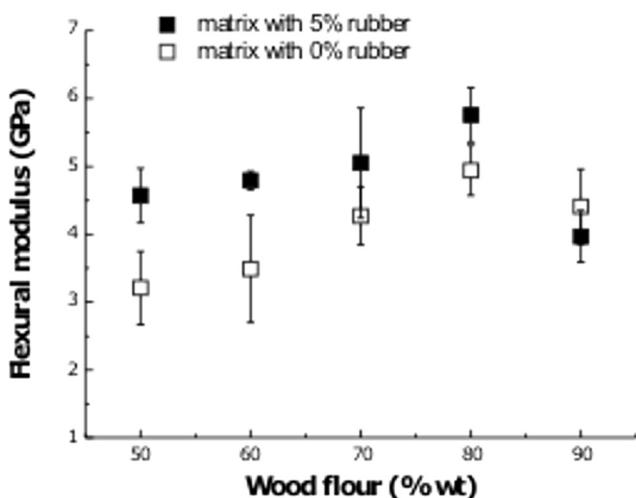


Figure 4 Flexural modulus as a function of the wood flour content for composite materials with 0 or 5 wt % rubber in the matrix.

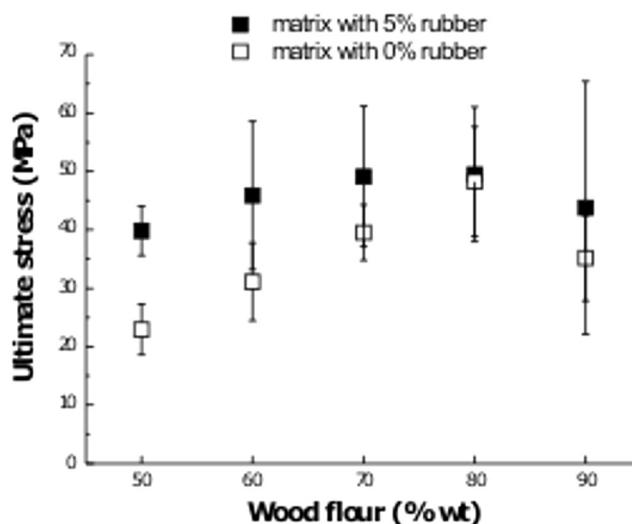


Figure 5 Ultimate stress as a function of the wood flour content for composite materials with 0 or 5 wt % rubber in the matrix.

a nonpolar material. The direct use of the natural latex is especially interesting in this context because its nonrubber constituents do not need to be removed since they play a positive role¹⁸ in the material performance.

Moisture absorption

Table I shows the EMC for materials containing different percentages of wood flour and 0 or 5% natural rubber after being exposed to 90% RH.

The same trend was observed in both materials, with and without rubber: the EMC increases with the polymer content in the composites. As stated in a previous work,⁹ the tannin matrix contains polar groups, which favor water absorption. Also, there are no important differences with the addition of natural rubber, probably because of the small concentration considered.

Table II presents the results obtained for composite materials containing 50% wood flour and natural rubber contents varying from 0 to 20 wt %. With these high contents of rubber, it was possible to

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TABLE III
Flexural Properties of Samples with 50 wt % Wood Flour as a Function of the Rubber Content in the Matrix

Natural rubber (wt %)	Flexural modulus (GPa)	Ultimate stress (MPa)	Ultimate deformation (1000×)
0	3.21 ± 0.54	22.9 ± 4.3	8.5 ± 1.4
5	4.57 ± 0.40	39.8 ± 4.2	8.9 ± 0.5
10	4.98 ± 0.41	41.6 ± 8.9	9.5 ± 0.8
15	5.25 ± 0.64	48.3 ± 7.8	9.9 ± 0.5
20	5.38 ± 0.32	52.1 ± 4.9	10.6 ± 1.0

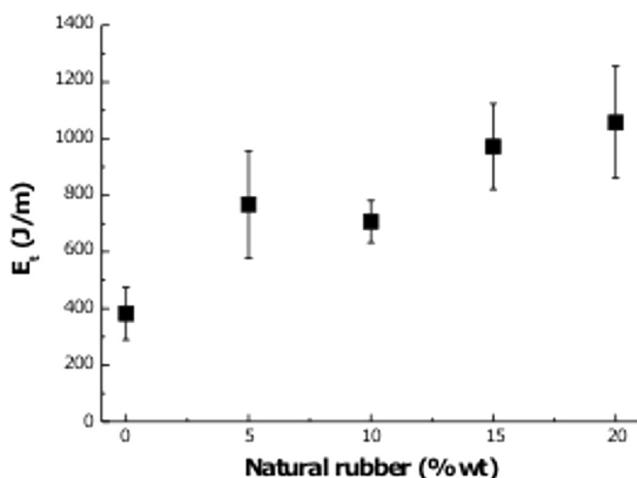


Figure 6 Total energy obtained in a dart impact test (E_t) as a function of the rubber content in the matrix for composite materials with 50% wood flour.

observe a measurable decrease in the EMC values between 5 and 10% rubber. The addition of high concentrations of a nonpolar material such as polyisoprene, the main component of the latex, which has a low affinity for water, leads to a decrease in the moisture absorption of the material.

F3 The values of the effective diffusion coefficient (D_{eff}), calculated from curve fitting [according to eq. (2)] of the experimental data of water absorption, are presented in Figure 3 as a function of the rubber content. The sorption kinetics seem to be more sensible to the presence of rubber in the formulation than the EMC; the added latex generates a more tortuous (indirect) path to water absorption. Thus, there is a large reduction in the D_{eff} values due to the addition of 5% rubber, but the decrease is more gradual with further increasing rubber content.

Flexural tests

F4 F5 Figures 4 and 5 present the flexural properties of composite materials containing 0 or 5 wt % natural rubber in the matrix formulation. The modulus and strength of the dry specimens increase with the wood flour content up to 80 wt % and then decrease for both samples with and without latex. For the

highest wood flour concentration used, the particle-particle interactions increase, and this effect reduces the level of filler-matrix interactions, thereby weakening the composite. Besides, there is an incomplete wetting of the particles because of the high wood flour content used in the composite formulation. The effect of the filler content on the mechanical properties of composites without latex addition was discussed in more detail in a previous article.⁹

A comparison of the properties of the two series of composites makes clear that the materials modified with latex present higher values of the modulus and ultimate stress. This unexpected result can be attributed to the interaction between the proteins present in the latex (where they act as surfactants) and the tannin extract. It is well known that the tannins interact with the proteins of animal skins in the process of tanning.⁵ Most of the published works have been dedicated to the study of the interactions generated between collagen (the most abundant protein in mammalian tissues) and different types of vegetable tannins.^{19–22} Because of the high complexity of the natural products involved, vegetable tannins and proteins in the skins, the mechanism of this interaction has not been completely clarified yet. However, it has been proposed that the fixation of tannins to proteins is due to the formation of strong hydrogen bonding, which results in the reduced hygroscopicity of the proteins and finally leads to the transformation of skins in strong leather.^{5,21,22} As reported by several authors,^{21,22} the Fourier transform infrared (FTIR) results have shown that bands assigned to the protein components in the latex suffer changes. The most important change is the broadening of the band around 3300 cm^{-1} , which is attributed to the hydrogen-bond interactions between the N–H groups of the amino acids in the proteins and the O–H groups of the tannins. This same broadening was observed in the FTIR curves of the latex and its mixture with the tannin-based resin. Thus, it is proposed that the protein component is responsible for the high cohesion of the composites modified with latex, which consequently present high modulus and strength values.

On the other hand, differences found in the mechanical properties corresponding to modified and

TABLE IV
Properties of Samples with 50 wt % Wood Flour and Different Percentages of Rubber (with Respect to the Matrix Weight) Tested in Dart Impact Tests

Natural rubber (wt %)	E_i/b (J/m)	E_p/b (J/m)	E_t/b (J/m)	DI	σ_d (MPa)
0	157.9 ± 19.4	224.0 ± 89.7	381.9 ± 92.1	0.57 ± 0.11	117.2 ± 23.8
5	193.6 ± 19.8	573.7 ± 205.3	767.3 ± 189.0	0.72 ± 0.07	156.3 ± 12.0
10	173.4 ± 35.9	508.4 ± 101.5	707.0 ± 74.8	0.68 ± 0.14	153.2 ± 6.6
15	309.9 ± 54.0	656.5 ± 131.6	972.0 ± 151.2	0.68 ± 0.08	143.3 ± 10.9
20	339.7 ± 145.0	717.7 ± 59.9	1057.4 ± 197.8	0.66 ± 0.08	127.1 ± 4.6

unmodified composites are more important at low percentages of wood flour. As an example, the modulus of the sample containing 50 wt % wood flour and 5 wt % natural rubber in the matrix formulation is 42% higher than the modulus of the sample without rubber. This difference decreases with the percentage of wood flour in the material, and for the sample of 90 wt % wood flour, the difference is insignificant.

This behavior can be expected because at low wood flour concentrations, the resulting concentration of latex with respect to the total weight of the sample is higher.

T3 Table III shows the flexural properties for composite materials with 50 wt % wood flour and modified with different percentages of latex. The modulus presents a clear increase with the modifier content, especially between 0 and 5 wt % rubber. The ultimate stress shows the same trend. The load transfer is more effective in the latex-modified composites. As expected from the incorporation of an elastomeric phase into a rigid matrix, the elongation at break increases with the natural rubber content.

Impact test

The falling dart impact test is widely used by the plastics industry to characterize the material response in the thickness direction. It provides a convenient method for studying surface embrittlement and methods of countering it through the use of additives.²³

F6 Figure 6 shows the total energy required to fully penetrate the specimens, normalized by the sample thickness, for different rubber contents. The energy absorbed presents a general trend of increasing with increasing latex content because the rubber phase introduces new mechanisms of energy consumption. The impact damage in a composite is a very complex process, in which the failure modes that can occur after initial elastic deformation are cracking and plastic deformation in the matrix, failure and fracture in the filler, filler–matrix debonding, filler pullout from the matrix, and stress relaxation.²⁴ The incorporation of rubber into this rigid composite material provokes a change in the matrix, allowing microlocal plastic deformation, so the total energy increases.

T4 Table IV shows the impact properties as a function of the latex content with respect to the total matrix weight. σ_d presents a high increase between 0 and 5% rubber and then decreases slightly. The role of the matrix is vital in composite behavior, protecting the fiber, transferring stresses, and, in some cases, alleviating brittle failure by providing alternative paths for crack growth.²⁵ The large change that occurs between 0 and 5% added rubber, partly due to the interaction of the protein component of the

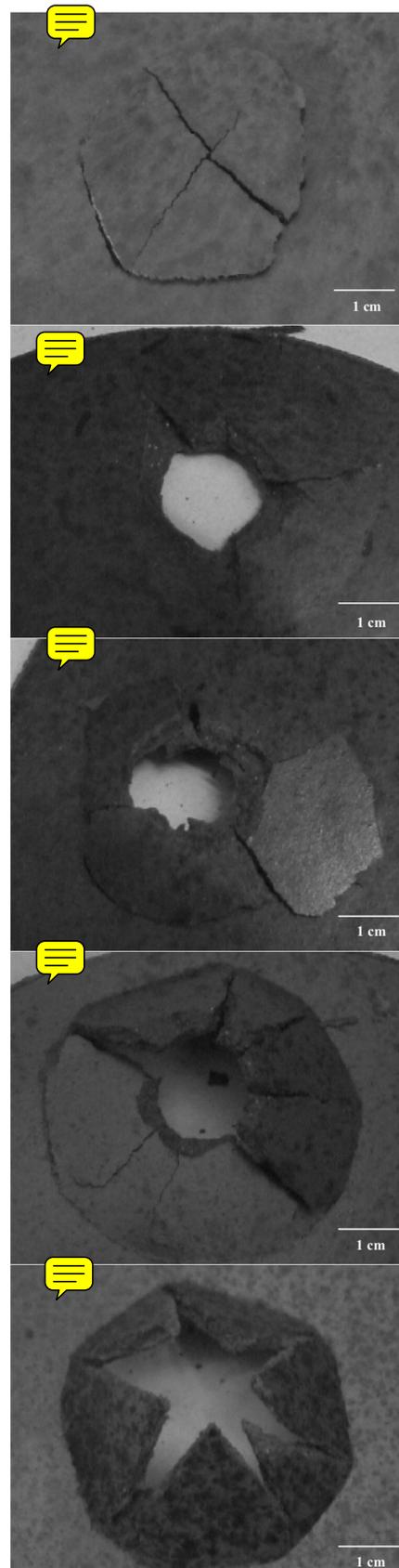


Figure 7 Photographs of samples with 50% wood flour and different rubber contents in the matrix after the impact test: (a) 0, (b) 5, (c) 10, (d) 15, and (e) 20%.

natural latex and the tannin, suggests an optimum concentration of the modifier by leading to the generation of more tortuous fracture paths. The incorporation of higher rubber amounts provokes a deleterious effect on the strength in the composites.

The initiation energy, shown in Table IV, also increases with the rubber content. This behavior can be attributed to the increasing difficulty for crack initiation, as more latex is incorporated into the formulation. Thus, the composite with 0% rubber exhibits brittle fracture, with the lowest propagation energy.

The DI as a function of the latex content in the material is also presented in Table IV. The increase is important between 0 and 5% modifier, and the differences become insignificant upon further latex incorporation. The calculated DI values are all above 0.5. In this type of test, a zero value would indicate that the material is behaving in a completely brittle manner. The larger the DI value is, the more energy is used in propagating the failure in comparison with that causing crack initiation.²⁶ Thus, the addition of the latex produces an increment of the total energy of fracture of about 2.7 times for the 20% natural rubber modified sample with respect to the unmodified composite. However, the DI varies slightly from 0.57 to 0.66, with a maximum at 0.72 for the 5 wt % rubber modified composite.

F7 Figure 7 shows photographs of the samples after impact tests. Some cracks run in a radial way from the central point of impact, whereas others follow a circular path around the same point. Circular cracks occur where the depression caused by the striker produces a large bending moment and a high level of out-of-plane curvature.²³ At low rubber contents, the circular crack, less effective in terms of toughness, interrupts the path of the radial cracks. As the latex content increases in the samples, the radial cracks seem to be longer. The sample with 20% natural rubber presents only radial cracks.

CONCLUSIONS

Composite materials made from a tannin adhesive, HEXA, and wood flour and modified with different natural rubber latex contents were prepared. The incorporation of natural latex allowed us to more easily prepare composites with low wood flour concentrations.

Although the latex contained mainly a nonpolar component, it did not lead to an important decrease in water absorption in the composites, but it retarded the kinetics of the sorption process.

The increase in the flexural properties with latex addition was attributed to the interaction between the protein contained in the latex and the tannin structure through a reaction similar to that occurring during the tanning of animal skin to become leather.

The impact properties improved with the addition of the latex, presenting the largest change between 0 and 5% rubber contents in the composites. As the rubber content increased, the materials consumed more energy to reach fracture.

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