5 th INTERNATIONAL SYMPOSIUM ON NATURAL POLYMERS AND COMPOSITES
8th Brazilian Symposium on the chemistry of lignins and other wood components

Paper 130

Tannin as a Partial Phenol Substitute in Thermoset Matrix of Jute Reinforced Composites

F.B. Oliveira, I.A.T.Razera, V. Barbosa Jr., E. Frollini*
Instituto de Química de São Carlos, Universidade de São Paulo
USP, C.P. 780, 13560-970 – São Carlos, SP, Brazil.
*elisabete@iqsc.usp.br

Abstract : *This work reports on the use of tannin, a natural macromolecule, as a partial substituent of phenol (raw material derived from non-renewable resource) in phenolic thermoset matrices of composites reinforced with vegetal fiber. Characterization by TG, DSC, infrared spectroscopy, scanning electron microscopy (SEM), and impact strength allowed the comparison the tannin-phenol matrix with the phenolic and lignophenolic matrices reinforced with jute fiber. The results obtained show that the presence of tannin resulted in a performance superior to those of lignophenolic and phenolic composites.*

Keywords: *composite, phenolic thermoset, lignin, tannin, jute, impact strength*

Introduction

The raw material used in the manufacture of phenolic resins is derived from non-renewable sources. However, tannin, a macromolecule of natural origin, presents the possibility of partially substituting phenol in the manufacture of phenolic resins as it forms an integrated network based on phenol and tannin units. It may constitute an interesting alternative from the economic and environmental viewpoints without the loss of resin properties.

Tannin has a complex structure [Pizzi, 2004, Bisand, 2003] including phenol-type rings and molar mass ranging from 500 and 20000 g/mol. It can be divided into hydrolysable and condensed, both normally soluble in water, with the exception of some with high molar mass.

Condensed tannins, also known as *Proanthocianides*, have flavonoid-type rings. These tannins have no ester bonds, as it occurs with hydrolysable tannins. It is the carbon-carbon type bonds that interconnect rings (Figure 1) that makes these tannins not easily hydrolysable.

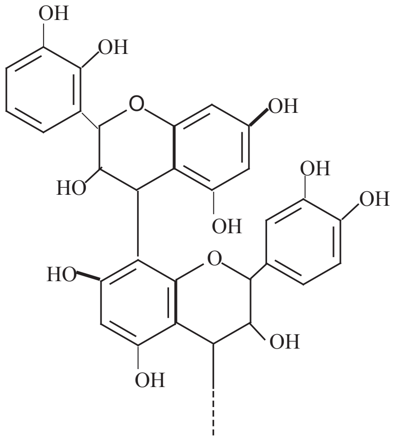


Figure 1: Representation of part of the chemical structure of condensed tannins

Condensed tannins are found in vegetal sources such as the Mimosa (or Acacia) tree. The presence of phenolic disubstituted rings in the structure of these tannins makes these rings be activated by electrophilic attack (such as by formaldehyde) due to the electron donating effect of hydroxyls. This factor, along with the fact that these macromolecules are resistant to hydrolysis, enables their use in the preparation of phenolic resins with the partial substitution of phenol.

This work is part of a broader project for the partial substitution of phenol in the preparation of phenolic resins by macromonomers in thermoset matrix composites reinforced with vegetal fibers [Paiva, 2001, Razera, 2004, Frollini, 2004, Paiva 2004]. Initial results for jute-reinforced composites in which tannin partially substituted the matrix phenol are here reported.

Experimental

Pre-polymer synthesis

A tannin-phenol pre-polymer was synthesized using tannin, phenol, formaldehyde, and potassium hydroxide (0.:1.38:1.0:0.06 w/w, respectively) under mechanical agitation. The solution was then cooled to room temperature and HCl was added until neutralization was achieved. Water was eliminated under reduced pressure.

Cure reaction and composite production

The thermoset and composites were obtained by mixing resorcinol (10%w/w) by mechanical stirring at 40 °C for 30 min. Compression molding was carried out in molds measuring 220 x 99.5 x 5 mm at 50 kgf/cm^2. Cure cycle parameters (40°C/0.25 h; 50°C/1 h; 85 °C/1 h;125°C/1.5 h) were previously determined by DSC measurements [Paiva, 2001] The jute fibers used in the preparation of the composites were pre-treated (Soxhlet) with cyclohexane/ethanol (1:1, v/v) for a period of 48 h to extract low molecular weight substances such as waxes, terpenes (natural impurities) and then with water for 24 h to extract inorganic contaminants. The fibers were dried in a circulating-air stove (60 °C) up to constant weight. Jute-reinforced composites (fiber length: 3.0 cm; 30%wt %) were obtained by adding the fibers to the pre-polymers. The mixture was submitted to mechanical stirring (0.5 h, 50 °C) before curing as described in the preparation of the thermoset. The composites were prepared with randomly oriented fibers.

Analyses

Fibers

Humidity content. Moisture content was determined according to ABNT (Associação Brasileira de Normas Técnicas, Brazilian Technical Standards Association), NBR9656.

Ash content. Ash content was determined considering the percentual difference between dried fiber sample weight before and after calcination for 4 h at 800 °C. At least three samples of each material were tested. Average values are reported in the next section.

Crystallinity index Crystallinity index (*Ic*) was determined by X-ray diffraction using a Rigaku Rota model RU-200B diffractometer (Rigaku, Japan) operating at 40 kV, 20 mA, and λ(Cu-K $_\alpha$) = 1540 Å. The crystallinity index was calculated using the Buschle-Diller and Zeronian equation: $I_c = 1 - I_1 / I_2$, where I_1 is the intensity at the minimum (2θ value between 18 and 19°) and I_2 is the intensity of the crystalline peak at the maximum (2θ value between 22 and 23°) [Razera, 2004]

Klason lignin content This method is based on the isolation of lignin by means of polysaccharide acidic hydrolysis (sulfuric acid, 72%) [Technical Association of Pulp and Paper Industry (TAPPI)T13m-54]. A minimum of three samples of untreated and treated fibers was tested. The average values are reported in the next section.

Cellulose and hemicellulose content The cellulose plus hemicellulose content (holocellulose content) was determined according to TAPPI T19m-54. A minimum of three samples of each material was tested. Average values are reported in the next section.

Microscopy. Scanning Electron Microscopy (SEM) was carried out in a Zeiss-Leica model 440 apparatus (Zeiss, Jena, Germany) at electron acceleration of 20 kV. Fibers were covered with a thin gold layer in a sputter-coating system before analysis.

Composites

Impact strength. Ten unnotched samples were cut from each plate and shaped according to ASTM D256 (63.5 x 12.7 x 4.0 mm). Impact strength was assessed using an Izod impact testor (Ceast Resil 25). Impact tests were carried out at room temperature with an impact speed of 4 m/s and incident energy of 5.5 J. As established in ASTM D256, at least five measures in each experiment were used to calculate the average values reported in the next section.

DSC analyses were carried out using a Shimadzu DSC equipment, model 50TA, 20 °C/min, under air atmospheres (10 mL/min). *Thermogravimetric analyses* (TG) were carried out using a Shimadzu model TGA-50TA apparatus. 20 °C/min under air atmospheres (10 mL/min).

Results and discussions

Table 1 shows the characterization results of jute fibers. Fibers were dried in oven prior to characterization. Humidity and ash content values are consistent with literature values for lignocellulosic materials (7.7 – 10% moisture and 0.5 – 1.0% ash) [Frollini, 2004] as well as the other data given in table 1.

Table 1: Characterization of jute fiber

Property	(%)
Humidity	10.3
Ash	1.0
NaOH 1% Soluble Material	10.6
Cellulose	60.0
Polyoses (hemicellulose)	22.1
Klason lignin	15,9

Tannin, the pre-polymer, and the tannin-phenol thermoset were analyzed by infrared spectroscopy. The three spectra (Figure 2) presented a broad and intense band in the 37000 – 3000 cm^{-1} region relative to the OH group vibrations. However, the pre-polymer spectrum shows a broader band due to the large quantity of $-CH_2-OH$ groups bound to the aromatic ring derived from the hydroxymethylation of the phenolic rings. It is also observed the presence of two little intense peaks around 830 and 750 cm^{-1} relative to *para* and *orto* substitutions of the aromatic ring, respectively. It was noticed that in the pre-polymer spectrum, the peak corresponding to the *orto* position is more intense, while in that of the thermoset, the ratio between the two is approximately one due to the interlinking reactions that occur in the *para* position.

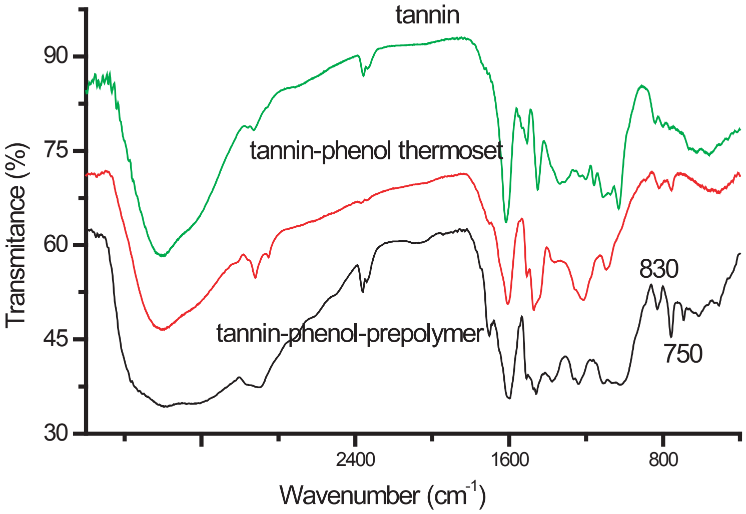
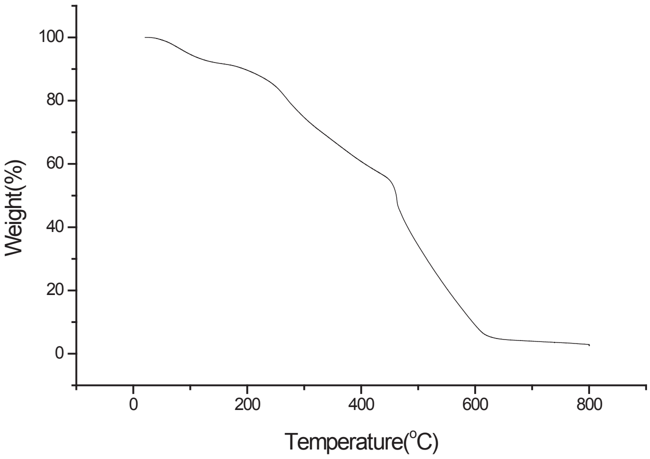


Figure 2: Infrared spectra of tannin, pre-polymer and thermoset tannin-phenolics

Figures 3 and 4 show TG curves for tannin and the tannin-phenol matrix composites, respectively.



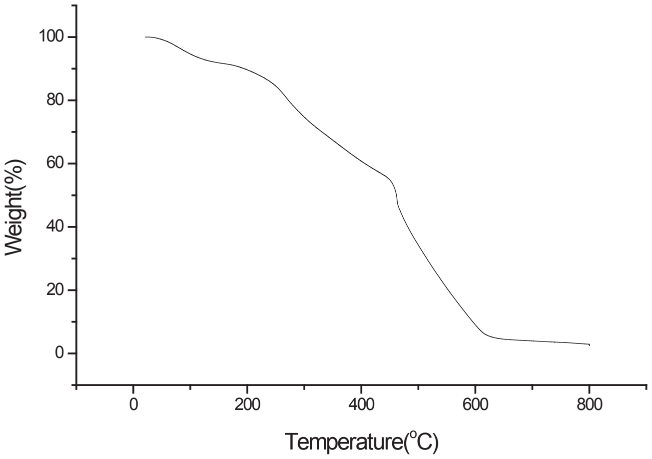


Figura 3: TG curve of tannin, air atmosphere, 10 mL/min, heating rate 20 °C/min

Figure 4: TG curve of tannin-phenol composite reinforced with jute fibers, air atmophere, 10 mL/min, heating rate 20 °C/min

In figure 4, it can be seen that the composite weight loss is significant from 200°C on, which may be attributed to the decomposition of tannin, as observed in figure 3, also incorporating the degradation of jute from approximately 250°C as a result of the degradation of the cellulose present in the lignocellulosic fiber [Paiva, 2004]. Figure 5 displays the DSC curve of the tannin-phenolic composite.

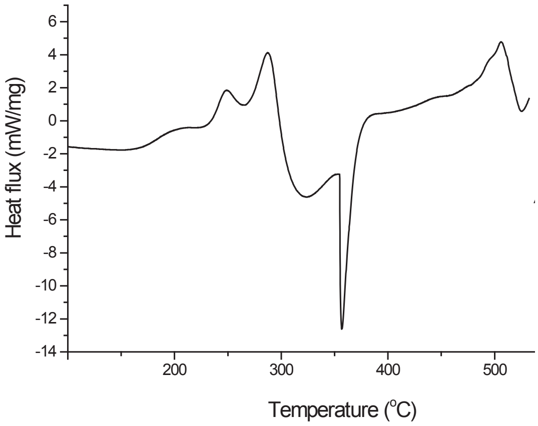


Figure 5: DSC curve of the tannin-phenolic composite reinforced with jute fibers, air atmosphere, 10 mL/min, heating rate 20 °C/min.

The DSC curve of the composite (Figure 5) shows several exothermic events between approximately 180 and 280 °C, which must be related mainly to the degradation of the tannin moiety incorporated into the matrix. Between 300 and 400 °C, two endothermic peaks are observed, which may be due to the release of volatiles in the process of decomposition of the matrix and also the lignocellulosic fiber. Around 500 °C, it is observed an exothermic peak, probably related to the degradation of the aromatic rings. SEM analyses of tannin-phenol composites were carried out (Figure 7).

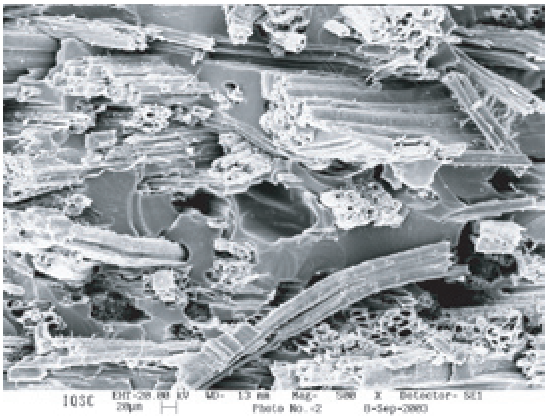


Figure 7: SEM images of the impact fracture surface of jute-reinforced tannin-phenol composite (x100)

Figure 7 shows some voids in the composite resulting from the detachment of fibers caused by the impact, indicating a poor adhesion region in the fiber/matrix interface. However, in other regions it can be observed that the fiber is entirely surrounded by the matrix, indicating a high adhesion region in the fiber/matrix interface.

In accordance to the results of Table 2, it is observed that the composite with tannin as a partial substituent of phenol presented impact strength higher than those of lignophenolic and phenolic composites, whose values were close to each other.

Table 2. Izod (*unnotched*) impact strength of jute-reinforced phenolic (PC), lignophenolic (LC), and tannin-phenolic (TC) composites and their respective standard deviations

Composites	PC	LC	TC
Impact Strength (J/m)	72.6 ± 6.5	74.3 ± 6.3	113.2 ± 13.9

The larger impact strength exhibited by the tannin-phenolic composite is a promising result. It may result from the better impregnation of the fiber/pre-polymer and more intense fiber/interface interactions in the composite in comparison to lignophenolic and phenolic composites.

Conclusion

The results obtained in the Izod impact strength assay show that the presence of tannin resulted in a performance superior to those of lignophenolic and phenolic composites. These initial results are extremely promising, showing that the substitution of phenol by tannin is viable.

Work aiming at the optimization of the pre-polymer synthesis and the cure steps, and to increase the percentage of tannin in the matrix as well as the use of other fibers, in addition to jute, as matrix reinforcing agents are under way.

Acknowledgements

E. F. is grateful to CNPq (National Research Council, Brazil) for a research productivity fellowship; to FAPESP (The State of São Paulo Research Foundation, Brazil), and TANAC SA (Montenegro, RS, Brazil) for financial support; to CAPES for research fellowships for IATR and FBO; and MEC/SESu for PET fellowship for VB Jr.

References:

Bisanda, E.T.N., Ogola, W.O., Tesha, J.V., Characterization of tannin resin blends for particle board applications, Cement & Concrete Composites, **25**, 593-598, 2003.

Frollini, E, Paiva, J.M.F, Trindade, W.G., Razera, I.A.T., Tita, S.P., *Lignophenolic and Phenolic Resins as matrix in vegetal fibers reinforced composites, In:* ***Natural Fibers**, **Polymers and Composites*** - Recent Advances, F. Wallenberger, N Weston, Eds., Kluwer Academic Publishers, 193-219, 2004.

Paiva, J. M. F.; Frollini, E. Sugarcane Bagasse Reinforced Phenolic and Lignophenolic Composites, *Journal of Applied Polymer Science*, 734-742, 2001.

Paiva, J.M.F., Trindade, W.G., Frollini, E., Pardini, L.C., *Polymer-Plastcs Technology Engineering*, **43**, 1174-1203, 2004.

Pizzi, A, Simon, C, George, B, Perrin, D., Triboulot, M. C., Tannin antioxidant characteristics in leather versus leather light stability: Models, Journal Applied Polymer Science, **91**, 1030-1040, 2004.

Razera, I. A. T.; Frollini E. Composites based on Jute Fibres and phenolic Matrices: Properties of fibers and composites. *Journal of Applied Polymer Science*, **91**, 1077-1085, 2004.