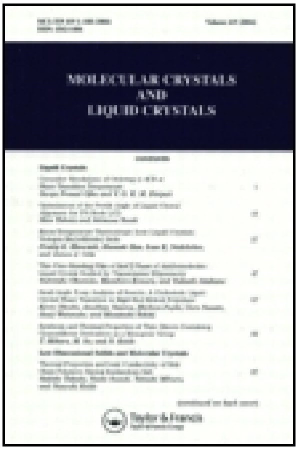

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Natural Composites: Polymeric Matrices Based on Vegetable Resources

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Natural Composites: Polymeric Matrices Based on Vegetable Resources

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The aim of this work has been to develop new composites using filler and resins obtained from renewable resources, combining low cost and good mechanical properties. The raw materials selected for the polymeric matrix were tannin extracts and plant oils. The tannin extracts are potential substitutes for phenol-formaldehyde wood-bonding adhesives and the vegetable oils can be functionalized to obtain unsaturated polyester resins to be further used in polymeric matrix formulations. Tannin and oil based composites using pine woodflour as filler were prepared and mechanically tested. The effect of the humidity on the mechanical properties was also evaluated.

Keywords: composites; mechanical properties; renewable resources

INTRODUCTION

The development of polymeric composites using cheap, renewable and widely available vegetable raw materials as sources for the matrix and filler components has been increasing, in both scientific studies and commercial applications, during the last decade, mainly because it presents environmental and economic advantages.

In particular, some developments have been driven by environmental considerations; this is the case of tannin based polymers, used to reduce phenol emissions of phenolic type resins.

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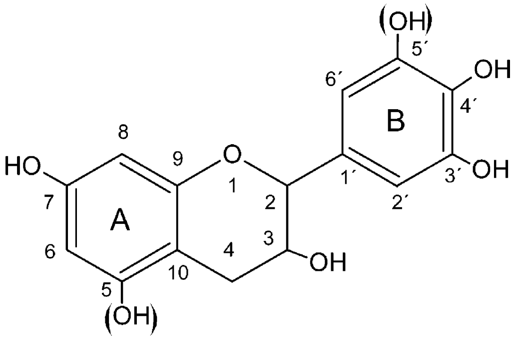


FIGURE 1 Flavan-3oil repeating unit in polyflavonoid tannin.

Polyflavonoid tannins are natural polyphenolic materials (Fig. 1) that can be crosslinked by reaction with formaldehyde or hexamethylenetetramine crosslinking agents, the last one leading to cured products with low formaldehyde emissions [1–3]. In the present study, this system was used as the polymer matrix of a pine woodflour composite.

Although most scientific and technological reports have focused on their use in the manufacture of adhesives (particleboards, plywood) [1], the use of these polymers in the manufacture of molding powders or fiber composite materials has not been fully developed.

Perhaps more rich in possibilities as a source of different polymers is the use of plant oils as natural source of different resins. There are many reports on natural fiber composites using commercial thermosetting resins or thermoplastic polymers [4,5], but the use of a polymeric matrix from natural sources such as plant oils is relatively new. Oils consist of triglyceride molecules, which are composed of three unsaturated fatty acid chains. An unsaturated polyester-like resin can be obtained by functionalizing the triglyceride molecules in two basic steps: glycerolisis to produce a monoglyceride and then reaction with maleic anhydride to produce a maleinated monoglyceride [6,7]. The product can be further mixed with styrene, the reactive comonomer, and cured via a free radical polymerization to give a crosslinked thermosetting polymer (Fig. 2). The matrix has a relatively low modulus, but the addition of rigid wood particles increases the material stiffness, improving its performance.

In this article, a brief report on the synthesis of these natural based polymers and the study of their performance as polymeric matrices in woodflour composites will be presented.

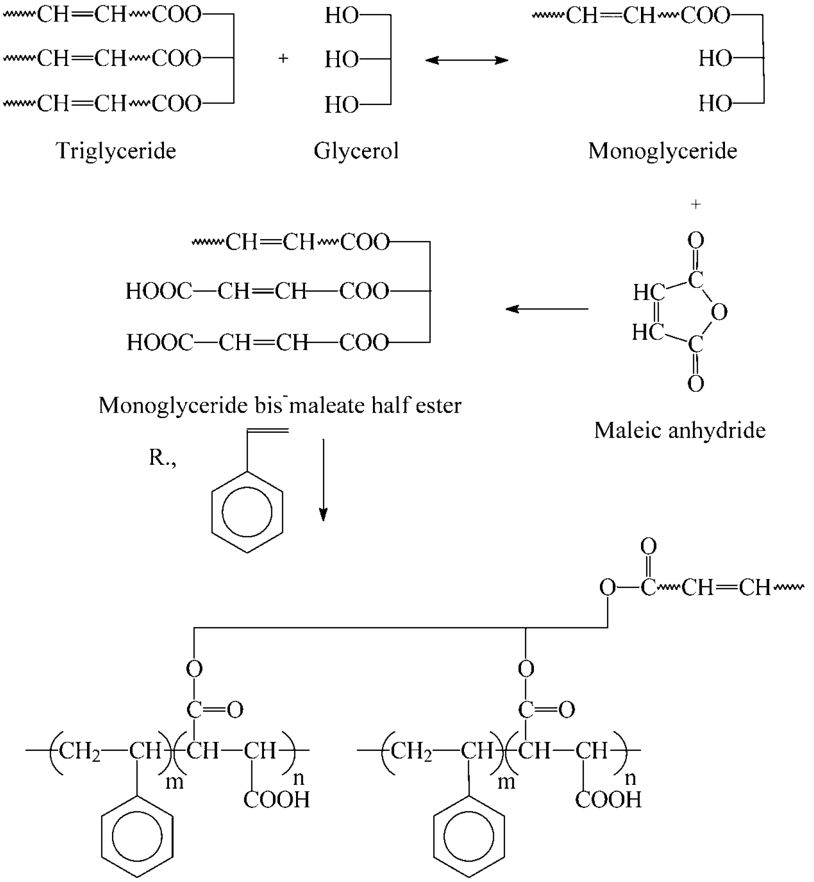


FIGURE 2 Synthesis and polymerisation of linseed oil monoglyceride maleates.

Materials

Tannin Based Matrix

Commercial quebracho tannin adhesive, Colatan GT100 (Unitan S.A.I.C., Argentine) was used as a 40% (by weight) aqueous solution. The hardener was hexamethylentetramine (Mallinckrodt, Argentine), in a proportion of 10% with respect to the mass of dried adhesive.

Oil Based Matrix

The natural resin was synthesized from linseed oil provided by Grainer S.A. (Entre Rios, Argentine), which was further crosslinked with styrene in a 60:40 weight proportion. The initiator was benzoyl peroxide (Lucidol 0.75, Akzo Chemical S.A.), 2.5% wt. with respect to the total reaction mixture. The synthesis and characterization of the matrix were carefully described in a previous publication [7].

In both systems, the chosen filler was pine woodflour. All the particles have particle sizes of 75 to 150 μm.

Preparation of the Styrene/Linseed Oil Resin Copolymers

The linseed oil resin was mixed with 20, 40, and 60% (by weight) of styrene and 2.5% (by weight) of benzoyl peroxide. The solution was heated to 40–50°C to achieve homogeneity. The mold consisted in two plane glasses previously treated with a silicone release agent, separated by a rubber cord and kept closed with metal clamps. The mixture-filled mold was placed in an oven at 50°C for 2 h, and the temperature was increased at the rate of 1°C/min up to 90°C. Curing took place at this temperature for 1.5 h and the sample was postcured a 150°C for another 1.5 h.

Compounding and Molding

The composite materials were prepared by mixing the dried filler and the reactive mixture in an intensive mixer at room temperature and 50 rpm. The resulting paste was filled in a cylindrical metal mold (145 mm of diameter and about 3 mm of thickness), and cured with different conditions depending of the system:

Tannin Adhesive/Woodflour Composites

The water (coming from the tannin adhesive) was evaporated from the mixture before curing at 160°C under pressure of 4.2 MPa for 30 min. The samples were prepared varying filler contents from 60 to 90% by weight with respect to total composite weight.

Linseed Oil Resin/Woodflour Composites

The mold was left open for 1.5 h at 50°C for degassing. Then, it was closed and the temperature was increased to 90°C. The mixture was cured at this temperature for 1.5 h under pressure, and then poscured a 150°C for another 1.5 h. Materials with different densities were obtained using different pressures (4 MPa and 8 MPa). Samples were prepared with varying filler contents, from 0 to 60% by weight with respect to total weight.

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

Composite densities were determined by picnometry using at least three specimens of each sample. The theoretical densities of the composites were calculated from the rule of mixture:

$$\frac{1}{\rho_c} = \frac{W_m}{\rho_m} + \frac{W_f}{\rho_f} \tag{1}$$

where ρ is the density and W is the weight fraction, and the subindexes c, m, and f corresponds to composite, matrix and filler, respectively. The woodflour density was taken as the density value of the cell walls, 1.53 g/cm^3 [8].

RESULTS AND DISCUSSION

Tannin Adhesive/Woodflour Composites

Figure 3 shows the fracture surface of a sample tested in three-point bending analysed by SEM (microscope Philips model SEM 505). Fiber breakage is the most common feature, indicating that there is a good adhesion between the matrix and the fiber (white arrows, Fig. 3).

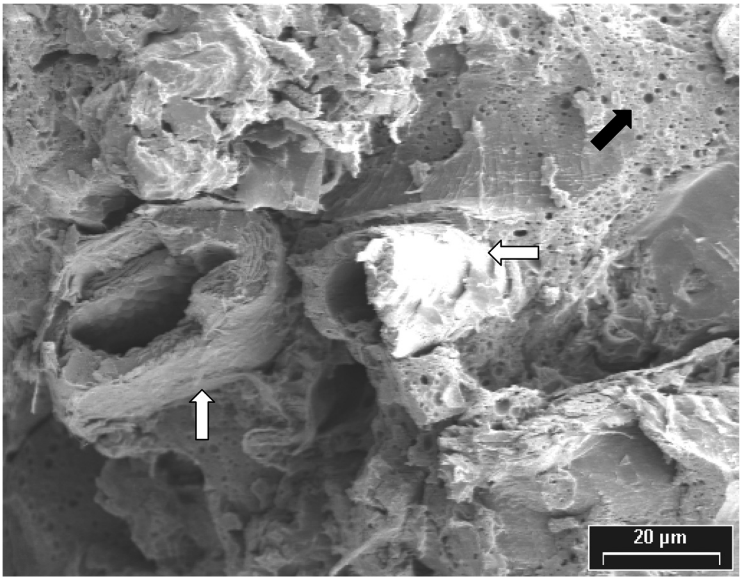


FIGURE 3 SEM micrographs of composites (×1000) showing surface fracture from flexural tests. Matrix microvoiding and interphase adhesion are indicated with arrows (black and white, respectively).

The lumen of the wood cells appears partially unfilled with the resin due to the high filler concentrations used (70% wt.). The amount of matrix is insufficient to perfectly coat all the individual filler particles and so direct aggregation of wood particles take place. The matrix presents a micro-foamed structure originated in the condensation reaction of the tannin adhesive with hexamethylentetramine during the cure molding process (black arrow, Fig. 3). This feature affects the density and water absorption of the composites.

Moisture Absorption

Figure 4 shows the equilibrium moisture content (EMC) reached by the materials as a function of the filler content at 60 and 90% relative humidity. The fitting curves were obtained using a simple rule of mixture [9]. 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 highly hygroscopic nature of the tannin matrix, which presents a high proportion of di- and tri- benzylamine bridges [3]. These groups are highly polar and favor water absorption. Besides

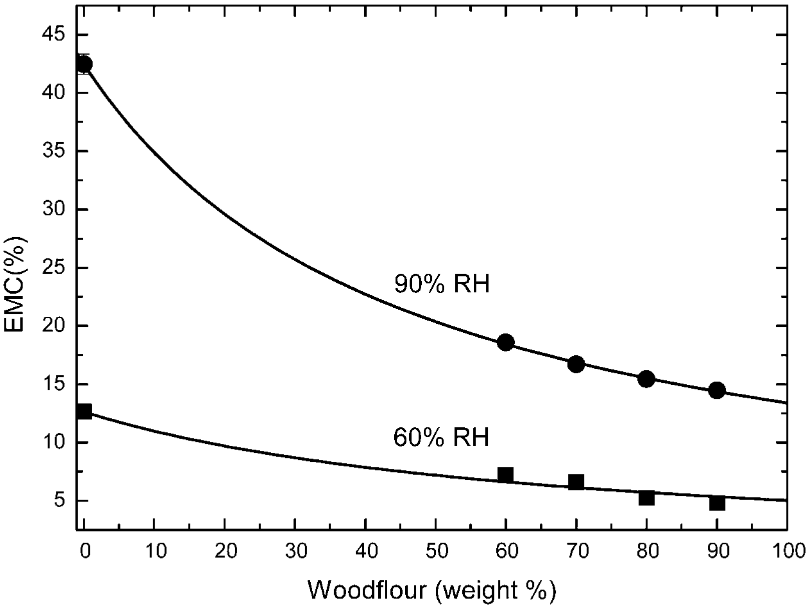


FIGURE 4 The final (equilibrium) moisture content (EMC) as a function of the wt% of filler at 60 y 90% RH.

the filler as well as the polymeric matrix have 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.

Flexural Tests

Three-point bending tests were performed in accordance to ASTM D790-93 standard.

Figure 5 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. As mentioned before, this could be explained by the incomplete wetting of the particles, due to the high content of filler used. A similar tendency was shown by the ultimate stress as a function of the concentration of woodflour (not shown).

Figure 5 also shows the comparison of the results obtained in three point bending tests from dry, wet and redried samples at different

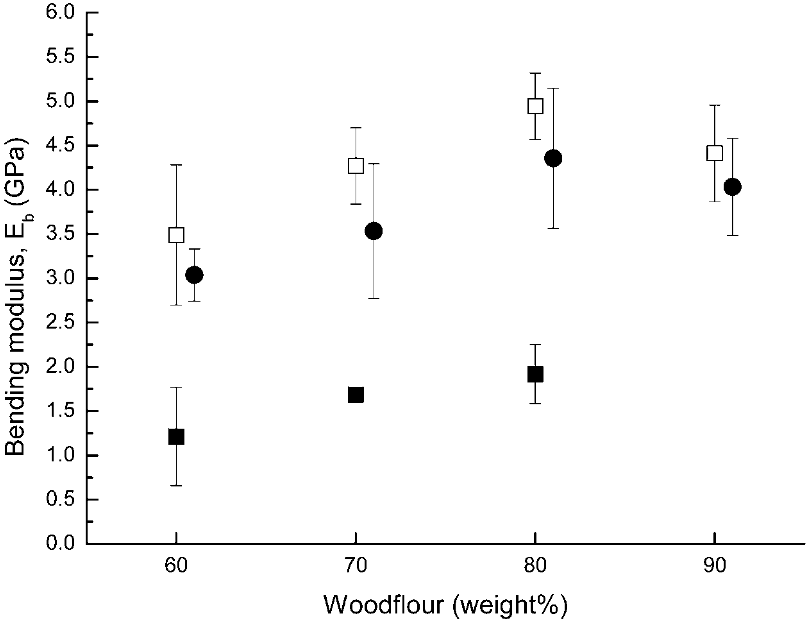


FIGURE 5 Comparison of flexural modulus of dry (■), wet (●) (moved for better visualization) and redry (□) samples for different filler weight percentages.

filler weight percentages. Regarding the properties of the wet samples at 90 RH (after 100 days), they exhibit an important reduction of the modulus due to moisture in the composites. However, the materials recover, although not completely, after re-drying, reaching property values close to those corresponding to the original dry materials.

Further studies are being conducted on the addition of natural rubber to these composites with the double purpose of reducing sensitivity to water and improving toughness.

Linseed Oil Resin

^{1}HNMR study of the linseed oil resin obtained indicated that the original unsaturations are still present at the end of the maleinization (5.3 ppm), while a new intense peak appears at 6.3 ppm, which is due to the maleic moieties. An acid proton signal (8.4 ppm) also appears, since maleic anhydride reacts to give a half ester and leaving a free carboxyl acid group [7].

Fracture Behavior

Fracture Toughness and Work of Fracture

Differences in fracture propagation mode are not completely reflected in the K_{IQ} factor, which does not describe completely the fracture behavior of these materials. Thus, the work of fracture (wof) that measures the energy necessary for driving the crack through the whole sample was also calculated. Notched specimens (ASTM D5045-93) were used for both tests.

In spite of the differences in the two approaches, the fracture tests showed the same tendency of the K_{IQ} and wof values (Fig. 6). All materials were fragile but the material prepared with 40% of styrene displayed the highest toughness [7].

Linseed Oil Composite Materials

Densities of the Composites and Void Volume Fractions

Table 1 shows the theoretical and experimental densities of the composites prepared with different percentages of woodflour and obtained using two different pressures. The experimental densities were similar to the theoretical values up concentrations of 30% of woodflour. For higher woodflour contents the void volume fraction increased. The use of higher pressure during curing allowed to improve sample connectivity and to increase its density. Results of samples prepared at a higher pressure (8 MPa) are also reported in Table 1.

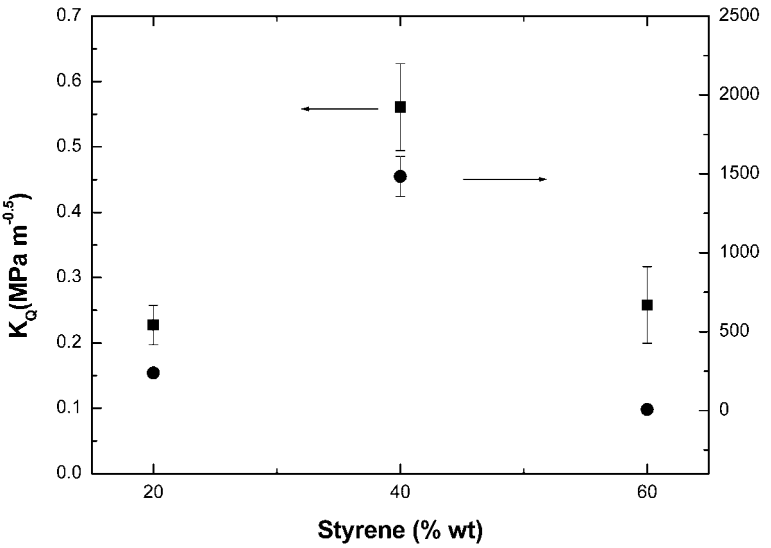


FIGURE 6 K_{IQ}(■) and WOF (●) values as a function of the percentage of styrene.

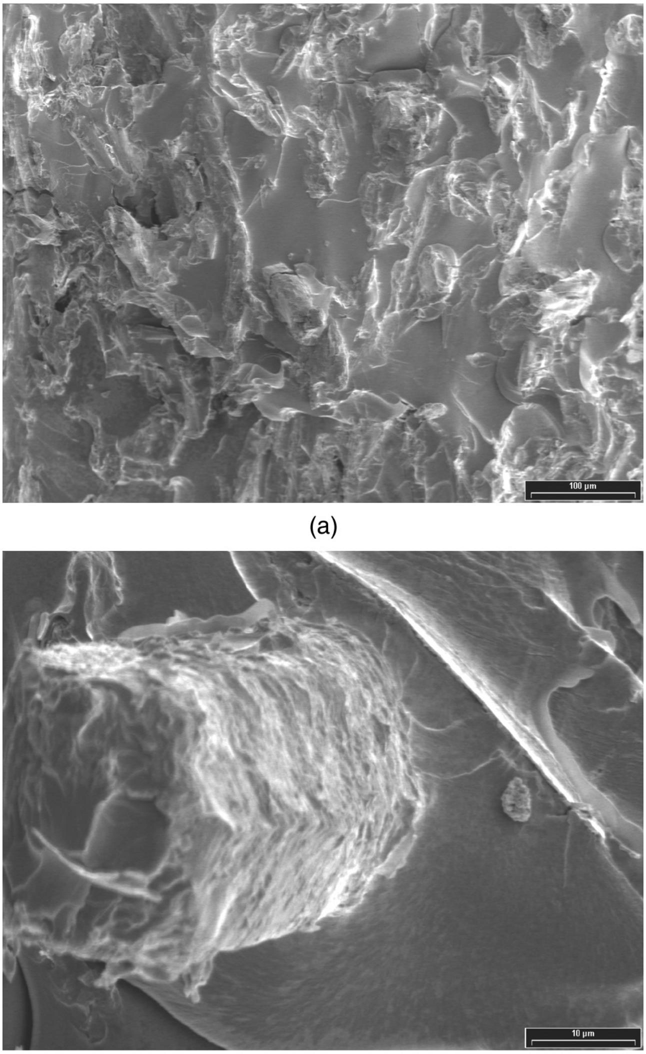
Microscopy Interfacial Adhesion

Figure 7a and 7b shows the micrographs (SEM) of the fracture surface of the composites with 30% by wt. of woodflour and zero void volume. The bulk matrix shows the characteristic features of fragile fracture. However, globally, the composite surface is substantially rougher (Fig. 7a) than the fracture surface of the neat resin (not shown) [10].

TABLE 1 Physical Properties of the Composites. All the Samples were Prepared Using a Pressure of 4 Mpa, Unless Specifically Indicated

Percentage of woodflour	Theoretical densities (g/cm^3)	Experimental densities (g/cm^3)	Porosity volume fraction, V_p
0	–	1.062 ± 0.001	0
20	1.133	1.138 ± 0.042	0
30*	1.169	1.191 ± 0.024	0
30	1.169	1.078 ± 0.010	0.08
40*	1.210	1.082 ± 0.003	0.1
40	1.210	1.001 ± 0.005	0.18
50	1.254	1.002 ± 0.026	0.201
60	1.301	1.051 ± 0.034	0.192

*Samples prepared under 8 MPa pressure.



(a)

(b)

FIGURE 7 SEM micrographs of composites with 30%wt woodflour and without voids, at two magnifications: a) ×200 and b) ×2000.

It can be observed that the capillaries of the wood particles are filled completely with the resin (Fig. 7b). Fiber pull out is not observed in any case. Micrograph 7b shows a short section of a filled particle with a completely resin coated surface. There is not clear differentiation

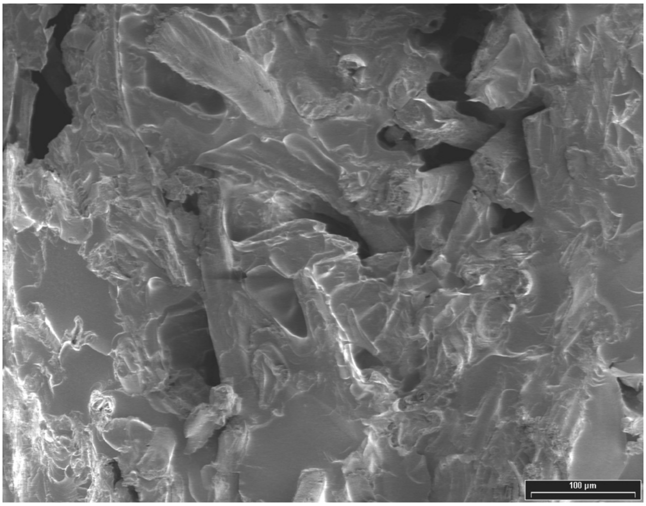


FIGURE 8 SEM micrograph of composite with 30%wt woodflour and 10% porosity, at magnification ×200.

between the bulk resin and the resin covering the filler surface. The adhesion filler-matrix is excellent in this system.

In the composites with higher void volume fraction, (Fig. 8, 30% wt. woodflour and 10% of porosity) the observation of the interphase region indicates that the compatibility between the two main phases is as excellent as in the high-density composites. However, the higher concentration of woodflour requires more resin for complete dispersion and wetting, and it can be seen that although the fibers are resin coated, there are voids in the structure as the result of the mechanical interlocking of the rigid particles, and the increasing difficulty of obtaining a compacted structure at the processing pressure of 4 MPa.

Dynamic Mechanical Response

Figure 9 shows the temperature range of the transition in the tan δ. There is a dramatic increase in the position of the tan δ peak with increasing woodflour content. That must be related to a very strong interaction between matrix and filler. The reason is the presence of hydroxyl groups in the lignocellulosic filler capable of reaction with the free carboxylic group of the maleic moiety in the synthesized resin [11].

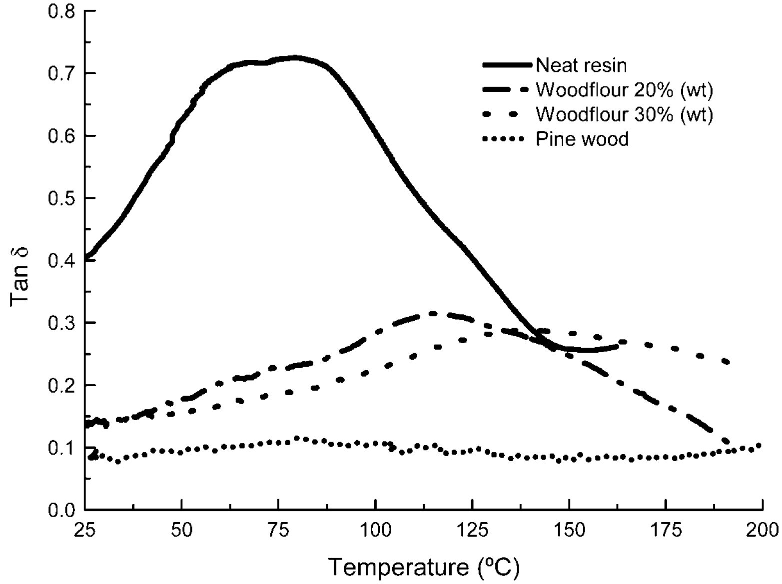


FIGURE 9 Temperature scans of tan δ for samples with no voids.

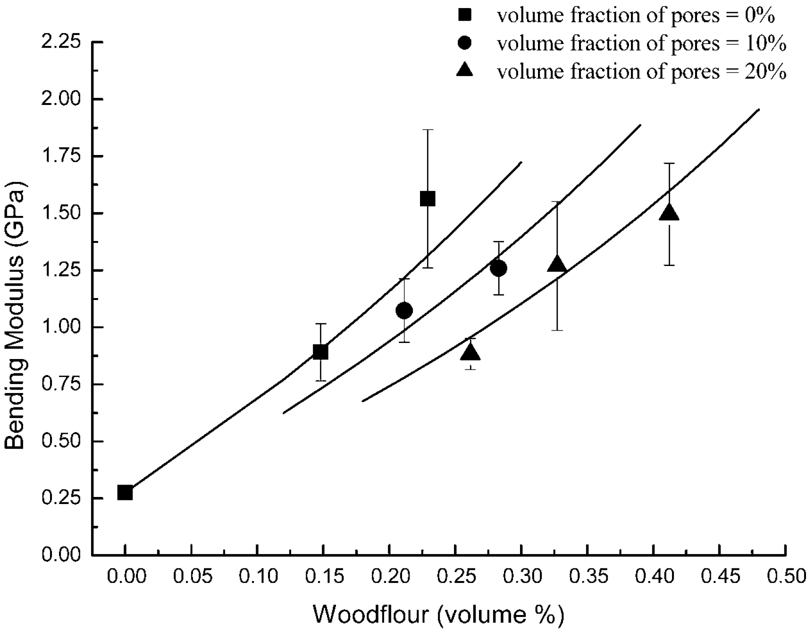


FIGURE 10 Experimental modulus of composites at various levels of woodflour content.

Flexural Tests

Figure 10 shows the bending modulus of the composites measured at room temperature as a function of filler content and for different void volume fractions. The moduli of the composites are higher than that of the neat thermoset even in those composites with high porosity, even when increasing void volume fraction reduces the modulus of the material.

Figure 11 shows the bending ultimate stress of materials (σ_c) with different volume fractions of filler (V_f) and of voids (V_v), showing the same trend as the modulus.

A modified version of Pukanszky equation [10,12] was used to fit data for different void volume contents, as shown:

$$\sigma_c = \sigma_{matrix}\left(\frac{1-(V_f+V_v)}{1+2.5\cdot(V_f+V_v)}\right)\cdot\exp(B\cdot V_f) \tag{2}$$

The parameter B is related to the filler matrix adhesion. $B \leq 3$ indicates a weak interface [13]. In the present case, all B values were much higher than 3, even for the porous materials; the interface is

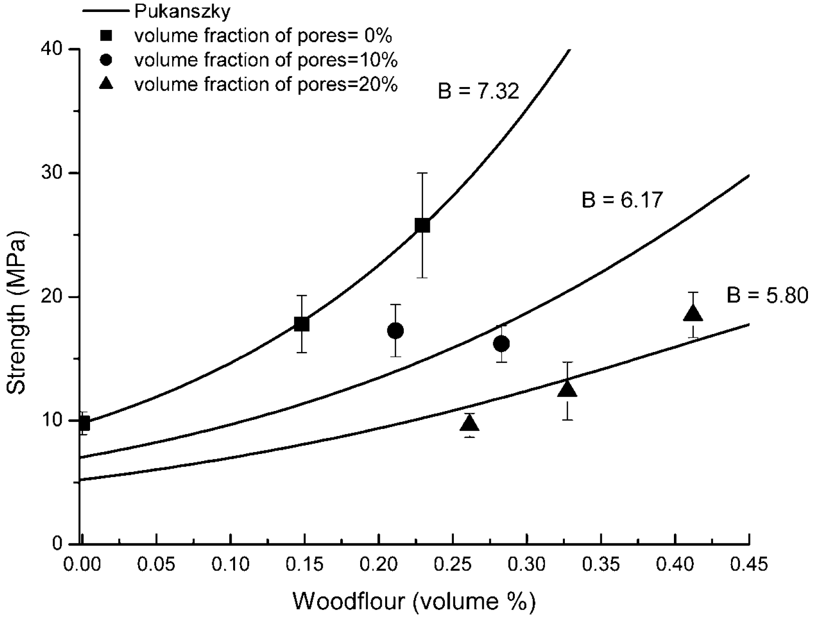


FIGURE 11 Experimental ultimate stress and theoretical values calculated from the Pukanszky model.

strong and a reinforcing effect is observed. Although, the adhesion at the interface is equally strong in all these materials, B decreases with increasing void content, because it is the only adjustable parameter of the model.

CONCLUSIONS

Tannin extracts and plant oils can be used as raw materials in the production of phenolic and unsaturated polyester types of resins. These polymers can be further used in the formulation of vegetable fiber/particle composites.

Tannin based composites are high modulus materials, but very sensitive to humid environments.

Linseed oil based copolymers show maximum properties at a ratio 60:40wt. oil based resin:styrene.

Oil based composites showed an excellent interfacial adhesion with vegetable fillers. SEM, DMA and mechanical properties confirmed this point. This feature added to easy processing make this resin very attractive for further use as vegetable composite matrices.

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