

Moisture absorption effects on the thermal and mechanical properties of wood flour/linseed oil resin composites

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Abstract: The thermal and mechanical behavior of new natural polymeric composite materials after exposure to humid environments must be well known and understood in order to predict their performance in final applications. For this reason, composites made from unsaturated polyesters based on linseed oil and filled with wood flour were exposed to environments of different relative humidities and their final properties were measured. In general, the equilibrium moisture content increased as the wood flour percentage increased. Dynamic mechanical tests performed in temperature scan mode were carried out in order to monitor the changes resulting from moisture absorption on the main transition temperature of the matrix (T_g). The temperature of this transition decreased as the amount of absorbed water increased, but the effect was partially reversible by re-drying the samples. The mechanical properties were also strongly affected by moisture. The flexural modulus and ultimate stress of the composites decreased after equilibration in humid environments.

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Keywords: wood flour composites; renewable resources; mechanical properties; moisture absorption; voids

INTRODUCTION

Polymeric materials prepared from natural products have gained increased importance due to threats of uncertain petroleum supply in the future and concerns about environmental pollution. Natural products offer some advantages: they are obtained from renewable resources, they are widely available and abundant, they constitute low-cost materials and they are potentially biodegradable.¹

Natural oils are predominantly composed of triglyceride molecules with three fatty acid chains from 16 to 22 carbon atoms in length and from 0 to 3 double bonds in each chain. Specifically, linseed oil has a high percentage of highly unsaturated fatty acid chains, and it is used principally in the paint and varnish industry. In Argentina, seed flax (or non-textile flax) is grown mostly in the northeast of the country for the production of linseed oil, of which a large percentage is exported. Triglyceride molecules can be modified to synthesize a new monomer with multiple functional sites and able to produce rigid polymers that can be used in composite formulations.^{2–4} The oil-based polymers used in this work are analogous to synthetic unsaturated polyesters but have different physical and mechanical properties.

Linseed oil resin can be further crosslinked with styrene by means of free radical polymerization and filled with pine wood flour in order to realize acceptable mechanical properties for practical structural applications.⁵

The mechanical properties of these new composites must be evaluated when exposed to humid environments, since their hygroscopicity may limit the type of applications for which they can be considered.⁶

All polymer composites absorb moisture in a humid atmosphere or during immersion. The amount absorbed is determined by the polar or nonpolar nature of the matrix and the filler, the fiber–matrix interface and the microvoid structure of the resulting composite. Wood flour is highly hygroscopic and can absorb or desorb moisture readily when subjected to changes in the relative humidity of the surrounding environment.⁷ Thus, water absorption is one of the limiting factors in the use of natural fiber-reinforced polymer composites.

Although different publications have dealt with the study of the effect of humidity on the mechanical behavior of wood flour/polymer composites,^{8,9} there are not many studies focused on the performances of natural oil resins and their composites. In the work reported here, composite materials made from a linseed oil resin and wood flour were exposed to humid environments. The aim was to determine the influence of the moisture content on the mechanical and thermomechanical properties of the different composites.

EXPERIMENTAL

Materials

The unsaturated resin was synthesized from linseed oil provided by Grainer SA (Entre Rios, Argentina),

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and was further crosslinked with styrene in a 60:40 weight proportion. The initiator was benzoyl peroxide (Lucidol 0.75, Akzo Chemical SA), added as 2.5 wt% with respect to total weight of the reactive mixture.

Composites were manufactured by adding dried pine wood flour (J Do Santos Freire, Buenos Aires, Argentina) to the reactive polymer system. All the wood flour particles used in the study were passed through mesh 100 (US Standard) and were retained by sieve 200, corresponding to average particle sizes ranging from 75 to 150 μm. The wood flour was dried at 75 °C for 48 h in a vacuum oven before use.

Linseed oil resin: synthesis and crosslinking

The reaction pathway of the resin synthesis used in this work is shown in Fig. 1 (steps (a) and (b)); this corresponds to the glycerolysis of linseed oil to obtain a monoglyceride, followed by the reaction with maleic anhydride to produce a maleinated monoglyceride. The details of the synthesis and characterization of the resin have been presented and discussed in a previous publication.³

The resin obtained was mixed with styrene and cured via free radical polymerization to obtain a crosslinked network^{3,10} (step (c) in Fig. 1).

Compounding and molding

Molded plaques of composite material were obtained by compounding the filler with the polyester resin in an intensive mixer (made in our laboratory) and working at room temperature and 50 rpm. The paste was cured in a metal mold (145 mm in diameter and about 3 mm thick), which was left open for 1.5 h at 50 °C. The mold was then closed and the temperature was increased to 90 °C. The mixture was cured at this temperature for 1.5 h under pressure, and then post-cured at 150 °C for another 1.5 h without pressing. Materials with different densities and void volume fractions were obtained using different pressures during curing (4 or 8 MPa). Samples were prepared with varying filler contents from 0 to 60 wt% with respect to total weight.

The volume fraction of voids (V_v) in the composites was estimated, assuming additivity of the volumes of matrix, filler and voids as

$$V_v = \frac{\rho_c \text{ theoretical} - \rho_c \text{ experimental}}{\rho_c \text{ theoretical}} \quad (1)$$

where $\rho_c \text{ experimental}$ is the density value of the composite measured by picnometry in degassed distilled water at room temperature. The duration of the test was sufficiently short to neglect absorption of the water

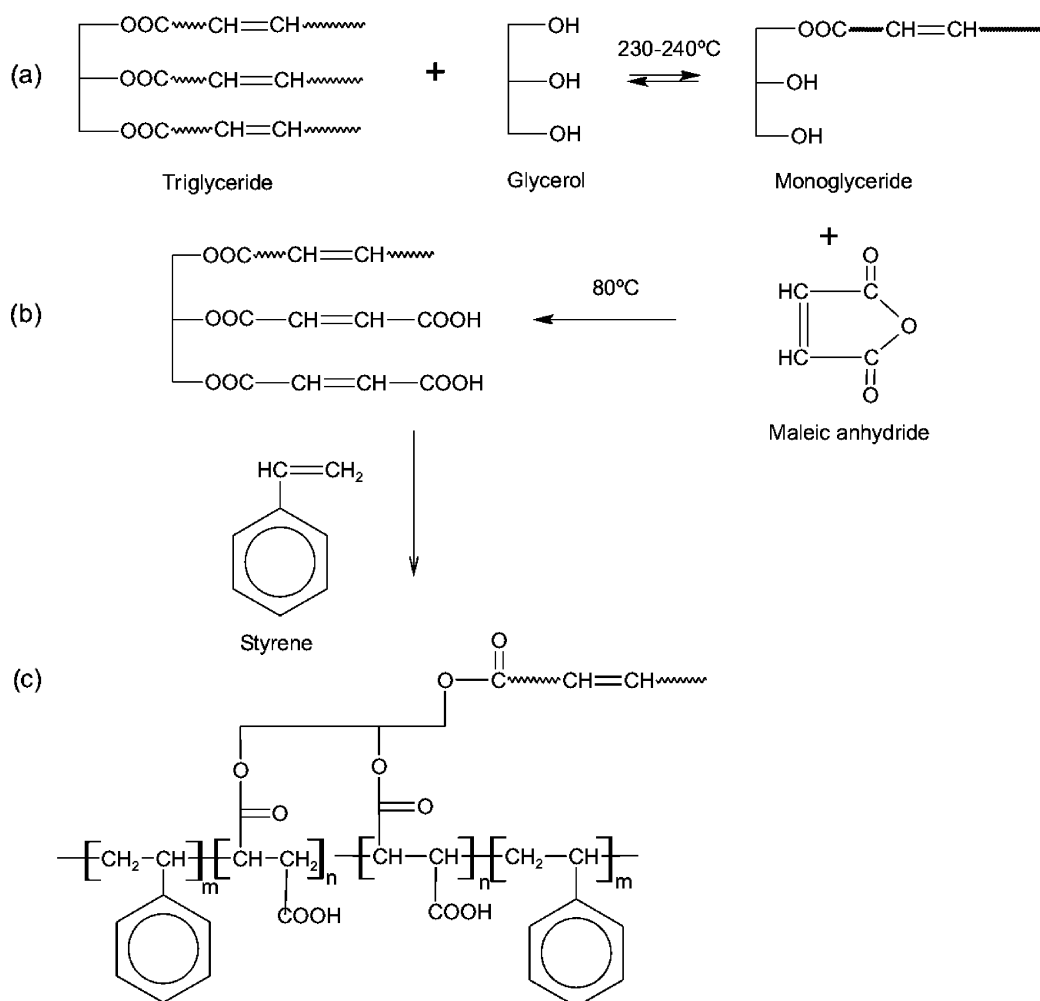


Figure 1. Synthesis and polymerization of oil monoglyceride maleates.

into the bulk of the sample. (The immersion of the sample for the test and further weighing was completed in 2 min, during which the most hygroscopic sample, 50 wt% of wood flour molded under low pressure, underwent an increment of only a 1 wt% due to water absorption.) The parameter $\rho_{c \text{ theoretical}}$ is the density obtained from the following equation:⁵

$$\frac{1}{\rho_{c \text{ theoretical}}} = \frac{w_{\text{matrix}}}{\rho_{\text{matrix}}} + \frac{w_{\text{filler}}}{\rho_{\text{filler}}} \quad (2)$$

where w_{matrix} and w_{filler} are the weight fractions of the matrix and wood flour, respectively, ρ_{matrix} is the density of the crosslinked polymer and was taken equal to 1.06 g cm^{-3} (experimental value)⁵ and ρ_{filler} is the wood flour density. Since the particles are compressed in the composite and the resin fills the cell lumens, ρ_{filler} was taken as the density of the cell walls in the wood, and equal to 1.53 g cm^{-3} .¹¹

Samples of the neat thermoset were also prepared by pouring the initially liquid resin/styrene mixture between two glass slides and curing the sample using the same thermal history as for the composites.

Moisture sorption test

Humid environments were prepared in hermetic boxes maintained at $15 \pm 2^\circ\text{C}$ and containing glycerol aqueous solutions with concentrations of 72 and 34 wt% to ensure 60 and 90% relative humidity (RH), respectively.¹²

Samples with different wood flour contents were dried until constant weight prior to exposure to the humid environments. The weight variations were recorded until no further change was detected.

All the samples were maintained in these conditions for a period long enough to reach their equilibrium moisture content (EMC). A period of 140 days was long enough for all the samples to achieve equilibrium, since no further change in their weights was detected. The determination of final humidity contents was performed on at least three specimens for each sample.

The percent moisture content, M (percent weight gain), calculated from the weight gain of the material as a function of time, t , was obtained using the following equation:

$$M(t) = \frac{(\text{Weight of wet material} - \text{Weight of dry material})}{\text{Weight of dry material}} \times 100 \quad (3)$$

EMC is the $M(t)$ value measured after equilibrium was reached (no further change of the weight with time).

Microscopy

SEM (Philips model SEM 505 scanning electron microscope) was used to obtain images of the central part of the fractured surfaces of samples after being tested using the three-point bending method. Specimens were previously coated with gold.

Mechanical tests

Dynamic mechanical tests

A Perkin Elmer dynamic mechanical analyzer (DMA 7e) was used to determine the loss tangent ($\tan \delta$) of the samples. Temperature scans were performed on samples under nitrogen atmosphere, using three-point bending geometry with a specimen platform of 15 mm length. Dynamic and static stresses were kept at 200 and 400 kPa, respectively, for the composites, and at 50 and 100 kPa, respectively, for the matrix. These forces were chosen in order to detect clearly the glass–rubber transition, while maintaining a good signal-to-noise ratio in the glassy as well as in the rubbery state. The frequency of the forced oscillations was fixed at 1 Hz and the heating rate was $10^\circ\text{C min}^{-1}$. The tests were carried out from 25 to 200°C . The specimens were cut to $20 \times 3 \times 2 \text{ mm}^3$, and the linear dimensions were measured to 0.01 mm. At least two replicate determinations were made for each sample to ensure the reproducibility of results. The time between sample preparation and testing was 240 days for the unfilled polymer and 100 days for the composites.

Three-point bending

These tests were carried out in accordance with ASTM D 790-93 standards, using an Instron 8501 universal testing machine at a crosshead speed of 2 mm min^{-1} . The bending modulus, ultimate stress and ultimate deformation were determined from the stress–strain curves. The dimensions of the specimens were approximately $2.5 \times 10 \times 60 \text{ mm}^3$ and were cut from molded plates, with linear dimensions measured to 0.01 mm. At least four specimens of each sample were tested. The dry, and never exposed to humidity, samples were tested during the two weeks following their preparation. The wet and re-dried samples were tested after to reach the equilibrium moisture during their exposure to humid environments (140 days).

RESULTS AND DISCUSSION

Densities and void volume fractions

The experimental and theoretical density values of the composite materials were used to calculate the void volume fractions of the composites (Eqns (1) and (2)).⁵ The estimated values should include voids produced by air pockets in the sample as well as voids corresponding to empty lumens since the wood flour density was taken equal to that of the cellulose, and thus close to the density of the cell walls. However, the contributions of empty lumens are negligible in these materials at relatively low wood flour concentrations. The results presented in Table 1 show that the use of higher pressure during curing allowed one to improve sample connectivity, and to decrease the presence of voids, thus obtaining a more compacted material. At wood flour concentrations higher than 30 wt%,

Table 1. Void volume fractions as a function of wood flour content

Wood flour content (wt%)	Molding pressure (MPa)	Void volume fraction, V_v	Nominal void volume (%)
0	4	0	0
20	4	0.00 ± 0.02	0
30	8	-0.02 ± 0.02	0
30	4	0.078 ± 0.008	10
40	8	0.106 ± 0.004	10
40	4	0.17 ± 0.02	20
50	4	0.20 ± 0.02	20
60	4	0.19 ± 0.03	20

packing voids and a few incompletely filled lumens appear.⁵ The presence of voids clearly increased with the volume fraction of filler at a given pressure. These voids are the result of direct mechanical interlocking of the wood flour particles, which creates space for air pocket formation. However, it is possible to obtain a more compact material (lower void volume content) by using a higher pressure during the composite curing step. This higher pressure forces the resin to enter and fill these spaces, improving filler wetting and increasing material density.

Taking into account the void volume fractions calculated, the samples were grouped as having nominal void volume equal to 0, 10 and 20%.

Moisture sorption

Table 2 shows the equilibrium (final) moisture content (EMC) of composites prepared with different wood flour percentages and void volume fractions, by conditioning in 60 and 90% RH environments. In general and as expected, the moisture saturation levels increase as the filler concentration increases due to the hygroscopic nature of wood flour. When the RH of the environment increases, the EMC also increases. The values of EMC measured for these systems are higher than those reported previously for similar composite materials formulated with a commercial polyester resin and eucalyptus wood flour. At 60% RH, the reported EMC values were 0.34 and 1.04 for composites

Table 2. Equilibrium moisture content (based on the dry weight of the sample) for different materials after equilibration in 60% and 90% RH

Wood flour content (wt%)	Equilibrium moisture content, EMC (%)	
	60% RH	90% RH
0% void volume		
0	2.0 ± 0.2	3.86 ± 0.09
20	3.1 ± 0.1	7.7 ± 0.9
30	3.68 ± 0.08	9.2 ± 0.2
10% void volume		
30	3.7 ± 0.1	8.8 ± 0.2
40	3.8 ± 0.1	10.3 ± 0.2
20% void volume		
40	4.0 ± 0.1	11.4 ± 0.3
50	4.82 ± 0.03	11.45 ± 0.08
60	4.62 ± 0.08	10.8 ± 0.6

containing 0 and 20 wt%, respectively, of eucalyptus wood flour.⁹ In the present case, the matrix itself is more hygroscopic than the synthetic analog, probably because the linseed oil-based matrix contains a larger amount of carboxylic groups that show affinity for the moisture.⁵

Mechanisms of moisture uptake in vegetable-filled composites may include diffusion through the matrix, the filler, the fiber–matrix interface and eventually through porosities in the matrix and interstitial spaces left by incomplete compaction of the particle–polymer paste during compression molding. Thus, moisture sorption depends on the hydrophilic character of the fiber and the matrix, and also on the composite interface and the overall microstructure.¹³ Analysis of the moisture uptake of the different samples indicates that the wood flour content is the variable that has the major effect on this property. In contrast, the presence of internal voids in the samples (or equivalently the lower density of the samples prepared at lower molding pressures) does not exert an important effect on the equilibrium moisture content of the composites. The only noticeable difference appears between the samples containing 40 wt% of wood flour that were molded under different pressures, when they were exposed to 90% RH (Table 1). This difference in the EMC values may be the result of a larger available internal interfacial area in the less compacted sample, which would allow more interactions of the hygroscopic material with moisture.

A simple rule of mixtures can be applied to predict the EMC of the composites:

$$100 \times \text{EMC} = W_{\text{filler}} \times \text{EMC}_{\text{filler}} + (100 - W_{\text{filler}}) \text{EMC}_{\text{matrix}} \quad (4)$$

where W_{filler} is the weight percentage of wood flour. This simple model represents very well the experimental findings (Fig. 2) using for $\text{EMC}_{\text{filler}}$ the reported values of 8.7 and 18.2% for 60 and 90% RH, respectively.⁹ The agreement is good for all measurements, even for samples containing voids.

Morphological analysis

Figure 3 shows SEM micrographs of the fracture surfaces of the samples tested in bending mode and conditioned in dry and humid environments. Figure 3(a) and (b) correspond to dry samples prepared with 0 and 20 wt% wood flour. Figure 3(c) and (d) correspond to the same composites but stored for 140 days at 90% RH.

Dry samples present essentially a fragile fracture. The fracture surface of the unfilled material (Fig. 3(a)) shows a smooth and featureless image even at high magnification ($\times 10\,000$). Figure 3(b) shows a $\times 350$ image of the filled composite. The fracture surface of the bulk matrix is smooth, indicating fragile fracture. There is no separation of the fibers from the matrix and a very good interaction between the two components can be inferred from the images. The strong adhesion

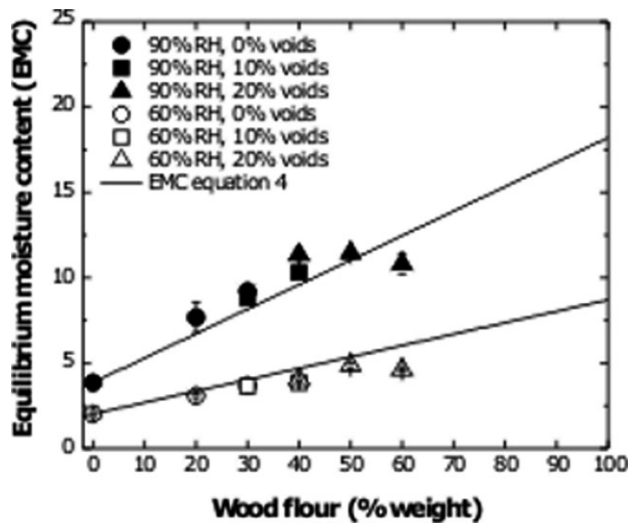


Figure 2. Comparison of theoretical EMC values (Eqn (4)) and experimental EMC values at different relative humidities.

that is observed at the interface has been already discussed in a previous publication.⁵

In contrast, humid samples show a completely different set of images, which indicates the strong effect

of water on these hygroscopic materials. Figure 3(c) ($\times 10\,000$) shows a much rougher surface than for the dry sample. This is the result of plastic deformation favored by the plasticizing effect of water on the polymer. Similarly, Fig. 3(d) ($\times 350$) shows plastic deformation of the polymeric phase. There seem to be ‘holes’, which are the result of deformation during fracture, since these features are absent in the image corresponding to the dry specimen.

Dynamic mechanical analysis

Table 3 presents the temperatures at which the maximum of the loss tangent curve, T_{α} (which is related to the glass transition temperature of the matrix), was measured for the materials without voids and containing 0, 20 and 30 wt% of filler. The data were recorded for dry, wet and re-dried samples. Table 3 does not include results of recently prepared samples, as indicated in the experimental section. The incorporation of wood flour to this matrix provokes a significant increment of the glass transition temperature, which is attributed to the strong fiber–matrix interactions. The hydroxyl groups in the lignocellulosic filler are capable of reacting with

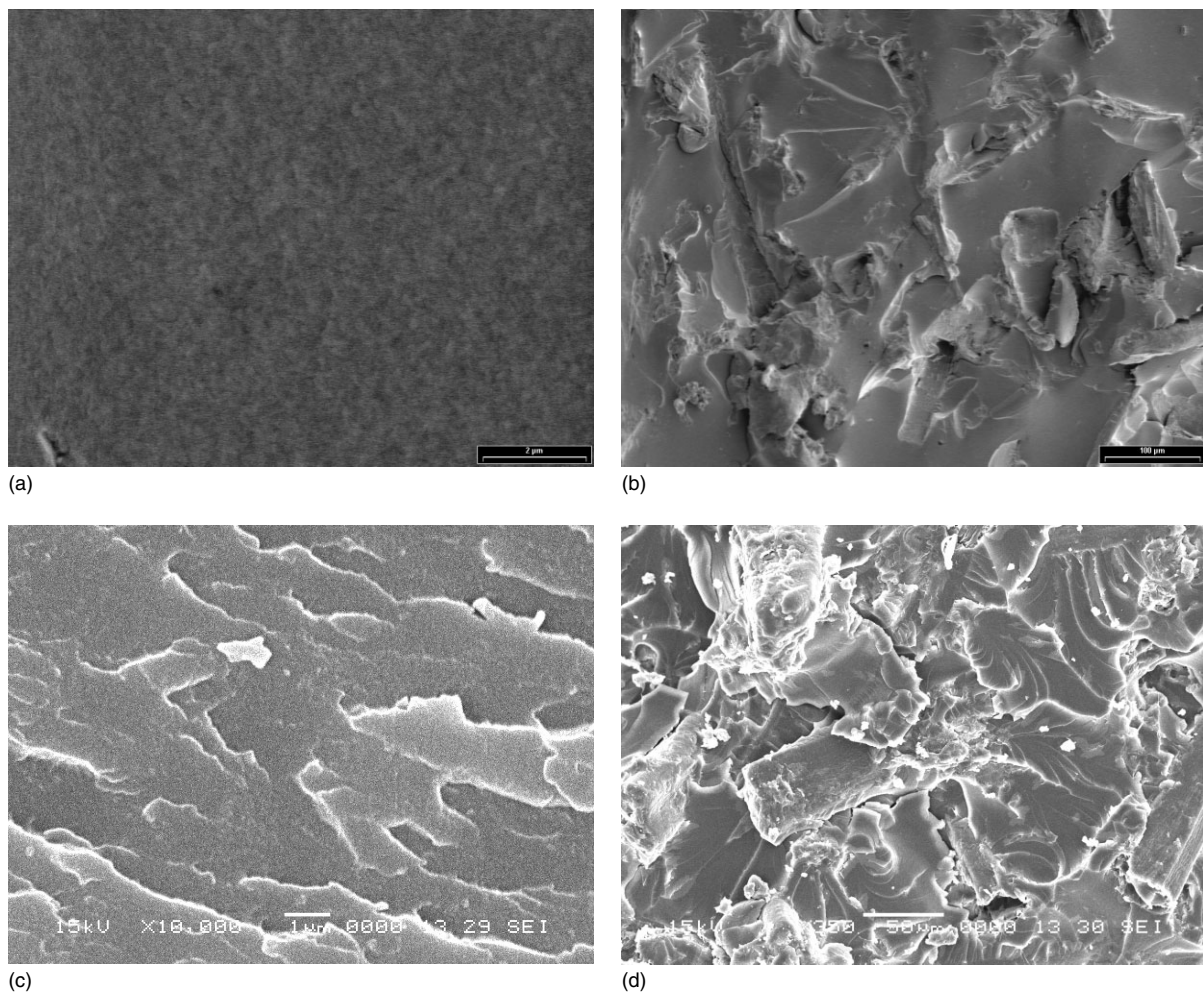


Figure 3. Fracture surfaces (SEM micrographs) of dry and wet (90% RH) samples after testing in three-point bending mode: (a) dry matrix, 0% wood flour ($\times 10\,000$); (b) dry composite, 20 wt% wood flour ($\times 350$); (c) wet matrix, 0% wood flour ($\times 10\,000$); (d) wet composite, 20 wt% wood flour ($\times 350$).

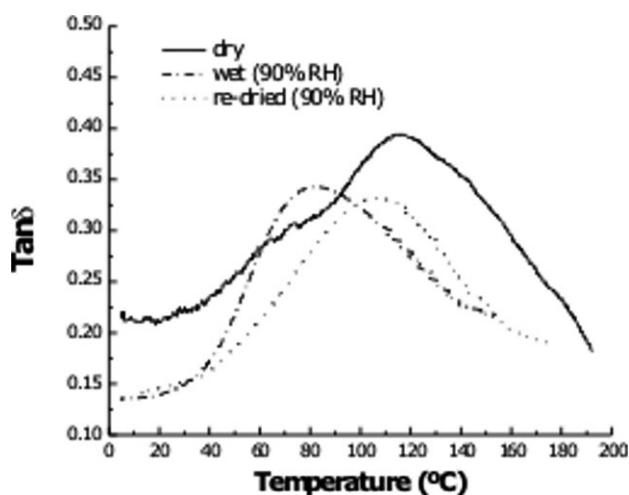
Table 3. Temperature (°C) of the maximum in the main $\tan \delta$ peak of materials without voids

Wood flour content (wt%)	Dry	Wet (60% RH)	Re-dried (60% RH)	Wet (90% RH)	Re-dried (90% RH)
0	84 ± 3	74 ± 3	82 ± 2	67 ± 2	79 ± 4
20	116.0 ± 0.3	105 ± 12	109 ± 10	79 ± 3	103.9 ± 0.4
30	142 ± 5	102.2	123 ± 3	74 ± 2	95 ± 9

the free carboxylic group of the maleic moieties in the synthesized resin, leading to a strong interfacial layer.⁵

Figure 4 shows the $\tan \delta$ curves corresponding to dry, wet (90% RH) and re-dried samples of the composite material with 20 wt% of wood flour, and illustrates the overall effect of humidity. The transitions observed through $\tan \delta$ cover an ample range of temperatures, indicating that many different relaxation mechanisms are involved. The effect of the humidity is visible through the shift towards lower temperatures of T_α measured for the composites conditioned in humid environments. This is related to the plasticizing effect of water molecules on the polymeric matrix. Water molecules absorbed in these materials act by disrupting intermolecular forces and increasing chain mobility; thus, the free volume of the polymer increases and the glass transition temperature of the material is reduced. Notice that this observation is in agreement with the more ductile fracture discussed in the morphological analysis. New plastic deformation mechanisms appear during fracture of the composites due to polymer plasticization. As expected, the higher RH in the environment (90% RH) produces a stronger effect on the thermomechanical properties.

While the matrix recovers almost completely in re-drying and presents a transition temperature close to that of the dry sample, the composites show an irreversible change as compared to the original dry samples. This effect may be due to partial hydrolysis of the ester groups in the matrix.⁸ This could be further enhanced by the larger water absorption of the composites. Breakage of bonds that attach dangling chains to the network may generate free chains that would act as plasticizers, even after re-drying.

**Figure 4.** $\tan \delta$ curves of dry, wet (90% RH) and re-dried samples for the composite material with 20 wt% of wood flour.

Flexural properties

Table 4 shows the results obtained for the bending modulus, ultimate stress and ultimate deformation of samples prepared with different wood flour contents, stored under different humidity conditions and also re-dried.

The bending properties of the never exposed to humid environments and recently prepared samples have been reported and analyzed in a previous publication.⁵ Those measurements were performed during the two weeks following the sample preparation and are also included in Table 4 (dry samples). In contrast, the rest of the data reported in Table 4 correspond to materials that have been stored for 140 days under humid environments at 60 and 90% RH, until equilibrium (wet samples), and to these same samples after re-drying until constant weight (re-dried).

The data reported for the recently prepared (dry) samples show that the flexural modulus and strength increased with the wood flour content. Moreover, a general decreasing trend of these properties is observed as the void volume fraction increases. As the rigidity of the composites increases with the percentage of wood flour, the ultimate deformation decreases, although there is no clear trend in the variation of this last property with the void volume fraction.

Regarding the effect of humidity, only the samples named wet and re-dried were compared, since both sets were tested at the same time after preparation. Comparison of the values reported for the mechanical properties of samples conditioned at 60 and 90% RH shows the plasticizing effect of moisture. The general trend is a decrease of the bending modulus and ultimate stress as the humidity of the environment increases, and consequently as the EMC of the samples increases. At higher moisture content in the sample, the stiffness of the cellulose fibers drops considerably, due to the softening of the disordered zones of the cellulose microfibrils.¹⁴

For the same reason, wet samples present higher values of ultimate deformation than those of re-dried composites. The plasticization effect is important, and actually leads to an enhancement of the diffusivity of water due to the increased polymer segment mobility.¹⁵ In particular, the unfilled polymer reached such large deformations in the wet conditions that it was not possible to measure the ultimate properties in bending tests.

Re-drying the samples leads to the recovery of rigidity. Composites prepared with a given wood flour content and subjected to different humid environments showed quite different properties under

Table 4. Flexural properties of aged composites^a. Samples were dry, wet and re-dried test pieces

Sample	0% nominal void volume						10% nominal void volume			20% nominal void volume		
	0 wt%	20 wt%	30 wt%	30 wt%	40 wt%	40 wt%	30 wt%	30 wt%	40 wt%	40 wt%	50 wt%	60 wt%
	wood flour	wood flour	wood flour	wood flour	wood flour	wood flour	wood flour	wood flour	wood flour	wood flour	wood flour	wood flour
Flexural modulus (GPa)	<i>Dry</i>	0.27 ± 0.01	0.89 ± 0.12	1.56 ± 0.3	1.07 ± 0.14	1.26 ± 0.12	0.88 ± 0.07	1.27 ± 0.28	0.88 ± 0.07	1.27 ± 0.28	0.88 ± 0.07	1.49 ± 0.22
	60% RH	1.01 ± 0.08	1.42 ± 0.18	1.32 ± 0.45	0.90 ± 0.13	1.24 ± 0.17	0.89 ± 0.07	1.44 ± 0.22	0.89 ± 0.07	1.44 ± 0.22	0.89 ± 0.07	1.55 ± 0.41
	90% RH	0.71 ± 0.03	0.73 ± 0.11	0.72 ± 0.10	0.57 ± 0.01	0.57 ± 0.10	0.38 ± 0.03	0.67 ± 0.06	0.38 ± 0.03	0.67 ± 0.06	0.38 ± 0.03	0.78 ± 0.16
	Re-dried 60% RH	1.26 ± 0.09	1.63 ± 0.49	1.97 ± 0.17	1.23 ± 0.06	1.68 ± 0.25	1.42 ± 0.28	1.75 ± 0.28	1.42 ± 0.28	1.75 ± 0.28	1.42 ± 0.28	1.61 ± 0.22
Re-dried 90% RH	–	1.11 ± 0.24	2.06 ± 0.43	1.12 ± 0.00	1.75 ± 0.13	1.36 ± 0.11	1.70 ± 0.25	1.36 ± 0.11	1.70 ± 0.25	1.36 ± 0.11	1.72 ± 0.36	
Ultimate stress (MPa)	<i>Dry</i>	9.8 ± 0.9	17.8 ± 2.3	25.8 ± 4.2	17.3 ± 2.1	16.2 ± 1.5	9.6 ± 1.0	12.4 ± 2.3	9.6 ± 1.0	12.4 ± 2.3	9.6 ± 1.0	18.5 ± 1.8
	60% RH	b	30.8	24 ± 11	14.8 ± 1.7	16.7 ± 2.7	11.5 ± 0.9	15.7 ± 2.5	11.5 ± 0.9	15.7 ± 2.5	11.5 ± 0.9	18.8 ± 3.8
	90% RH	b	17.4 ± 3.4	16.6 ± 3.1	12.1	10.4 ± 1.4	6.3 ± 0.2	8.6 ± 1.4	6.3 ± 0.2	8.6 ± 1.4	6.3 ± 0.2	12.8 ± 2.7
	Re-dried 60% RH	b	30.2 ± 2.5	27.5 ± 1.1	16.8	21.7 ± 3.0	13.8 ± 1.8	17.1 ± 4.2	13.8 ± 1.8	17.1 ± 4.2	13.8 ± 1.8	18.8 ± 0.2
Re-dried 90% RH	b	26.3	31.8 ± 5.3	21.3	20.4 ± 2.2	13.8 ± 1.1	18.4 ± 2.9	13.8 ± 1.1	18.4 ± 2.9	13.8 ± 1.1	21.8 ± 4.4	
Ultimate deformation (× 1000)	<i>Dry</i>	67 ± 4	40 ± 10	20 ± 3	22 ± 1	17 ± 1	16 ± 3	12.1 ± 0.5	16 ± 3	12.1 ± 0.5	16 ± 3	16 ± 2
	60% RH	b	22	25 ± 1	20.7 ± 0.4	18 ± 1	19 ± 6	13.6 ± 0.7	19 ± 6	13.6 ± 0.7	19 ± 6	15 ± 1
	90% RH	b	41 ± 2	41 ± 4	35	30 ± 4	29 ± 5	19 ± 2	29 ± 5	19 ± 2	24 ± 2	24 ± 2
	Re-dried 60% RH	b	26 ± 5	16 ± 2	15	16 ± 1	13 ± 2	11.4 ± 0.5	13 ± 2	11.4 ± 0.5	13 ± 2	14 ± 2
Re-dried 90% RH	b	23	16 ± 1	16 ± 1	26	14 ± 8	13.4 ± 0.8	13.3 ± 0.2	13.4 ± 0.8	13.3 ± 0.2	15 ± 2	

^a Numbers in *italic* are data obtained from test samples cut from freshly prepared composites and never subjected to humidity tests.

^b It was not possible to measure the ultimate properties in bending tests due to large deformations in wet conditions.

wet conditions, but recovered to reach similar properties after re-drying. As an example, the sample containing 30 wt% wood flour and essentially no voids had a modulus of 1.32 GPa after equilibration at 60% RH and 0.72 GPa if equilibrated at 90% RH. However, after re-drying the same samples reached 1.97 and 2.06 GPa, respectively.

The effect of voids can also be analyzed. The sample with 30 wt% wood flour and 10% void volume equilibrated at 90% RH had a bending modulus of 0.57 GPa and reached 1.12 GPa after re-drying. In both conditions, the measured moduli were lower than those measured for a sample without voids (20.8 and 45.6% lower, respectively).

Finally, Table 4 shows that the re-dried samples present higher rigidity than that of the recently prepared composites. This behavior is presently under investigation; however, preliminary results indicate that the material properties evolve mainly during the first month after preparation, to reach the high values reported for re-dried materials. Since linseed oil has been used traditionally as a drying oil in paints and coatings, and since the internal double bonds present in the glyceride chains show very low reactivity in the crosslinking reaction with styrene, they are still available in the final thermoset to undergo further oxidative polymerization. The consequence is a change of the properties of the material with time, due to this reaction that occurs as the result of the diffusion of oxygen into the sample. The occurrence of this process and the analysis of its characteristics are the subject of a future publication.

CONCLUSIONS

Mechanical and thermomechanical properties are affected by the presence of moisture in composites prepared with a linseed oil-based resin filled with wood flour.

The EMC of samples in environments of 60 and 90% RH increases with the filler content in the composites. Also, there are little differences in samples with and without voids, since the presence of voids in the structure may introduce different mechanisms of water sorption.

Absorbed moisture reduces the glass transition temperature of the neat resin and composites. This is attributed to the plasticizing effect of water in the samples. After re-drying, the original value of the glass transition temperature of the neat thermoset is almost completely recovered. In contrast, the composites present only partial recovery, probably

due to hydrolysis of the ester groups enhanced by the higher percentage of water absorbed.

The modulus and the ultimate stress decrease as the humidity of the environment increases, while the ultimate deformation increases. Specimens of a given sample present quite different properties if subjected to different humidity conditions (wet samples, 60 or 90% RH); however, after re-drying, both sets show similar properties (re-dried samples).

The comparison between the mechanical properties of recently prepared dry samples and re-dried samples shows an unexpected result. The moduli of the latter are higher than those of the former. The slow oxidative polymerization of linseed oil chains is proposed as being responsible for this effect, a process which is currently under study.

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