

# Dependence of the Mechanical Properties of Woodflour–Polymer Composites on the Moisture Content

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**ABSTRACT:** Woodflour of *Eucalyptus saligna* with two different chemical treatments (mercerization and esterification with maleic anhydride) was used as filler of an unsaturated polyester matrix. Woodflour was treated to increase the interfacial adhesion with the matrix, to improve the dispersion of the particles, and to decrease the water sorption properties of the final composite. The objective of this study was to determine the influence of the moisture content and the woodflour chemical modification on the physical and mechanical properties of the different composites. Results indicated that mechanical properties (compression and bending tests) were severely affected by moisture and chemical modifications. In wet conditions, the composites made from treated woodflour had the lowest flexural modulus and ultimate stress. It was found that this was a reversible effect, because the original values of the compression properties were recovered after drying. Temperature scans in dynamic mechanical tests showed that an irreversible change occurred during exposure to humid environments, probably due to the hydrolysis of the polyester matrix. Essentially, the same behavior was observed for matrix and composites; however, a wood-related transition overlapped the main transition in the case of wet composites. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 2069–2076, 1998

**Key words:** woodflour composites; mechanical properties; surface treatment; moisture absorption; fillers

## INTRODUCTION

Agrowastes and agroforest materials, for example, sawdust, wood fibers, sisal, bagasse, etc., are slowly penetrating the market of reinforced plastics and filled polymers presently dominated by glass fiber and other mineral reinforcements. The use of natural fibers is interesting because of their renewable nature, low cost, low density, and amenability to chemical modification.

Polymeric matrices filled with vegetable rein-

forcements offer a high specific stiffness and strength, flexibility during processing with no harm to the equipment, low density, and low cost per volume basis.<sup>1</sup>

Unfortunately, the frequent incompatibility between lignocellulosic materials and many polymeric matrices affects the degree of dispersion of the fibers in the matrix and the overall homogeneity of the composite structure. However, the use of compatibilizing and coupling agents for treating the fibers prior to, or as an addition, in the compounding step results in improved mechanical properties.<sup>2</sup>

On the other hand, all synthetic polymers absorb moisture in a humid atmosphere and when they are immersed in water. The sorption of water by nonpolar polymers containing a filler depends

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mainly on the nature of the filler.<sup>3</sup> Wood is a natural structure made of cellulose fibers in an amorphous matrix of hemicellulose and lignin. Cellulose, the main constituent of the cell wall of the wood, contains numerous hydroxyl groups that are strongly hydrophilic. Wood, therefore, is highly hygroscopic and could absorb or desorb moisture readily when subjected to changes in relative humidity of the environment (RH).<sup>4</sup> Then, woodflour-reinforced polymers can take up a high amount of water, which generally causes a reduction in mechanical properties.<sup>5</sup> Besides, the understanding of water-polymer interactions in polymeric composite materials is critical to the prediction of their behaviors when they are exposed to water or moisture.<sup>6</sup>

In this work woodflour of *Eucalyptus saligna* (Entre Rios, Argentina) with different chemical treatments has been used as a filler of an unsaturated polyester matrix. Woodflour was chemically treated to increase the interfacial adhesion with the matrix, to improve the dispersion of the particles, and to decrease the water sorption properties of the final composite. The aim of this work is to determine the influence of the moisture content and the woodflour chemical modification on the physical and mechanical properties of the different composites.

## EXPERIMENTAL

### Materials

Dry woodflour (particle average size lower than 57  $\mu\text{m}$ ) from *Eucalyptus saligna* (Entre Rios, Argentina) was the raw material used as filler. The treatments performed on the particles are detailed as follows: (1) Part of the woodflour was mercerized by soaking the particles in a 10% wt aqueous solution of NaOH for 1.5 h at room temperature, washed several times, and finally dried. (2) The NaOH-treated woodflour was then esterified by refluxing the fibers in a 4.08N solution of maleic anhydride (MAN) in xylene for 24 h; the unreacted MAN was eliminated by intensively washing the fibers in distilled water.

MAN (99% pure, Riedel-de Haën) was selected as a coupling agent for this system because it reacts with the —OH groups of woodflour during the esterification step and, in addition, the double bond of the anhydride can react with the unsaturations of the thermoset polyester matrix.

The effectiveness of this modification was es-

tablished by an analytical technique (acid number and saponification value<sup>7</sup>) and by weight gain; both results were in a good agreement, indicating an incorporation of 58.3 g of maleic anhydride per 100 g of neat woodflour.

A bisphenol A-fumarate solid unsaturated polyester (UPE) supplied by Perlinac S. A. (Argentina), RQ 426, has been used in this work. It was crosslinked with styrene in a 60 : 40 weight ratio (resin : styrene). The initiator was benzoyl peroxide (Lucidol 0.75, Akzo Chemical S.A.) added in an amount of 1.5% wt with respect to the total reactive mixture.

### Compounding and Molding

Samples of neat resin were obtained by pouring the reactive mixture inside a two-glass plate mold. The mold was left at room temperature for a day to facilitate the elimination of trapped air bubbles. Then, the sample was cured by heating at 80°C for 1.5 h, and finally postcured at 150°C for 2 h.

To obtain the composite material, filler and reactive mixture (including the initiator) were mixed for an hour in a Brabender-type mixer. The paste was filled in a metal mold (145 mm of diameter and about 3 mm of thickness), which was left open for 2 h at 50°C for degassing. Then the mold was closed and the temperature was increased to 80°C. The reaction was carried out under a pressure of 3.8 MPa for 1.5 h. After that time, it was postcured in an oven for 2 h at 150°C.

Different composite materials were prepared: (1) composites where the woodflour was incorporated "as received" (WC); (2) composites where the woodflour was mercerized (NaWC); and (3) composites where the woodflour was previously mercerized and then esterified with MAN (MANWC).

Filler content in the composites varied between 0 and 55% weight when possible. In fact, MANWC(55) still showed complete filler wetting, while it was impossible, for example, to obtain a good (homogeneous) composite with more than 35% of NaOH-treated filler due to the poor dispersion of the particles that were not wet appropriately by the matrix.

Specimens of each sample were dried in a vacuum oven for 24 h at 70°C before testing. Then, part of the samples were conditioned in environments of 60 or 90 relative humidity (RH) at 20°C.

### Moisture Sorption

Humid environments were prepared in hermetic boxes maintained at 20°C  $\pm$  2°C and containing

flasks with aqueous solutions of sulfuric acid (18 and 38 wt %) to ensure 90 and 60 RH, respectively.

Treated and untreated woodflour samples of about 1 g were dried until constant weight prior to be exposed to wet environments for short intervals of time, in which the weight changes were recorded.

The composite specimens were first dried and weighed in an analytical balance ( $\pm 0.001$  g). The final humidity content was determined on small specimens ( $6.5 \times 3.3 \times 3.3$  mm<sup>3</sup>) to reduce the time to reach the equilibrium value. The volume of the samples was calculated from the measurement of the dimensions ( $\pm 0.01$  mm) of each specimen (in the wet and dry conditions). The determinations of final humidity content and volume were performed on at least three specimens for each sample.

## Mechanical Testing

### Compression Tests

These tests were carried out on dry and wet (equilibrium moisture content) composites in accordance with ASTM D 695–85. The specimens were cut from the molded plates in the form of square bars of 3.3 mm width and approximately 6.5 mm in height. An Instron 8501 Universal testing machine was used, and all tests were performed at a crosshead speed of 0.5 mm/min. For each woodflour treatment and condition (wet, dry, redry), the tests were performed on at least three specimens.

### Flexural Tests

Three-point bending tests were performed on wet and dry composites in accordance with ASTM D 790–86, procedure A, on a Shimadzu Autograph S-500-C Universal testing machine. The composite specimens (70 mm long, 13 mm wide, and about 3 mm thick) were used at a loading span of 50 mm. The neat resin specimens were cut to a transversal area of  $12 \times 2.4$  mm<sup>2</sup> and tested using a span of 40 mm.

At least four specimens for each sample were tested.

### Dynamic Mechanical Tests

The loss tangent ( $\tan \delta$ ) of the wet and dry samples were evaluated in the bending mode (specimen platform of 15 mm length) using a Perkin-

**Table I** Equilibrium Moisture Contents (Based on the Dry Weight of the Samples) of Treated and Untreated Woodflour in Environments of 60 and 90 RH

Woodflour Treatment	60 RH	90 RH
Nontreated	8.70	18.22
Mercerized	11.21	29.43
Esterified	8.59	16.82

Elmer dynamic mechanical analyzer (DMA 7). The dynamic and static stresses were kept at  $3 \times 10^5$  and  $5 \times 10^5$  Pa, respectively, and the frequency of the forced oscillations was fixed in 1 Hz.  $\tan \delta$  was measured in a temperature range of 20–200°C using a heating rate of 10°C/min. The specimens were cut to  $20 \times 3 \times 2$  mm<sup>3</sup>, and the dimensions were measured up to 0.01 mm. At least two replicate determinations were made for each sample to ensure the reproducibility of results, with one exception, which is indicated in the table.

The tests were performed on previously acclimated samples (wet or dry, as required) in the nitrogen purged DMA chamber, and without a humidity-controlled environment.

## RESULTS AND DISCUSSION

### Moisture Sorption

Table I shows the final humidity content of untreated, mercerized, and esterified woodflours conditioned in 60 and 90 RH environments, respectively. NaOH-treated wood particles are much more hygroscopic than the others, as was expected. Moisture sorption is mainly due to hydrogen bonding of water molecules to the hydroxyl groups on the cell walls of the wood. In fact, mercerization increases the accessibility of water molecules to reactive regions, through the enlargement in the specific surface area; thus, the hygroscopicity of the filler is increased. Besides, the esterification of the woodflour with MAN reduces its hygroscopicity because a considerable amount of accessible —OH groups disappeared to become firmly bonded to the polar carboxylic groups of the maleic acid.

Unfortunately, although the MAN-treated woodflour shows the lowest moisture uptake, this value is rather similar to the one exhibited by the untreated sample, indicating, perhaps, that this way

**Table II** Equilibrium Moisture Content (Based on the Dry Weight of the Sample) and Volume Increment of Different Materials Due to Water Sorption Overtaken at 60 and 90 RH Atmospheres

Sample	Moisture Content (%)		Volume Increment (%)	
	60 RH	90 RH	60 RH	90 RH
Matrix	0.83 ± 0.37	1.00 ± 0.17	1.45 ± 0.14	2.03 ± 0.15
WC(40)	3.41 ± 0.79	6.22 ± 1.67	3.44 ± 0.88	8.81 ± 1.80
NaOHWC(35)	2.86 ± 0.45	5.83 ± 0.61	3.27 ± 1.20	7.00 ± 1.12
MANWC(40)	3.54 ± 0.41	6.55 ± 0.51	3.35 ± 0.51	8.25 ± 1.29
MANWC(55)	4.03 ± 0.42	10.64 ± 0.68	3.89 ± 1.61	10.43 ± 0.79

of chemical modification is not able to reduce the water affinity of the wood particles to a great extent.

Table II summarizes the equilibrium moisture content and the resulting volume expansion due to water sorption in 60 and 90 RH atmospheres for the matrix and the composites with similar filler concentration. The reported data were obtained after 140 days of exposure to the humid environments. As expected, samples acconditioned at 90 RH showed higher water sorption and volume change than those at 60 RH.

MANWC(55) showed the largest equilibrium moisture content, but it also corresponds to the highest filler percentage loaded into the matrix. In other words, the equilibrium values of MANWC(40) and WC(40) are comparable because the filler concentration is the same, and NaWC(35) exhibit a lower moisture content due to the lower filler percentage.

Moreover, results indicate that the MAN molecule added to the woodflour in one case, or the good mechanical anchorage between filler and matrix due to the rough surface of the mercerized fiber (which allows the resin to penetrate into the filler particles), are unable to reduce the hygroscopicity of these composites with respect to the WC one. Besides, the volume increment of all composites is rather important, so the composite dimensional stability is not significantly improved by the chemical treatments.

### Compression Tests

The final mechanical properties of the wet composites of similar filler concentration were measured. Table III shows the effect of water sorption on the compressive properties (modulus, yield stress, and ultimate strain) for the different composites as a function of the filler surface treatment. Dry properties are listed for comparison.

The physical and chemical changes of the woodflour due to the esterification reaction allowed preparation of more concentrated composites.

Previous results<sup>8</sup> indicated that dry compressive modulus and strength increased with the woodflour content of the composites. MAN-treated woodflour allowed using higher filler loads because of the improved dispersion, which besides the improved properties, should result in a cheaper product. The dry ultimate deformation of the materials decreased with increasing filler percentage, but again, in this case, the material made from MAN-treated woodflour was the less affected.

With respect to the behavior of the wet samples, it is noted that the compressive modulus of the composites diminishes with moisture content, while the matrix one is little affected. But in this case, the MANWC modulus is the most influenced by moisture sorption, showing for the samples conditioned at 90 RH, even lower values than the pure resin ones.

A similar behavior is observed for the yield stress, although the strength of the neat resin also diminishes with the increasing moisture content. It is observed that at 60 RH, all the filled samples exhibit comparable values, while at 90 RH the yield stress is worst for the composites made from esterified woodflour.

Regarding the ultimate deformation, in the wet state all the composites can resist larger strains without breaking than in dry conditions. It appears that woodflour acts as an elastomeric phase instead as a rigid particulate reinforcement<sup>9</sup>; hence, the humid filler enhances the deformation mechanisms in the matrix, increasing the ultimate strain of the final composite. On the contrary, the neat resin ultimate deformation determined from wet samples is lower than that obtained from dry specimens.

**Table III Compression Properties of Dry and Wet Materials**

Sample	Matrix	WC(40)	NaWC(35)	MANWC(40)	MANWC(55)	
Modulus (GPa)	Dry	2.50 ± 0.04	3.94 ± 0.33	3.56 ± 0.06	3.93 ± 0.31	4.44 ± 0.04
	60 RH	2.33 ± 0.34	3.38 ± 0.03	3.27 ± 0.18	2.33 ± 0.55	3.86 ± 0.13
	90 RH	2.35 ± 0.34	2.35 ± 0.57	2.17 ± 0.23	1.77 ± 0.07	1.86 ± 0.25
Yield Stress (MPa)	Dry	111.4 ± 4.05	140.9 ± 2.55	135.3 ± 4.95	138.6 ± 6.32	157.4 ± 2.85
	60 RH	106.7 ± 7.56	97.98 ± 0.43	111.8 ± 0.70	110.2 ± 17.1	114.5 ± 3.02
	90 RH	98.79 ± 3.34	80.85 ± 2.55	70.89 ± 2.72	68.69 ± 2.65	58.60 ± 0.93
Strain (mm/mm)	Dry	0.305 ± 0.07	0.084 ± 0.03	0.162 ± 0.03	0.207 ± 0.08	0.122 ± 0.02
	60 RH	0.260 ± 0.02	0.170 ± 0.01	0.211 ± 0.01	0.317 ± 0.06	0.166 ± 0.02
	90 RH	0.238 ± 0.05	0.145 ± 0.01	0.213 ± 0.01	0.226 ± 0.04	0.235 ± 0.04

Samples were conditioned at 60 RH or 90 RH during 140 days, respectively, before tested.

To study the effect of redrying on composite properties, compression tests were performed. Samples were dried until constant weight after reaching the equilibrium moisture content. Table IV shows the mechanical properties of samples previously acconditionated 140 days at 60 RH or at 90 RH and then redried and tested in comparison with compression properties determined from originally dry specimens. These determinations indicate that the matrix, as well as the composites, recovered the original modulus and yield stress values after redrying. This fact indicates that the moisture effect on these properties is not permanent. On the other hand, the ultimate strain is smaller in the redried samples than in the dry ones, which suggest that the water uptake introduces irreversible changes in the materials.

#### Flexural Tests

Table V shows the results obtained in three point bending tests of dry and wet samples for comparable filler weight percentages. The MANWC(40)

dry modulus is lower than that of the other composites, because the intensive chemical treatment given to this filler diminishes the woodflour mechanical properties.<sup>8</sup> Thus, a lower modulus than the values obtained from the other composites is observed. Nevertheless, the ultimate stress and deformation are similar for all the composites.

Regarding the wet properties, the matrix modulus remains unchanged with the moisture content. The values obtained at 60 RH for WC and MANWC are similar to the data reported for dry specimens, while the modulus of wet NaWC is lower than the dry one in about 14%. On the other hand, at 90 RH, composite samples exhibit an important reduction of the modulus due to the water uptake, mainly when the specimens were prepared with treated woodflour. At higher water content, the stiffness of the cellulose fibers drop considerably, due to the softening of the disordered zones of the cellulose microfibrils.<sup>3</sup>

Matrix ultimate stress is in all cases higher than that of the composites, even though it is reduced significantly by moisture. In the pure resin,

**Table IV Compression Properties of Dry and Redry Materials**

Sample	Matrix	WC(40)	NaWC(35)	MANWC(40)	MANWC(55)	
Modulus (GPa)	Dry	2.50 ± 0.04	3.94 ± 0.33	3.56 ± 0.06	3.93 ± 0.31	4.44 ± 0.04
	60 RH	2.68 ± 0.02	3.25 ± 0.20	3.83 ± 0.09	3.94	5.14 ± 0.13
	90 RH	2.39 ± 0.32	3.15 ± 0.28	3.67 ± 0.10	3.40 ± 0.29	4.57 ± 0.54
Yield Stress (MPa)	Dry	111.4 ± 4.05	140.9 ± 2.55	135.3 ± 4.95	138.6 ± 6.32	157.4 ± 2.85
	60 RH	106.6 ± 2.71	138.4 ± 6.21	134.5 ± 5.42	146.81	169.3 ± 0.19
	90 RH	107.0 ± 1.43	124.8 ± 6.07	133.0 ± 2.13	134.0 ± 10.8	154.9 ± 5.98
Strain (mm/mm)	Dry	0.305 ± 0.07	0.084 ± 0.03	0.162 ± 0.03	0.207 ± 0.08	0.122 ± 0.02
	60 RH	0.274 ± 0.09	0.072 ± 0.01	0.123 ± 0.01	0.126	0.147 ± 0.02
	90 RH	0.263 ± 0.02	0.081 ± 0.03	0.129 ± 0.01	0.164 ± 0.05	0.091 ± 0.01

Samples were conditioned at 60 RH or 90 RH during 140 days, respectively, before being dried and tested.

**Table V Flexural Properties of Dry and Wet Materials**

Sample	Matrix	WC(40)	NaWC(35)	MANWC(40)	
Flexural modulus (GPa)	Dry	3.28 ± 0.20	5.44 ± 0.22	5.47 ± 0.36	4.283 ± 0.21
	60 RH	3.21 ± 0.15	5.43 ± 0.34	4.70 ± 0.144	4.26 ± 0.209
	90 RH	3.28 ± 0.05	4.49 ± .013	3.612 ± 0.23	2.94 ± 0.10
Ultimate stress (MPa)	Dry	90.88 ± 20.17	54.06 ± 1.96	58.17 ± 3.12	52.46 ± 6.02
	60 RH	70.55 ± 24.22	52.57 ± 5.14	58.33 ± 8.12	49.51 ± 2.48
	90 RH	71.91 ± 19.18	36.53 ± 2.82	39.65 ± 5.80	35.64 ± 3.69
Ultimate deformation (×1000)	Dry	34.24 ± 9.33	9.94 ± 0.37	10.34 ± 0.22	10.39 ± 1.39
	60 RH	21.82 ± 6.52	9.66 ± 0.49	12.40 ± 1.36	11.63 ± 0.81
	90 RH	22.20 ± 6.36	9.20 ± 0.72	12.05 ± 1.30	10.26 ± 1.68

the loss of strength is mainly attributed to network degradation of the polymer (chemical scission of ester group<sup>6</sup>; hydrolysis<sup>10</sup>).

Composite wet strength shows the same behavior as the composite flexural modulus, although there are no notable differences with respect to the filler chemical modification. Raj et al.<sup>3</sup> pointed out that when the matrix–filler interface is accessible to the moisture from the environment, the wood fibers tend to swell. This results in the development of shear stresses at the interface, which leads to the ultimate debonding of the fiber. This results in a decline of the composite ultimate stress in the wet condition.

Concerning to the ultimate deformation, the matrix breaks at lower strains in the wet condition. On the contrary, composites show similar ultimate deformations in wet or dry states, as was also the case for compression tests.

### Dynamic Mechanical Test

In Table VI the temperature corresponding to the maximum of the loss tangent curve recorded for woodflour composites (containing approximately 40% by weight) are compared with that of the matrix. The results for the dry samples indicate

that the introduction of treated or untreated woodflour does not affect the glass transition of the matrix. Differences of 2–3°C between measurements of different samples are in the range of the expected experimental error.

Wet samples at 60 RH were tested after 140 days of storage in humid environment, while 90 RH specimens were studied after 80 days of storage. In the first case, a reduction in the temperature of the main transition peak of the UPE matrix was detected in the composites. A broadening of the peak was also observed in the tan  $\delta$  curve of the composites. A rather similar behavior is observed in the loss tangent peak obtained from samples conditioned at 90 RH. The slightly higher values measured at 90 RH may be the result of the shortest exposition time under this environment (e.g., samples do not achieve the water equilibrium content).

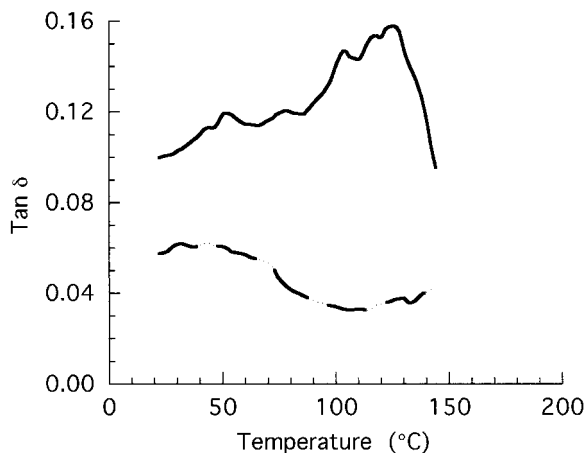
On the other hand, redried specimens did not completely recover the value of  $T_g$  corresponding to the original dry samples. An irrecoverable reduction (approximately 15°C at 60 RH and 10°C at 90 RH) was noticed in the matrix and composites. This was attributed to the hydrolysis of the polyester chains, which was more important after long exposure to humid environment.

**Table VI Temperature of Tan  $\delta$  (°C) Peak for Wet and Dry Samples**

Sample	Matrix	WC(40)	NaWC(35)	MANWC(40)
Dry	143.4 ± 0.08	140.93 ± 0.8	144.17 ± 0.50	142.59 ± 2.73
Wet (60 RH)	128.41 <sup>a</sup>	119.72 <sup>a</sup>	118–126	124–129
Redry (60 RH)	128.15 ± 0.46	127.27 ± 1.02	128.62 ± 1.44	129.74 ± 0.54
Wet (90)	129.68 ± 0.28	117–124	126.43 ± 1.58	128.64 ± 2.83
Redry (90 RH)	133.19 ± 0.46	132.27 ± 1.02		134.51 ± 0.14

Samples were conditioned at 60 RH or 90 RH during 140 or 80 days, respectively, before being tested (wet specimens) or dried and tested (redried specimens). A temperature range was reported when the width of maximum zone of tan  $\delta$  peak was broad.

<sup>a</sup> Only one sample was tested.



**Figure 1** Loss tangent,  $\tan \delta$ , as a function of the temperature for wood samples. (—) Dried for 2 h at 120°C; (---): immersed in distilled water for 24 h.

The water had also a plasticizing effect on the woodflour, which was investigated testing wood (*Eucalyptus saligna*) samples under similar conditions. Figure 1 shows the variation of  $\tan \delta$  for dry (2 h at 120°C) and wet wood (immersed in distilled water for 24 h) with temperature. It can be observed that wet wood exhibits a broad transition in the range of 80–130°C (which is absent in the dry sample) and a less important transition in the 40–80°C zone.

Wood devoid of moisture appears not to exhibit important thermal transition changes in the range of temperature studied. Other studies have shown that wood tends to soft at temperatures above 260°C.<sup>11</sup> Hon and Ou<sup>12</sup> reported transitions at –80 and at 250°C for dry untreated Southern yellow pine. The former was attributed to the motion of side groups such as methyl groups, which existed in lignin and hemicelluloses. The peak at 250°C was identified as the glass transition of wood polymeric components: the highly crystallized structure of the cell walls restricts the polymeric chain motions, imparting a good thermal stability to the material. A temperature scan of an *Eucalyptus saligna* sample (not shown in Fig. 1), realized in our laboratories showed a steep increase in  $\tan \delta$  at about 220°C. The test was stopped at that point because degradation takes place soon after the onset of the glass transition.<sup>13</sup>

The main transition peak (80–130°C), observed only for the moist sample, is thought to be related to the glass transition of wet wood, and the shift to lower temperatures observed with respect to dry samples is attributed to the plasticizing effect of water on the cell wall components.

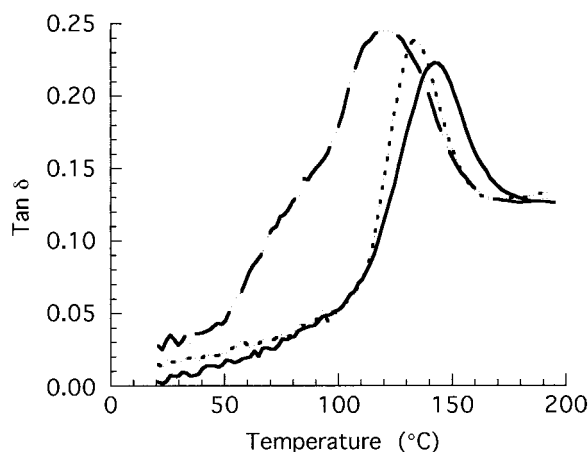
Figure 2 shows a comparison between the temperature scans of  $\tan \delta$  for WC(40) samples conditioned in three different ways: (a) dry, (b) wet at 90 RH, and (c) redried. Curves (a) and (c) are rather similar in height and width, but the peak in the sample (c) was shifted to a lower temperature (Table VI). As expected, the wet curve (b) is broader than the other two and the peak is shifted towards even lower temperatures than the previous one (c). This scan also exhibits a secondary broad transition in the 60–80°C range, in correspondence with the broad low temperature transition of the wet wood.

These last two figures help to understand that the change in the shape of the transition and the shift to lower temperature of the  $\tan \delta$  peak is due to the overlap of the glass transition of the UPE matrix and the transition suffered by the sawdust due to the plastification produced by water sorption.

Curve (c) indicates that after redrying the sawdust recover its original properties (at least in this respect) and the remaining shift in the glass transition of the matrix is attributed to the irreversible change caused by hydrolysis.

## CONCLUSIONS

It was demonstrated that the esterification of the woodflour with maleic anhydride is effective in reducing the hygroscopicity of the mercerized fibers, but the MAN-treated and untreated wood-



**Figure 2** Temperature scans of  $\tan \delta$  for WC(40) samples. (—) Dried for 24 h in vacuum at 70°C; (---) wet in a 90 RH environment; (----) dried (24 h in vacuum at 70°C) after exposure to humid (90 RH) environment.

flour reached similar equilibrium moisture content.

Mechanical properties (compressive and flexural) determined on wet samples are poor. In comparison with the behavior of the untreated woodflour composites, the measurements on composites made from NaOH-treated woodflour are lower, and the composites made with MAN-treated woodflour have the poorest behavior in wet condition. On the other hand, in all cases, the mechanical properties (except the ultimate strain) are worse as the humidity of the environment increases. This can be attributed to the detriment of the wood fiber strength in wet condition (untreated woodflour) added to an excessive degree of chemical modification (mercerization step, followed by a severe esterification reaction), which damages the reinforcement.

Moisture sorption diminishes the glass transition temperature of the neat resin and composites. A broad peak due to sawdust plastification overlaps the UPE main transition. Further redrying of the samples eliminates this contribution from the filler. The remaining decrease in  $T_g$  of all the samples (matrix and composites) is attributed to the irreversible hydrolysis of the polyester matrix.

Finally, it was found that the effects on compressive properties due to the absorbed water are mainly reversible, and the original values of these properties are recoverable by drying.

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