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Composites Made from Lignocellulosics and Thermoset Polymers

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Composites made from a stryrene/unsaturated polyester thermoset matrix and woodflours from different wood species have been prepared and tested. Pine (*Pino Eliottis*), eucaliptus (*Eucaliptus Saligna*) and marmelero (*Ruprechia Laxiflora*), a softwood and two semihard woods respectively, were selected for this study because of the availability and local abundance. The particles were used untreated and chemically modified with maleic anhydride (MAN). Thermogravimetric analysis and analytical techniques were used in the characterization of untreated and treated flours. Dispersion of the fibrous particles, as well as maximum filler concentration (accompanied by complete wetting of the wood fibers) was dependent on the treatment and on the wood species utilized. Bending and compression tests indicated some improvement in the performance of the composites, if the woodflour was previously esterified. Scanning electron microscopy (SEM) allowed to observe changes in the fracture surfaces due to MAN treatment of the fibers.

Keywords: lignocellulosics; thermosets; woodflours; chemical modifications; composites; mechanical properties

INTRODUCTION

The use of vegetal fibers and /or particles as reinforcement /filler of polymeric matrices has been enjoying a continuous growing interest in the past decade from the academic as well as the applied points of view. Applications go beyond the widely used particle boards and efforsts are

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being made to produce insumes for the construction, packaging and automotive industries among others.

Presently, sawdust (and woodflour) are considered wastes of the local forest industry in Argentina, which are partially burned to generate energy, or derived to the paper industry, while the major part is just accumulated, without any foreseen application and with the consequent environmental risk.

Unfortunately, the widespread use of these resources is hampered by the frequent incompatibility between lignocellulosic materials and many polymeric matrices, which affects the degree of dispersion of the fibers in the matrix and the macroscopic homogeneity of the structural piece. However, the addition of a compatibilizing and /or coupling agent to the filler or to the compounded material usually results in improved final properties.

On the other hand, there are chemical and morphological variations between different wood species, which in principle should correlate with different final properties of the woods and derived composites [1].

In previous publications, we reported the esterification of Eucaliptus Saligna with maleic anhydride (MAN), in order to improve the dispersion of the woodflour into an unsaturated polyester matrix and to modify the adhesion of the short fibers to the crosslinked resin [2,3]. In the present work, woodflours from different species, with and without chemical treatment, have been utilized. The final properties of composites made with a thermoset resin (styrene crosslinked-unsaturated polyester resin) were determined and the differences were discussed.

EXPERIMENTAL

Materials

The matrix is an unsaturated polyester resin (UPE) based on bisphenol A-fumarate (RQ 426, Perlinac S. A., Argentine), crosslinked with styrene in a 60:40 weight proportion with no additives. The initiator was benzoyl peroxide (Lucidol 0.75, Akzo Chemical S. A.), added in a proportion of 1.5% wt. with respect to the total reactive mixture.

Woodflours from pine (*Pino Eliottis*), eucaliptus (*Eucalyptus Saligna*) and marmelero (*Ruprechia Laxiflora*) were selected for this work, because of their availability and wide use in the region. Pine is a soft wood and eucaliptus and marmelero are considered semi hard woods. Only particles that pass through a sieve of mesh 250 (Tyler series) were utilized, thus the maximum particle average diameter was 57 μm.

Thermogravimetric Analysis

Thermogravimetric analysis were performed on samples of the different woodflours to study their degradation behavior. A Seiko Instruments SII Exstar 6000 thermogravimetric analyzer was used in these experiments. The loss weight thermograms and the corresponding derivative curves were obtained from temperature scans performed at 10°C/min from 30°C to 500°C under nitrogen atmosphere.

Chemical Modifications of the Woodflours

Woodflours were initially dried at 70°C for 24 hours in a vacuum oven and part of them were treated with an aqueous solution of NaOH (10% wt.). The particles were immersed in the solution during 1.5 hours at room temperature, then washed several times with distilled water, and finally, with ethanol.

Part of the NaOH treated woodflours was immersed a posteriori in a 0.6 N solution of MAN in xylene and heated at reflux temperature (140 °C) during 4 hours. After that, the esterified wood particles were separated from the xylene solution and intensively washed with distilled water in order to eliminate the unreacted anhydride. Finally, the woodflours were dried at 70 °C in a vacuum oven until constant weight was achieved. One sample of eucaliptus was treated during 7 hours to achieve a higher degree of esterification, then it was washed and dried as explained above.

Ester content of woodflour:

The ester content of the MAN modified woodflours was calculated from the acid and saponification values using the techniques described elsewhere [2, 4].

Equilibrium moisture content (EMC):

Controlled humid environments were prepared in hermetic boxes maintained at 20°C ± 2 °C and containing flasks with aqueous solutions of sulfuric acid (18 and 38 weight %) to ensure 90 and 60 of relative humidity (RH), respectively. Treated and untreated woodflour samples of about 1 g were dried until constant weight prior to be exposed to the wet environments. The weight changes due to moisture absorption were recorded until no further change was detected. The EMC was calculated as the difference between the final and the initial (dry) weight, ratioed by the later and it was expressed as a percentage value.

Compounding and Molding

Filler, resin and crosslinker (with the added initiator) were mixed in a Brabender type mixer (volume capacity ~60 cm^3) for about 30 min. The paste was filled in a metal mold (145 mm of diameter and about 3 mm of thickness) which was left open during 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 during 1.5 h. After that time, it was postcured in an oven for 2 hours at 150°C.

Plates of unfilled resin were obtained from pouring the reactive mixture between two glasses separated by a rubber cord and then clamped. The curing cycle was similar to that used in the cure of the composites, but no pressure was applied.

Mechanical Tests

Bending tests

Three point bending tests were also carried out at room temperature in a Shimadzu Autograph S-500-C Universal testing machine, using a crosshead speed of 1 mm/min and tested using a span of 50 mm. The composite test bars were cut from the molded plates (transversal area of 13 x 3 mm^2). The neat resin specimens were cut to a transversal area of 12 x 2.4 mm^2 and tested using a span of 40 mm (procedure A, ASTM D 790-86).

Compression tests

The compressive tests were carried out at room temperature at a crosshead speed of 0.5 mm/min. in an Instron 8501 Universal testing machine. Square bars (3.5 mm side) were cut from the molded plates. The aspect ratio of all the test specimens was kept between 1.5 and 2 according to ASTM recommendations (ASTM D 695-85).

Scanning Electron Microscopy (SEM)

The SEM photographs of the fracture surfaces of untreated and treated wood pine composites were obtained with a scanning electron microscope Philips model SEM 505, using gold coated samples.

RESULTS AND DISCUSSION

Woodflour Characterization

Thermogravimetric analysis of the untreated particles

In general, thermal decomposition of lignocellulosic materials show three main steps: (1) at temperatures lower than 100-120°C , (2) in the range between 120 to 300°C, and (3) above 300°C [5].

In the first step, absorbed moisture is lost. Weight losses at this step are usually around 5 %, depending on the morphological characteristics of the wood, the chemical composition and degree of sustitution of the cellulose -OH groups (if the wood has been chemically treated). In the second step, chain scissions occur and also water molecules are lost due to the intramolecular condensation of hydroxyls. Finally, in the third step, pyrolitic degradation of the wood components occur [6, 7].

According to the above scheme, there are esentially no qualitative variations between the degradation processes of the different wood species [8]. However significative differences can be observed in the specific temperatures of degradation, as well as in the percentage of losses that occurs at each step and in the final char residue.

In Figure 1 a and b the thermograms and derivative signals (DTG) obtained for the different untreated woodflours are shown. Pine and eucaliptus samples show a similar final region of degradation. The temperatures of the maximum of the DTG peaks appear at 285°C (shoulder) and 366°C for the pine sample, and at 287°C and 364°C for eucaliptus. The marmelero shows lower thermal stability than the other two species with a small shoulder at approximately 300°C and the main peak at 342°C (about 20°C below than pine and eucaliptus).

In the first period (dehydration) marmelero and pine loss about a 2.7% weight, while eucaliptus losses 6.4% of the original weight. In the

second region (between 120 to ~300°C) all woods loss 16-17% of their weight, and in the last step (above 300°C) pine losses 63% of their weight, while marmelero and eucaliptus loss 53 and 56%, respectively. The final char residues are 16.5, 20.2 and 27% for pine, eucaliptus and marmelero, respectively.

Chemical modification of the particles

The acid and saponification values listed in Table I were used to calculate the ester content of the different woodflours attributable to the chemical modification with MAN.

The saponification values measured for the NaOH treated flour were subtracted from the determinations of MAN treated samples, so that the original ester content of the woodflour is not considered in the calculation of bonded MAN[2]. Thus, the values reported in the last colum of Table I

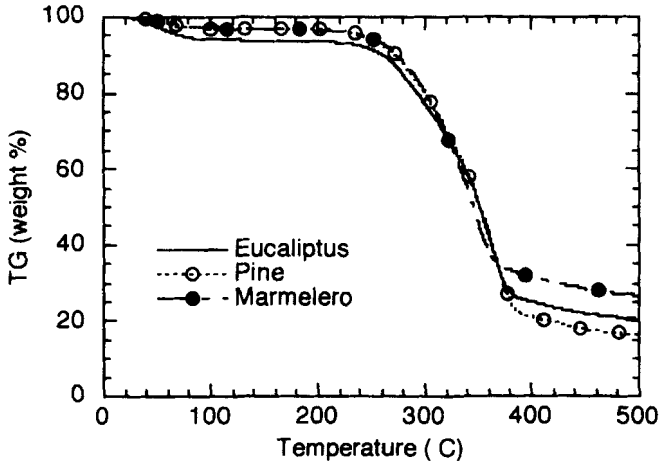

FIGURE 1 a Thermogram of the untreated woodflours.

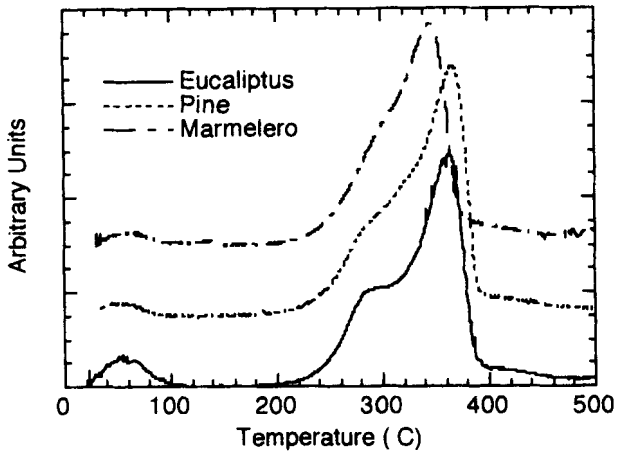

FIGURE 1 b DTG signal for the untreated woodflours.

TABLE I Acid number, saponification value (mg KOH/ g sample) and content of chemically bonded MAN (gMAN/100g woodflour) of the different woodflours.

Species	Treatment	Acid number	Saponific. value	MAN content
Pine	NaOH	negligible	43.5 ± 3.6	------
	MAN	89.5 ± 1.3	253.0 ± 4.8	26.54
Marmelero.	NaOH	negligible	49.2 ± 6.4	------
	MAN	100.8 ± 2.4	261.7 ± 6.9	24.23
Eucaliptus	NaOH	negligible	82.3± 0.6	------
	MAN	75.3 ± 0.4	214.1 ± 6.9	10.96
	MAN (7 hs)	120.9 ± 3.3	337.2 ± 1.8	30.58

indicate only the ester content in the wood particles due to the reaction with the anhydride. The efficiency of the reaction has also been verified previously, by using different techniques [9].

Water absorption

Table II shows the equilibrium moisture content (EMC) reached by the different samples when exposed to moisture and temperature controlled environments, room temperature with 60 and 90 % of relative humidity respectively. Alkaline treatment increases markedly the hygroscopicity of the samples (respect to the untreated ones). This effect was especially marked in the case of eucaliptus, for which the alkaline treatment caused that the water gain of the samples almost doubled the value of the original woodflour. On the other hand, esterification caused a noticeable reduction of the EMC of the particles, which is important considering that the hygroscopicity of the vegetable fillers is one of the most frequent disadvantages cited in literature.

TABLE II EMC (%) for the different woodflours.

Species	Treatment	EMC (%)	
		60 RH	90 RH
Pine	None	7.82	12.09
	NaOH	9.60	19.41
	MAN	5.74	9.09
Marmelero	None	7.12	13.38
	NaOH	8.70	16.33
	MAN	5.23	9.88
Eucaliptus	None	11.28	14.72
	NaOH	21.69	29.89
	MAN	9.81	12.91
	MAN (7 hs.)	8.54	10.38

Mechanical Tests

Compression

As other thermosets, crosslinked usaturated polyester resins (UPE) are highly rigid materials at room temperature exhibiting brittle behavior. As it also happens with thermoset epoxy resins, these materials break at low deformations when tested in tension with esentially no plastic deformation, and are very sensitive to any defect in the test specimen. However, they can show an important plastic deformation when tested in compression, since under these testing conditions propagation of internal microfisures is inhibited, and then, a real yielding of the samples can be observed [10]. Taking into account these characteristics of the matrix, the composites were tested in compression.

Figure 2 shows the typical curves corresponding to the composites obtained from pine woodflour untreated and esterified at filler loads of 40 %

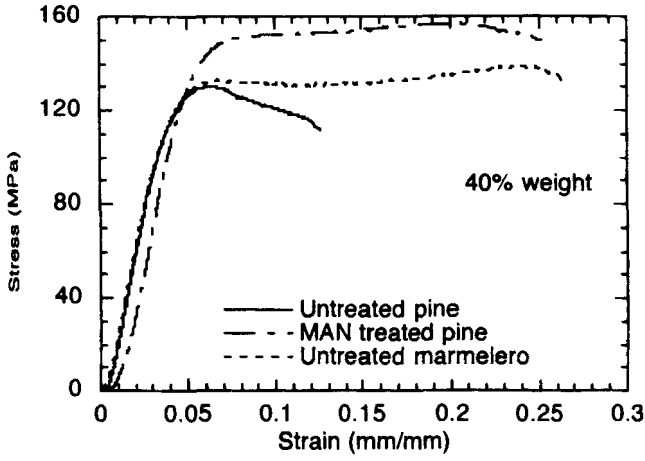

FIGURE 2 Typical curves of stress vs. deformation obtained in compression tests of three different composites.

with respect to the total weight of the sample. In the figure the behavior of the composite made with 40% of untreated particles of marmelero is also included. The simple observation of these curves indicates that treatment improves the resistance of the material to breakage, supporting a higher deformation before final rupture. It also shows that marmelero flour produces composites that break at comparable large deformations even without esterification treatment. The reason for this behavior is currently under study.

The summary of these results are reported in Table III, which also includes the results obtained from eucaliptus composites with similar chemical modifications. These results show that addition of woodflour increases the modulus of the composites, but contrary to the flexural behavior (discussed below), composites also show higher σ_{yield}. In all cases, the MAN treatment improves slightly the compressive modulus. The values of σ_{yield} do not show a significative difference in the case of the

TABLE III Compressive modulus (E_c), yield strength (σ_{yield}), ultimate deformation (r_u) and toughness for composites containing 40wt.% filler.

Samples	E_c (GPa)	σ_{yield} (Mpa)	r_u	Thoughness
Neat UPE	2.5 ± 0.1	111.4 ± 4.1	0.305 ± 0.074	33.7 ± 11.2
Pine untreated	3.7 ± 0.4	133.4 ± 9.5	0.171 ± 0.038	18.5 ± 7.6
MAN treat.	4.1 ± 0.3	145.6 ± 5.0	0.240 ± 0.089	33.1 ± 15.8
Marmelero				
untreated	3.7 ± 0.1	129.6 ± 2.0	0.248 ± 0.05	30.0 ± 7.2
MAN treat.	4.0 ± 0.3	135.0 ± 8.3	0.250 ± 0.06	30.8 ± 10.3
Eucaliptus				
untreated	3.9 ± 0.3	140.9 ± 2.6	0.084 ± 0.027	10.5 ± 3.8
MAN treat.	4.2 ± 0.3	138.2 ± 4.8	0.168 ± 0.041	26.4 ± 6.5
MAN (7 hs.)	4.1 ± 0.1	136.8 ± 0.8	0.214 ± 0.038	30.7 ± 7.4

composites made from eucaliptus flour, but there is an increment in the case of the other two treated woodflours. The final deformation of the samples (up to rupture) is increased quite significatively due to the particle treatment, in the case of pine and eucaliptus composites. However this improvement is almost negligible in the case of the marmelero composites.

Bending tests

Composites were also tested in flexion and the results are shown in Table IV. The reported results indicate that all composites behave more rigid than the unfilled crosslinked resin (neat UPE). The value reported for σ_{max} corresponds to the maximum stress supported by the bar and also to the ultimate stress before breakage.

The values of σ_{max} resulted similar for the pine and marmelero composites with some improvement if the particles were esterified. Composites made from eucaliptus showed the lowest values of σ_{max} without a definite trend.

TABLE IV Flexural properties of composites made with 40% of different wooflours.

Samples	E (GPa)	σ_{max} (MPa)	r
Neat UPE	2.9 ± 0.2	93.5 ± 0.6	0.036 ± 0.002
Pine untreat.	5.2 ± 0.1	60.9 ± 2.2	0.012 ± 0.001
MAN treat.	5.2 ± 0.3	62.0 ± 3.8	0.012 ± 0.001
Marmelero untreat.	4.9 ± 0.2	64.5 ± 6.5	0.013 ± 0.002
MAN treat.	5.4 ± 0.1	72.3 ± 4.3	0.014 ± 0.001
Eucaliptus untreat.	5.4 ± 0.2	54.1 ± 2.0	0.010 ± 0.001
MAN treat.	5.2 ± 0.2	52.8 ± 4.8	0.010 ± 0.001
MAN(7 hs)	5.1 ± 0.2	51.3 ± 3.1	0.010 ± 0.001

The values of the flexural modulus are similar for all the woodflours independently of the species or treatment. This kind of behavior is expected in this type of test [11].

The ultimate deformation was small and very similar for all the composites, although somewhat lower for the eucaliptus composites.

Scanning Electron Microscopy

Figure 3 a shows the fracture surface of a 40% composite made with untreated pine woodflour. The micrograph shows a very irregular surface, which is common to this type of samples. There are some holes and some depressions, where fibrous particles are missing probably because debonding occurred.

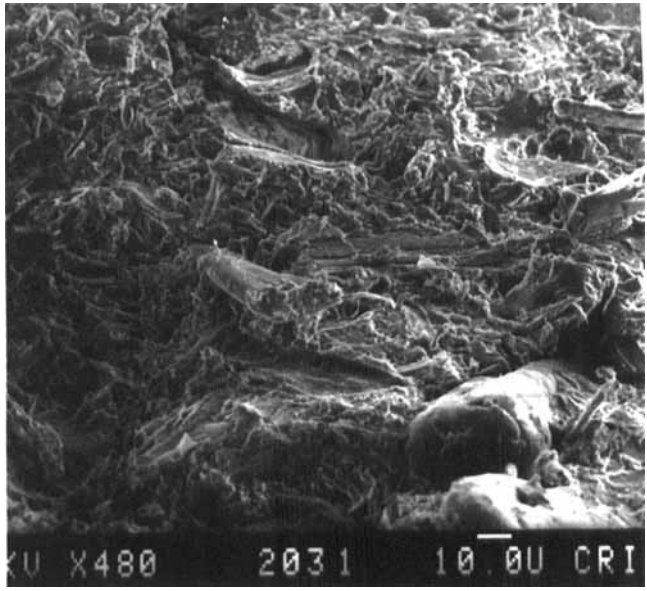

FIGURE 3 a Untreated pine woodflour -UPE composite at (40% filler). Magnification 480 X.

Composites behaved tougher under compression for MAN-treated woodflours.

The differences between a softwood, such as pine and a harder wood, such as eucaliptus were evident during the compounding step. Higher filler weight concentrations could be achieved using eucaliptus (a denser wood), due to easier dispersion and better wetting of the fibers.

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