Resin–Sisal and Wood Flour Composites Made from Unsaturated Polyester Thermosets

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Abstract

Short fibers and wood flour were selected as fillers in the production of two types of unsaturated polyester composites (bisphenolic and isophthalic-based thermosets). Sisal fibers were subjected to washing in order to remove the organic coating on the fibers (which were originally prepared for cord manufacture) and to maleic anhydride (MAN) esterification. The effect of these treatments on the thermomechanical properties of the composites, as well as on the mechanical properties (flexural and compression) and water absorption was investigated. All the results are coincident in showing the improved interfacial adhesion obtained by washing and mainly by esterification of the fibers. Additionally, hybrid wood flour sisal composites were prepared and their mechanical properties compared to those of the one-filler composites. The hybrid composites showed improved modulus and maximum stress.
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1. Introduction

Fillers are commonly added to polymer matrices in order to improve thermal and mechanical properties. There are, however, some adverse effects, e.g., toughness and ultimate elongation of polymers often suffer with the addition of fillers. However, composites continue to attract interest because their use helps to reduce the cost of the compounded polymers, while offering a wide range of attractive properties for different structural applications.

In many developing countries where natural fibers are abundant, economics and other related factors have led to apply locally appropriate technologies to utilize these natural fibers as effectively and economically as possible. Nowadays, due to

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the high specific mechanical properties, significant processing advantages, low cost and low density, natural fibers are being used worldwide to produce good quality fiber reinforced polymer composites for construction materials and other needs [1–4].

Natural fibers obtained from renewable resources are cheap, do not represent health hazards and provide an attractive alternative for reducing environmental pollution by offering new uses for waste or low cost materials. Natural fiber reinforced polymer composites constitute good substitutes for scarce wood and wood-based materials in some structural applications. One difficulty encountered during the incorporation of lignocellulosic fillers into a polymeric matrix (except for highly polar matrices, such as phenolics or urea–formaldehyde matrices) is the hydrogen bonding, which tends to hold the cellulose fibrils together. The polar nature of lignocellulosic-based fillers adversely affects the dispersion of such polar materials in most commonly used polymeric matrices [5].

The effect of the fillers on the final composite performance depends greatly on the shape and size of the particles, their composition, the particle/fiber distribution into the matrix, and the compatibility between the filler and polymer composition [6]. Several publications [7–11] have been focused on improving the quality of the interfacial bonding by treating the fibers with silane or isocyanate reactants, but showed no important improvement of the final composite performance. Recently, Bailey *et al.* found that the results obtained from classical sodium hydroxide plus acetic anhydride-based treatments exhibited a general increase of the flax fiber/unsaturated polyester adhesion [12]. Rong *et al.* [13] investigated the effect of sisal treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites. Their treatments included alkalization, acetylation, cyanoethylation, the use of silane coupling agent, and heating, and were carried out to modify not only the fiber surface but also its internal structure. Their results indicated that, in general, fiber treatments significantly improved adhesion at the interface and also favored the entrance of the matrix resin into the fibers, hindering the pull-out of the lignocellulosic cells. More recently, Idicula *et al.* [14] indicated that the use of fibers chemically treated with NaOH and polystyrene maleic anhydride (PSMA) allowed a significant increase of both thermal conductivity and density values of banana/sisal fiber–polyester composites, since the fiber modification allowed a better contact between the components (fiber/matrix) and reduced considerably the thermal contact resistance.

On the other hand, reinforcement by two or more fibers or by fibers with different aspect ratios or by a particulate and a fibrous reinforcement in a single matrix leads to hybrid composites. The contribution of the different components to the final properties is expected to result in a more favorable balance of properties in the resultant composite materials.

Previous reports in the literature have dealt mainly with the production and characterization of organic–inorganic hybrid composites. Thus, jute–glass, pineapple leaf fiber–glass or sisal–glass hybrid composites have been considered [15–19]. In

general, the presence of glass resulted in higher modulus of the material and reduced water absorption.

Of more interest to the present study are the publications that deal with natural fiber hybrid composites. Panels made from polymeric methyl diisocyanate and wood particles–wheat straw showed better properties than traditional wood particle-based panels, because of the higher aspect ratio of the straw fibers [20]. The adverse effect of humidity was investigated in cotton–kapok/polyester composites [21]. Jacob *et al.* [22] studied the mechanical properties and cure characteristics of sisal and oil palm hybrid fiber reinforced natural rubber composites. Paiva *et al.* [23] used plain weave hybrid ramie-cotton fabrics as reinforcement in polyester matrix and showed the high potential of ramie fibers and weak contribution of cotton fibers as reinforcement in lignocellulosic composites. Finally, the effect of the fiber orientation was addressed on a study of jute/cotton–phenolic composites [24].

The current study deals with the evaluation of the mechanical properties of composites made from two different unsaturated polyester resins filled with vegetable fibers and/or particles. Woodflour (particulate filler) is an abundant regional waste and sisal fibers are widely used in the region. In this study, sisal short fibers were considered as-received, washed and surface modified by esterification. Besides, hybrid composites (wood flour/sisal) were prepared and their mechanical and dynamic mechanical properties measured. Experimental results were analyzed to identify the effect of surface treatments on the sisal fibers. Additionally, the simultaneous addition of particulate–fibrous fillers to the thermoset resins was considered, with the aim of searching for enhanced final properties of the materials.

2. Experimental

2.1. Materials

The matrices selected for the study were two different unsaturated polyesters (UP), one based on bisphenol A-fumarate (RQ 426, Perlinac S.S., Argentina), and the other based on isophthalic acid (UB691, Ubyco S.A.I.C., Argentina). The characterization of the polymers by ^{1}H NMR showed the following molar composition:

- for the bisphenol-based resin: bis-phenol A 29.05%, fumaric acid 24.10% and propyleneglycol 46.85%;

- for the isophthalic-based resin: isophthalic acid 23.5%, fumaric acid 17.6%, succinic acid 11.7% and propyleneglycol 47.2% [25].

Both polymers were obtained as pellets in the neat solid state and were diluted in styrene (S) in a 60:40 weight ratio of UP:S. The crosslinking reaction was initiated with benzoyl peroxide (Lucidol 0.75, Akzo Chemical S.A.), 1.5 wt% with respect to the total reaction mixture.

A particulate filler, woodflour (WF) from *Eucalyptus sp.* (Entre Rios, Argentina, particle size below 147 μm) was used in this work.

Sisal fibers (S1) were obtained from twined sisal cords kindly supplied by Brascorda S.A. (Brazil) and individual fibers (S2) kindly supplied by Cellton (Brazil). Both fibers were cut to 10 mm length (average) before being utilized in the composite preparation.

2.2. Surface Modification

Woodflour was dried in a vacuum oven, at 70°C until reaching a constant weight, before being used in the composite preparation. Part of it was immersed in a 0.6 M solution of maleic anhydride (MAN, Merck, 99% purity) in xylene and then heated at reflux temperature (140°C) during 4 h for the reaction to take place [25–27]. The esterified wood particles were separated for scanning electron microscopy (SEM) from the xylene solution by centrifugation and then they were intensively washed with distilled water in order to eliminate the unreacted anhydride. The modified woodflour was further dried at 70°C in a vacuum oven until constant weight was achieved. The MAN content of the treated woodflour, determined by saponification and titration techniques [26–28], resulted in a value of 23 g MAN/100 g neat woodflour.

Similarly, part of the sisal fibers, S1, was also treated with MAN, but using acetone as a solvent, which resulted in a reaction temperature of 60°C, allowing us to achieve a lower degree of reaction and avoiding fiber degradation at high temperatures. The resulting content of attached MAN was 3.3 g MAN/100 g neat sisal.

Finally, part of the as-received sisal fibers (S1) was washed with acetone at room temperature in order to eliminate any surface coating present onto the fibers to facilitate the cording process.

2.3. Composite Fabrication

Fillers and fibers were dried and then mixed with the selected resin (UP + S) in a Brabender type mixer for about half an hour (chamber with 50 cm^3 capacity, rotor speed 50 rpm, room temperature). All samples were prepared at a total filler or fiber content of 40 wt%. Hybrid composites had also the same total amount of fillers (20% woodflour plus 20% of sisal fibers, S1). The mixture was then cured in a metal mold (diameter: 145 mm, thickness: 3 mm). The curing cycle was 2 h at 50°C (open mold), followed by 1.5 h at 80°C and 3.8 MPa (closed mold). The samples were post-cured at 150°C during 2 h without pressure. All test specimens were cut from these plaques and dried 24 h at 70°C under vacuum.

2.4. Scanning Electron Microscopy (SEM)

Surfaces of the different sisal fibers utilized in the study were examined using a scanning electron microscope (Philips model SEM 505). The samples were previously coated with gold.

2.5. Water Absorption

Rectangular slabs 35 mm long, 12 mm wide and 3 mm thick were used in the immersion tests. The specimens were dried until constant weight and then immersed in distilled water at room temperature. The weight gain was measured at different times, following the procedures described by ASTM D 570-81: *24 h Immersion* (procedure 6.1) and *Long-Term Immersion* (procedure 6.4). The final weight gain was obtained after stability, that is, when no changes were detected after three consecutive measurements.

2.6. Dynamic Mechanical Tests (DMA)

Dynamic mechanical measurements were performed by means of a Perkin-Elmer dynamic thermal analyzer (DMA 7). The tests were carried out using the temperature scan mode, with three-point bending fixture and a specimen platform of 15 mm length. Dynamic and static stresses were fixed at 3×10^5 and 5×10^5 Pa, respectively, and the frequency of the forced oscillations was fixed at 1 Hz. All specimens were cut to $20 \times 3 \times 2$ mm^3, and the linear dimensions were measured up to 0.01 mm.

2.7. Flexural Tests

Three-point bending tests were carried out at room temperature at a crosshead speed of 1 mm/min, using a Shimadzu Autograph S-500-C Universal testing machine. The specimen bars were cut to $70 \times 12 \times 3$ mm^3, conditioned according to ASTM D 790-86 — procedure A and tested using a 50 mm span.

2.8. Compression Tests

Compression 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 mm side) were cut from the molded plaques. The aspect ratio of all the samples was kept approximately equal to 2 (ASTM 695-85). Parallel faces were carefully machined and lubricated with molybdenum sulfide wax for testing.

3. Results and Discussion

In order to evaluate the effect of the intensive mixing (processing step) on the final length of sisal fibers, the uncured composites were extracted with acetone immediately after the mixing. Hence, the neat resin was dissolved in the solvent and the lengths of the remaining fibers were measured. It was found that the fiber length after mixing was reduced to about 3 mm (average) for the two types of sisal fibers used [29, 30].

On the other hand, the treatments (physical and chemical) affected the surface of the fibers. Figure 1 shows the surface of S1 and S2 unmodified sisal and S1 treated fibers. It can be observed that certain globular protrusions are present on the surface of 'as-received' fibers (Fig. 1A). When the fibers were washed with acetone
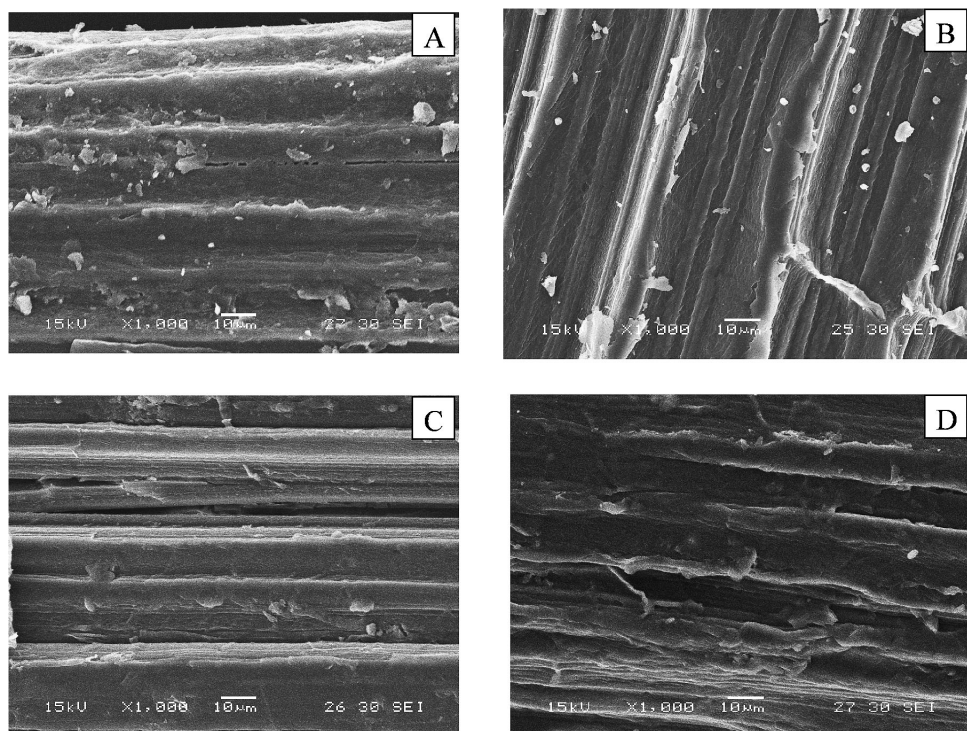
Figure 1. Scanning electron microscopy (SEM) of the fiber surfaces. (A) S1; (B) S2; (C) washed S1; (D) MAN-treated S1.

(Fig. 1C), these protrusions almost disappeared, leaving the rather rough surface of the sisal itself. The removal of the coating leads to a very different fiber surface which promotes the mechanical anchorage and, thus, an enhancement of the adhesion between the polymer matrix and fibers is expected. Consequently, the appearance of the S1 fiber surface after washing is very similar to that of the S2 fibers (Fig. 1B), which were procured with no surface coating. On the other hand, when the fibers were treated with MAN (Fig. 1D), the protrusions practically disappeared, leading to the formation of a rather smooth surface indicating that MAN is acting as a coating layer, evenly distributed onto the surface.

3.1. Water Absorption

Table 1 shows the results of the water absorption for the bisphenolic-based thermoset and derived composites. The first thing to be noted is that the composite prepared with 'as-received' sisal fibers (S1) is more prone to absorb water than that prepared with the same amount of wood flour. This general trend could be explained by the fact that wood flour particles are covered almost completely by the resin and, thus, particles are more restricted in swelling and water absorption is reduced [31, 32]. On the other hand, at the same concentration, fibers easily link with each other forming a connected hygroscopic route for the entrance of moisture. Al-

Table 1.
Water uptake of bisphenolic-based composites

Material/composite	24 h immersion	Long time immersion
Unfilled bisphenolic UP	0.30 ± 0.02	0.76 ± 0.05
Wood flour	1.58 ± 0.07	7.59 ± 0.23
Wood flour/S1	2.59 ± 0.01	9.82 ± 0.15
S1	4.84 ± 0.43	13.75 ± 0.47
Washed S1	2.68 ± 0.30	12.23 ± 0.58
MAN-treated S1	1.85 ± 0.28	10.37 ± 0.35
S2	2.32 ± 0.19	9.75 ± 0.92

though particles may also form aggregates, these aggregates are very probably less connected than those formed by fibers. Hybrid composites absorb water in quantities intermediate between those observed for the individual wood flour and sisal (S1) composites. S2-based composites absorb less moisture than S1 and washed S1-based composites, probably because S2 is low quality fiber, not approved for brushing and export. This kind of fiber suffered more mechanical wear during the extraction from the plant, so the surface quality is lower and this leads to more 'points' or defects for mechanical anchoring, actually improving the physical adhesion at the fiber–matrix interface.

As can also be seen in Table 1, washed sisal fibers composites are less susceptible to water uptake than 'as-received' sisal composites. This behavior would indicate the mechanical bonding matrix–fiber was improved and the interfacial adhesion increased. Washing eliminates the waxy coating of the S1 original fibers, allowing better contact at the interface with the polymer. Thus, it is more difficult for moisture to find an easy access through interfacial paths in these composites. Similar results have been reported previously for jute fabric unsaturated polyester composites [33], and for alkali-treated wood flour UP composites [26, 32]. On the contrary, the as-received fibers had a waxy coating that prevented the formation of a strong interface and hence water entered the material more easily. Additionally, when sisal fibers are MAN treated, the resulting composites absorbed less water because the available hydroxyls onto the surface of the lignocellulosic materials have diminished. At the same time and equally important, chemical bonds connecting the filler to the matrix could be formed through reaction of the C–C double bonds of the MAN moieties in the surface of the treated fibers with the unsaturated polyester and styrene during the curing of the thermoset [27]. Thus, the fiber's characteristics together with the strong interfacial adhesion make more difficult the water diffusion into the bulk composite.

Similar trends were obtained from the analysis of the behavior of the isophthalic polyester composites, although the moisture uptake is slightly lower than those of the bisphenolic-based samples (Table 2), which may imply a better interfacial adhesion in these composites.

Table 2.
Water uptake of isophthalic-based composites

Material/composite	24 h immersion	Long time immersion
Unfilled isophthalic UP	0.28 ± 0.05	0.98 ± 0.09
Wood flour	0.85 ± 0.01	5.43 ± 0.26
Wood flour/S1	1.74 ± 0.10	10.75 ± 0.46
S1	2.02 ± 0.32	11.68 ± 0.31

3.2. Dynamic Mechanical Tests

Figure 2A shows the storage moduli for the two thermosets and the corresponding composites prepared with 40 wt% sisal S1. The modulus of the neat isophthalic thermoset is higher than that based on the bisphenolic resin, 2.58 and 2.15 GPa at 40°C, respectively. There is essentially no difference between the values of the rubbery modulus of these materials (above 180°C). However, as noticed from Fig. 2B, the glass transition temperature of the isophthalic thermoset (taken as the temperature at the maximum in $\tan \delta$) is lower than that based on the bisphenolic one — 124°C and 134°C, respectively. The trend in these last values is in agreement with the T_g of the undiluted pellets that have T_g's (measured by DSC) of 35°C and 53°C, respectively. This would suggest a higher rigidity of the bisphenolic resin chains with respect to those of the isophthalic resin. The $\tan \delta$ peak corresponding to the bisphenolic derived network is also narrower. At room temperature, the behavior of both neat thermosets has clearly a larger elastic than viscous component.

Additionally, the composites present higher storage moduli at room temperature than the corresponding neat thermosets (3.43 and 4.2 GPa for the bisphenolic and the isophthalic networks at 40°C, respectively). The observed increments correspond to 59% and 62% with respect to the glassy modulus of the neat networks. This is due to the presence of the sisal fibers that contribute to the augmented rigidity of the system. As expected, this effect is more important at higher temperatures (rubbery region) showing increases of 14.4 and 7.9 times for the bisphenolic and isophthalic reinforced networks, respectively. It is interesting to observe that the rubbery modulus of the two composites is not the same, as it occurred with the neat thermosets. Since the type and weight percentage of sisal incorporated in the resins is the same for both composites, and the rubbery moduli of the neat networks were originally coincident, the same value of the rubbery modulus for the composites was expected. This is not the case, indicating that the crosslinking process has been more affected by the presence of the sisal in the case of the isophthalic resin. Paauw and Pizzi [34] have already reported the reduction of the heat of reaction in styrene crosslinked isophthalic resins containing different fillers, including wood flour. They observed an important reduction in the curing enthalpy of the reaction when it was conducted in the presence of 20% woodflour. They ascribed this result to two factors: first, woodflour is a highly absorbent filler and this high
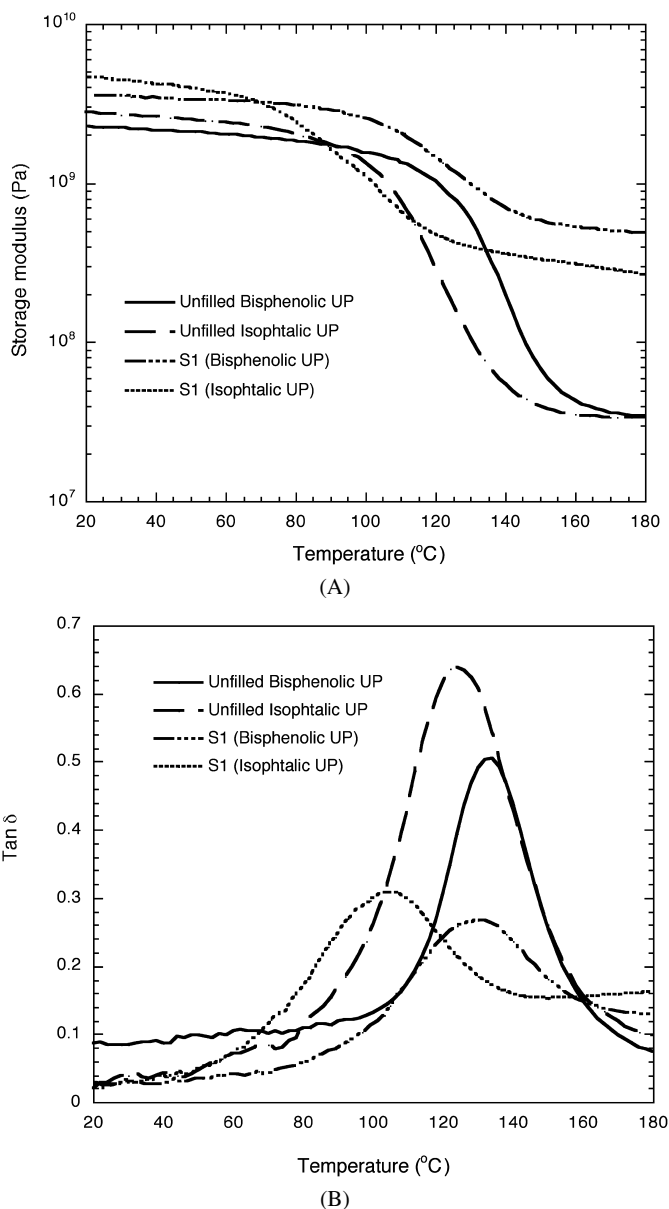
Figure 2. Thermomechanical properties of unfilled resins and S1 composites. (A) Storage modulus *vs*. temperature; (B) tan δ *vs*. temperature.

absorbance limits the mobility of the polymer chains by secondary forces' inter-action; and second, to the existence of a covalent bonds between the curing resin and filler. They indicated that the reaction between filler and matrix could be a free-radical one, which reduced the free-radicals available for resin crosslinking and, thus, contributing to enthalpy reduction.

On the other hand, the effect on T_g is more important in the isophthalic resin. Thus, although the two composites exhibit a shift of the main relaxation (tan δ peak) towards lower temperatures as compared to the tan δ peaks of the unfilled thermosets, the shift is comparatively larger in the case of the isophthalic composite ($\Delta T_g = 4°C$ and $20°C$, for the bisphenolic and isophthalic-based matrices, respectively). This may be a consequence of the changes produced in the crosslinked density of the materials (as discussed above, [34]) and also probably on some plastification produced by the addition of the fibers, through the humidity contained in the fibers, as well as the waxy coating present in untreated sisal. As expected, the height of the peak is lower in the composites as less material is involved in the relaxation due to the diluent effect of the fibers.

Figure 3 shows the effect of the addition of sisal fibers S1 (as-received, washed and MAN grafted) on the bisphenolic matrix. The effect of washing the fibers with acetone on the room temperature modulus of the material is mostly dependent on its cohesive density. Since there are better opportunities for mechanical anchorage of the resin on the fiber surface after washing, the cohesion of the material improves and the storage modulus at room temperature is higher. Notice also that this observation is in agreement with the results of water uptake at room temperature.

As the composites approach their glass transition temperature, their behavior depends more strongly on the crosslinking density of the networks. As already mentioned, the interactions at the interface can influence the reaction chemistry,
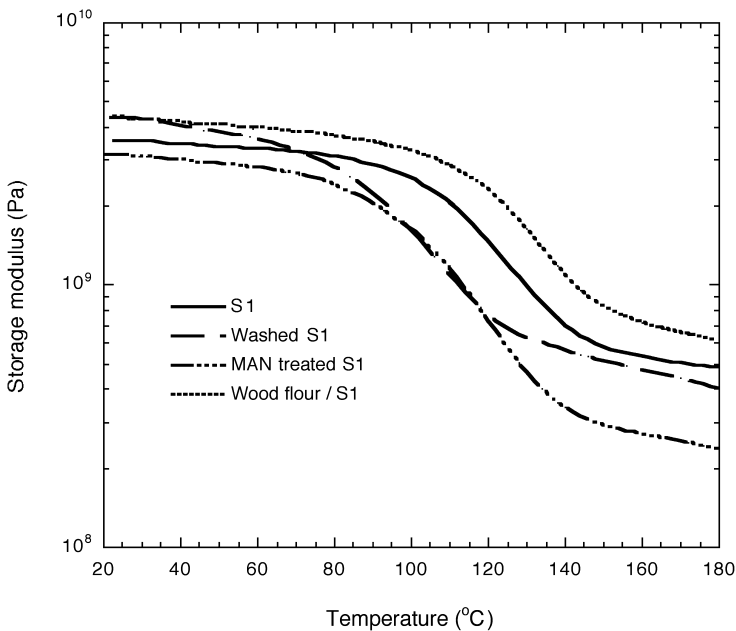
Figure 3. Storage modulus *vs.* temperature of S1 and wood flour/S1 composites (bisphenolic UP thermoset).

Table 3.

Main transition (as $\tan \delta$ peak) of the bisphenolic UP in the neat thermoset and derived sisal composites

Material/composite	T_g (°C)
Unfilled bisphenolic UP	133.2
S1	129.6
Washed S1	112.8
MAN-treated S1	125.2
Wood flour/S1	134.0

probably by preferential diffusion towards the fiber surface of one of the monomers or radical consumption [34], which leads to the decrease of the crossliking density of the final network and consequently to the reduction of the T_g of the matrix in the composite materials. The effect on the matrix temperature transition can be observed in Fig. 3 and is reported in Table 3.

The S1 bisphenolic composite shows a relatively modest decrease of 4°C in the T_g, with respect to the unfilled matrix. Washed sisal, which according to water absorpion results shows a larger interaction with the network, induces a decrease of 20.4°C in the T_g of the matrix. Washing helps to expose the surface of the sisal fibers, which interferes with the crosslinking of the resin. Esterification of the sisal (MAN-treated S1) partially covers the surface of sisal by attaching MAN moieties to the sisal surface. At the same time, attached MAN can react with the polymer unsaturations, chemically linking the matrix to the fibers. The result is an 8°C reduction of T_g with respect to the neat thermoset. Finally, the simultaneous addition of wood flour and sisal does not produce major changes in the matrix transition temperature. Apparently, sisal has a larger effect on the resin crosslinking than wood flour.

As mentioned above, the rubbery moduli of the composites (Fig. 3) are much higher than that of the neat thermoset due to the addition of the rigid fibers/particles. The modulus of sisal fibers has been reported to be 17.3 GPa [35], while the measured E' of the biphenolic thermoset in the rubbery state is much lower (35 MPa, Fig. 2). Differences are also noted between the different types of sisal composites tested. The lowest rubbery E' corresponds to the MAN-treated sisal fiber composite. Chemical bonding at the interface is expected in this case [26, 27, 32], which according to T_g measurements reduces polymer chain mobility, but it also reduces the crosslinking density in the matrix bulk.

The effect of the addition of a hybrid reinforcement (20 wt% of wood flour and 20 wt% of sisal) on the thermomechanical properties of the bisphenolic thermoset is also illustrated in Fig. 3. The storage modulus of this composite is higher than that of the S1 composite (actually, it is the highest of all the composites considered in the plot) in all the temperature range covered by the test. The particle size distribution affects the maximum packing fraction, i.e., mixtures of particles with different size

can pack more densely than monodispersed particles because the small ones can fill the interstitial space between the closely packed large particles to form more dense structures as Ahmed and Jones [6] have studied. These connected structures may be able to carry a larger portion of the load than the primary filler particles yielding a higher modulus in the composite.

3.3. Flexural Tests

The results obtained in flexural tests for the bisphenolic composites are shown in Table 4. The flexural moduli of the composites are higher than the ones measured for the neat thermoset (a logical consequence of using fillers/fibers that are more rigid than the polymeric matrix). Simultaneously, the flexural strength and the ultimate deformation diminish considerably in comparison to those of the unfilled material. The effect on ultimate deformation was expected due to the presence of rigid particles that restrict the matrix deformation. Moreover, the use of sisal fibers does not present any significant enhancement in comparison to the addition of woodflour, as can be seen in Table 4. Because of the important length reduction that the sisal fibers suffered during the mixing step (probably shorter lengths than the critical one are obtained), they act more as fillers than as reinforcements. However, the simultaneous use of both types of particles (sisal fibers and wood flour) allows the achievement of an increase in the composite flexural strength. It is interesting to highlight the fact that improved properties were also measured in dynamic mechanical testing of the materials, as discussed in the previous section. Besides, it should be noticed that after the maximum stress the behavior of the hybrid material is qualitatively intermediate to that of sisal and wood flour composites (Fig. 4A). That is, the material does not break catastrophically but some fiber pullout of partially attached fibers delay the final rupture of the material [36].

The use of surface treatments in sisal fibers and in wood flour caused no variation in the flexural modulus of the different composites. However, the analysis of the stress–strain curves shows some differences in the overall response of the material behavior. Figure 4B shows the curves corresponding to the flexural response of the bisphenolic thermoset–sisal composites for differently treated sisal fibers. The

Table 4.
Flexural properties of bisphenolic resin-based composites

| Material/composite	E (GPa)	σ_u (MPa)	ε ($\times 1000$)
Unfilled bisphenolic UP	2.9 ± 0.2	93.5 ± 0.6	36.12 ± 2.4
Wood flour	5.4 ± 0.2	54.1 ± 2.0	9.94 ± 0.4
Wood flour/S1	5.5 ± 0.2	59.4 ± 0.8	$12.0 \pm .0.1$
S1	5.4 ± 0.5	51.3 ± 3.2	12.2 ± 0.2
Washed S1	5.2 ± 0.5	54.4 ± 4.5	11.1 ± 1.2
S1 treated MAN	5.3 ± 0.4	53.4 ± 3.7	10.2 ± 0.6
S2	5.7 ± 0.5	50.0 ± 14.9	9.0 ± 1.8
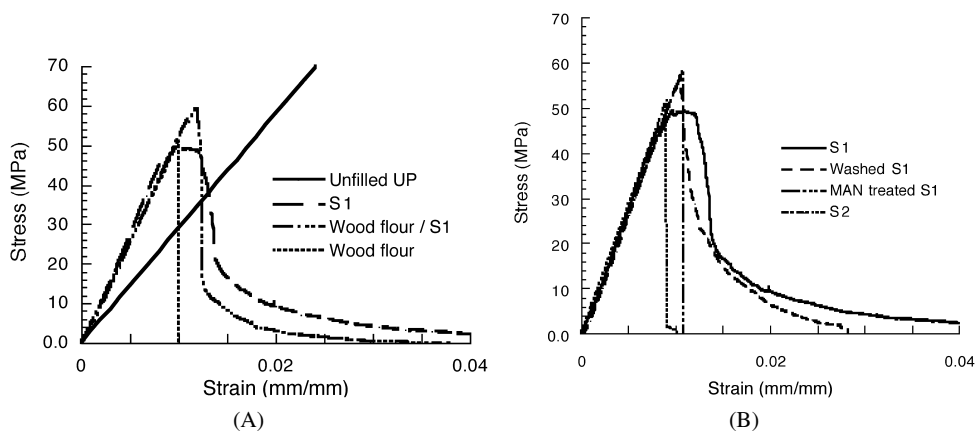
Figure 4. Flexural stress–strain curves. (A) Unfilled bisphenolic resin, wood flour, wood flour/S1 and S1 composites; (B) bisphenolic resin–sisal fiber composites.

curve corresponding to the untreated sisal composite shows an important non-linear response after reaching the maximum stress and before the final breakage of the material. After reaching the maximum stress there is a short plateau, during which fibers are pulled out from the matrix. After that, the fibers' contribution to load carrying is dramatically reduced, although some fibers attached to the matrix remain, since the stress drop is not catastrophic [36]. The use of S2 in the composite formulation led to composites with flexural modulus similar to that of the other sisal composites (Fig. 4B, Table 4). The interesting feature is the way in which this material fails as soon as the maximum stress is reached. This behavior is related to the lack of coatings in the S2 fibers (good mechanical anchorage of the matrix in the fibers) together with the compromised integrity of these fibers. S2 fibers were originally destined for uses different from cords, so they fail at lower strains than S1 fibers.

When the S1 fibers are washed, the waxy coating of the original sisal is removed and the fibers show a rougher surface prone to mechanical interlocking with the matrix and other fibers. Because of this, the stress required to unbond the fibers is shifted towards higher values. After that initial drop in stress, the behavior is similar to that of the untreated sisal since only weaker interfacial bonds remain.

After sisal esterification, the behavior changes again. The composite shows a maximum flexural stress close to that of the washed sisal composites, that is, strong interfacial forces are involved. However, because the interfacial interactions have been improved by the treatment and covalent bonds between fiber and matrix have been formed at the interface, the rupture of the composite is catastrophic, indicating that it is behaving as a monolithic material. In these conditions, fiber pull-out practically does not takes place and the material breaks through the matrix and fibers as a whole.

Figure 5 supports the above discussion on flexural behavior. The lengths of the pulled-out fibers are reduced with washing (B) and even more with MAN treatment (C) in comparison with the untreated fiber composite (A).
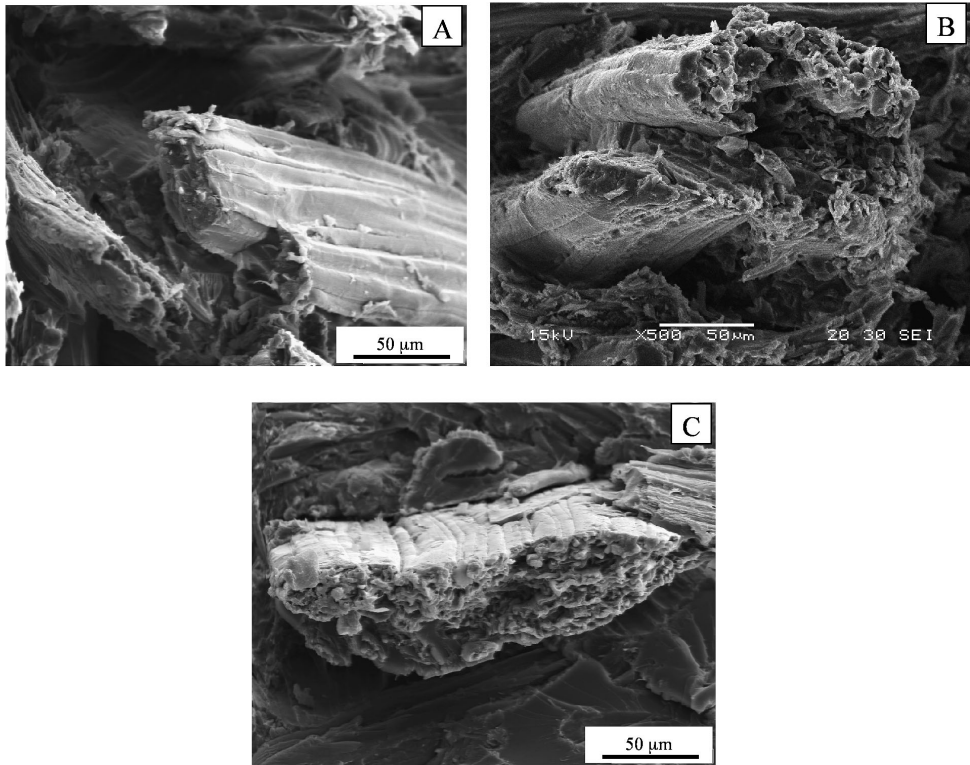
Figure 5. SEM of the fracture surfaces of the composites based on the bisphenolic polyester thermoset, containing 40 wt% sisal. (A) Untreated; (B) washed; (C) MAN treated.

Table 5.
Flexural properties of isophthalic resin-based composites

Material/composite	E (GPa)	σ_u (MPa)	ε ($\times 1000$)
Unfilled isophthalic UP	3.7 ± 0.1	85.5 ± 12.6	23.6 ± 3.2
Wood flour	5.2 ± 0.1	61.7 ± 4.9	11.4 ± 0.8
Wood flour/S1	5.8 ± 0.7	70.3 ± 2.9	11.5 ± 0.1
S1	5.2 ± 0.4	60.6 ± 3.2	12.2 ± 0.2

Flexural properties for composites obtained with the isophthalic polyester (Table 5) showed a similar tendency to that discussed for the bisphenolic one. However, in this case, there is a remarkable difference in the form of rupture of the material. All the samples, neat thermoset as well as composites, break catastrophically after reaching the maximum stress, all the deformation occuring in the linear regime. As in the case of the bisphenolic polyester composites, the simultaneous addition of woodflour and sisal to the isophthalic polyester matrix leads to a material with the highest modulus and flexural strength.
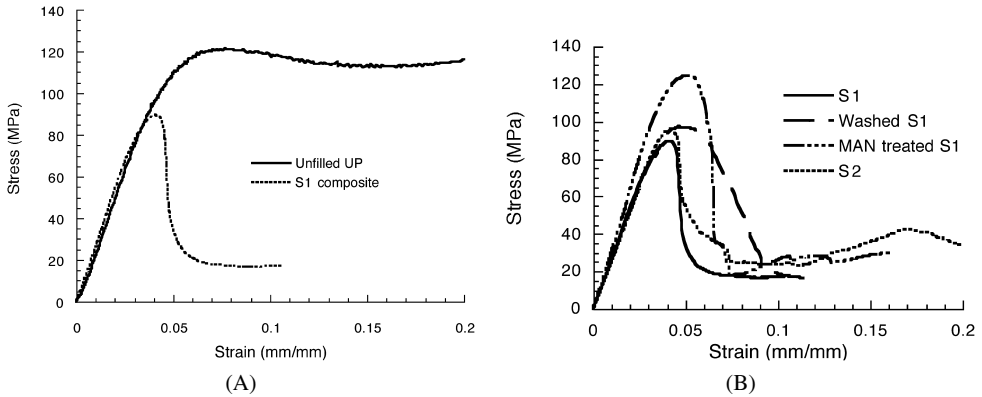
Figure 6. Compressive stress–strain curves. (A) Unfilled bisphenolic resin and S1 composite; (B) bisphenolic resin–sisal fiber composites.

3.4. Compression Tests

Thermoset materials subjected to compression can experience plastic deformation and such is the case for the composites prepared with any of the two UP resins presented in this study. In particular, Fig. 6A shows the effect of adding S1 to the bisphenolic UP thermoset. The inclusion of sisal short fibers into the polymer produces only a slight increment in the compression modulus of the material. This effect is quite different from the observed flexural behavior and indicates that the material response in compression is controlled mainly by the matrix properties. The yield stress is reduced and the material breaks at lower deformations. The three-dimensional arrangement of the fibers that are not strongly attached to the matrix may be responsible for the material's early failure.

The effect of surface treatment is illustrated in Fig. 6B, for the untreated, washed and esterified sisal fibers. The better interfacial adhesion between fiber and matrix obtained by simple washing leads to the delayed failure of the material, so a larger area under the stress–strain curve is observed. Notice that the S2 composite (sisal fibers supplied without coating) shows a similar behavior as the washed S1 composites, at least up to the yield point. This is attributed to the absence of surface coatings in S2 and in washed-S1 fibers leading to similar interfacial interactions in the composite. However, the S2 composites fail at smaller deformation and there is a larger standard error associated with the breakage of this material, which is consistent with the quality of the fibers. The initial integrity of S2 fibers has been more compromised than S1 during their extraction and handling, as was indicated in the Materials section.

Finally, the use of esterified fibers produces an improvement in the compression properties of the composite. The material is able to support plastic deformation without interfacial debonding up to higher stress values. This behavior has been already observed in MAN-treated wood flours-UP composites and was also related

Table 6.

Compressive properties of bisphenolic resin-based composites

Material/composite	E (GPa)	σ_y (MPa)
Unfilled bisphenolic UP	2.5 ± 0.02	111.4 ± 4
S1	2.9 ± 0.63	86.4 ± 14.8
Washed S1	2.6 ± 0.1	97.1 ± 12
MAN-treated S1	3.1 ± 0.70	126.8 ± 1.5
S2	2.5 ± 0.1	95.5 ± 4.1
Wood flour/S1	2.9 ± 0.40	110.2 ± 6.21

Table 7.

Compressive properties of isophthalic resin-based composites

Material/composites	E (GPa)	σ_y (MPa)
Unfilled isophatlic UP	3.03 ± 0.1	156.6 ± 5.0
Wood flour/S1	3.45 ± 0.5	142.8 ± 3.4
S1	3.03 ± 0.5	107.5 ± 16.5

to the better interface and improved dispersion of these materials as compared with untreated ones [26].

Table 6 summarizes the compression properties measured for the bisphenolic-based composites. The addition of the vegetable fibers/particles leads to a slight increase of the modulus of the bisphenolic thermoset under compression. A larger effect is observed on the yield stress (σ_y) of the materials. The simultaneous addition of wood flour and sisal (20 wt% each) leads to a composite with essentially the same modulus and yield stress as those of the neat thermoset. However, the addition of sisal fibers produces a reduction in the σ_y, with the exception of the MAN-treated sisal. The esterified sisal has a better interface with the UP resin and can sustain larger imposed loads, before yielding, as explained above.

Table 7 shows the compression results for the isophthalic-based thermoset and composites. As in the case of the bisphenolic composites, the addition of sisal reduces the properties of the base UP resin, but the addition of equal parts of wood-flour and sisal leads to a composite of similar yield stress and slightly improved modulus. This difference may originate in the relatively more easy dispersion of the wood flour particles, than the short sisal fibers.

4. Conclusions

The lignocellulosic fillers utilized, sisal and woodflour, interfere with the crosslinking reaction of the thermoset as judged from the decrease of the temperature of the main transition of the matrix. This effect is larger in the isophthalic-based network.

The treatment of the fibers reduces water uptake, through the formation of stronger interfacial adhesion. This is true for the MAN-treated fibers/particles, as well as for the just washed fibers, because of the formation of chemical and physical bonds, respectively.

The presence of the filler has different effects on the thermomechanical response of the composites: it reduces the glass transition temperature of the matrix, while in general it improves the modulus at room temperature and specially the rubbery modulus.

The addition of sisal fibers reduces the catastrophic breakage of the composites during flexural tests, even when short fibers have been used. The treatment of the fibers reduces this effect by improving the interfacial adhesion and, thus, reducing fiber pull-out.

The simultaneous addition of wood flour and sisal short fibers to produce hybrid composites improves the properties of the materials, produces higher maximum stresses and retaining some of the non-linear stepwise breakage typical of fibrous composites.

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