

Lignocellulosic materials and unsaturated polyester matrix composites: Interfacial modifications

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Abstract—The addition of particulate fillers (woodflour) and short fibers (sisal) into an unsaturated polyester matrix was performed and analyzed. The efficiency of the filler treatment was carefully investigated, in particular, esterification with two different anhydrides, maleic anhydride (MAN) and an alkenyl succinic anhydride (ASA). The reaction with MAN was performed under different experimental conditions in order to reach different degrees of esterification. The efficiency of the reactions was assessed by FTIR, titrimetric techniques and moisture absorption values. Esterification improves the wettability of the fillers by the resin, so that higher concentrations of filler could be incorporated in the composite. The reaction of the unsaturations of the attached anhydrides with the styrene co-monomer was confirmed by FTIR. This reaction was frequently invoked in the literature, but most times was not confirmed. Scanning electron microscopy study confirmed the improved adhesion of the fillers to the matrix. Surfaces of fractured esterified woodflour composites showed that the resin fills the hollow central regions of the woodflour cells (lumens) reducing capillarity effects during humidity or water sorption by the composites. Mechanical tests were performed on some of the composites to illustrate the effect of the covalent linkages created between the esterified lignocellulosics and the matrix. Tests in which the characteristics of the interphase played an important role were chosen in order to highlight differences resultant of the chemical co-reaction.

Keywords: Sisal; woodflour; esterification; interface; unsaturated polyester resins.

1. INTRODUCTION

Polymeric materials of commercial interest are usually mixed with fillers to improve thermal and mechanical properties and to reduce costs. However, the addition of fillers may also contribute to some adverse effects, such as a decrease of toughness and ultimate elongation of the polymers. Although traditionally inorganic fillers have been used in this area, since the beginning of the 1990s there has been a

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dramatic increase in the use of vegetable fillers with identical purpose. Presently, most of the commercially available composites use glass fibers as reinforcing agent [1], while carbon fibers are used in high performance applications. Synthetic fibers are stronger than vegetable ones [2], but when the specific composite properties [3] are important, the difference between both reinforcements becomes less critical, especially if low and medium performance applications (usually, high volume applications) are to be considered. In these cases, other aspects become important, such as end of life-time considerations, in which the lignocellulosic reinforcements offer advantages [4, 5].

The incorporation of vegetable fibers or particles into most polymers presents some difficulties, since dispersion is somehow prevented by the incompatibility between polar fillers and (usually) non-polar matrices. This drawback has been counteracted by chemically modifying the polymer or the filler or by adding compatibilizer agents. The increased compatibility results in improved dispersion of the particles and wetting of the fibers, so that higher concentrations of fibers or particles can be achieved in the composite, thus improving the processability and moldability of the mixtures.

Chemical modification of the fillers using silanes, isocyanates, acids and anhydrides has been reported in the literature [4, 10–13]: in some cases the goal was to change the texture of textile fibers, in others to improve the compatibility between filler and polymer in composite applications. Most commonly, the open literature deals with vegetable reinforcement or filling of thermoplastic polymers [4, 10, 11], and with less frequency with thermosets [12, 13]. The addition of vegetable fillers to the last type of matrices has the additional advantage of reducing the tendency of the resin to crack during cure by reducing the resin shrinkage.

Some authors have focused on the modification and characterization of the fibers. Yang *et al.* [14, 15] studied the relation of surface modification and tensile properties of sisal fibers, and found that the crystallinity and modulus could be improved by a simple thermal treatment, while other stronger chemical methods, which include alkali, sulfuric acid, conjoint alkali and sulfuric acid, benzol and alcohol dewax, acetylation, thermal/alkali or alkali/thermal treatments, produced increased ductility of the fibers reducing the modulus. To improve moisture resistance, Chand *et al.* [16] acetylated sisal fibers. Although the water absorption was reduced almost to one-half, the tensile strength of the fiber was reduced because of the loss of hemicellulose during acetylation.

On the other hand, the modification of fillers changes the interface characteristics in the produced composites. Fiber or particle modifications affect dispersion (filler wetting) and processability as mentioned above, as well as the final mechanical properties of the resulting material. In the case of vegetable fillers, it has been shown that the waxy substances originally present in the vegetables are responsible for poor wettability and adhesion characteristics [17].

Rong *et al.* [13] studied the effect of different treatments on sisal fibers added to an epoxy matrix and its effect on tensile and flexural properties. Ray *et al.* [12]

studied the effect of alkaline treatments on jute–vinylester composites. They found that there was an optimum time of reaction for the jute fibers, and that longer times of reaction led to less favourable properties in the final composites. A combination of alkali and diluted epoxy pretreatment for flax fibers was found to be the more efficient modification method to be used in epoxy–flax composites, probably due to the improved wetting and compatibility [18]. Hepworth *et al.* [19] took advantage of the swelling of flax cell walls with an urea solution, in order to introduce an epoxy alcoholic solution into those walls. This method improved the adhesion to an epoxy matrix and reinforced the original structure of the fibers producing stiffer, but less tough, unidirectional flax fiber composites.

In this work, we have investigated the chemical treatment of lignocellulosics, focusing on the identification of the material modifications at the chemical and topological levels. We also measured the effect of these changes on the hygroscopic characteristics of the materials and we investigated the covalent reaction between lignocellulosics and matrix components, which has been for years only inferred from changes in the macroscopic behavior of the composites. Finally, we present the results on selected properties of these materials, as an illustrative example of how the modifications performed on the fibers or particles affect the final composite behavior.

2. EXPERIMENTAL

2.1. Materials

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

2.1.2. Lignocellulosic materials. Two lignocellulosic materials were selected: one was a particulate filler (woodflour), the other a short fiber reinforcement (sisal). Both were subjected to similar chemical treatments.

Woodflour from *Eucalyptus sp.* (Entre Ríos, Argentina) was used as particulate filler. As an average, the major chemical components of woods [20] are carbohydrates (70–80%), lignin (20–30%) and extraneous materials that can be removed by a solvent (5–10%). Cellulose and hemicelluloses are the main component of the wood carbohydrate (40–50% and 20–30% of total wood, respectively). In the present work, only woodflour particles that passed through a sieve of mesh 250 (Tyler series) were used; thus the maximum particle average diameter was 57 μm . The aspect ratio was relatively low (1 to 5) and so the woodflour was considered a particulate material.

Sisal, kindly supplied by Brascorda S.A. (Brazil), was used as short fiber reinforcement. Fibers with an average diameter in the order of 160–330 μm were cut to a length of 10 mm (average) from twined samples. As in other vegetable

fibers, there are fluctuations in the composition of the fibers coming from different sources, but as indicative values, sisal fibers contain on average 78% cellulose, 10% hemicellulose and pectin, 8% lignin, 2% waxes and 1% ashes [21].

The reactants used in the chemical modification of the fillers were maleic anhydride, MAN (99% pure, Riedel-de Haën, Germany) and an alkenyl succinic anhydride (ASA, Lasar 2019 CF, Akzo Nobel), commercially distributed as paper sizing.

The fillers were subjected to chemical modifications as described below:

- (A) Alkaline treatment: the filler was immersed in an aqueous solution of NaOH (10% wt) for 1.5 hours at room temperature and then washed several times with distilled water.
- (B) Esterifications: The particles were reacted with MAN or ASA according to the procedures described in previous publications [22, 23]. Sisal fibers and one woodflour sample were prepared in the same way without alkaline pretreatment. Different weight gains were achieved by selecting different anhydride concentrations and reaction times. In all cases, the esterified particles or fibers were separated from the respective solutions and intensively washed with distilled water in order to eliminate the unreacted anhydrides. Finally, they were dried at 70°C under vacuum until constant weight was achieved.

2.2. Preparation of composites

The fillers or short fibers were incorporated into an intensive mixer together with a mixture of the unsaturated polyester resin, the corresponding amount of styrene (crosslinker) and catalyst. The compounding was performed at room temperature for 30 min with no appreciable reaction taking place during this step.

The filled resin was unloaded from the mixer as a viscous paste and introduced into an aluminium mold. The sample was heated at 50°C for 2 h, with the mold open to allow degassing, then the mold was closed to produce samples of 3 mm of thickness. The mixture was cured in a heated hydraulic press at 80°C and 3.8 MPa for 1.5 h and then postcured at 150°C for 2 h in an air circulating oven.

2.3. Physical and mechanical tests

2.3.1. Filler and short fiber characterization. The efficiency of the chemical treatments was verified using Fourier transform diffuse reflectance infrared spectroscopy (DRIFT) by adding 64 scans and using a 2 cm⁻¹ resolution. All the samples were used without KBr dilution. The equipment used was a Mattson Genesis II. The technique was used to identify chemical groups from the location of the absorption bands, and only in a semi-quantitative way to compare different degrees of esterification from the intensity of the corresponding peaks.

To confirm the presence of unsaturations in the ASA molecule, Raman spectroscopy was utilized. The equipment used was a Dilor Confocal Raman Microspectrometer.

The attached MAN or ASA content was calculated from saponification and acid values of the samples using the techniques described elsewhere [24]. The increase in acid or ester groups in the filler was calculated with respect to a blank sample subjected to the same pretreatments and solvent immersions as the sample.

The integrity and surface characteristics of the fillers were observed by scanning electron microscopy (SEM) using a Philips model SEM 505 microscope. The samples were previously coated with gold.

The water sorption characteristics of the woodflours or short sisal fibers with different treatments were determined as the equilibrium moisture content of the samples pre-conditioned at room temperature and 60% relative humidity. The water gain was measured by difference from the weight at the initial time of the test and the constant final weight of the sample.

2.3.2. Physical and mechanical characterization of the composites. The composites were fractured in liquid air (fragile fracture) and their surfaces were observed by scanning electron microscopy (SEM) using a Philips model SEM 505 microscope. The samples were previously coated with gold.

Mechanical tests were selected with the single objective of showing the changes in properties due to interface modifications produced by the lignocellulosic treatments.

Flexural tests were carried out on samples cut from compression molded plates, using a span of 50 mm (transversal area of $13 \times 3 \text{ mm}^2$), according to the procedure A, ASTM D 790-86, in a Shimadzu Autograph S-500-C Universal testing machine. A cross-head speed of 1.35 mm/min was utilized.

Activated creep experiments were performed at 100°C on woodflour composites using a Perkin Elmer dynamic mechanical analyzer (DMA 7). The tests were carried out using three-point bending geometry with a specimen platform of 15 mm length. The sample dimensions were maintained at $2 \times 3 \times 20 \text{ mm}^3$ with a precision of $\pm 0.01 \text{ mm}$ in the linear dimensions. The applied constant stress was 5.5 MPa for all the samples. The creep part of the test was performed over 30 min, followed by the recovery measurements after unloading. All the samples were dried previously to be tested.

Finally, Izod unnotched impact energy was measured on dry composites at room temperature in a Fractovis Ceast falling weight machine. The velocity of the test was set as 1 m/s and the striker minimum mass (3.6 kg) was used, thus the impact energy was 1.8 J.

3. RESULTS AND DISCUSSION

3.1. Woodflour esterification: maleic anhydride

The efficiency of the different chemical treatments of the particles and fibers was investigated by FTIR; in most of the cases, the diffuse reflectance infrared (DRIFT) scans of the neat samples were registered.

Figure 1 shows the spectra of the untreated and alkaline treated woodflour (A and B, respectively) in the region of $2000\text{--}600\text{ cm}^{-1}$. There is a change of the carbonyl zone where the peak corresponding to ester carbonyl absorption (1730 cm^{-1}) moves to lower frequencies because of the formation of ionic carboxylates (1590 cm^{-1}). It can also be seen that the peak located at 1240 cm^{-1} , which has been assigned to the C–O bond of the acetyl group in xylan, is broken into two smaller peaks at 1260 and 1230 cm^{-1} . The first one corresponds to vibrations in the guaiacyl structure of the lignin and the second to the syringyl structure [25]. The splitting of the original band is characteristic of the alkaline treatment of lignocellulosic materials and has been reported previously [25, 26].

The esterification reaction expected to occur between the wood or vegetable fibers with the MAN has been discussed in other previous publications [27, 28]. Figure 1

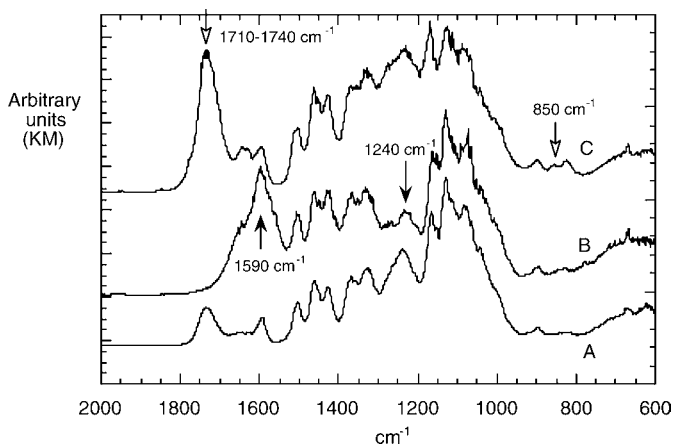


Figure 1. DRIFT spectra of the neat untreated woodflour (A), alkaline treated woodflour (B) and woodflour esterified with MAN without previous alkali treatment (C).

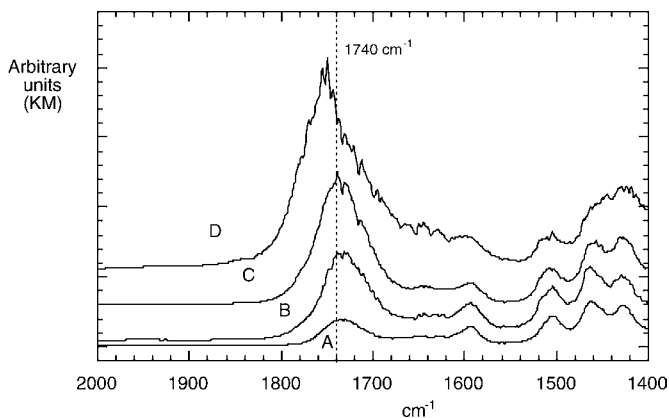


Figure 2. DRIFT spectra of woodflour treated with maleic anhydride at different lengths of time. (A) untreated; (B) 10%MAN (4 h); (C) 30%MAN (7 h); (D) 58%MAN (24 h).

also shows the spectrum of the sample esterified with MAN without previous alkali treatment (curve C). Comparison with the curve A shows that there is an increment in the intensity of the $1710\text{--}1740\text{ cm}^{-1}$ band, due to the new ester bonds formed by reaction of the OH groups in the wood with the anhydride. The absorption in this region corresponds to both the C=O groups in acid and ester groups attached to the filler [29]. The bands corresponding to the absorption of the unreacted maleic anhydride (1845 and 1780 cm^{-1}) have practically disappeared after washing the samples [28]. In the treated woodflour spectrum, it is possible to observe a new peak at 850 cm^{-1} related to the absorption of *cis* C=C, in conjunction with the carbonyl group [29].

The spectra obtained from the woodflour samples after reaction with MAN for different periods of time, are shown in Fig. 2. There is a strong increase in the absorbance of the band in the 1740 cm^{-1} region, which corresponds to an increase in the concentration of ester bonds between wood and maleic anhydride. The intensity is larger for the sample that was kept for a longer time in the reactor (curve D), but in these conditions the reaction is no longer confined to the surface OH; instead, the whole particle is involved. The overall structure is compromised, as may be seen in the gradual change of the $1400\text{--}1500\text{ cm}^{-1}$ zone of the curve D.

3.2. Woodflour esterification: alkenyl succinic anhydride

Figure 3 shows the transmission FTIR and Raman spectra of the alkenyl succinic anhydride used in the woodflour modification. The peaks corresponding to the anhydride IR absorption are clearly seen in the FTIR spectrum at 1780 and 1850 cm^{-1} , and appear less intense in the Raman spectrum. As is the case with many unsaturated fatty acids, in which the double bond is located approximately in the middle of the molecule, the 1650 cm^{-1} absorption peak characteristic of C=C absorption does not appear in the ASA's FTIR spectrum. However, it appears as a strong peak in the Raman spectrum, confirming the presence of the unsaturation in the chain.

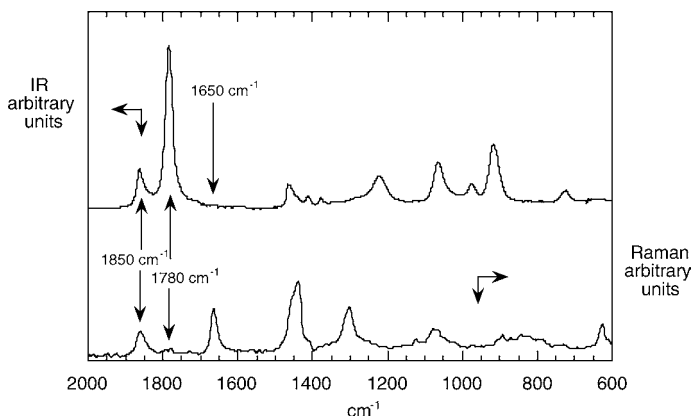


Figure 3. Transmission FTIR and Raman spectra of ASA.

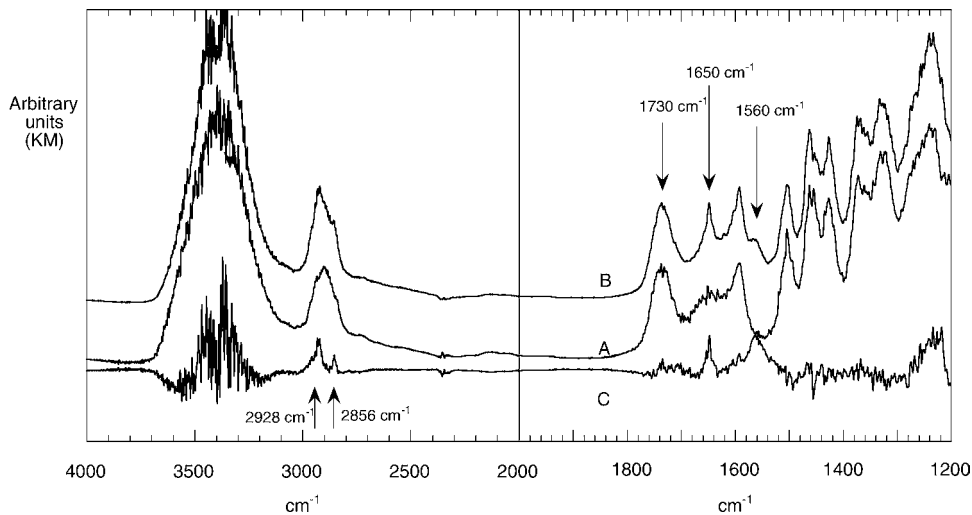


Figure 4. DRIFT spectra of the untreated woodflour (A); ASA treated woodflour (B) and difference spectrum (C).

Figure 4 shows the spectra of woodflour esterified with ASA and further washed to eliminate unreacted sizing (A) and that of the untreated woodflour (B) for reference. There is a slight increase in the intensity of the carbonyl absorption at 1730 cm^{-1} , while a new peak appears at 1650 cm^{-1} , which corresponds to the unsaturation of the attached ASA, since reaction with the wood breaks the symmetry of the molecule. There is also other new peak at 1560 cm^{-1} that has not been assigned. There is also a change in the shape of the C–H stretch bands in the $2900\text{--}3000\text{ cm}^{-1}$ region, which corresponds to the absorption of the CH groups of the attached ASA molecule. The location of the peaks can be seen more clearly in the difference spectra (C), at 2928 cm^{-1} , 2856 cm^{-1} , corresponding to the antisymmetric and symmetric CH_2 stretchings, respectively [30].

3.3. Saponification values

The qualitative changes observed by FTIR were further verified and quantified using titrimetric techniques to measure saponification and acid number in the different samples. The acid number measures the concentration of acid groups, while the saponification value measures the concentration of acid and ester groups. The difference between the measurements before and after esterification is due to the incorporation of the MAN to the lignocellulosic particles or fibers. Since MAN is expected to react as a monoacid, the increase in saponification values (Sap. after–Sap. before) should approximately double the increase in the acid number (Acid after–Acid before). Table 1 shows the results of the measurements, as well as the calculated values of the weight gained and the corresponding mmoles of MAN attached. The values of weight gains reported are calculated taking into account only the saponification values, while the results of the calculations considering the

Table 1.

Saponification values and Acid numbers of woodflour samples pretreated with alkali

Sample	Reaction time (h)	Acid number (mg KOH/g)	Saponif. value (mg KOH/g)	g MAN/100 g woodflour	mmol MAN/g woodflour
Alkaline	—	negligible	82.29 ± 0.55	—	—
10% MAN	4	75.33 ± 0.39	214.14 ± 6.85	13.02 (10.96)	1.33 (1.12)
30% MAN	7	120.87 ± 3.28	337.23 ± 1.83	28.65 (30.58)	2.92 (3.12)
58% MAN	24	228.99 ± 0.72	522.08 ± 18.03	62.37 (58.30)	6.36 (5.95)

Table 2.

Calculated weight gains of reacted anhydrides for woodflour and sisal samples without alkali pretreatment. Reaction time: 4 hours

Sample	g/100 g woodflour	mmol/g woodflour
MAN treated Sisal esterified	3.29 (3.31)	0.338
MAN treated woodflour	17.13 (20.30)	2.07
ASA treated woodflour	8.23	0.229

acid and saponification values are included in parentheses. As may be seen, there is no appreciable difference between the two ways of calculation (i.e. the increase in the concentration of ester groups due to reaction is approximately equal to the increase in the concentration of acid groups), confirming that maleic anhydride reacts only through one of the potential carboxylic acid groups. A similar behavior is expected for the reaction of the ASA molecule with the woodflour.

As expected, the longer the reaction times, the higher the saponification values measured. Although the alkaline pretreatment had been utilized in order to eliminate some wood matrix elements and to expose a higher concentration of OH groups in the cellulose for reaction, it was clear that esterification without this intermediate step is also possible. Even higher weight gains are obtained, as shown in Table 2 for MAN treated woodflour without pretreatment.

3.4. SEM microscopy

Figure 5 shows scanning micrographs (SEM) of different treated woodflours. The woodflour surface is severely affected by the alkaline treatment (Fig. B), exhibiting a very rough surface [27]. On the other hand, esterified particles have a rather smooth surface due to the MAN (Figs D and E) or ASA coating layer (Fig. C), which are evenly distributed onto the surface.

Figure 6 shows the untreated and MAN-treated sisal fibers. Figures A and B show the cross-section of the technical fibers. As can be seen, the treated fiber (B) presents a closer and more collapsed structure attributable to the MAN treatment when compared with the untreated fiber (A). Using greater magnification onto the external surface of both fibers, some protrusions along the length of the untreated fibers (C) can be observed, probably due to waxes and other low molar mass impurities.

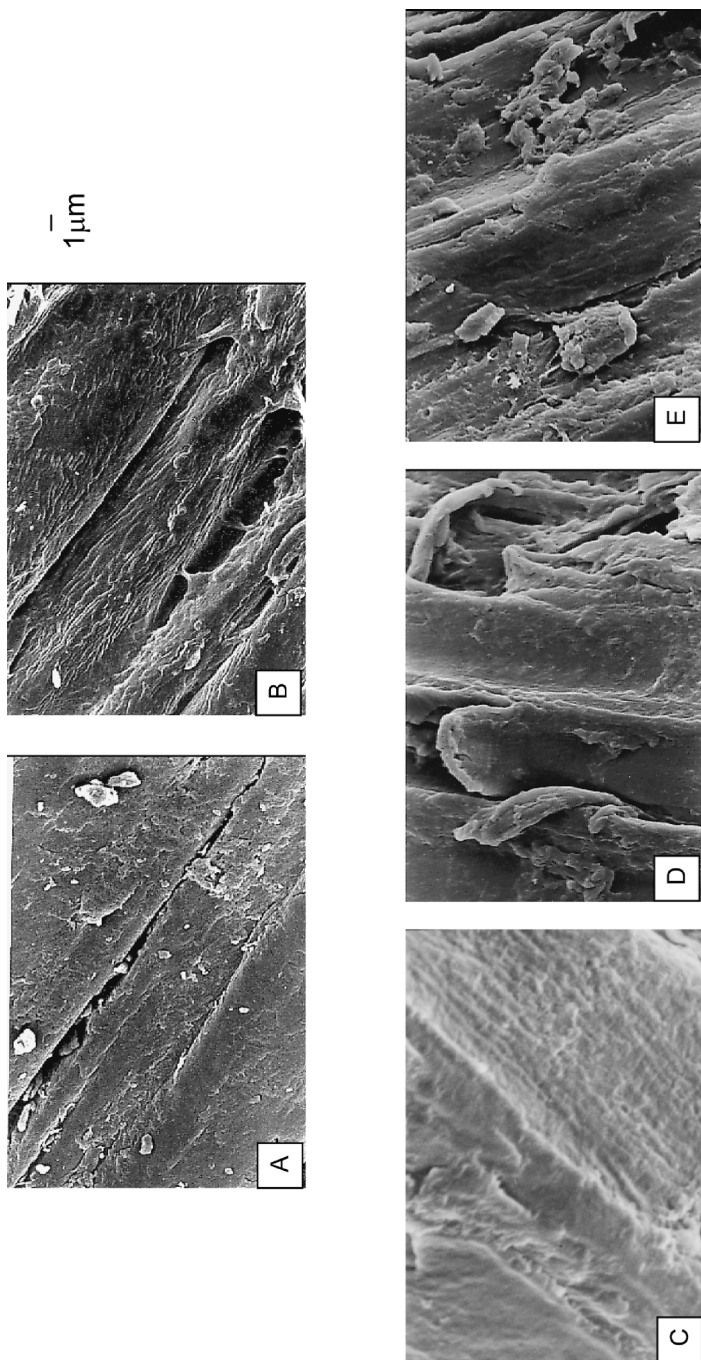


Figure 5. Scanning micrographs (SEM) for different woodflours. Untreated (A, Ref. [27]); NaOH treated (B, Ref. [27]); ASA treated (C); 10% MAN (D); 30% MAN (E).

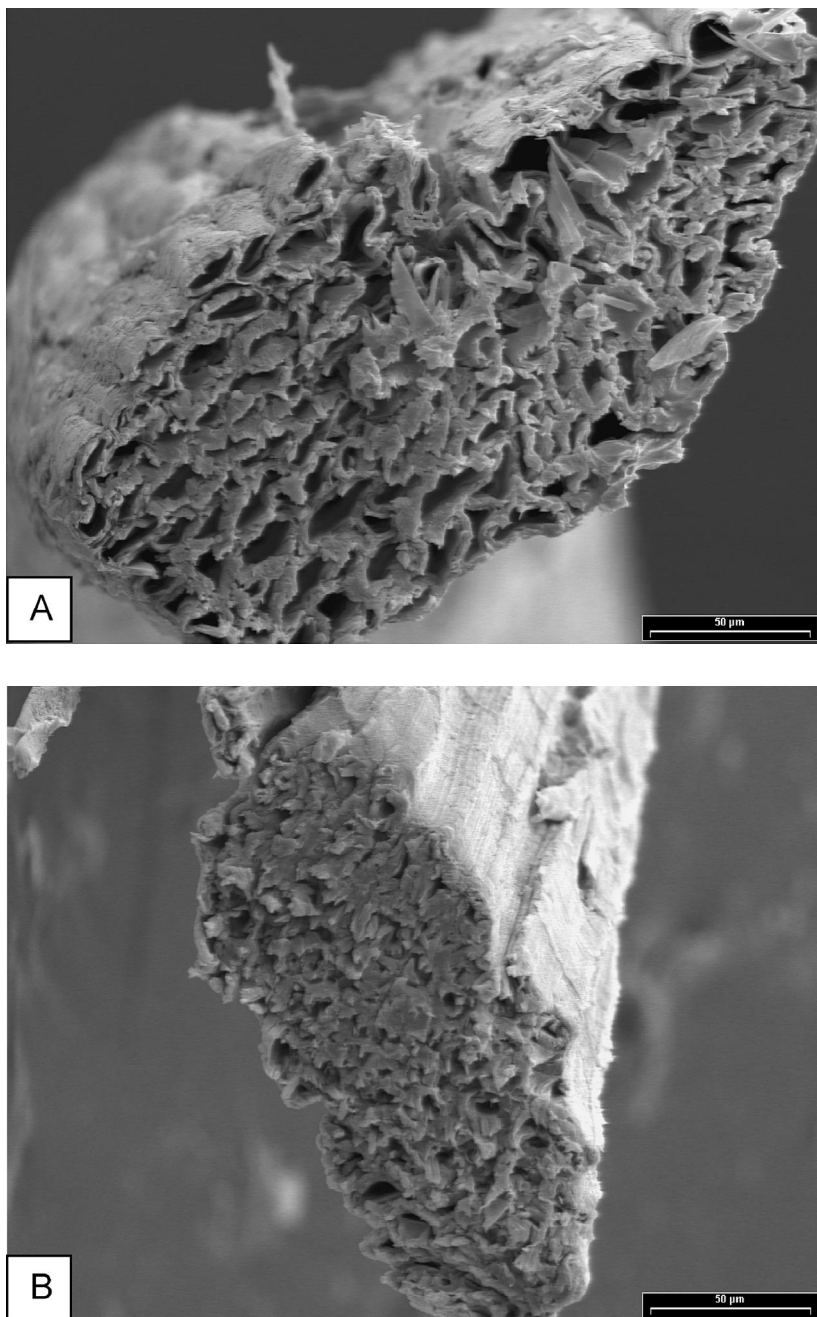


Figure 6. Scanning micrographs (SEM) for sisal technical fibers. (A) and (B) Cross section of untreated and treated sisal, respectively; (C) and (D) Surface of untreated and treated sisal, respectively.

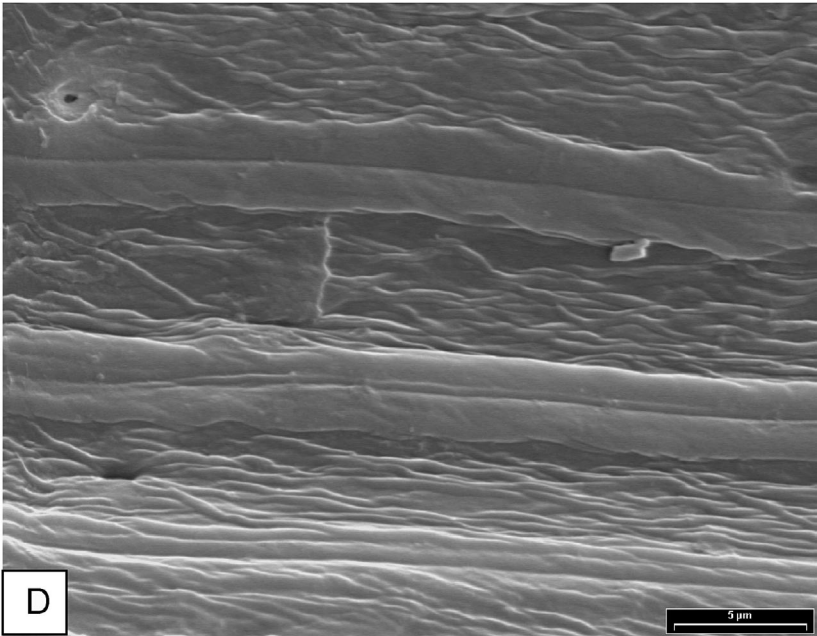
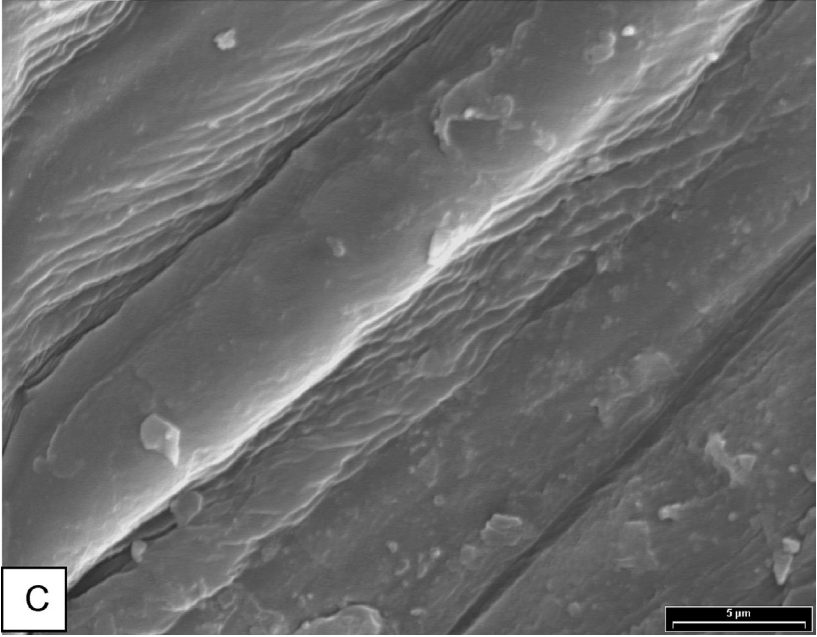


Figure 6. (Continued).

Table 3.

Equilibrium moisture content (EMC) of woodflours with different chemical treatments

Treatment	EMC (% weight gain) at 60 % RH
Untreated WF	11.28
Alkali treated WF	21.69
10% MAN treated WF	9.81
MAN treated WF (not pretreated)	6.18
ASA treated WF	6.18
Untreated sisal	8.35
MAN treated sisal	7.27

The surface of treated sisal fiber (D) shows a more leveled surface (less contrasting depths), presumably due to the attachment of the MAN molecules.

3.5. Water sorption of the fibers

The changes in the topology and chemistry of the woodflour particles described above have a direct correlation with the maximum amount of humidity that they are capable of absorbing under controlled conditions. Table 3 reports the equilibrium moisture content values (EMC) measured for the differently treated woodflour.

The alkali treatment reduces the content of lignin and hemicellulose that protect the cellulose fibers in the wood, and consequently a rougher and more open structure that also exposes a large concentration of cellulose hydroxyls and amorphous cellulose regions is available for water diffusion and physical bonding of the molecules to the particles. Consequently the values of humidity absorption increase after this treatment: the samples become more hygroscopic.

On the other hand, the MAN esterification generates a new protection for the particle surfaces, as was actually observed by SEM and consequently less water is physically bonded to the woodflour particles and the EMC is reduced. Similar effects of esterification on humidity sorption can be observed in the ASA-treated material and in the modified sisal fibers.

3.6. Reaction at the interphase

The aim of this part of the study was to confirm the co-reaction between modified lignocellulosics and the polyester matrix. Although the covalent bonding between filler and matrix has been frequently invoked in the literature [4, 31–33] to explain changes in the macroscopic properties, most times it has been not confirmed, because of the obvious complexity in identifying the reaction at the interphase of the composite. An exception would be the results discussed by Hill and Cetin [34], who demonstrated that methacrylic anhydride modified wood was able to form covalent bonds with styrene and methyl methacrylate monomers via free radical polymerization.

In the present work, samples of MAN esterified woodflour (no alkali pretreatment) were mixed with styrene monomer (80:20 by weight, respectively) and benzoyl

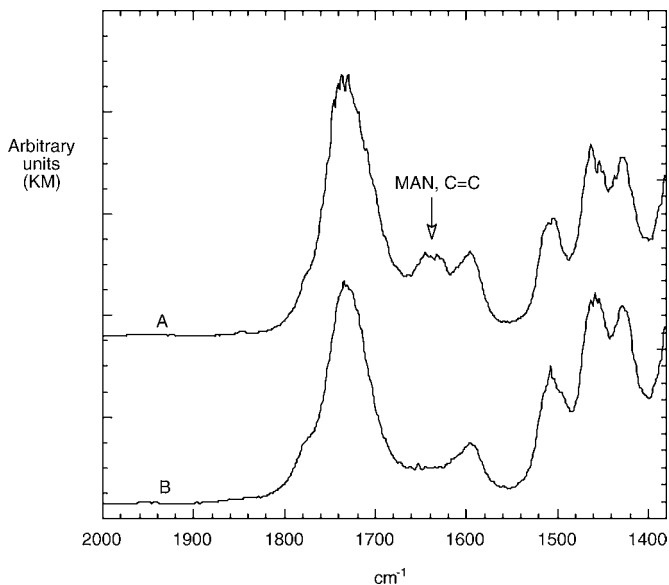


Figure 7. DRIFT spectra of esterified woodflour (A) and the same woodflour after being coreacted with styrene and extracted in toluene (B).

peroxide (1.5% by weight). This mixture (MaWFSt) was put into a mold and cured in a heated press as described in the composites preparation. The aim of this experiment was to check on the feasibility of the proposed co-reaction between the MAN attached to the woodflour and the unsaturated polyester resin, assuming that it occurs mainly through coreaction with styrene. The same test was performed with untreated woodflour mixed with styrene (WFSt).

The first observation was that the material obtained with the esterified woodflour showed a remarkable difference with respect to cohesion of the material obtained from untreated woodflour: the WFSt sample could be broken by simply applying bending forces by hand, powder-like debris was produced. The MaWFSt sample could be broken only using a hammer. In both cases, the pieces were further extracted in xylene to eliminate polystyrene homopolymer and finally, the dried material was analyzed by DRIFT technique. There were no changes in the DRIFT spectrum of the WFSt sample, as compared with that of the untreated woodflour.

Figure 7A shows the region of absorption of the C=C unsaturation of the attached MAN in the original esterified woodflour. It can be seen that the band disappears after reaction with styrene (Fig. 7B), indicating the copolymerization of the attached MAN. The presence of attached aromatic moieties is only insinuated in the corresponding absorption regions (1500, 1450 and the 700 cm^{-1}). This feature was to be expected according to the reactivity ratios of the participant species (styrene and wood-attached MAN); each co-reactant shows a much larger reactivity towards the other one than towards itself [35]. In a regular copolymerization this

would lead to a practically alternating copolymer (styrene–maleic anhydride) and in the present case to the multiple inter-linkage of the woodflour particles, which explains also the difficulty in breaking these samples.

Overall, the results confirm the previous assumption that the esterified lignocellulosic fillers can participate in the copolymerization reaction of the unsaturated polyester matrix [22, 28] through the reaction with styrene.

3.7. Interphase in lignocellulosics–UPE composites

3.7.1. Maximum filler concentration (woodflour). The mixing step of the preparation offered an eyes-on technique that allows woodflour composites to be graded according to the easiness of processing. The observations were used to determine the maximum amount of woodflour that could be incorporated into the polyester–styrene mixture. Low concentrations of woodflour particles (less than 20 wt%) led to fluid suspensions, while increasing amounts of particles produced thick pastes, until a point was reached where the product became a wetted powder.

In the case of the untreated woodflour, the maximum concentration achieved was approximately 45% by weight. Filler treatments changed the surface topology and chemical characteristics of particles, leading to changes in compatibility with the polymeric medium and to different mixing characteristics of the paste. Thus, the more rough and surface active alkaline treated WF could be incorporated up to a weight concentration of some 35–40%, while the 10% MAN-treated WF was added up to 60% approximately, still producing a thick, workable and homogeneous paste [22, 36]. In agreement with the above discussion, the lumens (hollow central section of the wood cell) of the 10% MAN woodflour were filled with the resin at all concentrations and up to 60% by weight (this feature is further discussed in a following section for a 30% MAN woodflour composite) while empty lumens were found in 40 wt% untreated woodflour composites [22], indicating that the compatibility and dispersion of the filler was improved by the chemical modification.

Unfortunately, the mixer used does not allow torque measurements to quantify the above observations, but further studies on the rheology of the pastes could be very valuable in modeling and optimizing larger scale processes.

3.7.2. Microscopy of the composites. Scanning electron microscopy (SEM) of untreated and MAN-treated sisal composites are shown in Fig. 8. Analysis of the micrographs of the composites shows that the treatment was effective in improving the interfacial adhesion, as the fiber appeared more tightly included in the resin and pieces of fiber surface were torn out for the case of MAN-treated sisal fibers (Fig. 8B). Besides some protrusions could still be seen on the untreated fiber surface (Fig. 8A) as observed previously in the original sisal fibers, indicating that almost no interaction was developed between fibers and matrix.

Additionally, Fig. 9 shows a MAN-treated woodflour composite (30% MAN sample) prepared at filler concentration of 40% by weight. The hollow central

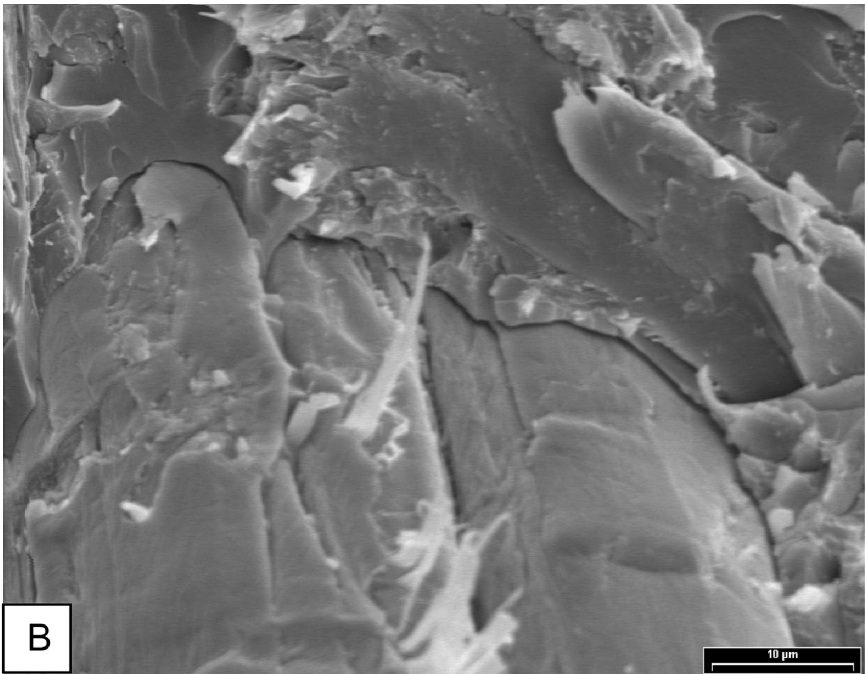
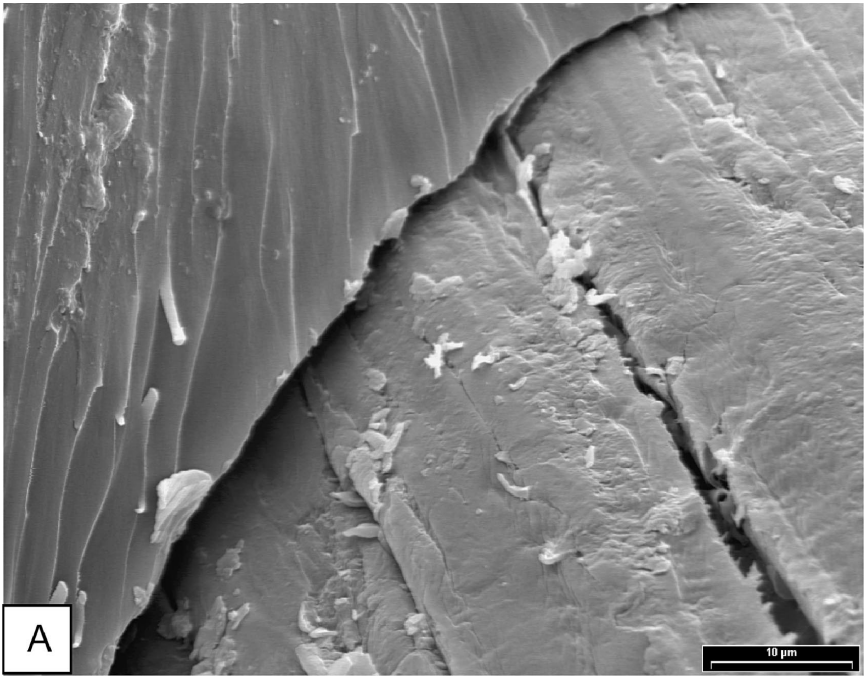


Figure 8. Scanning electron microscopy (SEM) of sisal composites. (A) untreated fibers; (B) MAN treated sisal.

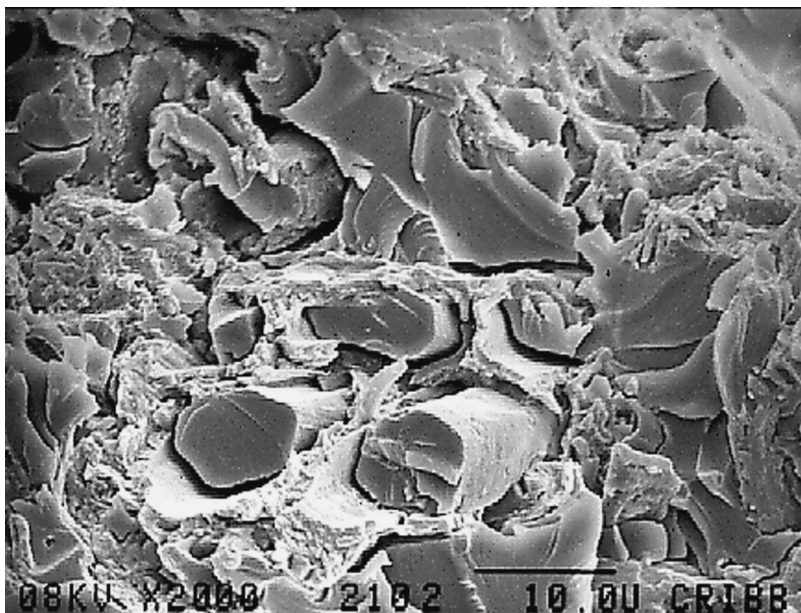


Figure 9. Scanning electron microscopy (SEM) of 30% MAN woodflour composite.

region of the wood cells, the lumen, can be seen. Because the fillers are treated and there is good wetting and compatibility between the particles and the polymer, the resin is able to penetrate the lumen. This feature is quite interesting, since it would readily reduce the empty spaces in the composites, while decreasing the capillarity effects during water or humidity sorption through the fillers ends. The effect of capillarity had been mentioned previously by Li *et al.* [33], who suggested sealing off the external surfaces of sisal composites using water-repellents, so as to keep water uptake in the material to a minimum.

3.8. Interphase effects on selected composite properties

The different treatments of the fillers had an important effect on the surface morphology of the particles or fibers, their chemistry and consequently their hygroscopicity. Moreover, these changes were shown to affect their dispersability in the polymer matrix. In this section, the effect of the filler treatments on the interface and selected mechanical properties of the formulated composites is analyzed.

3.8.1. Flexural properties (short sisal fibers). The comparison of the stress–deformation curves obtained in the flexural tests of short sisal fiber composites with different treatments can give interesting qualitative information with respect to the role of the interphase in the composites investigated.

In Fig. 10, representative curves of true stress *vs.* deformation for the composites prepared with the unsaturated polyester resin and sisal short fibers are shown. In this case, untreated sisal fibers, fibers washed in acetone and MAN-esterified fibers

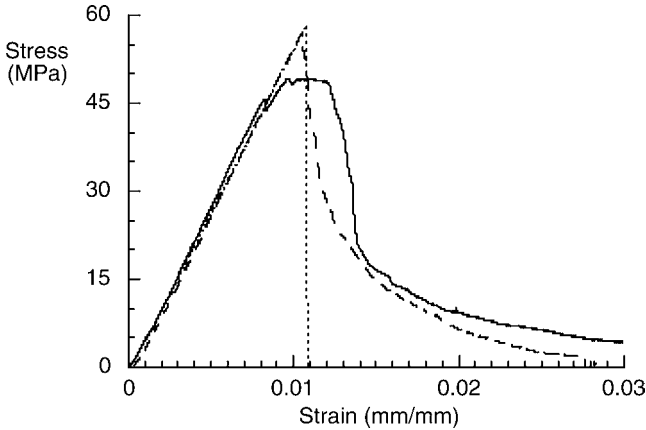


Figure 10. Representative curves of true stress vs. deformation for composites prepared with short sisal fibers. — Untreated fibers; ---- acetone washed fibers; ····· MAN treated fibers.

(Table 2) were utilized in the composite preparation at a weight concentration of 40%. Although little differences are observed in the value of the modulus of the materials, the maximum stress reached varies with the treatment and, even more revealing, the materials fail in a quite different form. If untreated sisal fibers are used, the stress–deformation curve reaches the maximum stress and after a short plateau, the stress drops and the curve becomes slightly serrated as deformation increases. The behavior is the result of the debonding of the fibers, which dissipates more energy as new surfaces are created during the breakage of the material. Consequently, the rupture of the material is progressive and not catastrophic.

After washing the sisal with acetone, original waxes of the sisal fibers are eliminated and better mechanical anchorage of the polymer to the fiber occurs. Because of that, there is less contribution from debonding and less energy is consumed in the rupture of the material. Accordingly, the area under the stress–deformation curve is lower due to a more marked drop of the stress value. There is still some contribution from debonding of the fibers.

Finally, when the fibers are treated with maleic anhydride, improved adhesion is expected between fibers and matrix. The maleic moieties chemically attached to the fibers can also participate in the free-radical copolymerization of the unsaturated resin and styrene, as presented in Fig. 7 and discussed in a previous section. This effect is clearly illustrated in the corresponding stress–deformation in Fig. 10. The strength of the interphase is strong in this material due to the covalent bonds formed between the two main phases, matrix and fibers. However, as a result, the composite behaves as a monolithic material, and simultaneous fracture of the resin matrix and the fibers occurs immediately after reaching the maximum stress.

Similar results have been discussed by Ray *et al.* [12] for composites made from untreated and alkaline treated jute and a vinyl ester resin. As the interface becomes stronger with the treatment, the contribution from fiber debonding to composite toughness disappears.

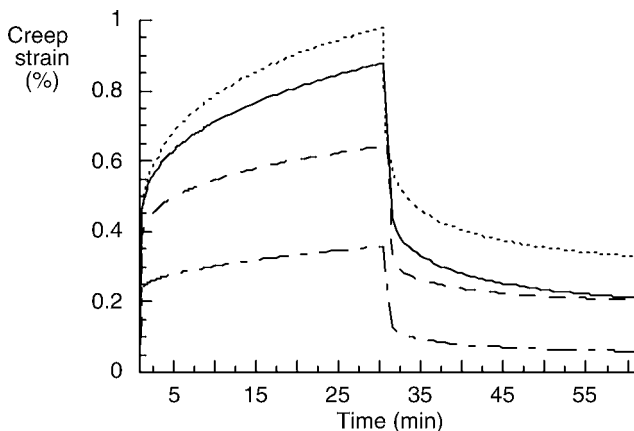


Figure 11. Creep curves for the neat resin and composites prepared at 40% by weight of woodflour with different esterification degrees. — UP resin; --- untreated woodflour composite; - · - · - 10% MAN composite; · · · · · 58% MAN composite.

3.8.2. Short-term creep experiments (woodflour particles). Creep tests are very revealing of differences in the strength of the woodflour composite interfaces, but this is a technique that has not been reported often for these materials in the literature. Short-term creep tests were performed on 40% woodflour samples with different filler treatments. The tests were performed at 100°C in order to accelerate the creep processes of the rigid thermoset composites.

Figure 11 shows the creep and creep recovery behavior of the neat resin and woodflour composites prepared at 40% by weight of woodflour with different degrees of esterification.

The addition of a rigid filler reduces the creep deformation of the network as observed by comparison of the neat polyester resin and the untreated woodflour composite. However, there is a more important reduction in the creep deformation if the woodflour has been treated with MAN. It is clear that the effect of changing the chemical nature of the woodflour surface produces a stronger adhesion between filler and matrix, which leads to reduced deformation. The advantages in using a 30% MAN-treated woodflour rather than a 10% MAN-treated woodflour is secondary. This probably occurs because at high degree of MAN grafting the filler surface is already saturated with the anhydride; also, the bulk of the woodflour is compromised and consequently so is the rigidity of the particles. This effect is clearer in the behavior of the 58% MAN-treated woodflour, in which the degree of esterification is so high that the woodflour properties are severely changed. Plastification may take place due to the chemical treatment [27, 37–40]. Analogously, other authors have also found optimum degrees of treatment for the fillers, above which properties deteriorate [12].

The 10% MAN-treated woodflour shows that not only the instantaneous deformation (deformation at time \rightarrow 0) is reduced but also the creep rate at longer times is lower. Consequently, the permanent set is also small. This improved creep behavior

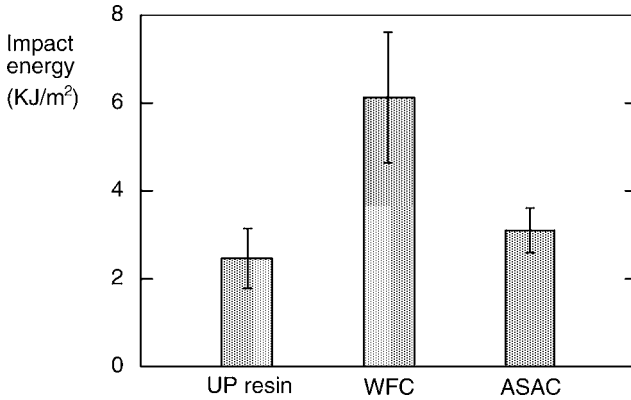


Figure 12. Izod impact strength of polyester resin and woodflour composites.

is the result of the increased strength of the interface, so that a much better transfer of the imposed load from the matrix to the rigid woodflour particles occurs and thus, the creep is reduced.

3.8.3. Impact properties (woodflour particles-ASA esterification). Figure 12 illustrates the effect of esterifying the woodflour particles with the relatively longer alkenyl succinic molecule, ASA. The Izod impact energy measured for the unfilled thermoset suffers an important increase by addition of untreated woodflour particles (WFC). Since the particles are not strongly attached to the matrix the measured impact strength is high, due to the mechanism by which the particles are separated from the matrix helping to create rough new surfaces during the fracture and thus, consuming more energy. Instead, if the particles are treated with ASA, the adhesion at the interface matrix–woodflour particles is improved; there is less separation of the particles from the matrix during fracture and less energy is consumed in the process of creating the new fracture surfaces. This is the reason for the observed trend in Fig. 12.

4. CONCLUSIONS

4.1. Fillers

Alkaline treatment and esterification with two different anhydrides were performed on woodflour and short sisal fibers. The overall results of the modifications were common for both lignocellulosic fillers as reinforcements.

Alkali treated fillers showed rougher surface micromorphologies than untreated fillers, while increased sensibility to humid environments was ascertained by measurements of the equilibrium moisture content (EMC) in controlled environments.

The degree of esterification of the filler can be tailored through selection of temperature and time of the reaction. MAN attachment to the fillers generated a

smoother surface and reduced their hygroscopicity. Similar results, although with lower weight gains were obtained with ASA esterification.

For all the treatments, DRIFT was shown to be an efficient technique to investigate the occurrence of the different reactions.

4.2. Composites

Esterification improved wetting and dispersion of the fillers in the resin, so that it was possible to reach higher maximum concentrations of woodflour in the polyester composites. The co-reaction of esterified fillers with the styrene was investigated and confirmed by DRIFT technique, which indicated undoubtedly the formation of covalent bonds between the treated filler and the polymer.

In general, the esterification method of the lignocellulosic filler/fibers produced unsaturated polyester composites of higher stiffness and resistance to creep, but reduced toughness. Both anhydrides showed similar trends. Because of the higher molar mass, ASA treatment was restricted to the filler surface, while it is possible to produce bulk changes in the filler by using MAN and long reaction times. Mechanical properties were however, reduced at high esterification levels.

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