

Sisal Fibers Treated with NaOH and Benzophenonetetracarboxylic Dianhydride as Reinforcement of Phenolic Matrix

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Received 8 May 2009; accepted 13 July 2009

DOI 10.1002/app.31113

Published online 27 August 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this work, composites based on a phenolic matrix and untreated- and treated sisal fibers were prepared. The treated sisal fibers used were those reacted with NaOH 2% solution and esterified using benzophenonetetracarboxylic dianhydride (BTDA). These treated fibers were modified with the objective of improving the adhesion of the fiber–matrix interface, which in turn influences the properties of the composites. BTDA was chosen as the esterifying agent to take advantage of the possibility of introducing the polar and aromatic groups that are also present in the matrix structure into the surface of the fiber, which could then intensify the interactions occurring in the fiber–matrix interface. The fibers were then analyzed by SEM and FTIR to ascertain their chemical composition. The results showed that the fibers had been

successfully modified. The composites (reinforced with 15%, w/w of 3.0 cm length sisal fiber randomly distributed) were characterized by SEM, impact strength, and water absorption capacity. In the tests conducted, the response of the composites was affected both by properties of the matrix and the fibers, besides the interfacial properties of the fiber–matrix. Overall, the results showed that the fiber treatment resulted in a composite that was less hygroscopic although with somewhat lower impact strength, when compared with the composite reinforced with untreated sisal fibers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 269–276, 2010

Key words: adhesion; surfaces; composites; fibers; modification; thermosets

INTRODUCTION

Over the past decade, there has been increasing interest bestowed on the development of new materials using natural resources, especially of renewable resources.^{1–3} This interest is mainly related to some advantages of these materials, the economic aspect being one of the more important. Besides, new- and stricter environmental policies have compelled industries to search for new materials that can substitute the traditional composite materials containing inorganic filler as the reinforced phase of its polymeric matrices.^{2,4–7}

Because of the advantages of natural fibers, cellulose-based fibers have been used as reinforcements in composite materials. In the automotive industry,

for example, natural fibers such as sisal, jute, cotton, and flax have begun to be used in trucks, cars, and buses, for bumpers, roofs, doors, panels, seats, etc.^{4,8} Furthermore, apart from the packaging- and electronic industries,⁴ natural fibers are now used in the aircraft industry (for seats and fuel tanks).

Compared with some synthetic fibers, the major advantages of natural fibers, besides cost, are low density, high specific properties, and modest abrasivity during processing, renewability, biodegradability, and almost unlimited availability.^{2,9–11} Sisal is one of the most used natural fibers because of its excellent mechanical properties and availability.^{12–16}

Despite all these advantages, when used as reinforcement for polymeric matrices natural fibers present some disadvantages, such as high moisture absorption, poor wettability, and incompatibility with some types of polymeric matrices.^{17–19} It is possible to improve these properties and make these fibers more compatible with some matrices. Fibers subjected to physical- and/or chemical treatments make it possible to use them to prepare composites with better fiber–matrix adhesion and less hygroscopic qualities, despite the loss of fiber strength that may occur simultaneously. Such treatments

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Contract grant sponsors: CNPq (National Research Council, Brazil) and FAPESP (The State of São Paulo Research Foundation, Brazil).

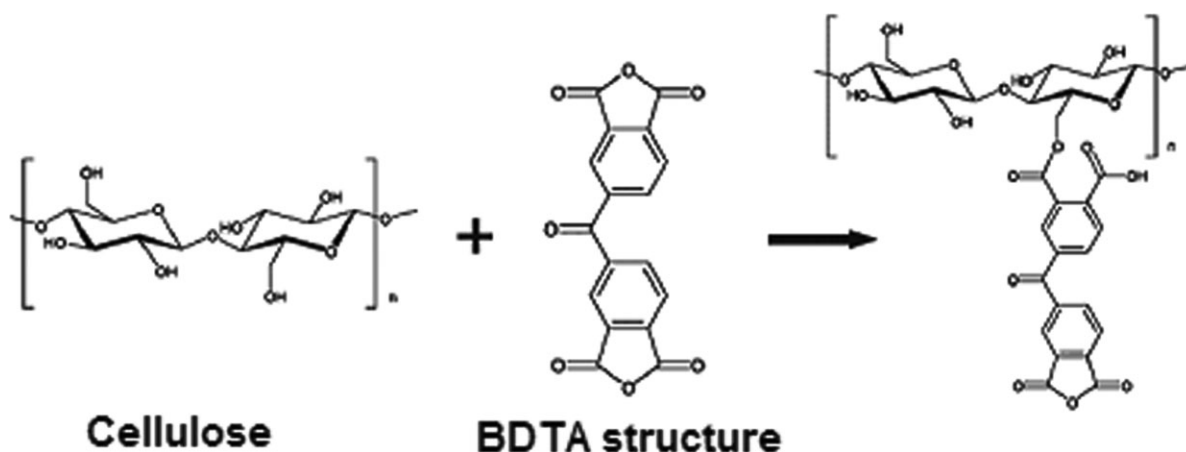


Figure 1 Example of BTDA modification on the cellulose surface.

must be selected according to the nature of polymeric matrix.^{3,13,17,20,21}

According to ASTM D1965, mercerization “is the process of subjecting a vegetable fiber to an interaction with a fairly concentrated aqueous solution of a strong base, to produce great swelling with resultant changes in the fine structure, dimension, morphology and mechanical properties.”³ Alkali treatment while partly removing hemicellulose and lignin also removes natural- and artificial impurities from fiber surfaces leading to improved adhesive characteristics of the fibers.²²

Chemical modification, esterification for instance, can also be used to modify the fiber surface. In this reaction, the cell wall hydroxyl (OH) groups of the fibers are replaced by coupling agents, which make the fibers less hydrophilic and, depending on the nature of the polymer used to prepare the composite, render them more compatible with the matrix.⁹ These modifications must, however, be limited to the superficial OH groups to preserve the integrity and thereby the mechanical strength of the fibers.¹⁰ Normally, esterification improves several properties of fibers such as the dispersion of lignocellulosic materials in the matrix, the wettability, as well as the dimensional stability, and the interface of the final composite.^{4,9}

In this work, aimed at improving adhesion at the interface, sisal fibers were submitted to mercerization and esterification (by reaction with benzophenonetetracarboxylic dianhydride, BTDA). Untreated- and treated fibers were used to reinforce thermoset phenolic matrices.

Phenolic resins present superior fire resistance and have a cost considerably lower than those of many others high performance resins. They also exhibit excellent dimensional and thermal stability, which makes this material more attractive for large-scale applications. The thermomechanical properties of phenolic resins are related to their high crosslinking density after curing, which also gives them low impact strength. This has contributed to the state of the art of the research of com-

posites based on phenolic matrix, as to increase impact strength, a property relatively low in phenolics, has become the objective of several researches in an effort to develop materials with better properties.³

BTDA was chosen to modify the sisal fibers because of the scope available to introduce polar- and aromatic groups into the fiber surface, which in turn could intensify the interactions at the interface fiber-matrix, as these groups are also present in the matrix structure.

EXPERIMENTAL

Fibers

The sisal fibers, *Agave sisalana*, used in this study were made available to us by courtesy of “Cachoeira do Brumado,” Mariana city, Minas Gerais State, Brazil.

The fibers were washed with distilled water and dried at room temperature for 48 h and then extracted (Soxhlet) with cyclohexane/ethanol (1 : 1, v/v) over a period of 48 h and dried using a stove. Mercerization (with 2% NaOH solution) was carried out at room temperature for 2 h. The fibers were washed with distilled water until the alkali was completely eliminated, after which they were dried in a stove at $100 \pm 5^\circ\text{C}$. Benzophenonetetracarboxylic dianhydride (BTDA) was used for the esterification reactions (Fig. 1) of mercerized fibers, which were carried out in acetone, with triethylamine as catalyst, for 48 h at 70°C . To each 1.0 g of sisal fiber, 2.5 g of the dianhydride (BTDA) was added with 1.5 mL of the catalyst (triethylamine). After the reaction had concluded, the fibers were washed with acetone and dried in a stove at $100 \pm 5^\circ\text{C}$, until constant weight was recorded.

Composites

Phenol, formaldehyde, and potassium hydroxide (in the proportion 1.38 : 1.0 : 0.06 w/w, respectively)

TABLE I
Composites Molding Cycle Cure

Time (min)	Temperature (°C)	Force (ton) (1 ton = 49.3 kg/cm ²)
30	75	5.0
30	75	7.5
30	85	10.0
30	85	12.5
30	85	15.0
30	95	17.5
30	105	20.0
60	115	20.0
90	125	20.0

were used to prepare the phenolic prepolymer. These reagents were mixed by mechanical stirring, under reflux (70°C). The solution was allowed to cool at room temperature and neutralized with HCl. Water was eliminated under reduced pressure.

Resorcinol 10% (w/w) was added and the system heated (at 50°C) for 30 min to dissolve the resorcinol completely. The phenolic resin was then ready to be mixed with the sisal fibers (15% w/w, 3.0 cm) and molded. The average thickness of sisal fibers was between 300 and 400 μm and can be variable in fibers along their length. Table I shows the molding cycle cure and the pressure used to produce the composites.

The mold was cooled to room temperature, under pressure. The composites were prepared with randomly oriented sisal fibers (treated and untreated).

Characterization

Cellulose-, hemicellulose-, lignin-, and ash contents of the sisal fibers were determined by methods specified by the TAPPI T19m-54, TAPPI T13m-54, and TAPPI T211om-85 standards. At least three samples of each material were tested, and the average values obtained are reported in the next section (Table II). For all these measurements, three trials were found to be a very reliable method.

Fourier Transformed Infrared (FTIR) spectroscopy was carried out in an Impact 410—Nicolet equipment in a transmittance mode by using KBr pellets methodology.

For arriving at the degree of crystallinity of the sisal fibers, X-ray diffractograms were recorded on a Shimadzu (XRD-600) X-ray diffractometer equipped with Fe radiation and Mn filter. The XRD patterns were obtained between 14° and 35° (2θ) at a scanning speed of 2°/min. The peak intensities were computed after subtracting the background and $K_{\alpha 2}$ contributions. The crystallinity index was then calculated using the Buschle-Diller and Zeronian (Buschle-Diller et al., 1992) eq. (1):

$$I_c = \frac{1 - I_1}{I_2} \quad (1)$$

where I_1 is the intensity at the minimum (2θ value between 22° and 23°), and I_2 is the intensity associated with the crystalline region of cellulose (2θ value between 28° and 29°).

The impact assays were performed on an Alfred J. Amsler & Co. – Schoffhausen 126/176 Charpy impact machine. The test method adopted was in conformity with the ASTM D256 method B. Nearly 15 samples (63.5 × 12.7 × 4.0 mm) per composite were analyzed.

A JEOL scanning electron microscope, model 5510, was used to analyze surface topographies of the untreated- and treated fibers and also of the impact-fractured surfaces of the composites after covering the samples with carbon in vapor phase (JEOL JEE 4C evaporator). The magnifications were variable according to the analyzed sample (Figs. 3–5).

The composites were evaluated for their water absorption capacity. The tests were carried out both after 24 h of immersion and up to saturation and were in accordance with the ASTM D570 standard (samples were of dimensions 76.2 × 25.4 × 3.2 mm).

RESULTS AND DISCUSSION

Sisal Fibers

Table II presents the chemical composition of the untreated- and alkali treated sisal fibers.

Several researchers reported that the climatic conditions, type of soil, extractive method, age, and digestion process influence not only the structure of fibers but also the chemical composition.^{4,21} However, in this work, values of the lignin-, cellulose-, and hemicellulose contents of sisal fibers obtained are consistent with those reported in the literature.^{4,23} Besides, the ash- and moisture contents

TABLE II
Composition of Sisal Fibers

Component	Untreated sisal fibers content (% w/w)	Sisal fibers treated with NaOH 2% content (% w/w)
Ash	0.9 ± 0.2	1.0 ± 0.1
Humidity	9.0 ± 0.5	7.0 ± 0.5
Extractives	3.5 ± 0.5	–
Total Klason Lignin	9.4 ± 1.0	9.0 ± 1
Cellulose	64.5 ± 0.5	74 ± 0.5
Hemicellulose	17.5 ± 0.5	7.0 ± 0.5
Holocellulose	82 ± 1	81 ± 2
(cellulose + hemicellulose)		

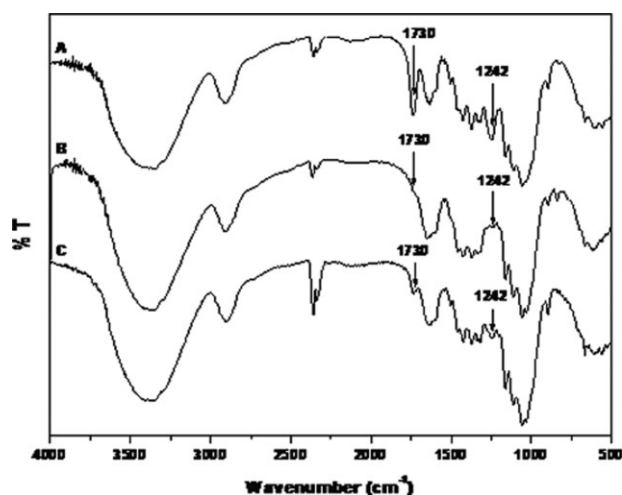


Figure 2 FTIR spectrum of sisal samples. (A) PCU (phenolic composite reinforced with untreated fibers); (B) PCM (phenolic composite reinforced with mercerized fibers); and (C) PCM_{BTDA} (phenolic composite reinforced with BTDA esterified fibers).

(Table II) of sisal fibers obtained are in agreement with the values reported in the literature for lignocellulosic fibers.^{4,14,22–24}

The analysis of the results of Table II reveals that the alkaline treatments changed the composition of the fibers, mainly hemicellulose. As was already observed for other lignocellulosic fibers,²² sisal hemicellulose is much more sensitive to the action of NaOH than lignin or cellulose. As the contents of holocellulose (cellulose + hemicellulose) had not changed the content of cellulose increased artificially because of the reduction of the hemicellulose content.

The concentration of the acids in the sisal groups increased from 1.36 (for untreated fibers) to 2.25 mmol/g (for fibers treated with BTDA). This result treated as an indication of effectiveness of the reaction, as carboxylic groups are introduced by esterification (Fig. 1). FTIR analyses of these fibers also indicate some modifications occurring in the samples after the treatments were carried out (Fig. 2).

It can be seen that the peak at 1730 cm^{-1} , present in the untreated sisal fiber, disappeared after treatment with NaOH 2%. The band in the spectrum near 1730 cm^{-1} is attributed mainly to C=O stretching vibration of the carbonyl- and acetyl groups in the “xylan” component of hemicellulose and also of the chemical groups of lignin.⁹ This peak (around 1730 cm^{-1}) reappeared after BTDA treatment, although with lower intensity, indicating that the esterification reaction had occurred. Another band around 1240 cm^{-1} that has disappeared after alkali treatment reappeared after the reaction with BTDA. This band near 1240 cm^{-1} corresponds to axial asymmetric strain of =C–O–C, common where

=C–O– occurs, e.g., in ether, ester, and phenol. Alkali treatment probably broke some ether bonds (α - and β -O-4) at the lignin molecule, which can explain the complete disappearance of this band in the FTIR spectrum.

Table III displays the results for the crystallinity index of the untreated- and treated sisal fibers.

According to some authors, the increase in the crystallinity index of alkali-treated fibers occurs because of the removal of cementing materials (such as lignin) and/or amorphous portions (such as lignin and hemicellulose) of the fibers, which leads to a better packing of the cellulose chains.^{4,25} The results shown in the Table III corroborate this finding, because nearly 50% of the hemicellulose present in the sisal fiber was extracted by the alkali treatment. In a general sense, it can be considered that the esterified fibers have lower crystallinity than the alkali-treated ones, which can be taken to be an indication that the reagent also reached the cellulose crystalline domains.

The SEM images showed some changes in the surface morphology of the treated sisal fibers (Fig. 4), when compared with the untreated fibers [Fig. 3(A,B)].

The presence of some parenchyma cells and impurities (e.g., dust and inorganic materials) on the surface of the untreated fibers can be seen [Fig. 3(A,B)].

On comparing the images of the Figure 4 with those in Figure 3, the removal of some natural- and artificial impurities of the sisal fibers by the alkali treatment after mercerization treatment (NaOH 2%) is discernible. According to Joseph et al.²⁶ the alkali treatment leads to fibrillation or a fiber separation process, i.e., break-down of the bundle of fiber composites into smaller fibers, leading to an increase in the effective surface area available for contact with the matrix. Despite the presence of some fissures (indicating the fibrillation) on the surfaces of the fibers, their integrity seems to have been preserved after the alkali treatment.

Figure 5 displays the SEM images of sisal fibers after reaction with BTDA.

As a result of the treatments, the fiber has acquired a rough surface topography as is evident from Figure 5(A,B). In Figure 5(B), it is possible to detect a crevice in the surface of the fiber that permits the polymer matrix to penetrate the fiber

TABLE III
Crystallinity Index of Untreated and Treated Sisal Fibers

Sisal fiber	% Crystallinity (I_c)
Untreated	76.8 ± 2.1
Alkali treated	85.4 ± 2.6
Alkali treated and reacted with BTDA	81.7 ± 2.3

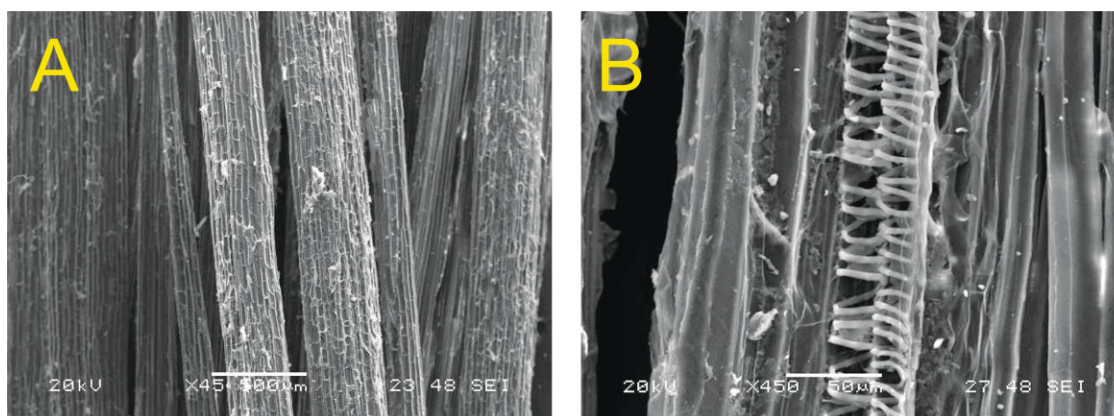


Figure 3 SEM micrographs of untreated sisal fibers (A and B). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

making the treated fibers adhere more firmly to the matrix.

The mercerization as also the esterification treatment produces an improvement in the wettability property; this fact was observed when the composites were processed and will be discussed later.

Composites

Figure 6 shows the impact strength of resin (PT) and the composites reinforced with untreated (PCU), mercerized (PCM), and esterified fibers (PCM-BTDA).

The impact strength of the phenolic composites is considerably higher than that of the phenolic thermoset (Fig. 6), indicating that fiber acts as effective reinforcement of phenolic matrices, as was already observed in previous studies.³ The composites reinforced with untreated mercerized fibers have practically the same impact strength as mercerized ones

and esterification of fibers leads to a composite with a lower impact strength. The esterification can promote a partial degradation of fibers that affects their mechanical properties and therefore their action as reinforcing agent.

However, the alkali and also the esterification facilitated the prepolymer flux in the lignocellulosics networks and then it was observed that due to the better wettability of the treated fibers, the composites they reinforced absorbed less water, as shown in Figure 7. In the case of the fibers treated with BTDA, the presence of polar groups and aromatic rings in both the fiber surface and the matrix probably collaborated to intensify the interactions between them. More efficient adhesion at the interface reduces the number of microcavities and thereby the number of water molecule clusters.²²

Besides the above considerations relating only to the hygroscopicity of fibers, it must be pointed out that hemicellulose is believed to be mainly

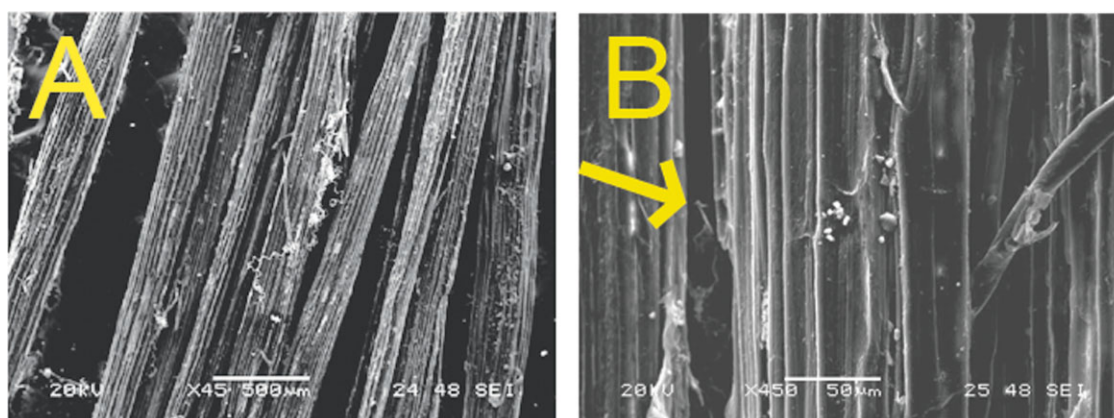


Figure 4 SEM micrographs of sisal fibers treated with NaOH (2%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

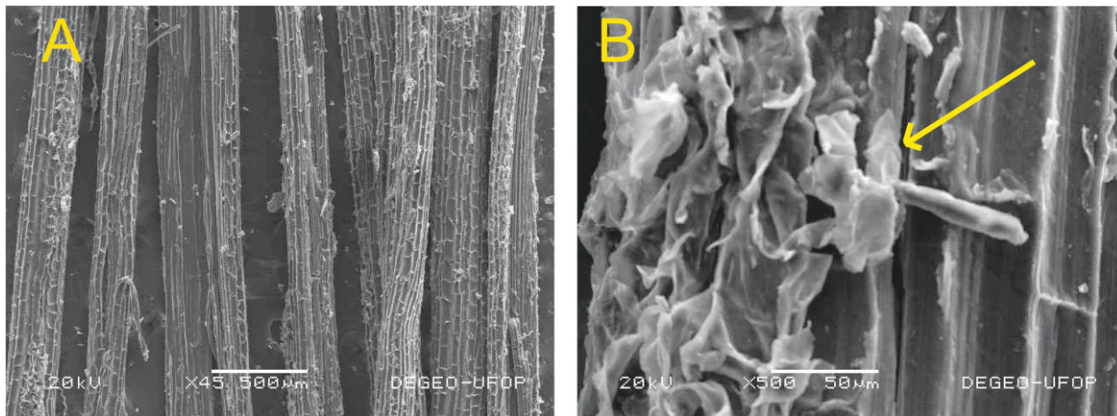


Figure 5 SEM micrographs of fibers treated with BTDA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

responsible for water uptake, as it is more accessible than the crystalline regions of the cellulose. Therefore, the extraction of hemicellulose by the alkali treatment probably further lowered the water absorption capacity of the composites reinforced with treated fibers, when compared with the composites reinforced with untreated fibers.

Figure 8 shows SEM micrographs of impact-fractured surfaces of the composites.

In Figure 8(A), the arrows indicate that the phenomenon of “pull out” that occurred to a greater extent in the composites with untreated fibers than in those with treated fibers (C and F). In (B) a better “pull out” phenomenon is visible where the fibers

have been uprooted from the matrix leaving behind a hole. This reveals the weak interfacial adhesion present between the matrix and untreated sisal fiber; in other words, it shows the incompatibility of fiber and matrix.

In the figures of the composites fibers treated with NaOH 2% and with BTDA (C and E), signs of both “pull out” (indicated by arrows in D) and some tearing of the fibers (indicated by arrow in F) are visible; in other words, the reduction of the “pull out” phenomenon and the occurrence of more at the broken fiber ends/sites suggest the failure occurred at the fibers due to the strong adhesion between the matrix and the treated fibers.

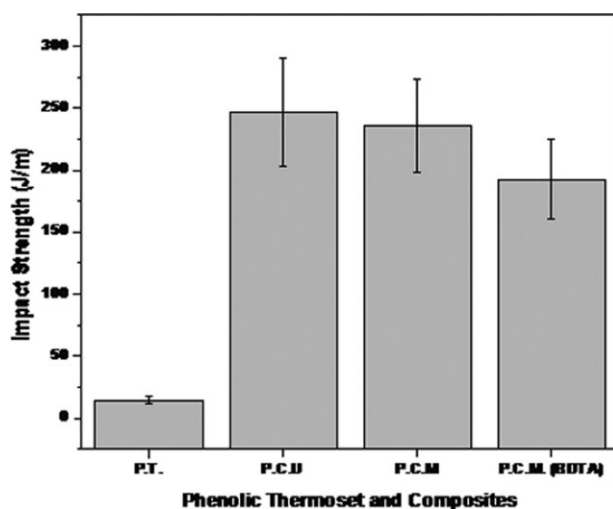


Figure 6 Impact strength of composites reinforced with untreated- and treated sisal fibers, where PT: phenolic thermoset, PCU: phenolic composite reinforced with untreated fibers, PCM: phenolic composite reinforced with mercerized fibers, and PCM_{BTDA} : phenolic composite reinforced with BTDA esterified fibers.

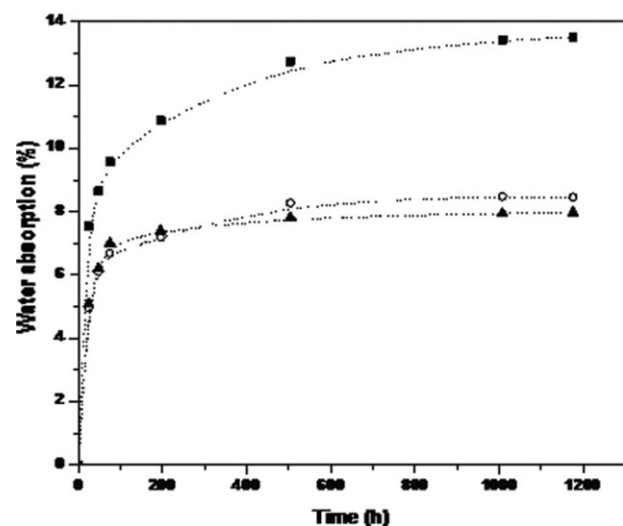


Figure 7 Water absorption as a function of time for: ■ PCU (phenolic composite reinforced with untreated fibers), ○ PCM (phenolic composite reinforced with mercerized fibers), and ▲ PCM_{BTDA} (phenolic composite reinforced with BTDA esterified fibers).

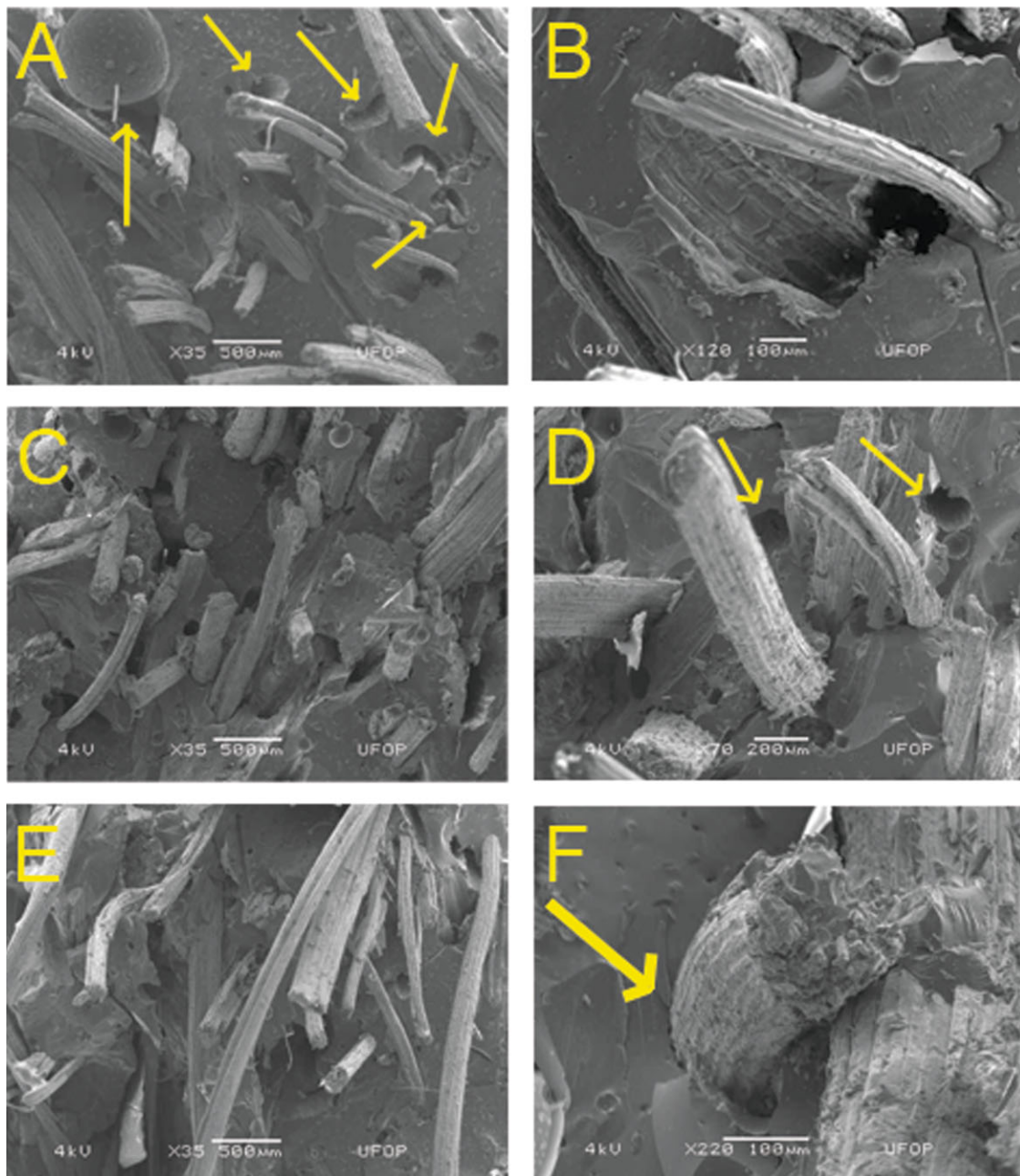


Figure 8 SEM micrographs of impact fracture surfaces of phenolic composites with untreated sisal fibers (A and B), with NaOH 2%-treated fibers (C and D) and with BTDA-treated sisal fibers (E and F). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

It was possible to improve the impact strength of the phenolic thermoset by means of reinforcing this polymer with sisal fibers and also to characterize the modifications attributed to the fibers and their influence on the composites. Although the impact strength of composites with treated fibers is lower than that of the composites with untreated fibers, the SEM micrographs of the impact fracture surfaces showed that all such treatments carried out improve interfacial adhesion between sisal and phenolic thermoset. The water

absorption capacity of the composites can be improved by modifying the sisal fiber surface by treatment with alkali and by esterification of the fibers with dianhydrides such as BTDA.

References

1. Satyanarayana, K. G.; Sukumaran, K.; Mukherjee, P. S.; Pavithran, C.; Pillai, S. G. K. *Cem Concr Compos* 1990, 12, 117.
2. Karlsson, S.; Espert, A.; Vilaplana, F. *Compos Part A Appl Sci Manuf* 2004, 35, 1267.

3. Frollini, E.; Paiva, J. M. F.; Trindade, W. G.; Razera, I. A. T.; Tita, S. P. In *Natural Fibers, Polymers and Composites—Recent Advances*; Wallenberger, F., Weston, N., Eds. Kluwer Academic Publishers: Boston, Dordrecht, New York, London, 2004, p 193.
4. Gassan, J.; Bledzki, A. K. *Prog Polym Sci* 1999, 24, 221.
5. Thomas, S.; Joseph, K.; Paul, A. *Compos Technol* 1997, 57, 67.
6. Trindade, W. G.; Hoareau, W. J. D.; Razera, I. A. T.; Castellan, A.; Frollini, E. *Biomacromolecules* 2005, 6, 2485.
7. Zárate, C. N.; Aranguren, M. I.; Reboredo, M. M. *J Appl Polym Sci* 2008, 107, 2977.
8. Schuh, T.; Gayer, U. In *Lignocellulosic-Plastics Composites*; Leão, A. L., Frollini, E., Carvalho, F. X., Eds.; UNESP-USP, São Carlos, São Paulo, Brazil, 1997.
9. Panayiotou, C.; Simon, F.; Zafeiropoulos, N. E.; Tserki, V. *Part A Appl Sci Manuf* 2005, 36, 1110.
10. Belgacem, M. N.; Gandini, A.; Pasquini, D.; Curvelo, A. A. S. *J Colloid Interface Sci* 2005, 295, 79.
11. Trindade, W. G.; Paiva, J. M. F.; Leão, A. L.; Frollini, E. *Macromol Mater Eng* 2008, 293.
12. Jacob, M.; Varughese, K. T.; Thomas, S. J. *Appl Polym Sci* 2006, 102, 416.
13. Megiatto, J. D., Jr.; Oliveira, F. B.; Rosa, D. S.; Gardrat, C.; Castellan, A.; Frollini, E. *Macromol Biosci* 2007, 7, 1121.
14. Oliveira, F. B. O.; Gardrat, C.; Enjalbal, C.; Frollini, E.; Castellan, A. *J Appl Polym Sci* 2008, 109, 2291.
15. Navarro, F.; Dávalos, F.; González-Cruz, R.; López-Dellamary, F.; Manríquez, R.; Turrado, J.; Ramos, J. *Appl Polym Sci* 2009, 112, 479.
16. Djidjelli, H.; Boukerrou, A.; Founas, R.; Rabouhi, A.; Kaci, M.; Farenc, J.; Martínez-Vega, J.-J.; Benachour, D. *J Appl Polym Sci* 2009, 106, 2925.
17. Wambua, P.; Ivens, J.; Verpoest, I. *Compos Sci Technol* 2003, 63, 9.
18. Buschle-Diller, G.; Zeronian, S. H. *J Appl Polym Sci* 1992, 45, 967.
19. Horeau, W.; Oliveira, S.; Siegmund, B.; Frollini, E.; Castellan, A. *Macromol Mat Eng* 2006, 291, 829.
20. Ansell, M. P.; Aziz, S. H.; Clark, S. J.; Panteny, S. R. *Compos Sci Technol* 2005, 65, 525.
21. Sydenstricker, T. H. D.; Mochnaz, S.; Amico, S. C. *Polym Test* 2003, 22, 375.
22. Razera, I. A. T.; Frollini, E. *J Appl Polym Sci* 2003, 91, 1077.
23. Li, Y.; Mai, Y.-W.; Ye, L. *Compos Sci Technol* 2000, 60, 2037.
24. Megiatto, J. D., Jr.; Hoareau, W.; Gardrat, C.; Frollini, E.; Castellan, A. *J Agric Food Chem* 2007, 55, 8576.
25. Rong, M. Z.; Zhang, M. O.; Liu, Y.; Yang, G. C.; Zeng, H. M. *Compos Sci Technol* 2001, 61, 1437.
26. Joseph, K.; Thomas, S.; Pavithran, C. *Polym* 1996, 37, 5139.