

Improvement of the Interfacial Compatibility Between Sugar Cane Bagasse Fibers and Polystyrene for Composites

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Sugar cane bagasse fibers were modified by surface treatments using either physical or chemical methods in order to improve their adhesion to polystyrene matrices. The surface treatment methods used were alkaline treatment, treatment with silane coupling agents, physical coating with polystyrene and grafting of polystyrene with and without crosslinker. Fiber modifications were monitored by Fourier Transform Infrared Spectroscopy (FTIR), Differential Thermal Analysis coupled with Thermogravimetric Analysis (DTA-TGA) and Scanning Electron Microscopy (SEM). On the other hand, the improvement of the adhesion between sugar cane modified fibers and polystyrene was assessed by micromechanical pull-out and by macromechanical Iosipescu tests. It was found, from Interfacial Shear Strength values (IFSS), that substantial improvements in fiber-matrix compatibility were achieved. According to micro- and macromechanical test results, the IFSS increased for all treated fibers as compared to non-treated fibers. Particularly, both the coating the fibers or grafting with polystyrene using crosslinker resulted in substantial adhesion improvement to the polystyrene matrix in comparison with the non-treated fibers and fibers treated by alkaline and silane methods only. *Polym. Compos.* 25:134–145, 2004. © 2004 Society of Plastics Engineers.

1. INTRODUCTION

Natural fibers are important because of the interest in their use in the development of low cost “eco-friendly” natural fiber-composites. Indeed, the mechanical properties of natural fibers containing cellulose in composite materials (1, 2) are the subject of current international research projects. This is especially important if such fibers are residues of agroindustrial processes and if their raw-properties are acceptable for

composites, making their purification to pure cellulose unnecessary. Examples of such natural fibers are residues from pineapple (3), banana (4), rice (5), coconut (6) and sugar cane (7) processing. From society’s point of view and owing to the pressure of environmental groups leading to new environmental regulations, the production of natural fiber-composites has gained great attention, since it is recognized that natural fibers are cheap, highly available and renewable. Natural cellulosic fiber-polypropylene composites are being used in the automobile industry, and their usage is growing in general (8). One of these natural materials available in great quantities is sugar cane bagasse, a solid residue obtained after the extraction of the juice of sugar cane

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in the sugar industry. Early reports (9, 10) show that the main components of sugar cane bagasse are cellulose (~46%), hemicellulose (~30%) and lignin (~15%), with minor quantities of water-soluble compounds, silica, fat and waxes.

In the literature, we find reports on the use of sugar cane bagasse wastes in construction material-composites (11), in composites with cement (12) and in composites with the following polymer matrices: phenol-formaldehyde resins (7), polyethylene (13), poly(ethylene-co-vinyl acetate) (EVA) (14, 15) and poly(vinyl alcohol) (16). However, in most of these reports, sugar cane bagasse fibers were only washed before being used, and to our knowledge, the chemical and/or physical modification of these fibers for its use as reinforcement in composite materials has not been extensively reported.

The presence of hydroxyl groups on the surface of the cellulose fibers is, of course, synonymous with both high energy and a hydrophilic character. On the contrary, most of the polymeric matrices used for composites, such as polyethylene, polystyrene, and polypropylene, have a modest cohesive energy and a strong hydrophobic character (nonpolar materials). In order to profitably use these lignocellulosic fibers as reinforcing agents for polymers and improve the interfacial compatibility in the composite, it is essential to lower the ensuing interfacial energy. It is obviously easier to approach this problem by considering means of reducing the surface energy of the natural fibers.

In general it is known that the interfacial compatibility between the constituents plays a key role in the reinforcing properties of composites (17). In the case of cellulosic fiber-polymeric composites, the hydrophilic nature of natural fibers adversely affects adhesion to a hydrophobic matrix, and as a result may cause a loss of strength. To prevent this, the fiber surface has to be modified in order to promote adhesion. Also, the modification of these cellulosic fibers should improve (a) their thermal stability, (b) their surface adhesion characteristics, and (c) the dispersion of the fibers in the case of thermoplastic composites (1). In the literature, there are several reports on the chemical modification of natural fibers aiming at better fiber-matrix interfacial compatibility in composite preparation (18). These methods include bleaching of fibers (19), alkaline and silane treatments (17, 20, 21), acetylation (22) and cyanoethylation (20, 21) reactions, treatment/coating with polymers, most of them containing maleic anhydride groups (17, 23–25), treatment with alkyl

isocyanates (23, 26), grafting polymerization of vinyl monomers (20, 21) and other special treatment methods (27). To our knowledge, in the case of sugar cane bagasse, only alkaline treatments (12, 17) have been reported for this purpose. In this work, sugar cane bagasse fibers were modified by an alkaline treatment, the use of silane coupling agents, coating with polystyrene and grafting of polystyrene (with and without crosslinker). The goal was to achieve better interfacial compatibility between sugar cane bagasse fibers and the polystyrene matrix as a first step in obtaining composites with good properties and recycling possibilities.

2. EXPERIMENTAL

2.1 Materials

Sugar cane bagasse fibers were kindly supplied by the sugar cane industry "Emiliano Zapata" in Zacatepec, Morelos, México. Raw sugar cane bagasse fibers were separated using a sieving machine and sieves of mesh sizes 4, 8, 12, 16, and 30. For the following treatments only the fibers that passed through sieves of mesh size 12 and retained in sieves of mesh size 16 (mesh size according to ASTM standards) were used. The sieving procedure took 20 min and yielded 274.6 g of fibers of mesh size 16 from 1 kg of starting material. 3-(trimethoxysilyl)propylmethacrylate (TMPS), acetic acid, toluene (HPLC grade), ethanol (anhydrous), polystyrene ($M_w = 280,000 \text{ g mol}^{-1}$), styrene, divinylbenzene (DVB), t-butylcatechol inhibitor-remover and 2,2'-azo-bis-isobutyronitrile (AIBN) were purchased from Aldrich Chemicals and used without further purification. Ethanol, dichloromethane and sodium hydroxide, reagent grade, were purchased from Productos Químicos Monterrey and polystyrene for the matrix ($M_w = 171,000 \text{ g mol}^{-1}$) was supplied by Pemex. Deionized water was obtained from a nanopore purifying system installed in our laboratory.

2.2 Fiber Treatment Methods

Table 1 shows the keywords that are used throughout this paper, which were chosen according to the different treatments applied to the fibers. After each treatment, the fibers were stored in sealed plastic poly(ethylene) bags.

FIBNA: 1 g of bagasse fibers was dispersed in 40 mL of deionized water and the dispersion was heated up to 80°C with stirring for 2 h. Then, the water was decanted and the fibers were rinsed with deionized water until full elimination of less dense fibers and

Table 1. Treatment Methods for Sugar Cane Bagasse Fibers.

Keyword	Treatment
FIBNA	Fibers washed with deionized-water and extracted with toluene-methanol (1:1 v/v).
FIBAL	FIBNA treated with NaOH (1N) at room temperature for two hours.
FIBSI	FIBAL silanized with 3-(trimethoxysilyl)propylmethacrylate (TMPS).
IFIBSI	FIBSI grafted with polystyrene.
IFIBSIE	FIBSI grafted with polystyrene and divinylbenzene as a crosslinker.
FIBCOAT	FIBAL impregnated with a diluted solution of polystyrene.

until the water turned colorless. Then, the fibers were pre-dried for 5 h using hot air from a hair dryer, assembled to a box of polystyrene foam in which the wet fibers were placed. Afterwards, the fibers were dried in a vacuum oven (−25 inches of Hg) at 60°C for 15 h. Finally the fibers were extracted using a soxhlet apparatus for 12 h with a solution of toluene-methanol (1:1 v/v) followed by another drying cycle in a vacuum oven.

FIBAL: 1 g of FIBNA fibers was dispersed in 40 ml of 1N NaOH solution. The mixture was stirred for 2 h at room temperature. The fibers were then separated by filtration and rinsed with several amounts of deionized water until neutral pH was reached. After rinsing, the fibers were dried using a vacuum oven (−25 inches of Hg) at 60°C for 15 h.

FIBSI: A 2% solution by volume of TMPS in water was prepared. The pH of the solution was adjusted to ~3.5 with acetic acid. After that, the solution was kept for 2 h at room temperature allowing full hydrolyzation of the TMPS; then 1 g of FIBAL was dispersed in 30 ml of this TMPS-reaction solution for 1 h. Then, the solution was decanted and the fibers were dried in a vacuum oven (−25 in of Hg) at 110–120°C during ~30 min. Finally the fibers were rinsed with ethanol, dried at room temperature and later in vacuum (−25 in of Hg) for 1 h at 60°C.

FIBSI: 0.3 g of FIBSI, 10 ml of toluene and 0.015 g of AIBN were placed into a Schlenk-flask. The system was immersed in a Dewar-flask containing acetone/dry ice mixture and it was evacuated for 1 min and then flushed with argon. This procedure was repeated three times to eliminate any oxygen leaving the flask under positive argon atmosphere. When the flask reached room temperature, it was heated to 60°C, and after 5 min, 25 mL of a solution of styrene in toluene (1M) was added to the flask. Then, the flask was stirred gently for 14 h at 60°C to graft-polymerize styrene onto the fibers. Finally the flask was cooled down to room temperature, the solution was decanted over filter paper and the fibers were rinsed two times with cold toluene under continuous stirring for 30 min at room temperature. Then the fibers were dried in vacuum (−25 in of Hg) at 25°C for 12 h. After that, the fibers were extracted using soxhlet equipment for 12 h with dichloromethane as a solvent to eliminate any non-grafted polystyrene formed during the graft-polymerization. Finally the fibers were dried at room temperature during 12 h and later in a vacuum oven (−25 in of Hg at 60°C for 12 h).

IFIBSIE: For this treatment the same procedure applied to IFIBSI fibers was used, only that, DVB (3 mol% with respect to styrene) was added in the 25 mL of 1M solution of styrene in toluene.

FIBCOAT: 1 g of FIBAL fibers was dispersed in 30 mL of a 5% w/w polystyrene-toluene solution using polystyrene with $M_w = 280,000 \text{ g mol}^{-1}$. The mixture was stirred during 2 h at room temperature. Then, the solution was decanted and fibers were dried at room temperature for 12 h and later in a vacuum oven (−25 in of Hg at 60°C for 12 h).

2.3 Chemical and Physical Characterization of the Treated Fibers

2.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR Spectra of neat and treated fibers were obtained by mixing the samples with KBr and preparing conventional wafers using a laboratory press. The samples were analyzed by the transmission mode with a resolution of 4 cm^{-1} and strong numerical apodization. The absorption range studied was from 4000 cm^{-1} to 400 cm^{-1} using a FTIR Perkin-Elmer spectrophotometer, series 1600.

2.3.2 Thermal Analysis

Fibers were characterized using a simultaneous DTA-TGA thermal analysis equipment from Stanton Redcroft (STA-780), using the following conditions: Weight of sample: 8–10 mg, Heating rate: $20^\circ\text{C}/\text{min}$, Atmosphere: dry air-flow (30 mL/min), Reference: Calcinated Alumina, Sample Holder: Platinum. The study was performed for a temperature-range: 20–600°C.

2.3.3 Scanning Electron Microscopy (SEM)

Treated and not-treated fibers were placed in a vacuum chamber (JEE-400 JEOL) and a thin layer of gold was deposited onto them to diminish charging effects. Then, SEM micro-photographs were obtained using a SEM JSM-5300 JEOL, at 10 keV. Two magnification levels were studied $200\times$ and $5000\times$.

2.4. Evaluation of Interfacial Properties

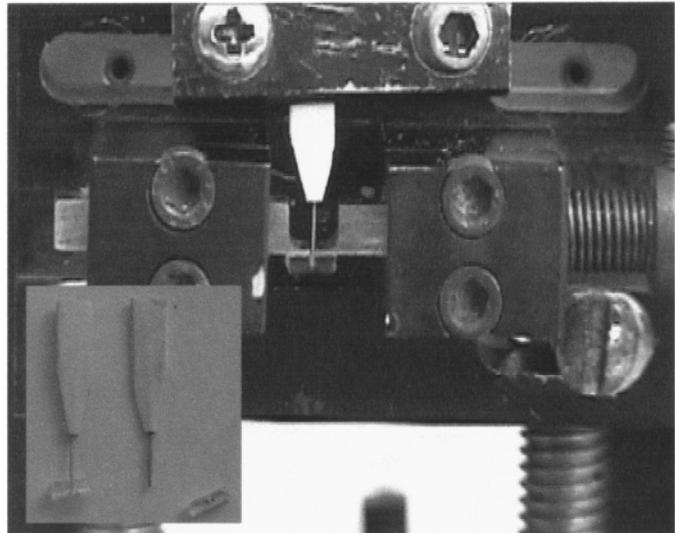
2.4.1 Micromechanical Evaluation

The pull-out specimens used for this test were prepared using the following procedure: polystyrene-sheets ($M_w = 171,000 \text{ g mol}^{-1}$) of dimensions $3 \times 110 \times 1 \text{ mm}$, were prepared using a Carver Press model C at a pressure of 4.5 ton and a temperature of 180°C . These sheets were perforated (diameter of 1 mm) and were placed between the plates of the Carver Press at room temperature. One fiber of sugar cane bagasse with a minimum length of 1.5 cm was inserted in each perforation; after that, a pressure of 1 ton and a temperature of 120°C were applied for 5 min. Finally, the specimens were cut and the embedded length and apparent diameter of each specimen was measured by using an optical microscope with a 1 mm^2 graduated mesh. The specimens were held from the polymer side and a tensile force was applied to the free end of the embedded fiber using a microtensile testing machine equipped with an 18 Kg load cell and a cross-head speed of $0.2 \text{ mm}/\text{min}$ (Fig. 1). The average interfacial shear strength (IFSS) was calculated by using Eq 1:

$$\tau = \frac{F}{\pi dl} \quad (1)$$

where F is the maximum load measured prior to the fiber-polymer matrix debonding, d is the fiber diameter and l is the fiber embedded length in polymer matrix.

Fig. 1. Micromechanical testing arrangement.



2.4.2 Macromechanical Evaluation

Sugar cane bagasse fibers-polystyrene composites were prepared with a fiber concentration of 20% by weight of fibers respecting to polystyrene matrix ($M_w = 171,000 \text{ g mol}^{-1}$). Test specimens for the Iosipescu test were elaborated according to the ASTM D-5379 norm described in (17). The measurements were performed using an Instron Universal Testing machine with a Wyoming Test Fixture accessory (Fig. 2), using a 500 Kg load cell at a crosshead speed of 1 mm/min. The average interfacial shear strength (IFSS) was calculated by using Eq 2.

$$\tau = \frac{F}{bt} \quad (2)$$

where F is the maximum load applied prior to fracture, b is the specimen thickness and t is the effective distance between notches (Fig. 2).

3. RESULTS AND DISCUSSION

3.1 FTIR Analysis

From the FTIR technique used we expected evidence of the chemical transformations occurred to sugar cane bagasse after each treatment.

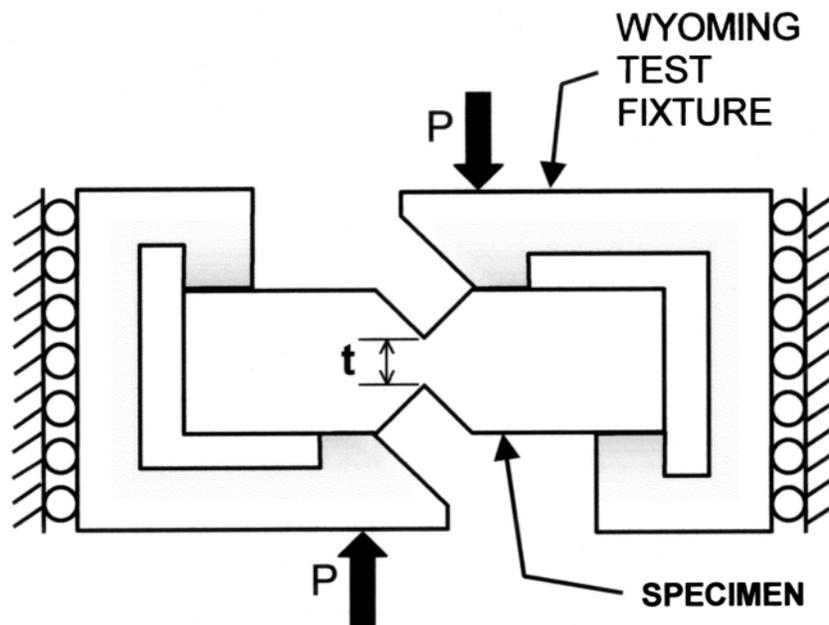


Fig. 2. Wyoming Test Fixture accessory.

We observed in the spectrum of FIBNA-fibers a strong absorption band at 1728 cm^{-1} corresponding to C=O stretching vibration from hemicellulose and lignin (Fig. 3). This absorption does not appear in the FIBAL spectrum. Other typical absorption bands of lignin in FIBNA spectrum are at 1510 cm^{-1} (aromatic skeleton vibration) and at 1263 cm^{-1} , which are weaker in FIBAL spectrum. This is indicative of hemicellulose and lignin being partially eliminated after treatment, in agreement with reports in the literature (17, 28–30) saying that the treatment of natural fibers with diluted alkaline solution removes mainly hemicellulose and lignin present on the surface of natural fibers. After the silanization treatment, we observed in the spectrum of FIBSI-fibers (Fig. 3) a double absorption band at 1719 cm^{-1} corresponding to the C=O stretching vibration of the methacrylate group, at 1602 cm^{-1} and 747 cm^{-1} bands for the C=C bond, at 670 cm^{-1} a C-H olefinic vibration and an absorption increment between 1000 and 1100 cm^{-1} corresponding to Si-O-Si and Si-O-C vibrations; all these vibrations were expected after the silanization treatment. After graft-polymerization reaction on the fibers, we observed in the spectrum of IFIBSI-fibers (Fig. 3, bottom) a decrease of absorption bands corresponding to C=C vibrations (747 cm^{-1} and $\sim 1602\text{ cm}^{-1}$) as compared to

those in the spectrum of FIBSI-fibers. We take this as evidence that the double bonds located at the end of each silane reacted with the styrene to form polystyrene (PS) grafted to the fibers. Furthermore, the spectrum for IFIBSI-fibers shows an increment in the absorption band at 1505.6 cm^{-1} , corresponding to aromatic ring vibrations of polystyrene. These changes were also observed by comparing the spectra of FIBSI fibers with IFIBSIE fibers (IFIBSI with crosslinker). Evidence for PS-grafting can be observed better in Fig. 4, which shows the difference-spectrum between FIBSI and IFIBSIE compared with the spectrum of pure polystyrene. This confirms additionally that PS-grafting on the fiber was successful. In the case of the fibers after the coating procedure with polystyrene, their spectrum (FIBCOAT, here not shown) shows absorption bands for the aromatic ring vibrations of polystyrene at 695 cm^{-1} , 751 cm^{-1} and at 1505.6 cm^{-1} . This confirmed the presence of a polystyrene coating over the fiber.

In summary, FTIR-Analysis confirmed the expected chemical changes after each treatment.

3.2 Thermal Analysis

It is well known (31–33) that cellulose, hemicellulose and lignin are the main components of natural

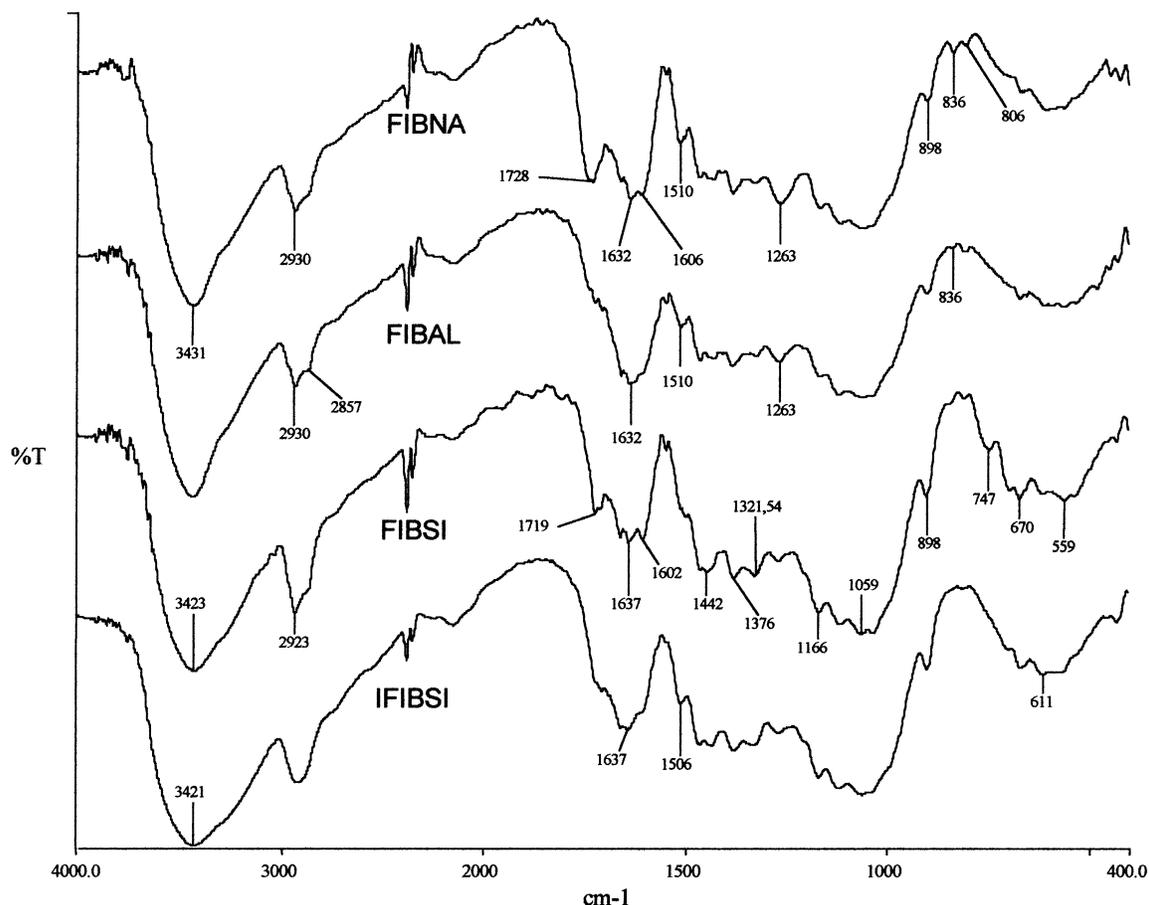


Fig. 3. FTIR-spectra of FIBNA, FIBAL, FIBSI and IFIBSI fibers.

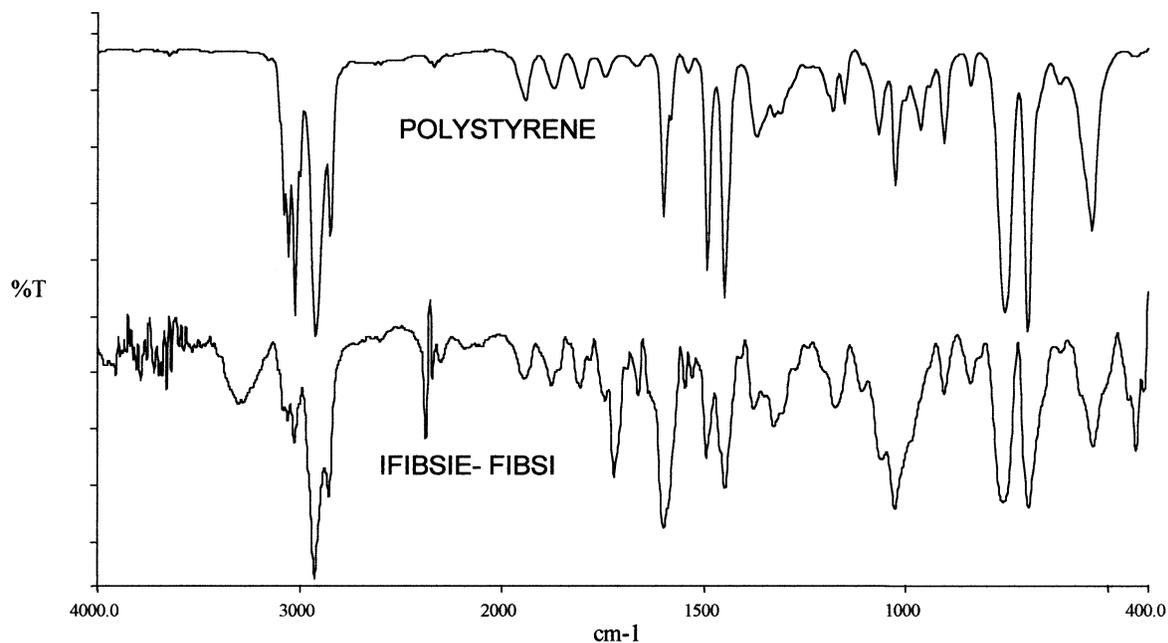


Fig. 4. Comparison of FTIR spectrum of polystyrene and the spectrum difference between FIBSI and IFIBSIE fibers.

fibers and that they show different thermal stabilities. The hemicellulose is the least thermally stable compound and lignin the most thermally stable. Figure 5 shows DTA thermograms of the fibers, which were measured in dry air atmosphere. The DTA thermogram of FIBNA-fibers shows a small endothermic deflection at 78°C, which corresponds to adsorbed moisture. The exothermic signal at 310°C was assigned to the initial degradation of hemicellulose and lignin (33). The exothermic signal at 372°C corresponds to degradation of amorphous polysaccharides, mainly hemicellulose, while the exothermic signal at 462°C corresponds to degradation of mixtures of lignin-hemicellulose complex and cellulose-hemicellulose complex (32), and the small exothermic signal at 497°C corresponds to the final degradation of the lignin fraction, which is not forming a complex. The DTA thermogram of FIBAL does not show the exothermic signal at 372°C present in the FIBNA thermogram, indicating the absence of amorphous hemicellulose. This is confirmed by our own FTIR spectra analysis and by literature reports (31). The exothermic signals at 388°C and 435°C were assigned to the cellulose-hemicellulose complex and to the lignin-hemicellulose complex, respectively. The small exothermic signal at 497°C, assigned to lignin in the FIBNA thermogram, is not present in the FIBAL thermogram. On the other hand, the DTA thermogram of FIBCOAT shows two new exothermic signals at 372°C and 481°C. These signals were assigned to the polystyrene coating, while the signals for the mixture of complexes appear at a slightly higher temperature than in the FIBAL thermogram. The DTA thermograms of FIBSI, IFIBSI and IFIBSIE fibers are similar. Nevertheless the two main exothermic steps appear at higher temperatures, and a

broadening of the peak at 499°C was observed in the case of IFIBSIE fibers. This may be due to the presence of crosslinked polystyrene.

Table 2 lists the moisture and the residue content of the samples obtained after TGA-analysis. The FIBAL fiber had higher moisture content than the FIBNA fiber because the alkaline treatment generated a rough surface, as can be seen from the SEM-analysis (Fig. 6b). The FIBCOAT fiber shows less moisture content than the FIBAL fiber because of the presence of polystyrene on the surface; however, the moisture content is higher than for the PS-grafted samples IFIBSI and IFIBSIE. The FIBSI fibers have less moisture content than the FIBAL fibers. This may be due to the hydrophobic nature of TMPS. Surprisingly, the IFIBSIE-fibers have more moisture than the FIBSI and IFIBSI fibers. Since the crosslinked polystyrene does not cover all the fiber surface and is instead distributed as dots (see Fig. 6e), this may allow moisture to reach the hydrophilic part of the fibers (cellulose), resulting in higher moisture absorption, as expected.

On the other hand, the FIBAL fibers had more residue at 600°C in dry air than the FIBNA fibers because of the elimination of hemicellulose from the fibers. Remember that hemicellulose is less thermally stable in these fibers. The FIBSI fibers have slightly more residue than the FIBAL fibers mainly because of silicon present in TMPS. The FIBCOAT fibers have less residue than the FIBAL, while the IFIBSI and IFIBSIE fibers have less residue than the FIBSI fibers because of the amount of physical deposited or grafted polystyrene respectively. In general, fibers with polystyrene present have less residue, because polystyrene decomposes without solid residues at temperatures lower than 600°C (34).

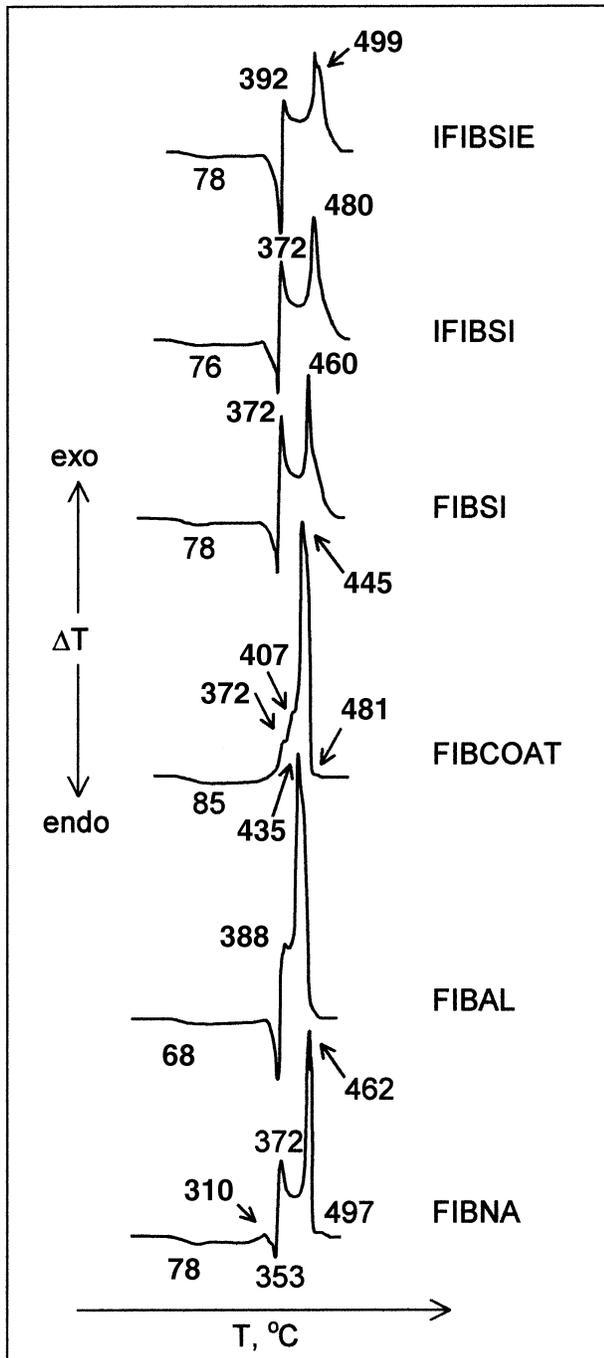


Fig. 5. DTA of fibers in dry air atmosphere.

In summary, the thermal analysis results showed that, with exception of the alkaline treatment, all the treatment methods used increased the hydrophobicity of the fibers. Since the polystyrene matrix is also hydrophobic, we expected that the treated fibers could build a better interface with polystyrene than the non-treated fibers. In addition, the thermal analysis showed also that the thermal stability of the fibers increased

Table 2. TGA Analysis of Fibers as a Function of Treatment.

Sample	Moist (%)	Residue at 600°C (%)
FIBNA	4.2	5.5
FIBAL	5.5	7.2
FIBCOAT	4.5	2.9
FIBSI	3.4	7.8
IFIBSI	2.7	5.8
IFIBSIE	4.2	2.2

when the silane treatment was used followed by grafting methods (IFIBSI and IFIBSIE). This could be advantageous when the processing of the composites is considered.

3.3 SEM Analysis

If we aim to obtain a good interfacial interaction in polymer composite materials, the characteristics of the surface of the fiber reinforcement, which are not going to be altered much during the composite preparation, are crucial. Therefore we undertook SEM analysis to study how the treatment methods applied to the fibers affected their surface characteristics.

The fiber surface morphology is shown in the SEM micrographs (Fig. 6). As can be seen, the alkaline treatment (Fig. 6b) roughens the surface, because of the partial removal of hemicellulose, lignin and other soluble materials. As a result, FIBAL fibers have more sites available for physical interlocking with the matrix in a composite. Figure 6c shows that the FIBSI fiber surface closely resembles the FIBAL fibers. The SEM micrograph of the FIBCOAT fibers (Fig. 6d) reveals a smooth surface. Therefore we conclude that a layer of polystyrene is deposited on the surface of the fiber. In comparing the surfaces of IFIBSI (Fig. 6e) and IFIBSIE (Fig. 6f) with the surface of FIBSI fibers, the difference is seen with the IFIBSIE fibers, which shows polystyrene-aggregations distributed as dots along the fiber surface. These results confirm that the surface of sugar cane bagasse fibers was modified by these treatments.

3.4 Micromechanical Evaluation

So far, it has been shown that the treatment methods used effectively change the surface and thermal properties of the fibers. How these changes influence the interfacial properties with polystyrene is demonstrated by the pull-out test.

Figure 7 shows the dependence of the maximum force of debonding versus embedded area of fibers after each treatment. The lines are the linear regression analysis of the data obtained for each treatment. Different slopes were obtained, indicating that the interfacial interactions increased with the treatments made to the fiber in this order:

FIBNA < FIBAL < FIBSI ≪ IFIBSI < FIBCOAT < IFIBSIE

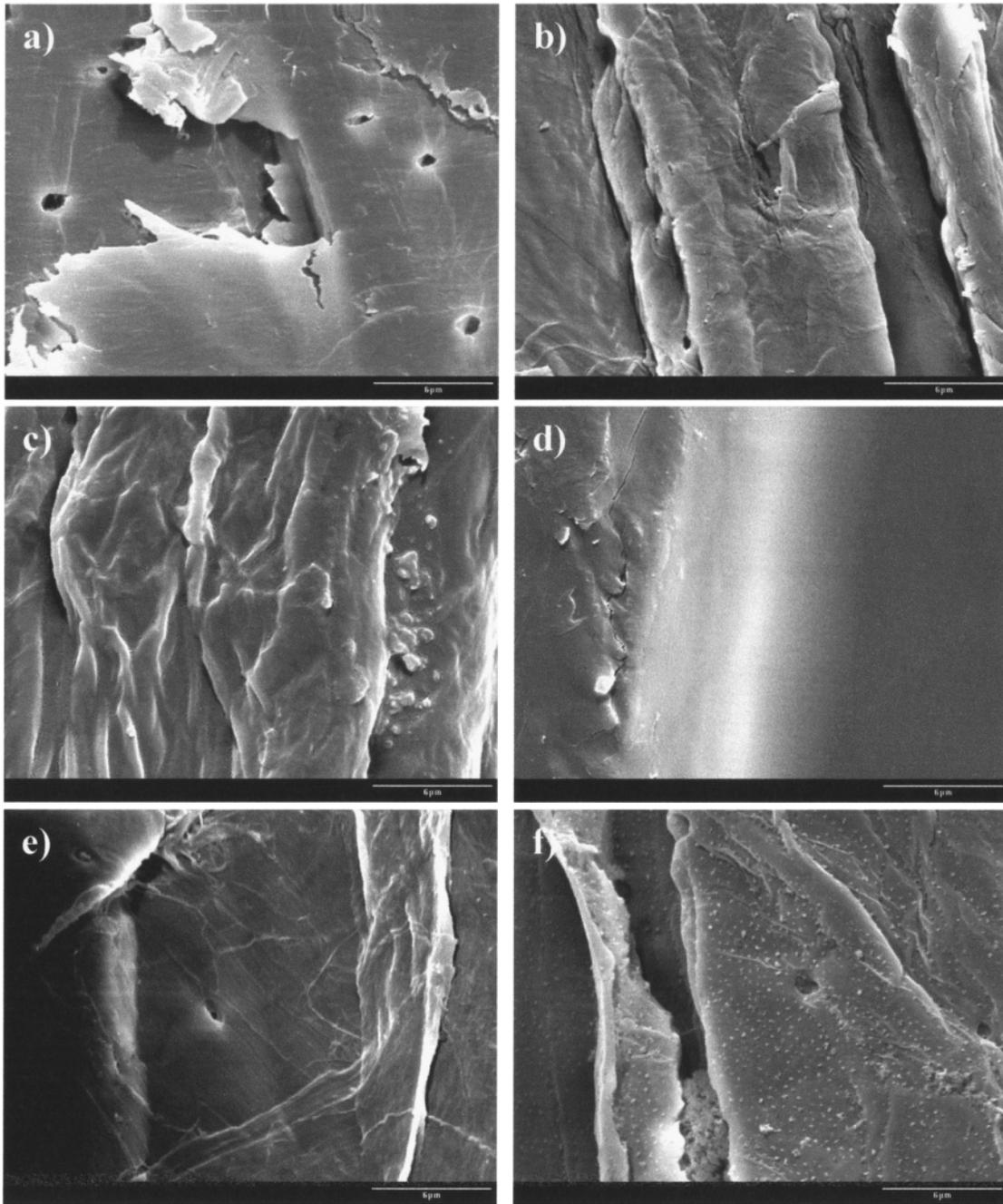


Fig. 6. SEM of a) FIBNA, b) FIBAL, c) FIBSI, d) FIBCOAT, e) IFIBSI and f) IFIBSIE fibers.

The scattering in the data is due to the nature of natural fibers used, since their diameters vary from fiber to fiber; only the embedded fiber length could be controlled using the procedure described in the **Experimental** section.

Figure 8 shows the interfacial shear strength (IFSS) calculated using the mean area of the fibers with Eq 1; see also Table 3. FIBAL-polystyrene had a higher IFSS than FIBNA-polystyrene owing to mechanical interlocking of the matrix with the rough fibers. This

effect has been reported in the literature (17). FIBSI-polystyrene has a slightly higher IFSS than FIBAL-polystyrene. This is possible because TMPS has a hydrophilic group attached to the fiber and a hydrophobic group interacting with polystyrene, allowing better compatibility with the hydrophobic matrix. Because of its hydrophobicity, it was also the fiber with the lowest moisture absorption. The IFSS of IFIBSI-polystyrene was significantly higher than the IFSS of FIBSI-polystyrene, mainly because of interdiffusion of chains

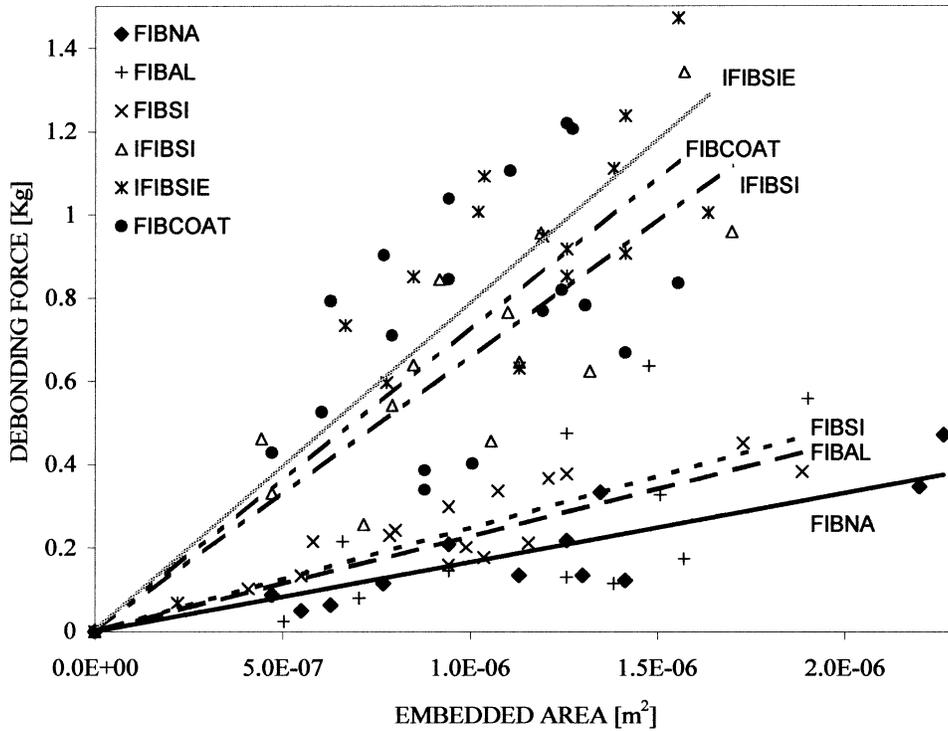


Fig. 7. Maximum force of debonding versus embedded fiber area for all treatments.

of polystyrene from the matrix to the chains of polystyrene grafted to the fiber. However, the IFSS of FIBCOAT-polystyrene is slightly higher than that of IFIBSI-polystyrene. This may have two origins: i) A more homogeneous wetting of the fiber with polystyrene occurs during the coating treatment, because

polystyrene in solution can reach all the microcavities of the fibers generating a good coating (see Fig. 6d) and lowering the surface energy of the fibers, therefore promoting a better miscibility with the matrix (38), resulting finally in an improved fiber-matrix mechanical interlocking; and ii) Because the polystyrene

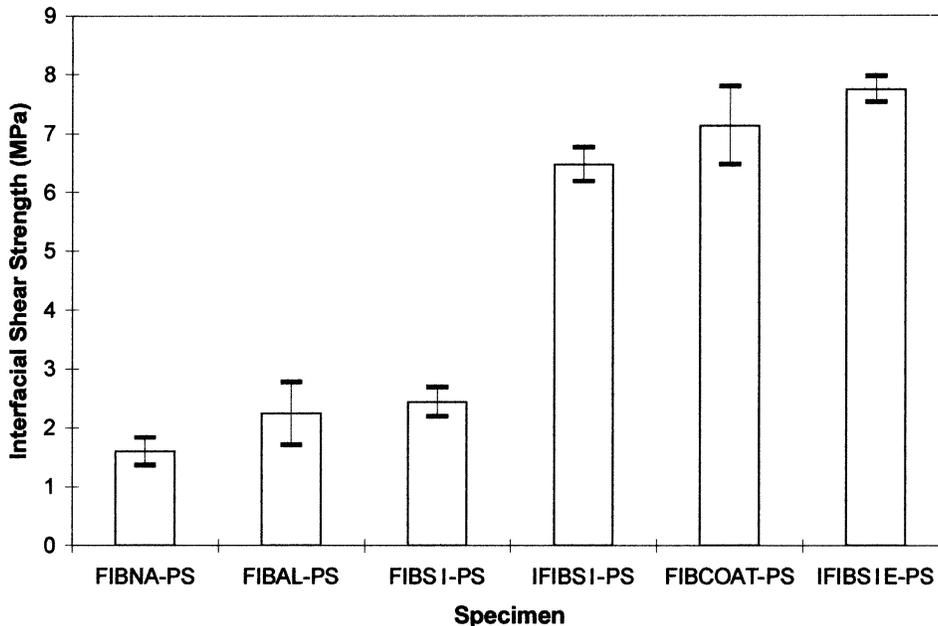


Fig. 8. Interfacial shear strength for modified fibers evaluated by pull-out test.

Table 3. IFSS and R² for the Linear Regression Analysis From Pull-out Testing.

Sample	IFSS [Mpa]	R ²
FIBNA	1.63	0.77
FIBAL	2.24	0.47
FIBSI	2.44	0.75
IFIBSI	6.47	0.71
FIBCOAT	7.13	0.34
IFIBSIE	7.74	0.77

chains in the surface of the fiber may be shorter in IFIBSI fibers than in FIBCOAT fibers, the longer polystyrene chains in FIBCOAT may show improved interdiffusion with the chains of the polystyrene matrix. The later can be expected from the molecular weight of the non-grafted polystyrene produced simultaneously by the graft-polymerization method used in IFIBSI ($M_w = 64,400 \text{ g mol}^{-1}$), versus the $M_w = 280,000 \text{ g mol}^{-1}$ of the polystyrene used for generating FIBCOAT fibers.

The positive role of natural fiber coating with a matrix polymer prior to composite preparation was already highlighted in Reference 17 and explained in terms of a better mechanical interlocking interaction fiber-matrix. Nevertheless, the major IFSS response obtained in this work was for IFIBSIE-polystyrene, in part because of a good interdiffusion between chains of polystyrene in the matrix and the grafted polystyrene with crosslinker. Besides this, the surface features generated during the crosslinking reaction (Fig. 6f) gave more interlocking sites that contributed to the IFSS also. Table 3 shows the linear regression analysis of the IFSS (from Fig. 7) for each treatment. A bad fit for FIBAL and FIBCOAT treatments is observed, which could be a result of differences in the surface morphology of these fibers within the same treatment. On the other hand, the fit for the other treatments, around $R^2 > 0.7$, is reasonably good,

given the fact that we are dealing with natural fibers, and is comparable with reported results of pull-out and microbond testing (17, 22, 27, 35, 36). Nevertheless, taking the scattering of the data into consideration we can group the IFSS results discussed into three groups: non treated fibers < alkaline or silanized fibers \ll polystyrene-grafted or coated fibers.

Finally, it was found that all treatments applied to the sugar cane bagasse fibers improved the binding properties of their interface with polystyrene, compared with untreated natural fiber. The IFSS-Value of 7.74 MPa obtained for IFIBSIE-polystyrene is in the same range of values reported in the literature using the pull-out or microbond-test for other surface-treated natural fiber-thermoplastic composites (Table 4).

The 375% increase in IFSS, achieved through a combination of treatments, shows how different interfacial-interactions can be exploited in a synergistic way by surface treatment techniques. This high increment in IFSS is comparable to the results reported in References 17 and 37 however higher. Interestingly, in the work of Valadez-Gonzalez *et al.* (17) the increase of IFSS was also achieved through a combination of treatments.

The IFSS-Value obtained for treated sugar cane bagasse fibers is lower than that reported for treated flax and treated henequen fibers. Although a simple comparison is not always useful, for a given application of natural fiber composites we need to consider additionally that the low cost and high availability of sugar cane bagasse, which is a waste product of sugar industry, offer an advantage over flax and henequen, which most likely need to be harvested for the purpose of composite preparation.

3.5. Macromechanical Evaluation

It is known that results from micromechanical testing cannot be quantitatively extrapolated to macromechanical performance. Nevertheless, the trend shown

Table 4. IFSS in Natural Fiber-Thermoplastic Composites by Micromechanical Testing.

Fiber	Matrix	IFSS [Mpa] non-treated	IFSS [Mpa] best treatment	Increment [%]	Method	Ref.
Sugar cane bagasse	Polystyrene	1.63	7.74	375	Pull-out	This work
Pineapple	Poly(hydroxybutyrate-co-valerate)	8.23	—	—	Microbond	(35)
Henequen	Poly(hydroxybutyrate-co-valerate)	5.24	—	—	Microbond	(36)
Henequen	HD-Polyethylene	2.2	9.0	309	Pull-out	(17)
Wood	Polystyrene	~3.2	10.0	~212	Microdrop	(37)
Wood	Polyethylene 1	0.4–0.8	1.92	137	Pull-out	(22)
	Polyethylene 2	2.0	3.1	55		
Wood	Polypropylene	1.5–2.0	2.0–2.45	20	Pull-out	(24)
Flax	Polypropylene	9.6	16.3	70	Microbond	(23)
Flax	LD-Polyethylene	5.5	6.2	12.7	Pull-out	
	HD-Polyethylene	9.1	10.1	11.0	Pull-out	(27)
	Polypropylene	10.6	—	—	Pull-out	
	Maleic Anhyd.-Polypropylene	11.4	—	—	Pull-out	
Regen. Cellulose	Polystyrene	2.7	3.4	26	Microdrop	(38)

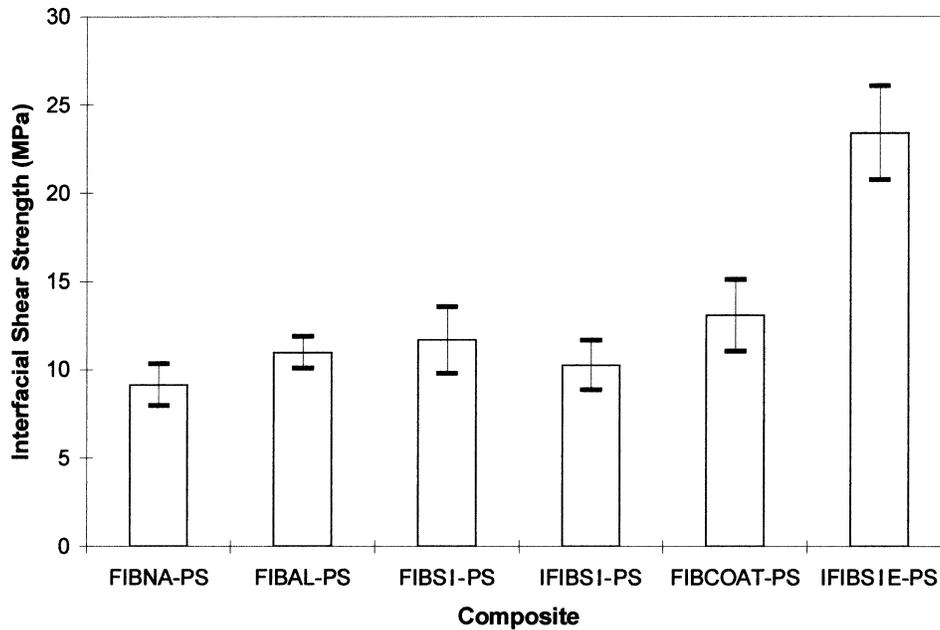


Fig. 9. Interfacial shear strength for modified fibers evaluated by Iosipescu test.

in the micromechanical behavior should qualitatively correspond with the macromechanical performance if sources of variability can be constrained to a certain level. We used the Iosipescu test to evaluate the IFSS of composites by macromechanical testing in the expectation of showing how the observed micromechanical behavior corresponds to the macromechanical performance in terms of IFSS.

The specimens evaluated by Iosipescu test showed, as expected, a behavior very similar to that observed in micromechanical pull-out testing. Figure 9 shows that the IFSS increases in the order: FIBNA < IFIBSI < FIBAL < FIBSI < FIBCOAT < IFIBSIE.

The IFSS increased from 12% for composites with IFIBSI fibers up to 156% for composites with IFIBSIE fibers as compared to composites with FIBNA fibers. A comparison between the percentages of improvement of the IFSS recorded by micro- and macromechanical testing are shown in Table 5. It is important to keep in mind that the response to the mechanical stress in composites also depends on the size of the fibers, the fraction in volume or in weight of the fibers in the composite, and the type of arrangement and distribution

of the fibers in the matrix material, while these factors do not affect the micromechanical evaluation using only one fiber at a time. Although we tried to keep all these factors constant, the random arrangement and distribution of the fibers in the composite could vary since it depends also on the wettability of the fibers with the matrix polymer, a property that most likely changed after each treatment method used.

The only variation, in the order of improvement of IFSS, as compared with the pull-out testing results, is for the composite with IFIBSI fibers. Differences in the distribution of fibers during composite preparation could be responsible for this slight change. In general terms, the macromechanical testing results qualitatively confirmed the behavior expected from the micromechanical evaluation.

4. CONCLUSIONS

Several chemical and physical modifications of the sugar cane bagasse fibers were conducted to improve their surface properties for a better compatibility with polystyrene. The surface modification of these fibers was assessed by: FTIR, SEM and DTA-TGA analysis.

Table 5. Comparison of IFSS-Improvement by Micro- and Macromechanical Evaluations.

Micromechanical pull-out test		Macromechanical Iosipescu test	
Composite	IFSS-Improvement as compared to FIBNA-PS [%]	Composite	IFSS-Improvement as compared to FIBNA-PS [%]
FIBAL-PS	37	FIBAL-PS	20
FIBSI-PS	50	FIBSI-PS	28
IFIBSI-PS	297	IFIBSI-PS	12
FIBCOAT-PS	337	FIBCOAT-PS	43
IFIBSIE-PS	375	IFIBSIE-PS	156

The influence of each treatment on the adhesion of sugar cane bagasse to polystyrene was studied using pull-out and Iosipescu testings. The alkaline treatment removed hemicelluloses and lignin mainly from the surface of FIBNA fibers generating a surface with more roughness and a higher surface area. These changes promoted a higher absorption of moisture and a better mechanical interaction between the FIBAL fibers and polystyrene as compared with FIBNA-fibers. As a result the IFSS increased approximately by 37%/20% according to micromechanical/macromechanical testing results respectively. The treatment made to FIBAL fibers with TMPS resulted in a small increase of adhesion with the polystyrene matrix. This is probably due to the expected increase in hydrophobicity of the fiber surface. The IFSS increased 13%/8% according to micromechanical/macromechanical testing results respectively as compared to FIBAL-polystyrene. Also, the incorporated methacrylate-groups of TMPS served as anchoring units for the polystyrene grafting treatments IFBSI and IFBSIE. The polystyrene-grafted fibers showed a substantial improvement in the thermal stability and up to 375%/156% increase in interfacial shear strength (IFSS) according to micromechanical/macro mechanical test results respectively, as compared to the FIBNA-polystyrene. This is probably due to a combination of interdiffusion of polystyrene grafted chains with the matrix and mechanical interlocking with the rough surface. Finally, a simple polystyrene coating of the fibers resulted in a substantial increase in IFSS, resulting from interdiffusion of chains in a well-covered surface (lower surface energy), but nevertheless lower than the IFSS for IFBSIE-polystyrene. Herewith the importance of appropriate fiber-treatment is demonstrated for the generation of a better interfacial compatibility in sugar cane bagasse-polystyrene composites.

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REFERENCES

1. D. Nabi-Saheb and J. P. Jog, *Adv. Polym. Technol.*, **18**, 351 (1999).
2. S. J. Eichhorn, C. A. Baillie, N. Zafeiropoulos, L. Y. Mwaikambo, M. P. Ansell, A. Dufresne, K. M. Entwistle, P. J. Herrera-Franco, G. C. Escamilla, L. Groom, M. Hughes, C. Hill, T. G. Rials, and P. M. Wild, *J. Mat. Sci.*, **36**, 2107 (2001).
3. L. U. Devi, S. S. Bhagawan, and S. Thomas, *J. Appl. Polym. Sci.*, **64**, 1739 (1997).
4. W. H. Zhu, B. C. Tobias, and R. S. P. Coutts, *J. Mater. Sci. Lett.*, **14**, 508 (1995).
5. R. Salgado-Delgado, *Tesis de Maestría*, Instituto Tecnológico de Tijuana, Tijuana B. C., México (1999).
6. C. F. Jasso-Gastinel, P. Lopez-Carrillo, and E. Mendizabal-Mijares, *Polym. Eng. Sci.*, **32**, 443 (1992).
7. C. N. Zárate, M. I. Aranguren, and M. M. Reboredo, *J. Appl. Polym. Sci.*, **77**, 1832 (2000).
8. Natural fiber composites industry registered 40–50% growth in the USA in 2000, according to: http://www.klinegroup.com/press/6_200103.htm.
9. I. O. Salyer and A. M. Usmani, *Ind. Eng. Chem. Prod. Res. Dev.*, **21**, 13 (1982).
10. C. A. Cruz-Ramos, *Mechanical Properties of Reinforced Thermoplastics*, p. 65, Elsevier Applied Science Publishers, London and New York (1986).
11. A. M. Usmani, G. L. Ball III, I. O. Salyer, D. W. Werkmeister, and B. S. Bryant, *J. Elast. Plast.*, **12**, 18 (1980).
12. V. M. Poblano, *Tesis de Licenciatura*, Instituto Tecnológico de Zacatepec, Zacatepec Morelos, México (1996).
13. R. G. Raj and B. V. Kokta, *Eur. Polym. J.*, **27**, 1121 (1991).
14. E. C. McLaughlin, *J. Mat. Sci.*, **15**, 886 (1980).
15. G. C. Stael, M. I. B. Tavares, and J. R. M. d'Almeida, *Polym. Plast. Technol. Eng.*, **40**, 217 (2001).
16. E. Chiellini, P. Cinelli, A. Corti, E. R. Kenawy, E. Grillo-Fernandes, and R. Solaro, *Macromol. Symp.*, **152**, 83 (2000).
17. A. Valadez-Gonzalez, J. M. Cervantes-Uc, R. Olayo, and P. J. Herrera-Franco, *Compos.: B: Eng.*, **30**, 309 (1999).
18. A. K. Bledzki and J. Gassan, *Prog. Polym. Sci.*, **24**, 221 (1999).
19. S. S. Tripathy, G. Levita, and L. Di Landro, *Polym. Compos.*, **22**, 815 (2001).
20. J. Rout, M. Misra, S. S. Tripathy, S. K. Nayak, and A. K. Mohanty, *Polym. Compos.*, **22**, 468 (2001).
21. J. Rout, M. Misra, S. S. Tripathy, S. K. Nayak, and A. K. Mohanty, *Polym. Compos.*, **22**, 770 (2001).
22. A. R. Sanadi, R. M. Rowell, and R. A. Young, *J. Mat. Sci.*, **28**, 6347 (1993).
23. C. Joly, M. Kofman, and R. Gauthier, *J. M. S.-Pure Appl. Chem.*, **A33**, 1981 (1996).
24. M. Kazayawoko, J. J. Balatinez, and L. M. Matuana, *J. Mat. Sci.*, **34**, 6189 (1999).
25. D. Feng, D. F. Caulfield, and A. R. Sanadi, *Polym. Compos.*, **22**, 506 (2001).
26. J. Kuruvilla, T. Sabu, and C. Pavithran, *J. Reinf. Plas. Compos.*, **12**, 139 (1993).
27. A. Stamboulis, A. Baillie, and E. Schulz, *Angew. Makromol. Chem.*, **272**, 117 (1999).
28. R. López, V. M. Poblano, A. Licea-Claverie, M. Avalos, A. Alvarez-Castillo, and V. M. Castaño, *Adv. Composites Mater.*, **9**, 99 (2000).
29. J. Gassan and A. K. Bledzki, *Compos. Sci. Technol.*, **59**, 1303 (1999).
30. E. T. N. Bisanda, *Appl. Compos. Mat.*, **7**, 331 (2000).
31. T. Nguyen, E. Zavarin, E. M. Barral II, *J. M. S.-Rev. Macromol. Chem.*, **C20**, 1 (1981).
32. S. Tsujiyama and A. Miyamori, *Thermochim. Acta*, **351**, 177 (2000).
33. K. Bilba and A. Ouensaga, *J. Anal. Appl. Pyrol.*, **38**, 61 (1996).
34. J. Brandrup, E. H. Immergut, and E. A. Grulke, *Polymer Handbook, Fourth Edition*, p. V-92. John Wiley & Sons, New York-Chichester-Weinheim (1999).
35. S. Luo and A. N. Netravali, *J. Mat. Sci.*, **34**, 3709 (1999).
36. S. Luo and A. N. Netravali, *J. Adhesion Sci. Technol.*, **15**, 423 (2001).
37. F. P. Liu, M. P. Wolcott, D. J. Gardner, and T. G. Rials, *Compos. Interf.*, **2**, 419 (1994).
38. J. A. Trejo-O'Reilly, J. Y. Cavaillé, M. Paillet, A. Gandini, P. J. Herrera-Franco, and J. Cauich, *Polym. Compos.*, **21**, 65 (2000).