

# Effect of Fiber Surface Modification on the Mechanical Properties of Sisal Fiber-Reinforced Benzoxazine/Epoxy Composites Based on Aliphatic Diamine Benzoxazine

Suchada Tragoonwichian,<sup>1</sup> Nantaya Yanumet,<sup>1</sup> Hatsuo Ishida<sup>2</sup>

<sup>1</sup>*Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand*

<sup>2</sup>*Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106-7202*

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**ABSTRACT:** Sisal fibers were incorporated into a mixture of benzoxazine and bisphenol A type epoxy resins to form a unidirectionally reinforced composite. Surface modifications of the sisal fibers were carried out with sodium hydroxide,  $\gamma$ -aminopropyltrimethoxysilane, and  $\gamma$ -glycidoxypropyltrimethoxysilane. The surface treatments led to changes in the morphology, chemical groups, and hydrophilicity of the fibers. The effect of the fiber surface treatments on the fiber–matrix interfacial adhesion and mechanical properties of the composites were also

studied. The results showed that surface treatments with sodium hydroxide and a silane coupling agent led to improved fiber–matrix adhesion; this could be seen in the scanning electron micrographs of the fractured surfaces from mechanical testing and the reduction in the impact strength of the composites made from treated fibers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2925–2935, 2007

**Key words:** adhesion; composites; reinforcement

## INTRODUCTION

Natural fibers are receiving attention as reinforcements in polymer composites. Compared with conventional reinforcing fibers, such as glass and carbon fibers, natural fibers have a number of benefits, including low density, high specific strength and modulus, biodegradability, and low cost. There have been many studies using cellulosic fibers to reinforce both thermosets and thermoplastics.<sup>1–8</sup> These studies show that natural fiber materials have the potential to compete with glass fibers in composite materials. However, because of the poor wettability toward polymers resulting from the hydrophilicity of the cellulosic fibers, the adhesion between the fibers and the polymer matrix is generally insufficient. To optimize this interface, physical and chemical methods have been used. Aziz and Ansell<sup>2</sup> obtained an improvement in the flexural strength and flexural modulus of long hemp/kenaf fiber–polyester composites after a treatment with a sodium hydroxide (NaOH) solution, and scanning electron microscopy (SEM) results showed that alkalization could eliminate surface impurities. Mishra et al.<sup>3</sup> found that the mechanical properties of maleic anhydride

treated natural fiber composites were higher than those of untreated fiber composites. Abdelmouleh et al.<sup>4</sup> treated cellulosic fibers with silane coupling agents and obtained fiber surfaces with higher hydrophobicity.

In this study, sisal fiber, a leaf fiber from *Agave sisalana*, was incorporated into a mixture of a benzoxazine resin and a bisphenol A type epoxy resin to form a unidirectionally reinforced composite. Polybenzoxazine is a novel polymer with good dimensional stability, high heat resistance, and low moisture absorption. The epoxy resin was added to improve the toughness and processability of polybenzoxazine. Surface treatments with alkaline and silane coupling agents were applied to this system. The alkali treatment was expected to remove hemicellulose from the fibers, thus making the cellulose fibrils and hence their hydroxyl groups more exposed on the fiber surface. Thus, after the alkali treatment, the condensation reaction between silanol groups of silane and hydroxyl groups of the sisal fibers could occur more readily. Two silane coupling agents,  $\gamma$ -aminopropyltrimethoxysilane ( $\gamma$ -APS) and  $\gamma$ -glycidoxypropyltrimethoxysilane ( $\gamma$ -GPS), were used. The effect of the surface treatment on the mechanical properties of the composites was studied.

## EXPERIMENTAL

### Materials

Sisal fibers with diameters ranging from 100 to 300  $\mu\text{m}$  and 100 cm long were obtained from growers in Petchburi Province, Thailand. A bisphenol A type epoxy resin (epoxy equivalent weight = 184–194 g/

Correspondence to: N. Yanumet (nantaya.y@chula.ac.th).

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equiv) was supplied by Thai Epoxy and Allied Products Co., Ltd.

$\gamma$ -APS (>97%),  $\gamma$ -GPS (98%), and ethylenediamine (>99%) were purchased from Aldrich Co. (St. Louis, MO). Paraformaldehyde (>95%), phenol (>99.5%), and NaOH were purchased from Merck Co. (Hohenbrunn, Germany). All chemicals were used without further purification.

### Fiber surface treatment

#### Alkalization

NaOH solutions were prepared with concentrations of 2, 4, and 6 wt %. Fibers were placed in the NaOH solutions at room temperature for 1, 5, and 24 h. The treated fibers were rinsed several times with distilled water until they were neutral. Then, the fibers were dried in an oven for 2 h at 110°C.

#### Silanization

Aqueous solutions of  $\gamma$ -APS and  $\gamma$ -GPS were prepared with concentrations of 0.1 and 0.5 vol %. The pH of the  $\gamma$ -GPS solution was adjusted to 5.5 by hydrochloric acid. The fibers were soaked in the silane solutions for 2 h. The obtained fibers were dried in an oven for 2 h at 110°C.

When silane treatments followed the alkali treatment, the alkali-treated fibers, after being taken out of the alkali solution and rinsed until they were neutral, were squeezed to remove excess water and were then placed directly in the silane solutions for the silanization step.

### Fiber characterization

SEM (JSM 5200, JEOL, Tokyo, Japan; 20 kV) was used to study the surface morphology of the treated fibers. The fiber sample was coated with gold for 4 min before being analyzed. Fourier transform infrared/attenuated reflection spectroscopy (FTIR-ATR) with a ZnSe plate was used to analyze the chemical groups present on the fiber surface. The spectrometer was a Nexus 670 (Nicolet, Madison, WI) with 32 scans at a 4-cm<sup>-1</sup> resolution in the frequency range of 4000–400 cm<sup>-1</sup>. Thermogravimetric analysis (TGA) of the sisal fibers was performed with a Pyris Diamond high-resolution TG-DTA apparatus (PerkinElmer, Wellesley, MA) at a heating rate of 10°C/min with a nitrogen purge with a purge rate of 200 mL/min.

For contact-angle measurements (with a DSA 10-Mk2 contact-angle measurement instrument from Krüss, Hamburg, Germany), the fibers were cut into short segments 3 mm long, and 60 mg of the cut fibers was pressed by a hydraulic press of 8 tons for 5 min to form a disc 13 mm in diameter and 0.45 mm thick. The dynamic contact angles of a water droplet placed on the surface of the disc were measured at every 0.1 s

for 2 s. The curve of the contact angle versus time was recorded for later analysis.

Tensile tests of single sisal fibers were carried out with a Lloyd LRX universal testing machine (Hants, UK). A gauge length of 50 mm was employed with a crosshead speed of 10 mm/min in accordance with ASTM C1557-03. Twenty single fibers of 15 cm were tested. The cross-sectional area of fibers was determined by SEM.

### Preparation of the composites

Sisal fibers were cut into 17-cm lengths and dried in an oven at 60°C overnight to remove the moisture. The diamine-based benzoxazine was synthesized from phenol, paraformaldehyde, and ethylenediamine according to Allen and Ishida.<sup>5</sup> The benzoxazine and epoxy resin were mixed with 50 wt % epoxy without any hardeners or catalysts and then melted and degassed in a vacuum oven at 120°C for 1 h to remove any remaining volatiles. The composite was prepared with a Wabash compression press (Wabash, IN). In the compression-molding process, the mold, measuring 17 cm × 13 cm, was first coated with a silicone mold-release agent and preheated to 140°C. The molten monomer was poured into the preheated mold to fill up to 50% of the mold. Sisal fibers weighing 14.7 g, which amounted to 10 vol % of the composite, were laid unidirectionally in the mold. Because the fibers were fairly stiff and straight in their natural state and were as long as the mold, there was no problem in aligning the fibers to keep them unidirectionally oriented during molding. After the laying of the fibers, the remaining 50% of the resin required to fill the mold was poured onto the laid fibers. The composite was cured according to the temperature program shown in Table I. The thickness of the composite was 3 mm.

### Mechanical testing

Tensile and flexural tests of the composite samples were carried out on an Instron 4206 universal testing machine (Norwood, MA) according to ASTM D 638-96 and ASTM D 790-96a, respectively. Tensile tests were conducted with 10 dumbbell-shaped specimens

TABLE I  
Temperature Program for the  
Compression-Molding Process

Temperature (°C)	Time (min)
140	30 <sup>a</sup>
160	30 <sup>a</sup>
180	60 <sup>b</sup>

<sup>a</sup> Mold unclosed.

<sup>b</sup> Mold closed and compressed by a force of 10 tons.

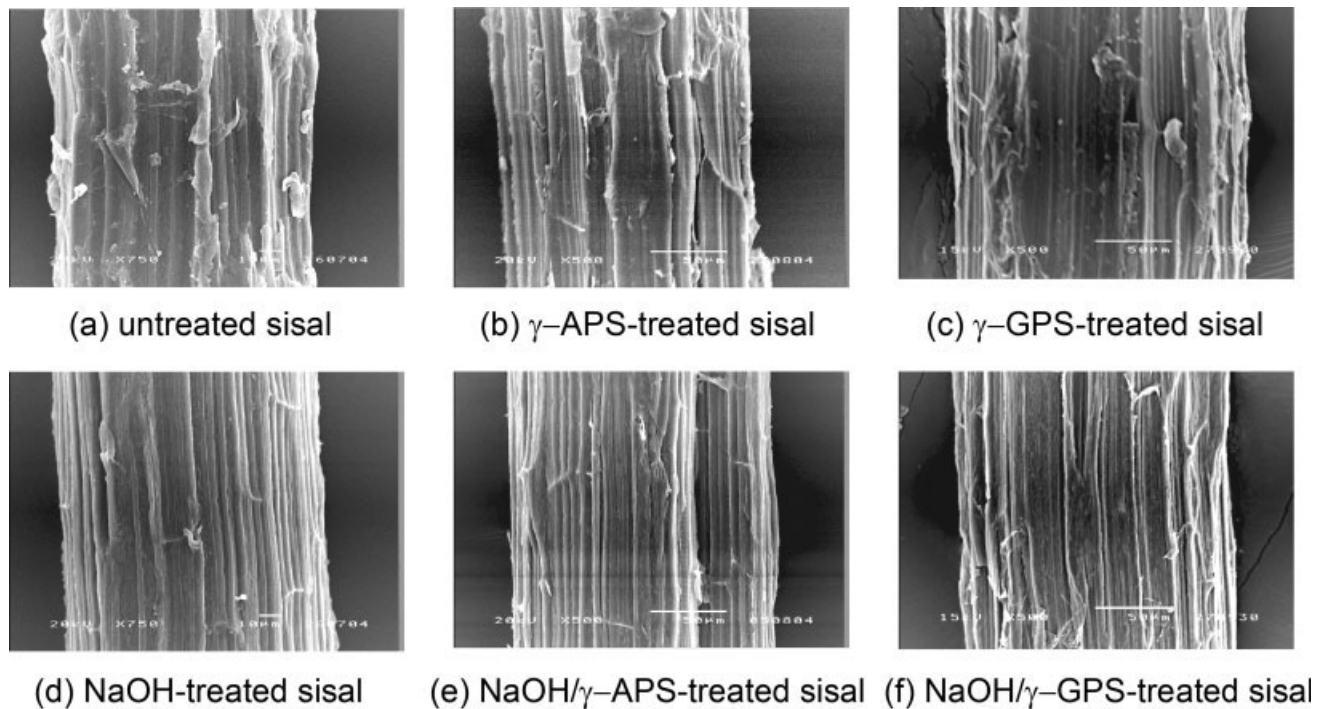


Figure 1 SEM micrographs of the untreated and modified sisal fibers.

140 mm long, a crosshead speed of 5 mm/min, and a gauge length of 50 mm. For flexural tests, five rectangular test specimens of each sample measuring  $62 \times 12.7 \times 3 \text{ mm}^3$  were used at a crosshead speed of 1.28 mm/min in a three-point loading fitted with a 100-kN load cell. Impact tests were performed on a Zwick 5113 pendulum impact tester (Ulm, Germany) in accordance with ASTM D 256-97. Five rectangular test specimens with dimensions of  $62 \times 12.7 \times 3 \text{ mm}^3$  were used. All reported values are the averages of the five tests.

## RESULTS AND DISCUSSION

### Fiber surface treatment

#### Alkali treatment

The alkali treatment promotes the partial removal of the hemicellulose, wax, and lignin present on the fiber surface,<sup>2</sup> leading to changes in the fiber morphology and chemical composition. The change in the surface morphology of the treated fibers was studied by SEM. For untreated sisal and NaOH-treated sisal, Figure 1 shows that the lumps of the cementing materials in the untreated fiber were removed by the NaOH treatment, revealing the surface underneath containing long crevices running along the length of the fiber.

The effect of the alkali treatment on the amount of weight loss of the fibers was studied with NaOH solutions of different concentrations and with different times of treatment. Figure 2 shows that the weight-loss percentage of the sisal fibers increased with the

NaOH concentration. The weight-loss percentage was high initially, and this was followed by a more gradual weight loss at a longer treatment time. In agreement with other lignocellulosic fibers, the significant weight loss of the sisal fiber after the alkali treatment could be ascribed to the partial dissolution of hemicellulose.<sup>2,6</sup>

Figures 3 and 4 show Fourier transform infrared (FTIR) spectra of untreated and NaOH-treated sisal fibers. The intensity of the carbonyl stretching peak at  $1730 \text{ cm}^{-1}$ , corresponding to hemicellulose of the fibers,<sup>6</sup> was continuously reduced when the treatment

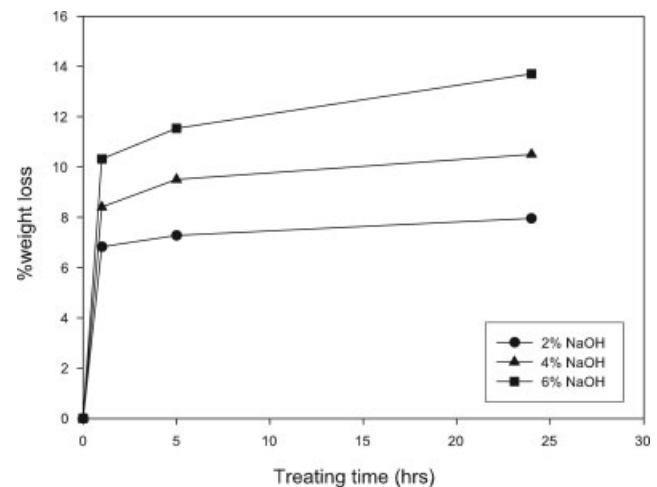
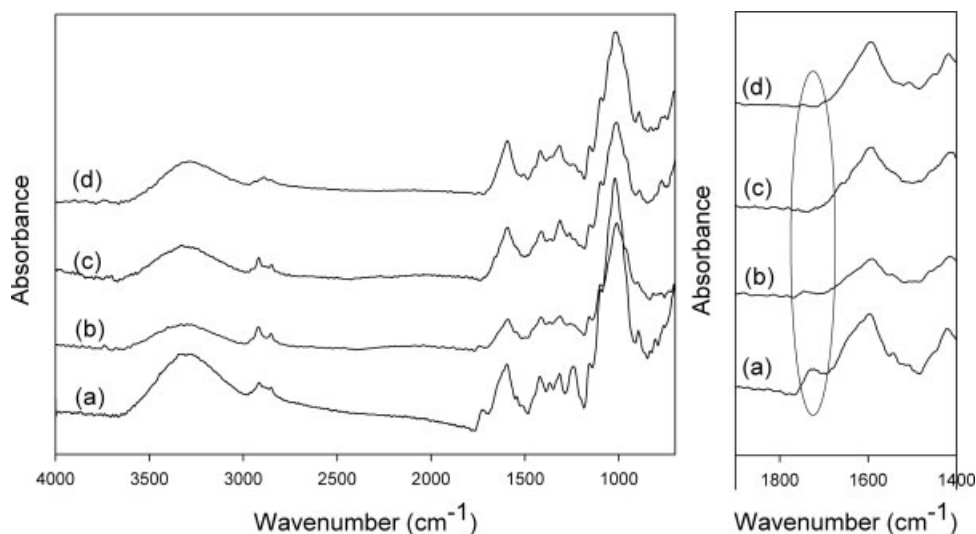


Figure 2 Weight-loss percentage of sisal fibers after NaOH treatments at different times.



**Figure 3** FTIR spectra of (a) untreated fibers and (b–d) NaOH-treated fibers with treatment times of (b) 1, (c) 5, and (d) 24 h with a NaOH concentration of 6%.

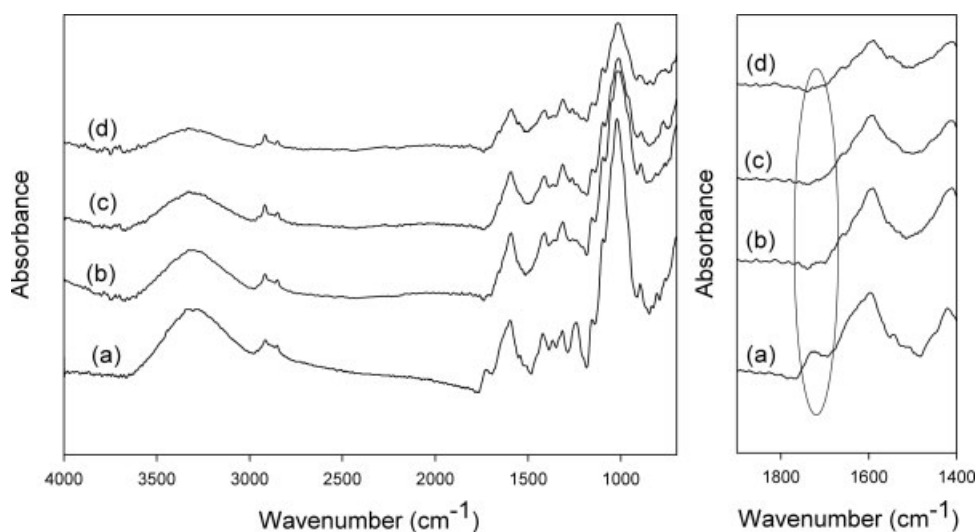
time and NaOH concentration increased until it could no longer be perceived for the 5-h curve in Figure 3 and 6% curve in Figure 4. A 6% concentration and a 5-h treatment period, during which hemicellulose at the fiber surface was mostly removed, were chosen as the conditions of NaOH treatment for the next experimental part.

Figure 5 shows the TGA and differential thermogravimetry (DTG) thermograms of untreated fibers and fibers treated with 6% NaOH for 5 h. The thermogram of the untreated fibers shows two decomposition steps. The first peak appears at 300°C and corresponds to the thermal decomposition of hemicellulose and the glycosidic links of cellulose. The second one appears around 360°C because of the thermal decomposition

of  $\alpha$ -cellulose.<sup>9</sup> In the case of NaOH-treated fibers, the peak at 300°C is not present, and this confirms the removal of hemicellulose during the treatment, leaving the more stable  $\alpha$ -cellulose; hence, the TGA thermogram for the treated fibers was found to move to a higher temperature with a higher char yield. Similar results were obtained by Valadez-Gonzalez et al.<sup>10</sup>

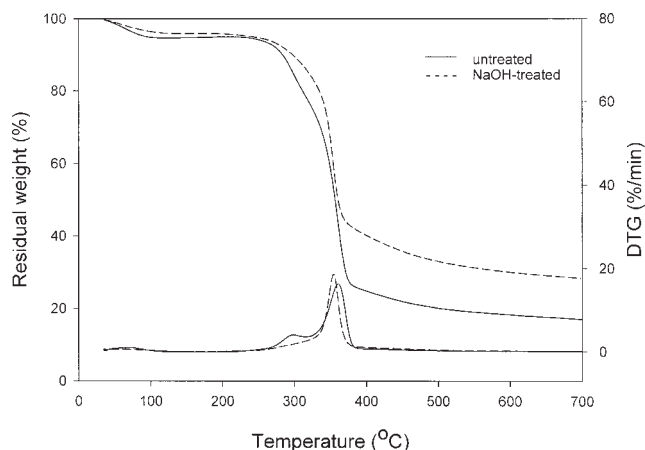
#### Silane treatment

Figure 1 shows the SEM micrographs of the  $\gamma$ -APS-treated fiber and the  $\gamma$ -GPS-treated fiber. There is no dramatic change in the surface morphology of the silane-treated fiber compared with that of the untreated one, and the surface morphologies of the NaOH/



**Figure 4** FTIR spectra of (a) untreated fibers and (b–d) NaOH-treated fibers at concentrations of (b) 2, (c) 4, and (d) 6% for 5 h.





**Figure 5** Thermograms of untreated fibers and fibers treated by 6% NaOH for 5 h.

$\gamma$ -APS-treated and NaOH/ $\gamma$ -GPS-treated fibers are also not visibly different from that of the NaOH-treated fiber. The results show that a silane coupling agent forms only a thin film on the silane-treated fiber surface.

FTIR-ATR was used to analyze the chemical functionalities present on the surface. Because of the small quantities of silanes present on the fiber surface, the analysis was based on the spectral differences between the treated and untreated samples. The difference spectra of  $\gamma$ -APS- and  $\gamma$ -GPS-treated sisal surfaces are shown in Figures 6 and 7, respectively. In general, free  $\text{NH}_2$  groups show a band around  $1600\text{ cm}^{-1}$ . Figure 6 shows that  $\gamma$ -APS-treated fibers have a distinctive absorbance peak at  $1575\text{ cm}^{-1}$ . This band is the typical deformation mode of  $\text{NH}_2$  groups hydrogen-bonded to the OH functions of both silanol moieties and cellulosic fiber.<sup>4,11,12</sup> The band around  $1130\text{ cm}^{-1}$  is related to the Si—O—C group, whereas the absorption band at  $1030\text{ cm}^{-1}$  corresponds to the Si—O—Si bond.<sup>4</sup>

The Si—O—Si bond is indicative of the existence of polysilsesquioxane deposited on the fiber, and the Si—O—C bond could confirm the occurrence of a condensation reaction between the silane coupling agent and the sisal fiber. The Si—O—C group is also present in the unhydrolyzed silane. However, the conditions adopted in this study do not leave the unhydrolyzed species at a detectable concentration.<sup>13</sup> Although the observation of the Si—O—C-related band might seem to indicate the presence of the interfacial bond, the weakness of the band and complex spectral features necessitate further study before conclusive statements can be made.

The changes in the water contact angle on the sisal sheets after treatments with  $\gamma$ -APS, NaOH/ $\gamma$ -APS,  $\gamma$ -GPS, and NaOH/ $\gamma$ -GPS are shown in Figure 8, which presents the dynamic acquisition of the values of the contact angle with time. The dynamic contact angle of

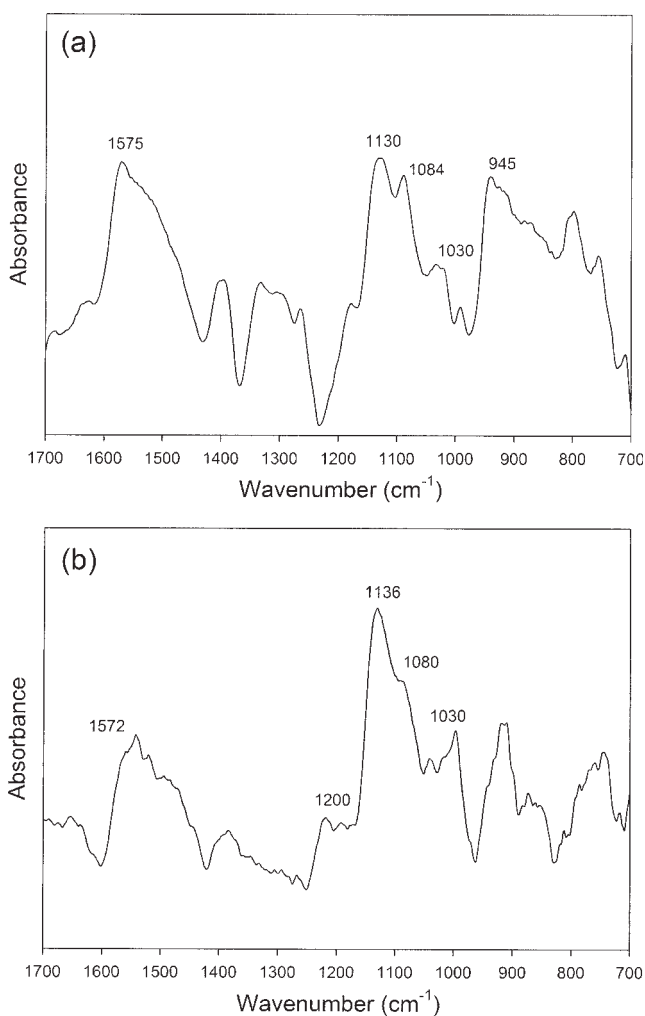
the untreated fiber had an initial value of  $62^\circ$ , which decreased sharply to below  $10^\circ$  after 0.6 s. The silane-treated fiber, on the other hand, had a higher initial contact angle, which decreased only slightly and gradually with time up to the end of the experiment at 1.7 s. The results show that the silane-treated fiber was more hydrophobic than the untreated fiber. With 0.1%  $\gamma$ -APS, the initial contact angles increased from  $62^\circ$  for the untreated sample to  $72^\circ$ . This increment resulted from the  $\gamma$ -APS configuration, which was assumed to orient its polar  $\text{NH}_2$  heads toward the fiber surface and form hydrogen bonds with the cellulose hydroxyl groups. Such a configuration would leave the methylene sequence exposed at the surface, thus providing the hydrophobic character.<sup>4</sup> The higher concentration of  $\gamma$ -APS of 0.5% resulted in a higher contact angle of about  $83^\circ$ . González-Benito et al.<sup>14</sup> investigated the dynamic contact angles of modified glass fibers and found that silanization with  $\gamma$ -APS reduced the solid surface tension, showing the nonpolar character of the coating, and this agrees with the contact-angle results in this study.

The NaOH treatment coupled with the  $\gamma$ -APS treatment showed almost the same result as the treatment with only silane in the case of 0.1%  $\gamma$ -APS. However, in the case of the 0.5%  $\gamma$ -APS treatment, the NaOH treatment enhanced the hydrophobic character, as can be seen from the highest value of the contact angle at  $89^\circ$ . From the results, it can be concluded that the alkali treatment removed some hemicellulose from the fibers, thus making cellulose fibrils and their hydroxyl groups more exposed to the fiber surface. After the alkali treatment, the condensation between the silanol groups of silane and the hydroxyl groups of the sisal fibers could occur more readily than that without the alkali treatment.

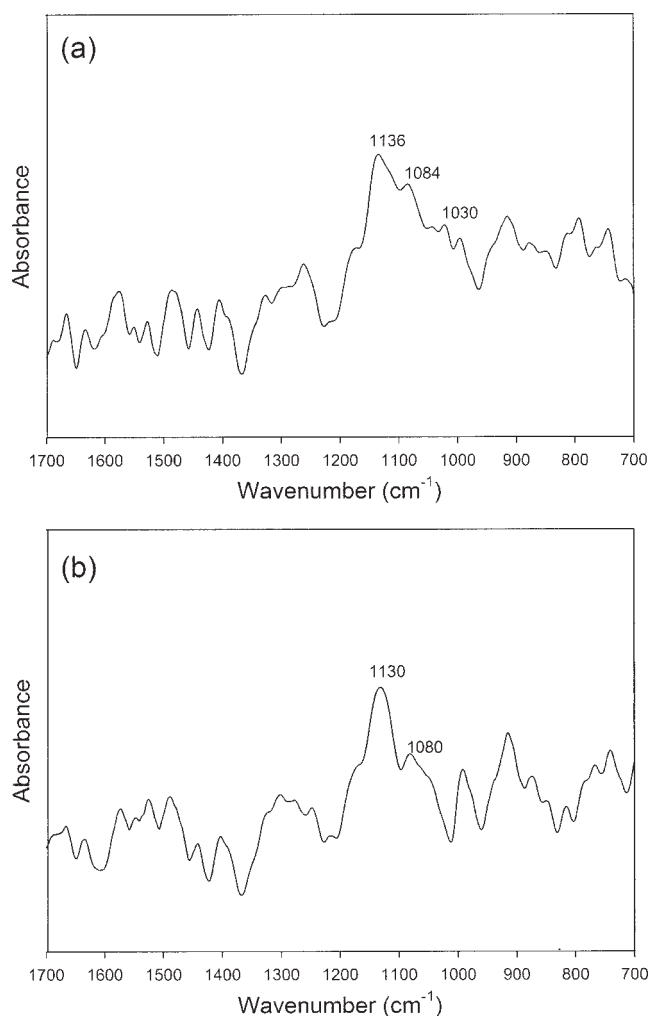
In the cases of  $\gamma$ -GPS treatment, the initial contact angle increased from  $62^\circ$  for the untreated sample to  $72^\circ$  with 0.1%  $\gamma$ -GPS and to  $77^\circ$  with 0.5%  $\gamma$ -GPS. As in the case of the  $\gamma$ -APS treatment, fibers treated with 0.1% and 0.5%  $\gamma$ -GPS after the alkaline treatment showed the highest values of the contact angle. From these results, it can be concluded that silane was deposited onto the fiber surface, providing more hydrophobic character, and the alkali treatment enhanced the efficiency of the deposition.

### Effect of fiber surface modification on the mechanical properties of the composites

The mechanical performance of a fiber-reinforced composite primarily depends on three factors: (1) the strength and modulus of the fibers, (2) the strength and toughness of the matrix, and (3) the effectiveness of fiber–matrix bonding in transferring stress across the interface. For a unidirectional composite, the longitudinal tensile response is mainly governed by the



**Figure 6** Difference spectra of (a)  $\gamma$ -APS-treated and untreated fibers and (b) NaOH/ $\gamma$ -APS-treated and NaOH-treated fibers.



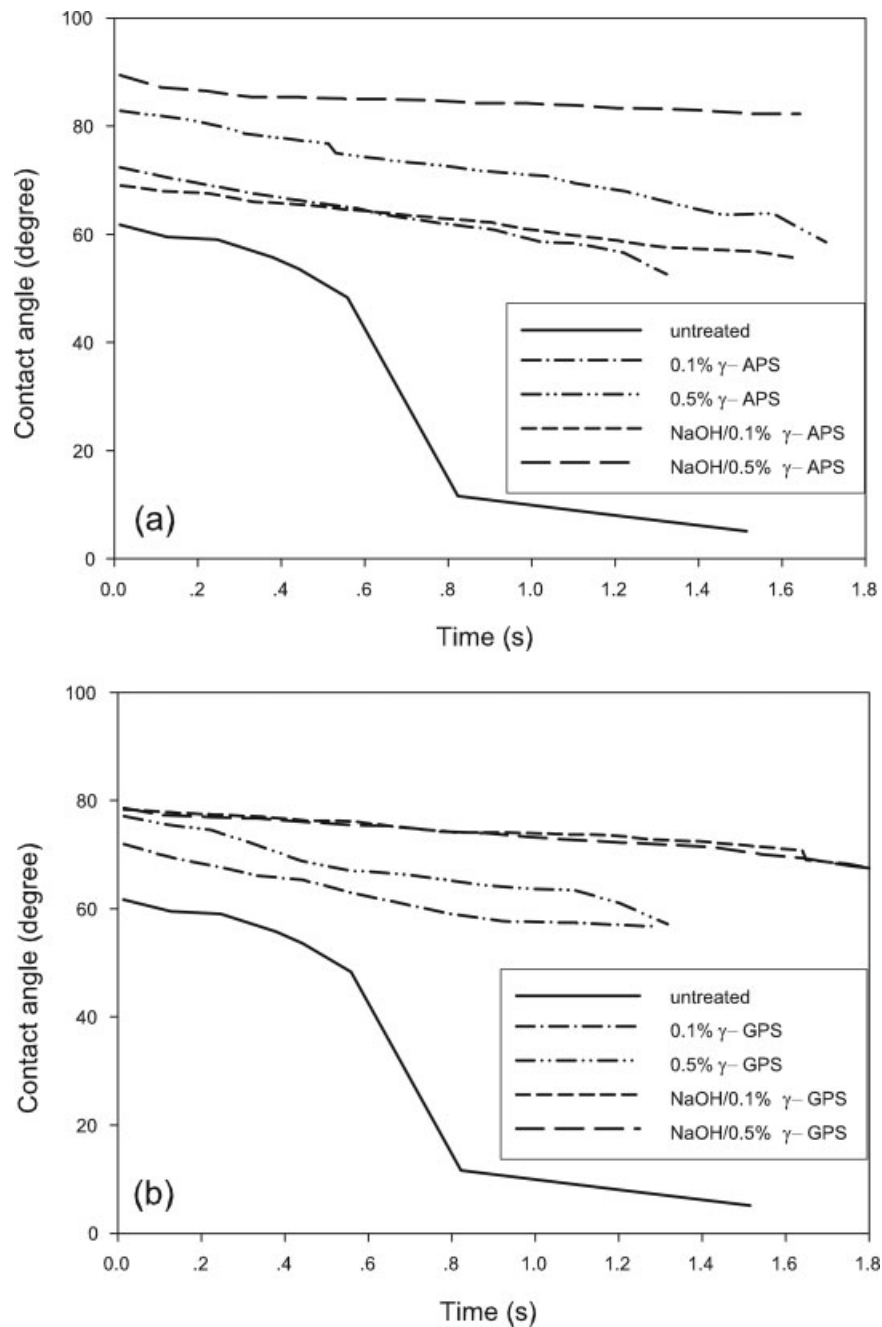
**Figure 7** Difference spectra of (a)  $\gamma$ -GPS-treated and untreated fibers and (b) NaOH/ $\gamma$ -GPS-treated and NaOH-treated fibers.

fiber properties, whereas the transverse response is strongly dependent on the matrix properties.<sup>15</sup> Thus, the effect of the surface treatment on the longitudinal mechanical properties will be discussed on the basis of two factors: the strength of the fibers and interfacial bonding.

Figure 9(a–c) shows the tensile, flexural, and impact properties of the composites, respectively. In general, the standard deviations are relatively high, especially in the tensile properties. This is due partly to the inherent nonhomogeneity of the natural fiber and to the nonuniform fiber distribution in the composite, which can be expected in the hand-lay method. However, the results will be discussed on the basis of the average values obtained. In Figure 9(a), the NaOH-treated sisal composites show an average tensile strength less than that of the untreated sisal composites. According to the previous study described in the Alkali Treatment section, the NaOH treatment partly removes the cementing materials, lignin and hemicellulose, in sisal

fibers, so this could reduce the strength of the fiber. The tensile strength of the fiber before and after the alkali treatment was determined, and it was found that tensile strength of the fiber decreased from 489.9 to 243.6 MPa after treatment in 6% NaOH for 5 h at room temperature. Although the fiber–matrix adhesion may be improved and the stress may be transferred well to the fibers, it cannot compensate for the reduction in the fiber strength, so the tensile strength of the composites is not as high as that of the untreated sisal composites.

The average tensile modulus of the NaOH-treated sisal composites, however, is higher than that of the untreated one. After the NaOH treatment, the sisal fiber surface is rougher, and the static frictional force is increased. Thus, the fiber–matrix adhesion is enhanced by mechanical interlocking. It is believed that the vacancies outside and inside the fiber left by the NaOH treatment facilitate penetration of the resin, which replaces the removed cementing materials.<sup>6</sup>



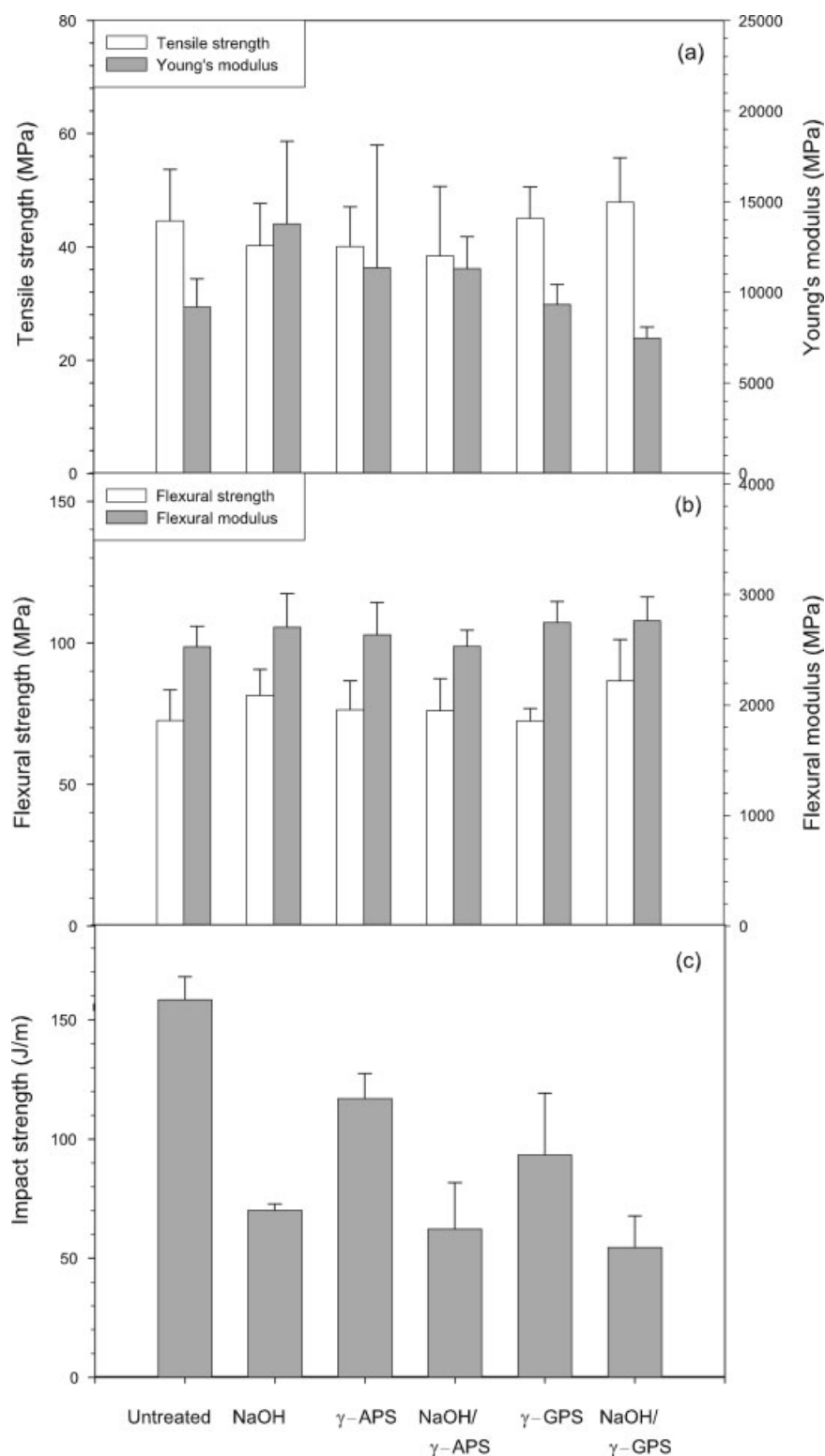
**Figure 8** Water contact angles of untreated fibers and sisal fibers treated with (a)  $\gamma$ -APS and (b)  $\gamma$ -GPS.

Because the immigrated resin is connected to the bulk matrix, forming a network, the higher rigidity of the composite is also reflected in the decrease in its extensibility, so the modulus is increased.

The improved adhesion between the treated fibers and the polymer matrix can be clearly seen in the SEM micrographs of the tensile fracture surface of the unidirectional sisal-benzoxazine/epoxy composites, as shown in Figure 10. With a weak interfacial bond, the fracture is more likely to lead to interfacial debonding and extensive fiber pullout. If bonding is strong, the failure

mode is fiber breakage at the fracture point, resulting in a fairly smooth surface across the section.<sup>15</sup> For the untreated sisal composite, the failure mechanism is interface debonding; the composite shows the surface with the fiber pulled out from the matrix. On the other hand, the fracture of the NaOH-treated fiber occurs at the crack plane in the composite.

Figure 9(a) shows the tensile properties of the sisal-benzoxazine/epoxy composites with different fiber surface modifications. The  $\gamma$ -APS-treated sisal composite and the NaOH/ $\gamma$ -APS-treated sisal composite

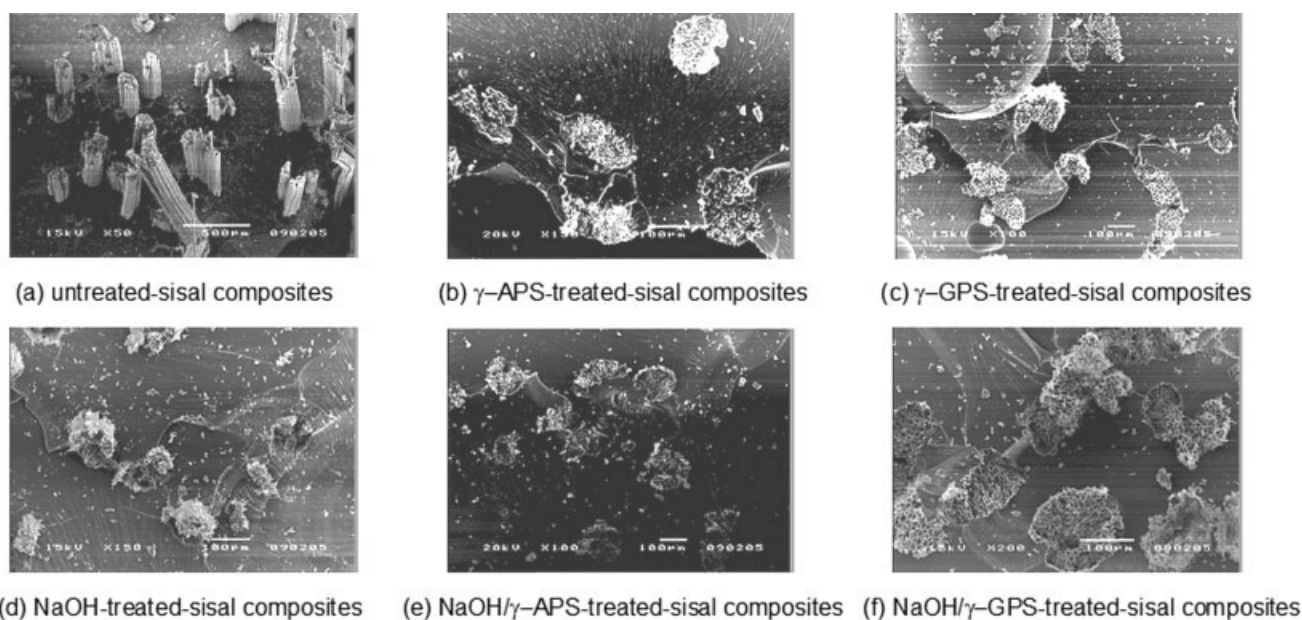


**Figure 9** Effects of fiber surface modifications on the mechanical properties of sisal-benzoxazine/epoxy composites: (a) tensile properties, (b) flexural properties, and (c) impact strength.

show similar tensile properties. The average tensile strength of these composites is lower than that of the untreated sisal composite. Figure 11 shows that the average tensile strength of the  $\gamma$ -APS-treated sisal

fiber is reduced because the fiber treatment with the aminosilane is performed under a basic condition (the natural pH of the silane solution exceeds 10 when alkoxy groups of  $\gamma$ -APS are hydrolyzed in water<sup>13</sup>)





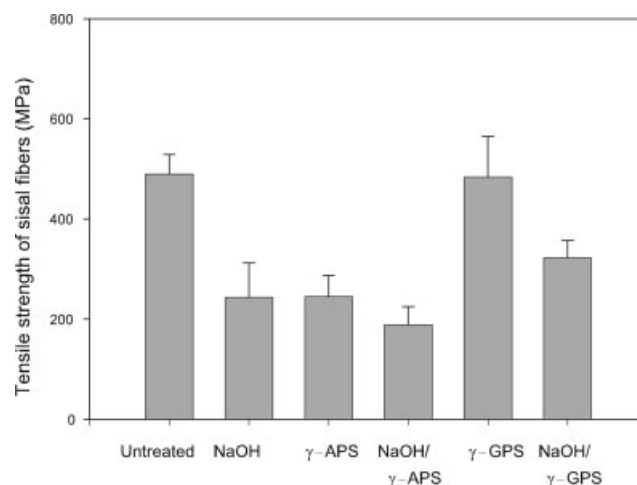
**Figure 10** SEM micrographs of tensile fracture surfaces of sisal-benzoxazine/epoxy composites with untreated and treated fibers.

like the alkaline treatment, and thus some cementing materials of the fibers may be partially removed. The tensile strength of the NaOH/ $\gamma$ -APS-treated sisal fiber is lower than that of the sisal fiber treated by only  $\gamma$ -APS. This reduction of the fiber tensile strength causes a lower composite tensile strength than that of the untreated one. However, the relatively high average modulus of  $\gamma$ -APS-treated sisal composites compared with that of untreated sisal composites reveals less tensile strain at break and better interfacial interaction, which can be explained as in the case of the alkaline treatment. The SEM micrographs of the tensile fracture surfaces give supporting evidence. The SEM results do not reveal fiber pullout, and this indicates good adhesion between the matrix and fiber. The improvement of interfacial bonding in the  $\gamma$ -APS-treated sisal composite might be the result of hydrogen bonding between amino groups on the  $\gamma$ -APS-treated fiber and hydroxyl groups in the polymer matrix.

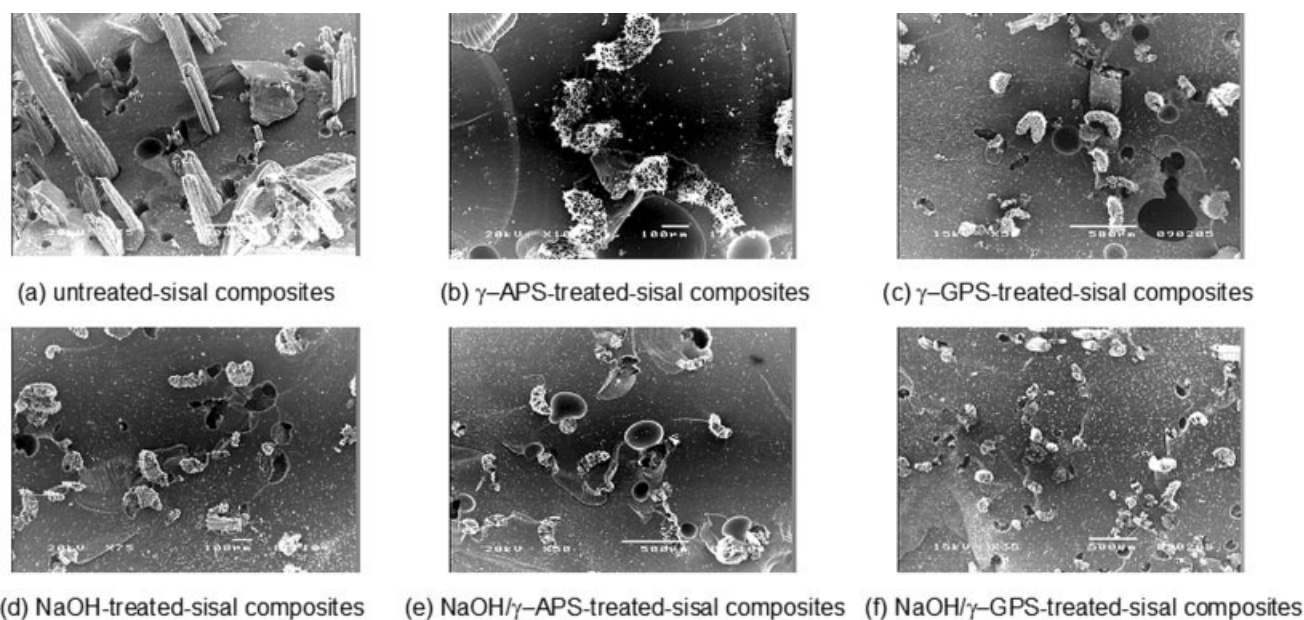
The  $\gamma$ -GPS-treated sisal composites show an average tensile strength higher than that of the  $\gamma$ -APS-treated sisal composites. Compared with the  $\gamma$ -APS-treated sisal, which might form a hydrogen bond to the polymer matrix, the  $\gamma$ -GPS-treated sisal fiber can bond covalently with the hydroxyl groups of the polymer matrix while minimizing the damage on the fiber during the treatment. Thus, in terms of interfacial bonding, the  $\gamma$ -GPS-treated sisal composite is better than the  $\gamma$ -APS-treated sisal composite. In terms of the strength of the treated fibers, the pH of the solution in the  $\gamma$ -GPS treatment is about 5.5. Thus, it does not affect the fiber strength, as shown in Figure 11.

Additionally, the hydrogen bonding of the amino group of  $\gamma$ -APS to the fiber surface might reduce the reactivity to the matrix. The results from both factors make the tensile strength of the  $\gamma$ -GPS-treated sisal composite higher than that of the  $\gamma$ -APS-treated sisal composite.

When the sisal fiber was first treated with the NaOH solution and then by  $\gamma$ -GPS, the average tensile strength was improved. It is believed that  $\gamma$ -GPS can react easily with cellulose microfibrils in the NaOH-treated sisal fibers because the alkaline treatment removes some hemicellulose and makes cellulose more exposed to the fiber surface. Thus, the NaOH/ $\gamma$ -GPS treatment leads to an interfacial interaction



**Figure 11** Dependence of the tensile strength of sisal fibers on the surface treatments.



**Figure 12** SEM micrographs of impact fracture surfaces of sisal-benzoxazine/epoxy composites with untreated and treated fibers.

stronger than that in the case of an individual  $\gamma$ -GPS or NaOH treatment. The highest average tensile strength of the NaOH/ $\gamma$ -GPS-treated sisal composite gives supporting evidence.

Making a comparison with the tensile properties, Rong et al.<sup>6</sup> showed that the flexural failure of composites depends mainly on the fiber/matrix interface rather than the fiber strength. In general, the flexural strength and flexural modulus are slightly improved by the fiber surface treatments. According to Figure 9(b), the NaOH/ $\gamma$ -GPS-treated sisal composite has the highest average flexural strength and the highest average flexural modulus. This result agrees with the results from the tensile tests, which show that the NaOH/ $\gamma$ -GPS treatment gives the best interfacial bonding in this work.

For the Izod impact test shown in Figure 9(c), in all cases of fiber surface treatment, the average impact strengths of the treated fiber composites are lower than that of the untreated one. In most fiber-reinforced composites, a significant part of the energy absorption during impact takes place through the fiber-pullout process.<sup>7</sup> The low impact strength of treated fiber composites is due to the improved bonding of the treated fiber with the polymer matrix, which results in the fracture of the fiber at the crack plane, as can be seen in Figure 12. The untreated fiber composites show the impact failure with many fibers pulled out. In contrast, in the case of the treated fiber composites, more tearing of the fibers can be observed, together with a few cavities left by pulled-out fibers.

If the lower impact strength (less energy absorption from the fiber pullout process) means better interfacial

adhesion, the effect of different surface treatments can be concluded as follows:

1. The NaOH treatment coupled with the silane treatment results in better adhesion than the individual silane treatment or NaOH treatment.
2. The  $\gamma$ -GPS treatment gives better fiber-matrix bonding than the  $\gamma$ -APS treatment. This agrees with the results of tests of the tensile strength and flexural strength.

## CONCLUSIONS

The surface modifications of sisal fibers with NaOH,  $\gamma$ -APS, and  $\gamma$ -GPS led to changes in the morphology, chemical groups, and hydrophilicity of the fibers. When treated sisal fibers were incorporated into a benzoxazine/epoxy resin to form a unidirectionally reinforced composite, fiber-matrix adhesion was better, and this led to improved mechanical properties of the composites. However, the conditions of the fiber treatment significantly affected the fiber strength and composite properties. The  $\gamma$ -GPS treatment led to good fiber-matrix bonding while minimizing the damage to the fiber during the treatment. The NaOH treatment coupled with the silane treatment resulted in better adhesion than the individual silane treatment or NaOH treatment.

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