

# Scanning Electron Microscopy Study of Chemically Modified Coir Fibers

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**ABSTRACT:** Chemical-surface modification of coir fibers was done by dewaxing, using an alkali treatment (5% and 10% NaOH), vinyl grafting with methyl methacrylate (MMA) and cyanoethylation. The chemically modified fibers were characterized by Fourier transform infrared (FTIR) spectroscopy. In addition, the surface features of untreated, dewaxed, alkali-treated, grafted, and cyanoethylated coir fibers were studied using scanning electron microscopy (SEM). Progressive changes in surface morphology were observed. SEM observations showed the removal of tyloses from the surface of coir as a result of alkali treatment (5%), resulting in a rough fiber surface with regularly spaced pits. At a lower percentage of grafting (PMMA), the surfaces became more or less uniform, while the surfaces of the coir fibers with a higher percentage of grafting were increasingly covered with grafted materials, resulting in canal-like cavities between the overgrowths of the grafted materials on the unit cells. Cyanoethylated coir-fiber surfaces showed an insufficient deposit of cyanoethyl groups. SEM analysis of the samples was corroborated by measurements of a mechanical property (maximum stress at break). © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1169–1177, 2001

**Key words:** coir fiber; tyloses; unit cell; tensile strength

## INTRODUCTION

Coir is a versatile lignocellulosic fiber obtained from coconut trees (*Cocos nucifera*) and is available in very large quantities, on the order of 5 million tons a year worldwide. Coir consists of cellulose fibers with hemicellulose and lignin as the bonding materials for the fibers. Therefore,

the coir fiber is in a sense a fibrous composite material.

Coir has several valuable physical properties that stem from its structure. Among the most useful properties are length, fineness, strength, rigidity, wettability, resistivity,<sup>1</sup> and resistance to dampness. These properties make the coir fiber extremely useful for various domestic and commercial applications. Another important application for coir, developed over the last few decades, is as part of the preparation of composites of different polymers,<sup>2,3</sup> In most of these applications coir fiber is used in both its natural and modified forms. A study on the surface morphology of a

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fiber that can be used in both its natural and chemically modified forms will be more helpful because user of the fiber will be applicable to several meaningful purposes. Several previous studies<sup>4–8</sup> sought to understand the structure, mechanical properties, and chemical-treatment effects on the properties of coir fiber. Mercerization, essentially a simple alkali treatment, is a well-known commercial process that largely improves the luster of textile fibers such as cotton and their reactivity toward dyes. Prasad et al.<sup>9</sup> studied the effect of an alkali treatment on the microstructure, surface topography, and tensile strength of coir fiber, while Sreenivasan et al.<sup>10</sup> studied the effect of an alkali treatment on the fine structure of coir fiber.

Graft copolymerization of vinyl monomers is one of the universal, effective, and accessible methods for chemical modification of high-molecular-weight compounds, in particular of natural polymers.<sup>11,12</sup> It is known that grafting takes place in two ways, either by interaction of the monomer at the surface of the cellulosic structure or at random within the cellulose molecule. Surface grafting may lead to different effects on the properties than those produced by volumetric grafts located throughout the fiber. To improve the resistance of the cellulosic fiber against abrasion or to make fiber hydrophobic, surface grafting may be done. Kundu et al.<sup>13</sup> examined microscopically the transverse section of polyacrylonitrile-grafted jute fiber. They observed that the fibers were almost completely penetrated by polymer deposits, although the polymer concentration appeared to be greater near the surface. Hebeish<sup>14</sup> observed that it wasn't possible to compare the grafting mechanism used for one cellulosic material with that used with another, as grafting onto hydrocellulose was found to be more of a surface phenomenon, while grafting onto swollen cotton and viscose take place inside the fiber. Iwakura et al.<sup>15</sup> observed a cross section of cellulose grafted with glycidyl methacrylate (GMA) and found that when initiated by Ce(IV) ions, the grafting of GMA starts from the surface of the fiber and as the grafting ratio is increased, it progresses toward the center.

Despite all the previous reports on chemical modifications of coir fiber, the literature survey reveals no systematic work exclusively on the morphological changes of coir fiber resulting from various chemical modifications of the fiber surface, observed with the help of scanning electron microscopy (SEM). The present work primarily

elaborates on SEM observations of the changes in surface topology brought about by different chemical treatments such as dewaxing, mercerization, grafting with MMA, and cyanoethylation. In addition to the SEM study, the procedure for the chemical modifications adopted and the characterization of the modified fiber by FTIR are briefly reported.

## EXPERIMENTAL

### Materials

Used in these experiments were raw Bristol coir fiber, alkali-treated (5% and 10% NaOH solutions) coir fiber, MMA-grafted coir fiber, and cyanoethylated coir fiber.

Raw Bristol coir fibers were first subjected to Soxhlet extraction with acetone for about 24 h, followed by washing with distilled water and air-drying. The fibers were then extracted in a 1:2 (v/v) mixture of ethanol and benzene for 72 h to dewax the sample, followed by washing with distilled water and air-drying. The fibers thus obtained were referred to as dewaxed or defatted fibers.

### Treatment with Alkali

The defatted fibers were immersed in different concentrations of an NaOH solution (5% and 10%) at 30°C for 1 h, after which the fibers were washed repeatedly with water and then air-dried.

### Graft Copolymerization

Graft copolymerization of methyl methacrylate (MMA) onto 5% alkali-treated coir fiber was carried out by the usual method<sup>16</sup> in an aqueous medium using Cu(II)—IO<sub>4</sub><sup>-</sup> as the initiator system. The homopolymer PMMA [poly(methyl methacrylate)], along with the grafted coir fibers, was filtered off, washed with distilled water, and dried in a vacuum oven. Finally, the grafted fibers were extracted with acetone in a Soxhlet apparatus for 12 h to dissolve all the homopolymers and subjected to drying overnight in a vacuum oven. The process of extraction and drying in a vacuum oven continued until a constant weight of the grafted fiber was obtained. The percentage of grafting was estimated as follows:

$$\% \text{ of grafting} = \frac{\text{dry wt. of grafted coir} - \text{dry wt. of original coir}}{\text{dry wt. of original coir}} \times 100$$

### Cyanoethylation

Cyanoethylation of 5% alkali-treated coir fibers was carried out by refluxing the fibers with AN (Acrylonitrile), acetone, and pyridine (catalyst) at 60°C for 2 h. After the reaction was over, the fibers were washed with dilute acetic acid, acetone, and distilled water and then air-dried.

### FTIR Spectra

FTIR spectra in the form of KBr pellets of the finely ground fiber samples were recorded on a JASCO-5300 FTIR spectrophotometer.

### Scanning Electron Microscopy

Scanning electron microscopy (SEM) of fiber the samples was recorded using a JEOL-JSM 35 CF scanning electron microscope with the following specifications—accelerating voltage: 10–15 KV; image mode: secondary electron image; working distance: 15 mm. Since the fibers were nonconducting, they were coated with 10 nm of gold using the sputtering technique.

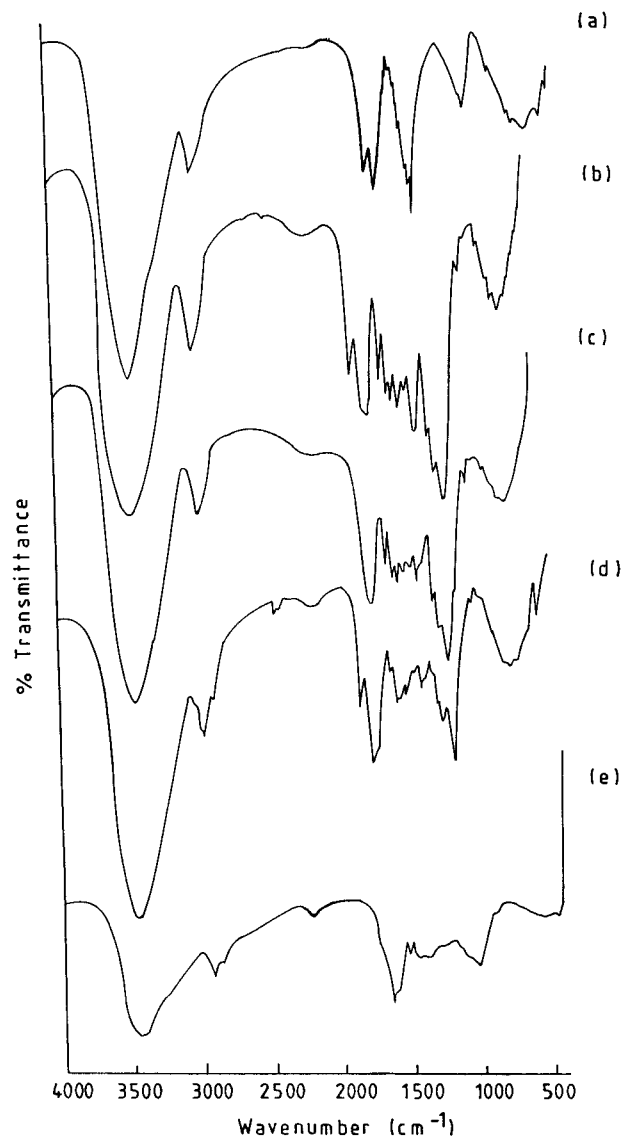
### Mechanical Property

The maximum stress at break of the coir fibers was determined by Universal Testing Machine LR 100 K at a gauge length of 150 mm and strain rate of 450 mm per minute. Each result was reported as an average of 10 fibers.

## RESULTS AND DISCUSSION

### Characterization of Chemically Modified Coir Fibers by FTIR

The characterization of modified coir fibers constitutes an important part of our investigation. The FTIR spectra of the untreated and chemically modified coir fiber are shown in Figure 1. The spectra from Figure 1(a–e) represent, respectively, the untreated, dewaxed, alkali treated (5%), MMA grafted (~10%), and cyanoethylated coir fibers. In all these spectra a broad and intense peak centering at  $\sim 3400\text{ cm}^{-1}$  can be seen, the result of the hydrogen-bonded O–H stretching vibration from the cellulose structure of the coir fiber. When comparing Figure 1(a–d) with Figure 1(e), we find that the OH peak at  $\sim 3400\text{ cm}^{-1}$  is relatively weaker in case of the latter (cyanoethylated fiber). This decrease in intensity corroborates the reaction of AN with the OH



**Figure 1** FTIR Spectra of different chemically modified coir fibers: (a) untreated, (b) dewaxed, (c) alkali treated (5%); (d) MMA grafted (~10%); (e) cyanoethylated.

groups of cellulose during cyanoethylation. This reaction destroys a large number of OH groups of the cellulose structure. The minor variations in the positions of the OH peak in all the above figures also indicates the participation of OH groups in these chemical reactions either directly or indirectly. Another interesting feature can be observed when comparing Figure 1(a–c) with Figure 1(d). It was expected that the grafting of MMA onto the fiber would take place at the site of OH group, with the OH peak intensity expected to decrease as a consequence. However, in our case,

the OH peak for the MMA-grafted fiber [Fig. 1(d)] is as intense as for the other fibers [Fig. 1(a–c)]. Two reasons may account for this: either the grafting site may be other than that OH group, or it may be a pseudografting process, in which the PMMA is not covalently bonded with the fiber backbone but rather is deposited on the surface with strong physical adsorptive forces. The less intense peak in all these spectra, at  $\sim 2900\text{ cm}^{-1}$ , results from the aliphatic C–H stretching vibration. A sharp peak in the region around  $\sim 1720\text{ cm}^{-1}$  in the untreated and dewaxed fibers [Fig. 1(a) and Fig. 1(b), respectively] can be seen. This peak results from the carbonyl absorption of the hemicellulose. The peak at  $\sim 1720\text{ cm}^{-1}$  is also absent in Figure 1(c) (the alkali-treated coir fiber) and Figure 1(e) (the cyanoethylated coir fiber). This might be because of the removal of the reducible hemicellulose during alkali-treatment and cyanoethylation processes. The presence of the said peak in Figure 1(d) (the MMA-grafted coir fiber) is a result of the C=O stretching of the ester function present in the PMMA unit. The weak peak at  $\sim 2200\text{ cm}^{-1}$  seen in Figure 1(e) (the cyanoethylated fiber) results from  $\text{—C}\equiv\text{N}$  stretching. The weak band in the case of the cyanoethylated coir as against a sharp and strong  $\text{—C}\equiv\text{N}$  peak normally found for the PAN-grafted fibers may be because in cyanoethylated coir, only a single AN molecule adds per OH group of cellulose macromolecule. A positive test for nitrogen by Lassaigne's test<sup>17</sup> confirmed the presence of nitrogen in the cyanoethylated coir. A similar observation for cyanoethylated pineapple leaf fiber has been reported previously.<sup>18</sup>

### SEM Analysis

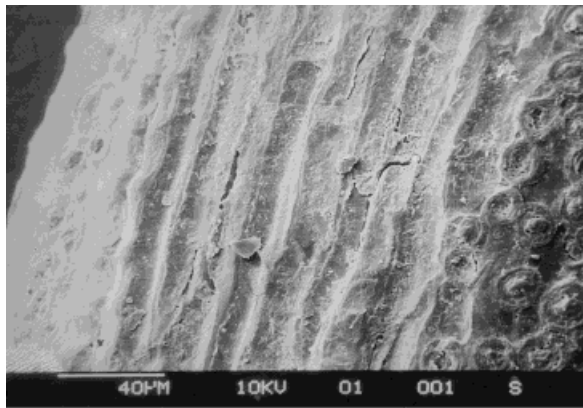
SEM pictures of untreated coir-fiber surfaces at increasing magnifications are shown in Figure 2(a–c). From all three pictures it can be observed that the unit cells run longitudinally with more or less parallel orientations. The intercellular gaps, in the form of shallow longitudinal cavities, can be clearly marked as the unit cells are partially exposed. The intercellular space is filled up by the binder lignin and by fatty substances that hold the unit cells firmly in the fiber. At several places, particularly to the right of Figure 2(a), a large number of globular protrusions or patches around  $10\text{ }\mu\text{m}$  in diameter and embedded in the fiber surface at regular intervals can be observed. These have been designated "tyloses." A small

number of surface cracks also can be observed in these micrographs, which are especially clear in Figure 2(b,c).

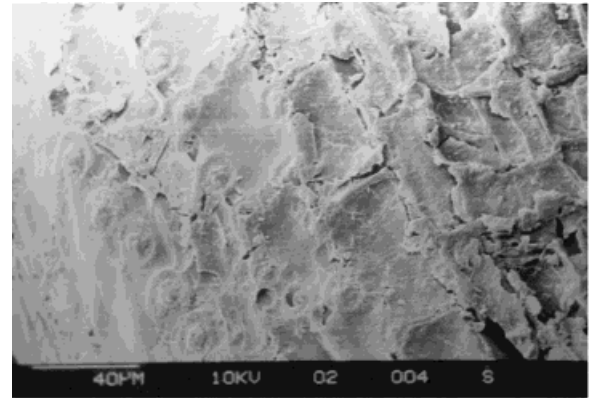
SEM pictures of the dewaxed coir fiber at increasing magnifications are shown in Figure 3(a–c). In these pictures are apparent a larger number of surface cracks, or pit formations, compared to Figure 2(a–c). These might occur because of the partial removal of wax and fatty substances during treatment with the dewaxing solvent mixture. Very interestingly, the parallel unit cells look partially split due to the removal of fatty materials. From the data in Table I it can be found that the tensile strength of the dewaxed fiber is greater than that of the untreated fiber. This might be because of the increase in the degree of orderly arrangement of the cellulose and lignin structure present in the fiber. However, the ordering isn't evident from the SEM pictures of the dewaxed fibers.

Micrographs with increasing magnifications of the 5% alkali-treated fiber are shown in Figure 4(a,b). The pictures show a large number of regularly placed holes or pits on the surfaces. These are most possibly from the removal of fatty-deposit tyloses on the surface. Given the large number of these pits, it can be considered that a large number of the tyloses, globular fatty deposits, were lying hidden inside the surfaces of the untreated fiber. These were therefore not revealed in the untreated fiber, only partially revealed in the dewaxed fiber, and largely revealed in the fiber treated with 5% alkali. At this lower concentration of alkali treatment, thickening of the cell walls does not occur, and hence the shrinkage of the unit cells does not take place. This can be verified by comparing the nature of the unit cells and the intercellular gaps for untreated and 5% alkali-treated fibers. Barring the formation of pits, the overall surface morphology between the two does not change much. Table I shows the tensile strength of 5% alkali-treated fiber ( $80.70\text{ N/mm}^2$ ) is much less than that for the untreated fiber ( $108.29\text{ N/mm}^2$ ). The reduction in strength  $\text{m}^2$  might a result of the formation of a large number of pits on the fiber surface.

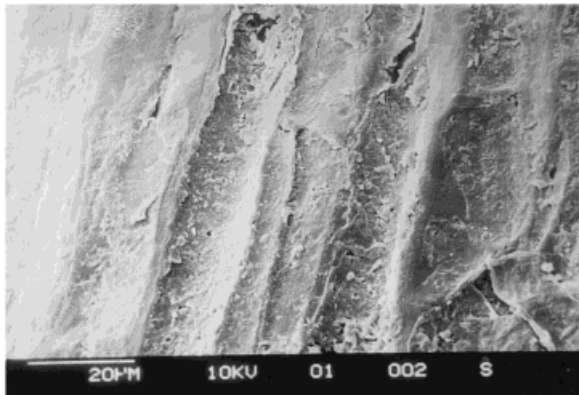
Figure 5(a–c) shows SEM pictures of 10% alkali-treated fiber. Figure 5(a) reveals only a small number of pits compared to the 5% alkali-treated fiber [Fig. 4(a)]. In addition to the reduction in the number of pits, the intercellular gaps are also considerably reduced in the 10% alkali-treated fiber. This might be because the thickening of the cell walls and the consequent shrinkage of the unit cells only occur at a higher concentra-



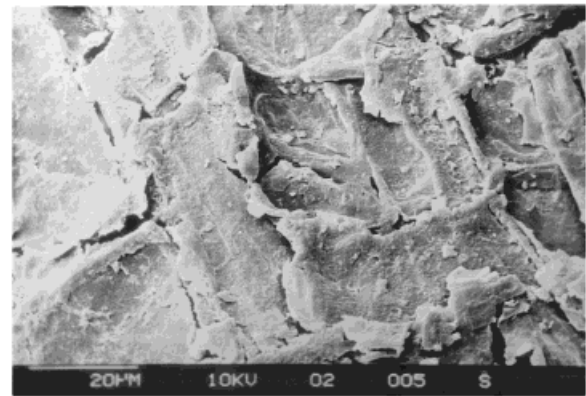
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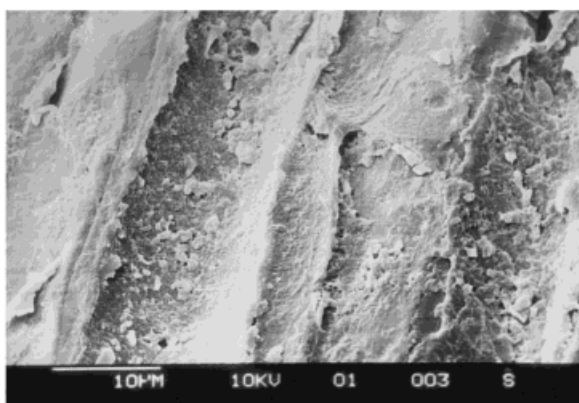
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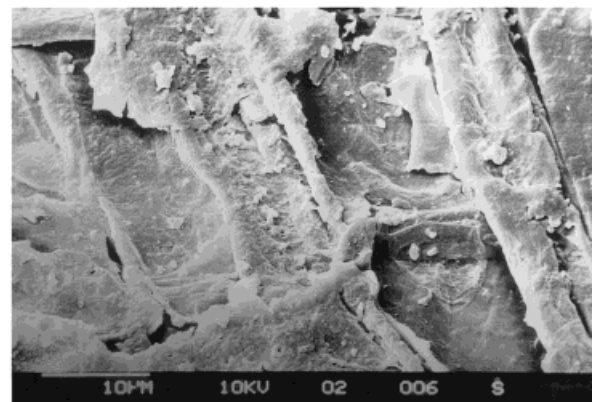
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**b**



**c**



**c**

**Figure 2** SEM of untreated coir fiber: (a) magnification  $\times 500$ ; (b) magnification  $\times 1000$ ; (c) magnification  $\times 2000$ .

**Figure 3** SEM of dewaxed coir fiber: (a) magnification  $\times 500$ ; (b) magnification  $\times 1000$ ; (c) magnification  $\times 2000$ .

**Table I Tensile Strength of Untreated and Chemically Modified Coir Fiber**

Modifications	Maximum Stress at Break (N/mm <sup>2</sup> )
Untreated	108.29
Defatted	171.304
5% alkali treated	80.70
10% alkali treated	259.7
8.56% MMA grafted	175.812
17.65% MMA grafted	111.524
Cyanoethylated	252.742

Strain rate = 450 mm/min, gripping length = 150 mm.

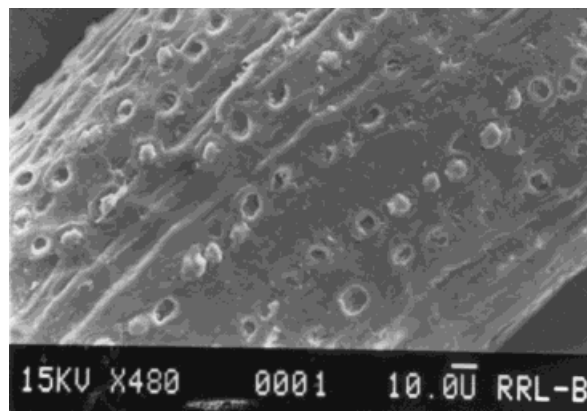
tion of alkali (10%). Similar results were observed by Prasad et al.<sup>9</sup> The higher tensile strength of the 10% alkali-treated fiber (259.7 N/mm<sup>2</sup>), as shown in Table I, is for the above reason.

SEM pictures of 8.56% MMA-grafted coir fiber are shown in Figure 6(a–c). All these pictures show PMMA grafts have been deposited in the intercellular gaps and on the surface of the unit cells. A comparison of Figure 6 with Figure 4 clarifies this point—the intercellular gaps have been reduced because of deposition of PMMA grafts. These grafts caused the surface to become more or less uniform and smooth, which in turn might be the cause of the increase in strength of the 8.56% MMA-grafted fiber (175.812 N/mm<sup>2</sup>) as compared to the untreated fiber (108.29 N/mm<sup>2</sup>), as shown in Table I. The deposition of a foreign substance, PMMA, on the fiber surface can more clearly be seen in Figure 6(c).

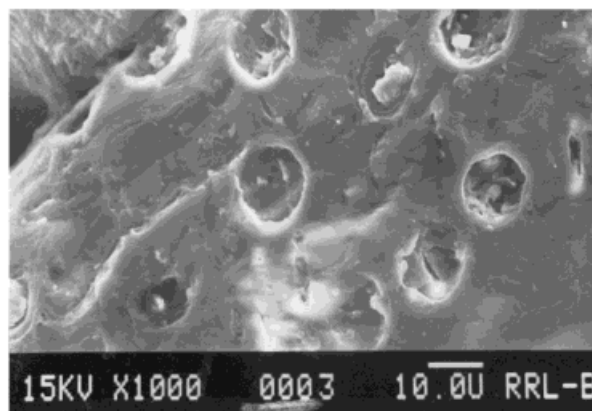
SEM pictures of 17.65% MMA-grafted fiber are shown in Figure 7(a–c). In these cases a very typical and interesting result can be observed. The deposit of the PMMA grafts takes place more on the surface of the unit cells than in the intercellular gaps. This results in deep canal-like cavities in between the overgrowths of the unit cells. Although the cause of such unusual observation is not clear, Kundu et al.<sup>13</sup> have ascribed it to an increase in the pressure of the grafting material. The PMMA units in the 17.65% MMA-grafted fiber are more amorphous, reducing the fiber's degree of crystallinity and hence causing a large in reduction in strength (111.524 N/mm<sup>2</sup>) compared to that of the 8.56%–MMA grafted fiber (175.81 N/mm<sup>2</sup>). However, the strength of this fiber is nearly the same as that of the untreated fiber.

SEM pictures of cyanoethylated coir fiber, shown in Figure 8(a–c), reveal that the intercel-

lular gaps have been reduced because of the cyanoethyl moieties bonded onto the fiber surfaces. But an appreciable quantity of pits can also be seen in these pictures, although the pits are not as deep as those found in the 5% alkali-treated fiber. This may be because of an insufficient deposit of cyanoethyl groups on the pits found in the 5% alkali treated-fiber, unlike those with 8.56% MMA grafting. It may be recalled that both MMA

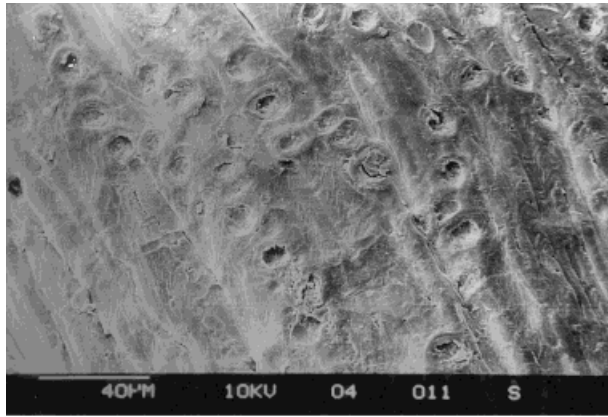


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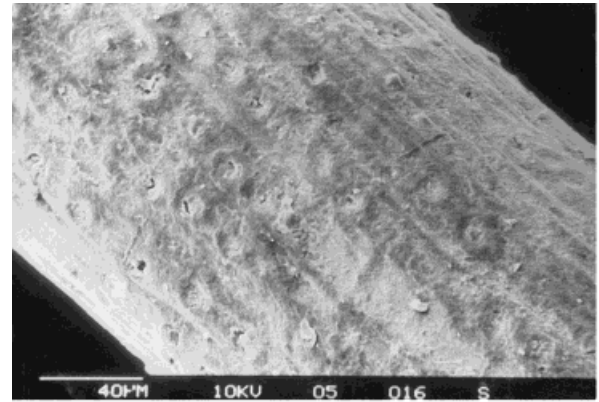


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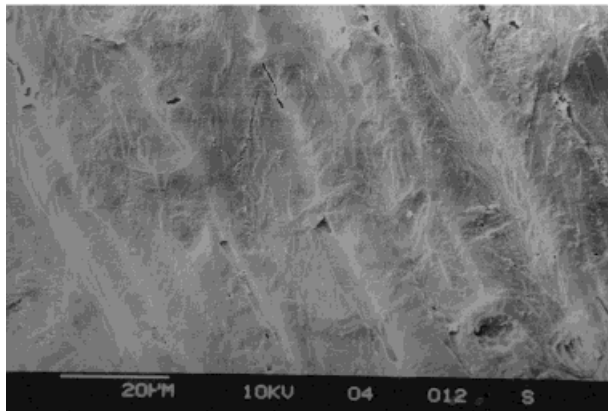
**Figure 4** SEM of 5% alkali-treated fiber: (a) magnification  $\times 480$ ; (b) magnification  $\times 1000$ .



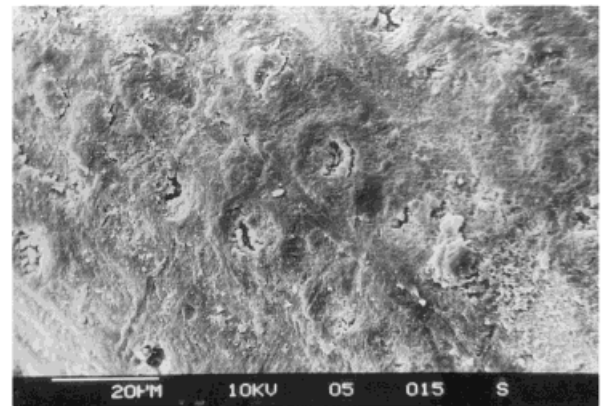
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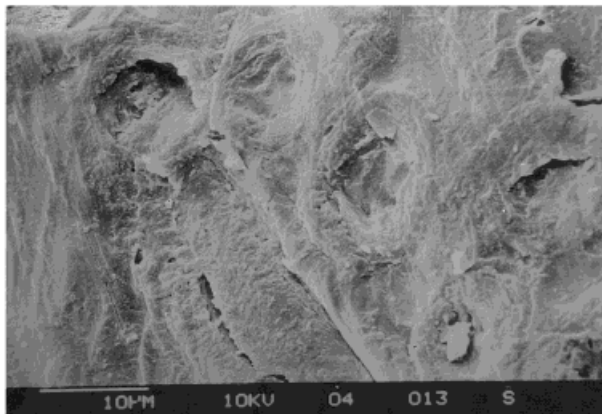
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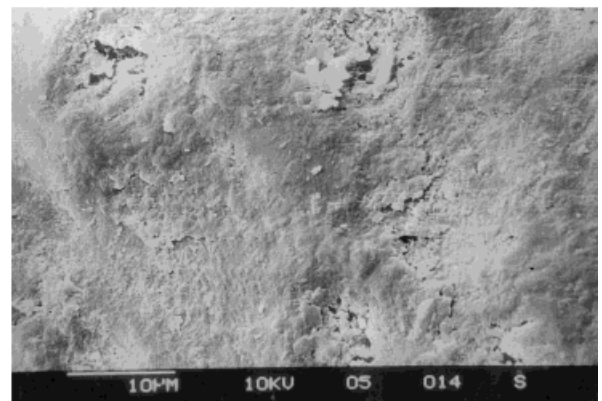
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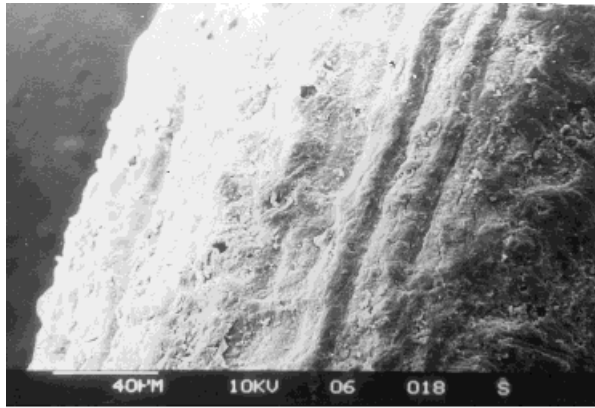
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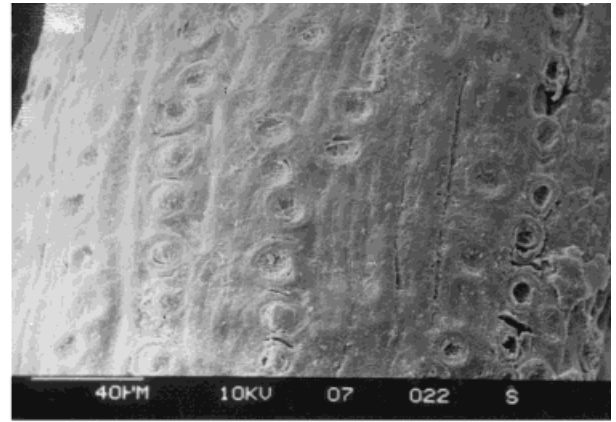
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**Figure 5** SEM of 10% alkali-treated coir fiber: (a) magnification  $\times 500$ ; (b) magnification  $\times 1000$ ; (c) magnification  $\times 2000$ .

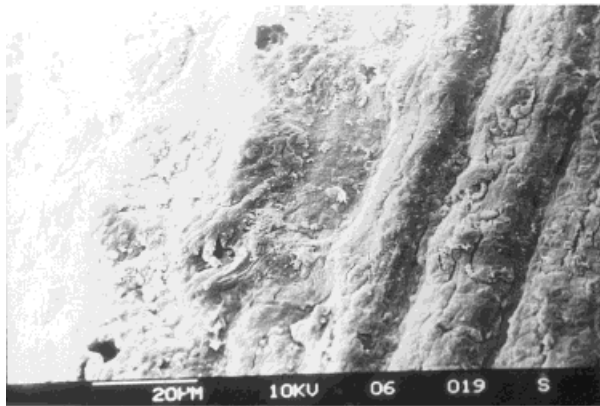
**Figure 6** SEM of 8.56% MMA-grafted coir fiber: (a) magnification  $\times 500$ ; (b) magnification  $\times 1000$ ; (c) magnification  $\times 2000$ .



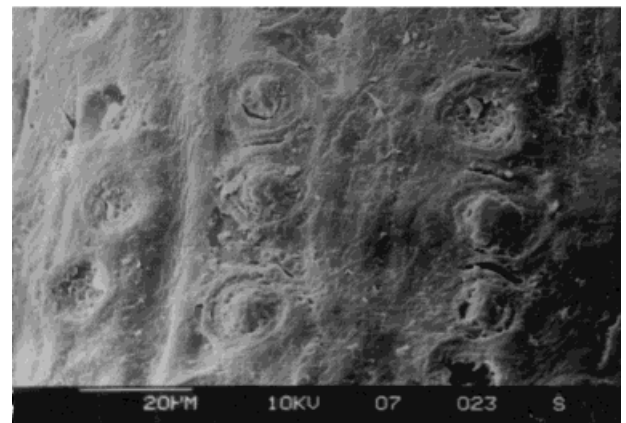
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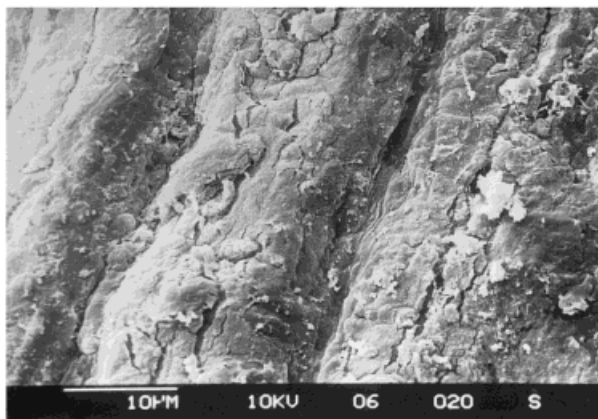
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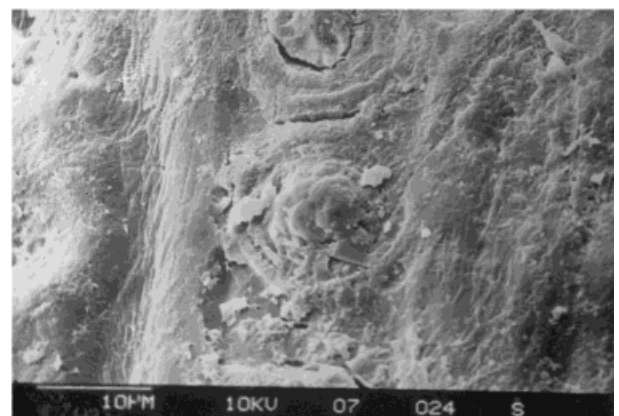
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**Figure 7** SEM of 17.65% MMA-grafted coir fiber: (a) magnification  $\times 500$ ; (b) magnification  $\times 1000$ ; (c) magnification  $\times 2000$ .

**Figure 8** SEM of cyanoethylated coir fiber: (a) magnification  $\times 500$ ; (b) magnification  $\times 1000$ ; (c) magnification  $\times 2000$ .



grafting and cyanoethylation are done after the 5% alkali treatment. The large increase in strength in cyanoethylated fiber may be a result of the increase in the degree of crystallinity for the ordering of the cyanoethyl groups.

## CONCLUSIONS

In this article we have reported four different chemical modifications of coir fiber and our study of the morphology of the modified fibers using SEM. The mechanical property (maximum stress at break) of these fibers has been determined and compared with the untreated fiber. SEM features correlated satisfactorily with the mechanical properties of the modified fibers. The 10% alkali treated, MMA-grafted and cyanoethylated fibers produced the best results. It is expected that these chemically modified fibers might prove to be successful candidates for polymer composites.

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