Surface Modification of Coir Fibers. II. Cu(II)- IO_4^- Initiated Graft Copolymerization of Acrylonitrile onto Chemically Modified Coir Fibers

J. ROUT,[1] M. MISRA,[2] S. S. TRIPATHY,[1] S. K. NAYAK,[3] A. K. MOHANTY[2]

[1] Polymer and Composites Laboratory, Postgraduate Department of Chemistry, Ravenshaw College, Cuttack, Orissa, India

[2] Composite Materials and Structures Center, Michigan State University, 2100 Engineering Building, East Lansing, Michigan 48824-1226

[3] Central Institute of Plastic Engineering & Technology, B-25, CNI Complex, Patia, Bhubaneswar, Orissa, India

ABSTRACT: A study of the graft copolymerization of acrylonitrile (AN) onto chemically modified coir fibers was carried out using a $CuSO_4$ and $NaIO_4$ combination as the initiator in an aqueous medium in a temperature range of 50–70°C. The graft yield was influenced by the reaction time, temperature, concentration of $CuSO_4$, concentration of $NaIO_4$, and monomer concentration. Grafting was also carried out in the presence of inorganic salts and organic solvents. A combination of copper(II) and sodium periodate (Cu^{2+}-IO_4^-) in an aqueous medium with an IO_4^- concentration of 0.005 mol L^{-1} and a Cu^{2+} concentration of 0.004 mol L^{-1} produced optimum grafting. The chemically modified and AN grafted fibers were characterized by FTIR and scanning electron microscopy (SEM). The SEM studies revealed that grafting not only takes place on the surface of the fibers but also penetrates the fiber matrix. The tensile properties like the maximum stress at break and extension at break of untreated, chemically modified, and AN grafted coir fibers were evaluated and compared. The extent of absorption of water of untreated, chemically modified, and grafted coir fibers was determined. It was found that grafting of AN imparts hydrophobicity onto coir fibers. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 75–82, 2002; DOI 10.1002/app.10221

Key words: periodate; graft copolymerization; mechanical property; coir fiber

INTRODUCTION

Coir is a versatile lignocellulosic fiber obtained from coconut trees (*Cocos nucifera*), which grow extensively in tropical countries. Coir is a hard and tough fiber.[1] Each fiber is polygonal to round in section. It is a multicellular fiber with a central pore called a lacuna. Each cell is round or polygonal in shape and $(0.3–1.0) \times 10^{-3}$ m long with a 12–14 μm diameter or width. The chemical constituents of pure coir are cellulose (32–43%), lignin (40–45%), hemicellulose (0.15–0.25%), pectin (2.75–4%),[2–4] and moisture (8%). Several studies[5–7] were carried out to understand the structure, mechanical properties, and effect of chemical treatments on coir fibers. Because of its hard wearing quality, durability, and other advantages it is used for making a wide variety of floor fur-

nishing materials, yarn, rope, and so forth. However, these traditional coir products consume only a small percentage of the potential total world production of coconut husk. Hence, research and development efforts have been underway to utilize coir as a reinforcement in polymer composites. Because coir fiber absorbs a great deal of moisture,[7] it proves to be a poor reinforcing agent with different polymeric matrices. Hence, for better utilization of this important lignocellulosic fiber as a reinforcement, suitable chemical modification is required. This communication is an aspect of our research program in this field of investigation.

Graft copolymerization is a well-established technique for the modification of the physical and chemical characteristics of high molecular weight compounds, particularly natural polymers.[8,9] Extensive research[10–15] was carried out to accomplish efficient graft copolymerization of various monomers onto jute and cellulosic materials. However, very little work was undertaken on grafting onto coir fiber, which is an important lignocellulosic fiber. It was reported earlier that IO_4^- (sodium periodate) induced vinyl grafting onto cellulose[16] and wool.[17] A combination of the Cu^{2+}-IO_4^- concentrations was found efficient to induce graft copolymerization onto dewaxed jute.[18] Thus, there are reasons for the use of this initiator system for vinyl grafting onto coir fiber. We recently reported[19] grafting of methyl methacrylate (MMA) onto chemically modified fiber using $CuSO_4$-KIO_4 as the initiating system. In the present communication we wish to report the study of $CuSO_4$-$NaIO_4$ as the initiator for graft copolymerization of acrylonitrile (AN) onto chemically modified coir fiber in an aqueous medium.

EXPERIMENTAL

Materials

Bristol coir fibers were obtained from Aerocom Industry (Orissa, India). The fibers were procured from the coconuts produced in the coastal regions of Orissa, India, and were subjected to a retting process for 3–6 weeks before the use. The fibers were scoured with hot detergent solution (2%) at 70°C for 1 h, washed with distilled water, and finally dried in a vacuum oven at 70°C. The fibers were then extracted in a 1:2 mixture of ethanol and benzene for 72 h to dewax the sample. The dewaxed fibers thus obtained were treated with 5% NaOH solution for 1 h at 30°C, then washed thoroughly with distilled water to obtain chemically modified fiber. The purpose of the NaOH treatment is to carry out the mercerization and swelling of the fiber so that the chemically modified fiber can undergo the grafting reaction efficiently.

The AN monomer was washed with 5% NaOH and 3% orthophosphoric acid followed by repeated washings with conductivity water, drying over anhydrous calcium chloride, and storing in a refrigerator for use. The conductivity water was used for the preparation of all solutions. All chemicals like $NaIO_4$, $CuSO_4 \cdot 5H_2O$, and other reagents were AR grade.

Graft Copolymerization

Graft copolymerization was carried out in a specially designed reaction vessel with outlet and inlet systems for passage of N_2. The required amount of chemically modified fiber was taken in the reaction vessel into which the required amount of monomer (AN) was added, and the fibers were allowed to soak with the monomer for about 10 min. The appropriate quantity of $CuSO_4$ solution of known concentration was added followed by conductivity water. The reaction vessels were deaerated by passing oxygen-free nitrogen for 20 min and then sealing them air tight by rubber capping. The vessels were kept in a constant temperature bath until the mixture attained thermal equilibrium, after which a required amount of $NaIO_4$ solution was added and the reaction was carried out for the desired time. A fiber/liquor ratio of 1:50 was maintained for each experiment. After the desired time, the reactions were arrested by quenching the vessels in ice-cold water.

The grafted samples were washed well by extraction with several portions of water, given a light soaping to remove the loosely adhering poly(AN) (PAN) homopolymers, and then washed with water and dried.[20] On further extraction with dimethyl formamide (DMF) for about 24 h at 30°C, the grafted samples showed a negligible weight loss. This observation was reported earlier.[20,21] Hence, all the results are based on the increase in weight of the fiber after grafting and thorough soaping and washing. The percentage of grafting is calculated by the dry weight determined after storing the materials in a weighing bottle over P_2O_5 at room temperature in a vaccum

desiccator until constant weight was obtained. The percentage of grafting was calculated on a dry weight basis.

graft yield

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

FTIR Spectra

FTIR spectra in the form of KBr pellets of fiber samples were recorded on a Jasco-5300 FTIR spectrometer. The fibers were dried in a vacuum oven at 100°C for 1 h, then ground into fine powder followed by mixing with KBr (fiber/KBr = 1:9) to prepare the pellets for FTIR spectral study.

Scanning Electron Microscopy (SEM)

The SEM micrographs of fiber samples were recorded using a Jeol JSM-T330A scanning electron microscope with original magnifications ×1000, ×500, and ×75.

Tensile Properties

The tensile properties of the coir fibers were determined using a universal testing machine (LR-100K, Lloyds Instrument Ltd., U.K.) at a strain rate of 450 mm/min and a gripping length of 150 mm at 23°C and 58% relative humidity. The tensile strength was measured according to ASTM D 638.

Water Absorption

About 0.200 g of each of the untreated, chemically modified, and grafted fibers were oven dried at 70°C until a constant weight was obtained. The oven dried samples were then immersed in distilled water for 24 h at 23 ± 1°C. After the test period, the samples were removed from the water, dried with a cotton cloth, and reweighed. This is referred to as the wet weight of the fibers.

% water absorption

$$= \frac{\text{wt. of wet fiber} - \text{wt. of oven dry fiber}}{\text{wt. of oven dry fiber}} \times 100$$

RESULTS AND DISCUSSION

Effect of Variation of Time

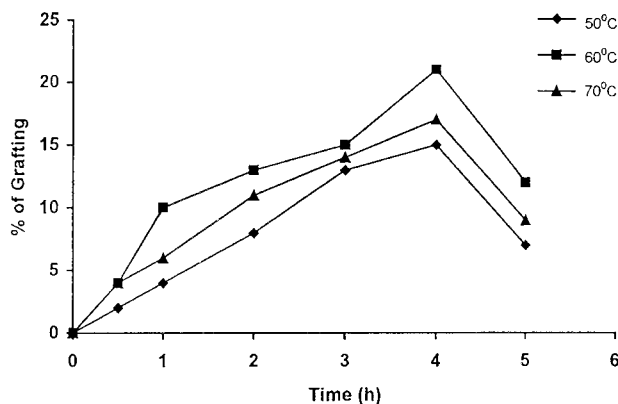Figure 1 shows the effect of time on the graft yield at 50, 60, and 70°C. In each case the graft yield

Figure 1   The effect of time on the graft yield of 0.1 g of coir and using the following concentrations: [AN] = 0.759 mol L^{-1}, [IO$_4^-$] = 0.005 mol L^{-1}, and [Cu^{2+}] = 0.004 mol L^{-1}.

increased steadily with time up to 4 h and thereafter decreased. This may be attributed to partial dissolution of the grafted fibers with the prolonged incubation period. Similar observations were also reported while studying graft copolymerization of vinyl monomers onto pineapple leaf fiber (PALF)[21] and graft copolymerization of MMA onto chemically modified coir fibers.[19] Within 4 h the graft yields follow an increasing trend with the time of polymerization, and thus an optimum graft yield was obtained within 4 h of the experiment. The graft yield is found to be greater at 60°C compared to 50 and 70°C at each time period of grafting studied. The decrease in graft yield at 70°C might be due to the partial dissolution of the graft chain at this high temperature.

Effect of Variation of IO$_4^-$ Concentration

The relevant data are presented graphically in Figure 2 and show the effect of the IO$_4^-$ concentration on the graft yield at three different temperatures. The percentage of graft yield increases with the IO$_4^-$ concentration up to 0.009 mol L^{-1}. This trend of increasing graft yield may be attributable to the creation of a greater number of grafting sites with the increase in oxidant. A further increase of the IO$_4^-$ concentration shows a decreasing trend that may be due to the formation of an increased amount of homopolymers. A larger amount of homopolymer was extracted in the sample using a higher IO$_4^-$ concentration (>0.009 mol L^{-1}) than samples using a lower IO$_4^-$ concentration (<0.009 mol L^{-1}). This corrobo-
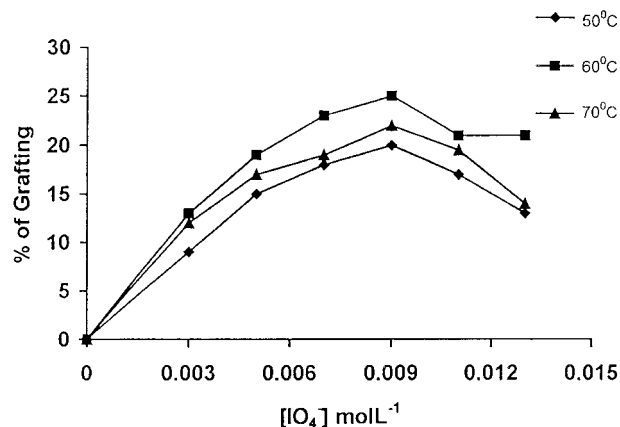
Figure 2 The effect of the IO_4^- concentration with a time of 4 h and 0.1 g of coir and using the following concentrations: [AN] = 0.759 mol L^{-1} and [Cu^{2+}] = 0.004 mol L^{-1}.

rates the decrease in graft yield at a IO_4^- concentration higher than 0.009 mol L^{-1}.

Effect of Variation of Cu^{2+} Concentration

It is observed that neither $NaIO_4$ nor $CuSO_4$ induced graft copolymerization of AN in the presence of coir when used separately. However, Cu^{2+} coupled with IO_4^- is an effective redox initiating system. The effect of the Cu^{2+} concentration was studied by varying the concentration of Cu^{2+} from 0.002 to 0.012 mol L^{-1} at three different temperatures by keeping the concentrations of all other reagents fixed (Fig. 3). The Cu^{2+} concentration of about 0.006 mol L^{-1} produced the optimum per-
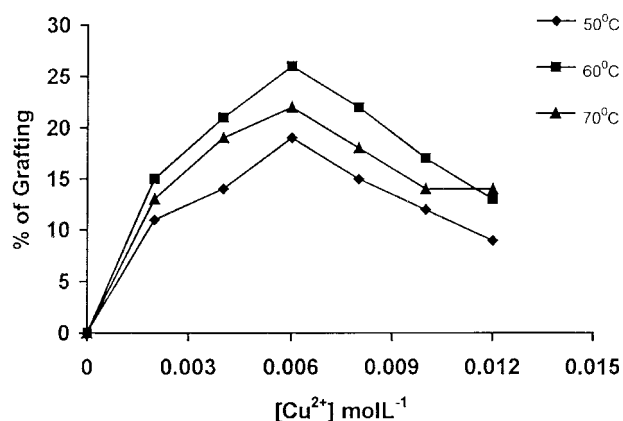

Figure 3 The effect of the Cu^{2+} concentration with a time of 4 h and 0.1 g of coir and using the following concentrations: [AN] = 0.759 mol L^{-1} and [IO_4^-] = 0.005 mol L^{-1}.

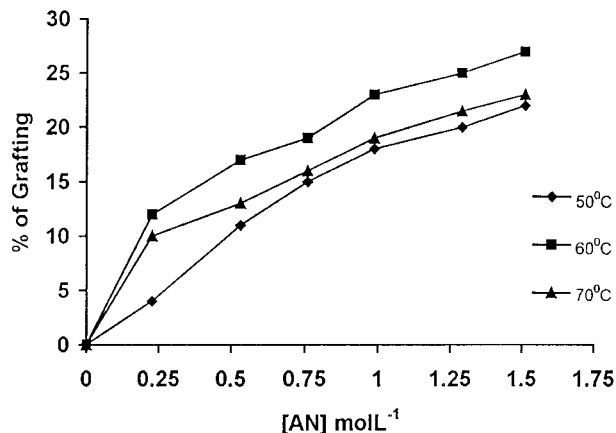**Figure 4** The effect of the AN concentration with a time of 4 h and 0.1 g of coir and using the following concentrations: [IO_4^-] = 0.005 mol L^{-1} and [Cu^{2+}] = 0.004 mol L^{-1}.

centage of grafting. The graft yield decreased with the increase in the Cu^{2+} concentration above 0.006 mol L^{-1}. The decrease in the graft yield with the increase of the Cu^{2+} concentration above 0.006 mol L^{-1} may be due to the fact that at a higher Cu^{2+} concentration, the periodate ion forms a redox couple with Cu^{2+} and favors homopolymer formation.[18]

Effect of Monomer Concentration

The effect of the variation of the monomer (AN) concentration on the grafting percentage at three different temperatures is represented in Figure 4. The graft yield increases with an increase in the monomer concentration from 0.227 to 1.51 mol L^{-1}. Similar observations were also reported in Ce(IV)-*N*-acetylglycine initiated grafting of AN onto chemically modified PALF.[22]

Effect of Coir Fiber Amount

Figure 5 shows the effect of the amount of coir fiber on the graft yield. It is observed that, within the range studied, the graft yield increased with an increasing amount of fiber up to an optimum value (0.100 g) and then decreased. The decrease in the graft yield beyond an optimum amount may be due to the insufficient quantity of monomer for the larger amount of fiber.

Effect of Reaction Medium

The graft copolymerization of the vinyl monomer is greatly influenced by the reaction medium. The
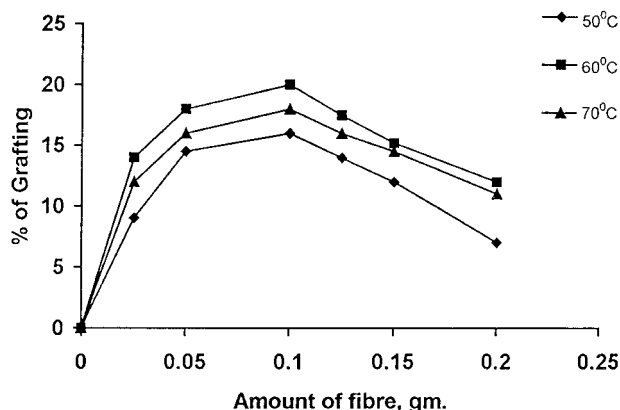
Figure 5 The effect of the amount of coir fiber with a time of 4 h and using the following concentrations: [AN] = 0.759 mol L^{-1}, [IO_4^-] = 0.005 mol L^{-1}, and [Cu^{2+}] = 0.004 mol L^{-1}.

effect of different inorganic salts and organic solvents on the graft yield is reported in Table I. The graft yield has the following order when an equivalent molar concentration of salts is added into the reaction mixture:

$$\text{Control} > \text{Ba(NO}_3)_2 > \text{Pb(NO}_3)_2 = \text{Na}_2\text{SO}_3$$
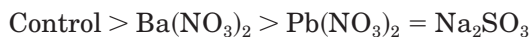
The cause of the decrease of the graft yield in the presence of inorganic salts, although not clear, might be the inhibiting effect of the metal ion on the production of free-radical sites on the cellulosic chain of the natural coir fiber.

Similarly, the effect of various organic solvents when added in equal proportion (5%, v/v) follows the following order:

$$\text{Control} > \text{CH}_3\text{COOH} > \text{CH}_3\text{OH}$$
$$> \text{DMF} > \text{Benzene}$$
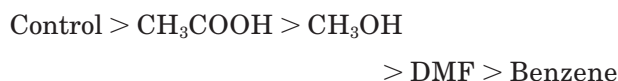
The cause of the decrease in the percentage of grafting in the presence of different organic solvents under the present investigations might be the decrease in the net polarity of the medium, which reduces the ease of formation of the free-radical sites on the fiber.[19] It may be reiterated here that the grafting reaction is being carried out in an aqueous medium and the addition of a small amount of another solvent in place of water reduces the net polarity of the medium for which the graft yield decreases.

Reaction Mechanism

As a lone initiator, IO_4^- fails to induce graft copolymerization of AN onto coir fibers while IO_4^- in combination with the Cu^{2+} ion acts as an effective initiating system. This might be due to the following reasons. The phenolic structure of lignin acts as a strong inhibitor to kill the free radicals formed from periodate. The periodate ion, being a strong oxidant, reacts with lignin and converts it to its quinonoid form. The reaction between the phenolic structure of lignin and the periodate ion is already established.[23] However, in the presence of the Cu^{2+} ion the lignin is bound with the metal ion[18] and thus inhibiting action is prevented. As a result, IO_4^- becomes free to produce free radicals and hence induce grafting of AN onto coir. The detailed mechanism was already proposed in our previous publication.[19]

Characterization

FTIR Spectra

The FTIR spectra of chemically modified coir fiber and AN grafted coir fiber are shown in Figures 6 and 7, respectively. The chemically modified fiber and AN grafted fiber both show characteristic broad absorption of hydroxyl groups at around ~3400 cm^{-1}. From Figure 7 it is observed that AN grafted coir fiber shows an additional band for the nitrile group at 2243 cm^{-1}, thereby confirming the occurrence of grafting. It is also observed that with the increase of the percentage of grafting the intensity of the nitrile peak increases (Fig. 7). It is expected that grafting of AN onto the fiber should take place at the site of the OH group; thus, the OH peak intensity is consequently expected to decrease. However, in our case the OH peak of the AN grafted fiber is as intense as the chemically modified fiber, which is possibly due to the large concentration of the —OH group of coir fiber. A similar observation was also reported in the IR spectra of MMA grafted coir fiber.[19]

Table I   Effect of Reaction Medium on Grafting

Solvent 5% (v/v)	Grafting (%)	[Salt] 0.01 mol L^{-1}	Grafting (%)
Control	21	Control	21
Acetic acid	8	Ba(NO$_3$)$_2$	12
Methanol	7	Pb(NO$_3$)$_2$	0
DMF	6	Na$_2$SO$_3$	0
Benzene	2		

Reaction conditions: 0.1 g coir; [AN] = 0.759 mol L^{-1}, [IO_4^-] = 0.005 mol L^{-1}, and [Cu^{2+}] = 0.004 mol L^{-1}; 60°C; and 4 h.
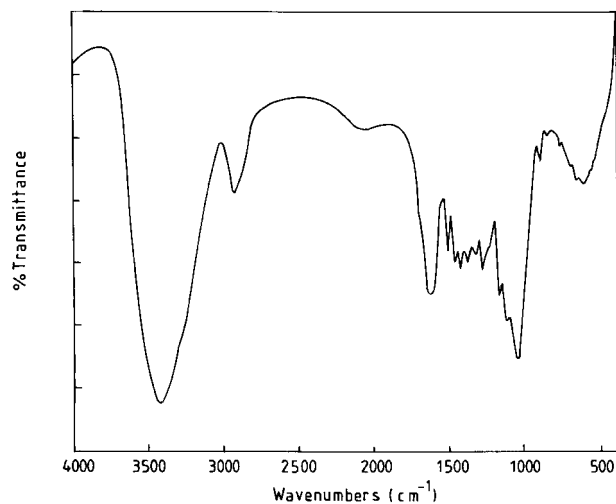
Figure 6 The FTIR spectrum of chemically modified coir fiber.

Tensile Properties

The tensile properties like the maximum stress at break and extension at break of untreated, chemically modified, and AN grafted coir fibers are shown in Table II. For each type of fiber a minimum of 10 fibers are tested and the average values are determined. Chemically modified coir fibers show an appreciable decrease in maximum stress at break (80.70 N/mm^2), which may be due to leaching out of the outer cuticle layer, leading to pit formations on the fiber surface. The SEM
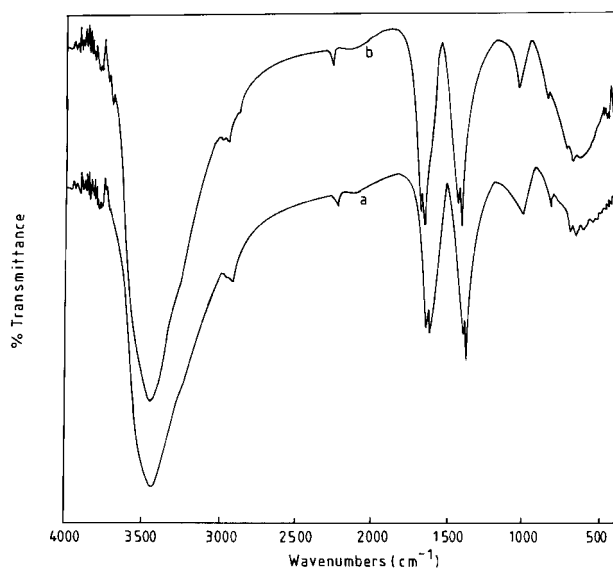

Figure 7 FTIR spectra of AN grafted coir with (a) ~10% and (b) ~20% grafting.

Table II Tensile and Water Absorption Properties of Untreated, Chemically Modified, and AN-Grafted Fibers

| Sample	Maximum Stress at Break (N/mm^2)	Extension at Break (%)	Water Absorption (%)
Untreated	108.29	15.49	38.91
Chemically modified	80.70	14.44	43.47
AN grafted			
6.5%	119.67	12.67	27.34
10%	148.3	12.32	23.47
15%	97.14	9.31	22.98

observation reveals the above fact. However, the extension at break (%) value of the chemically modified fiber does not change much. Grafting of chemically modified fibers with AN to 6.5% brings about an increase in the maximum stress at break (119.67 N/mm^2). The maximum stress at break value increases with the increase in the percentage of AN grafting up to 10%. More than an 83% increase in maximum stress at break is observed for 10% AN grafted fiber in comparison to chemically modified fibers. A further increase in AN grafting shows a reduction in the maximum stress at break in comparison to 6.5 and 10% AN grafted fibers. The reason for the decrease in the strength at the higher percentage of grafting may be a decrease in the orderly arrangement of PAN units and hence the degree of crystallinity. It was found that the extension at break (%) value decreases with AN grafting. This may be due to the large increase in the brittleness of the fiber by grafting with AN.

SEM Observations

The SEM micrographs of chemically modified and AN grafted coir fiber are shown in Figure 8(a,b) respectively. In Figure 8(a) there are lots of deep depressions observed that are due to removal of the intercellular binding materials and the cuticle layer. A comparison of the micrographs of the chemically modified coir and AN grafted coir shows that the pits in the chemically modified fibers are no longer present in the grafted fibers and a considerable amount of PAN is grafted onto the fiber surface. Again a comparison of the cross sections of chemically modified coir fiber [Fig. 9(a)] and AN grafted coir fiber [Fig. 9(b)] shows
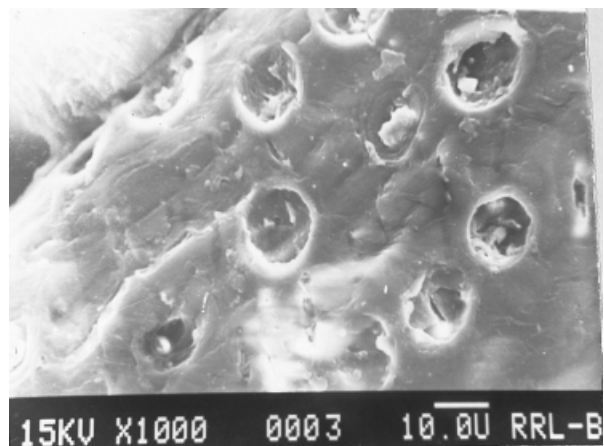
(a)
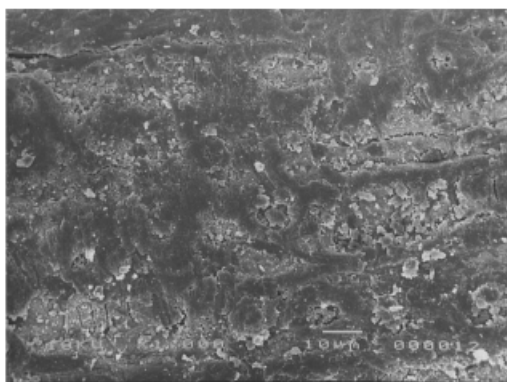
(b)

Figure 8 The SEM of fiber surfaces of chemically modified and AN grafted coirs (original magnifications ×1000).

that a considerable amount of grafted molecules enter the fiber matrix, causing the lumen size to be reduced in the AN grafted coir fiber. Similar observations were also reported earlier.[11]

Water Absorption

The percentage of water absorption (extent of hydrophobicity) of untreated, chemically modified, and AN grafted coir fibers were determined and are presented in Table II. The data in Table II clearly indicate that grafting of AN onto coir fiber brings about a significant reduction in the water absorption (enhanced hydrophobicity) of the coir fiber. These grafted fibers may therefore serve as ideal reinforcement for fabrication of fiber reinforced polymers with reduced water absorption behavior.

CONCLUSION

The results of the present investigation established that significant hydrophobicity and improved mechanical strength might be imparted to coir fibers through AN grafting using a Cu^{2+}-IO_4^- combination as the initiator in an aqueous medium. Fibers with 10% AN grafting show an appreciable increase in maximum stress at break (148.3 N/mm^2). A comparison of micrographs of chemically modified and AN grafted fibers show that a considerable amount of PAN is grafted onto the fiber surface. Based on the above studies, it is expected that these modified fibers may be used as good reinforcing materials for developing fiber reinforced polymer composites.
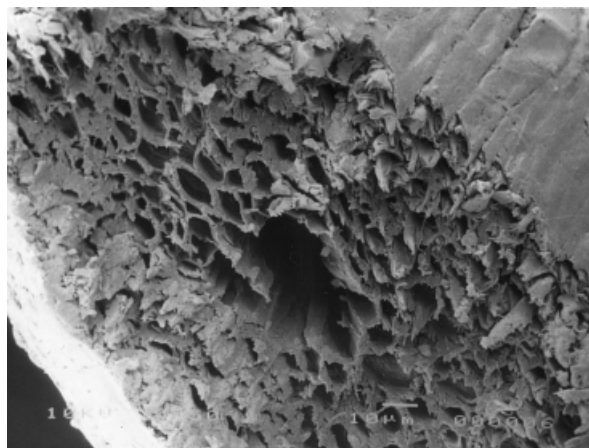
(a)
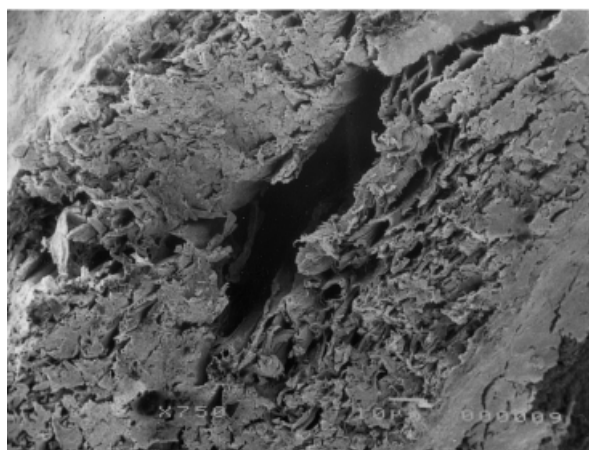
(b)

Figure 9 The SEM cross section of chemically modified coir (original magnification ×500) and AN grafted coir (original magnification ×750).

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