

Effect of Chemical Modification on FTIR Spectra. I. Physical and Chemical Behavior of Coir

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SYNOPSIS

Coir fibers were chemically modified through alkali treatment, and crosslinking with formaldehyde, *para*-phenylene diamine, phthalic anhydride, and combined crosslinking-cyanoethylation reactions in appropriate solvent and catalyst. The parent and chemically modified coir were characterized by FTIR spectra. The percent moisture regain, tensile strength, and behavior toward some chemical reagents (solubility %) of parent and chemically modified fibers have also been evaluated. The modified fibers showed significant hydrophobicity, improved tensile strength, and good chemical resistance. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

During recent years there has been increasing effort to exploit the possible use of agrowaste/lignocellulosic fiber like jute, sisal, palm, ramie, coir, etc. as reinforcement in part replacement of expensive synthetic fibers like glass, carbon, boron, borosilicate, etc. in composites for various industrial applications.^{1,2} However, the high moisture content of these natural fibers is detrimental to the amenability and ideal bonding characteristics with matrix resins and as a result delamination of fiber reinforced plastics (FRPs) was a commercial failure.³ Attempts are now being taken to impart significant hydrophobicity and improved mechanical properties to these fibers. Such studies have only begun, however, and few reports on jute⁴⁻¹⁸ and coir¹⁹⁻²⁵ are available. However, much skillful experimental technique and effort are needed to achieve a full commercial benefit in this area of composite research. In this laboratory we are applying a simple route with cheap chemicals to bring about abrupt reduction in moisture content to impart absolute hydrophobicity, improved mechanical properties, and chemical resistance to coir, an abundant lignocellulosic fiber in the coastal belt

of India. Coir has 36–43% cellulose, 40–45% lignin, 0.15–0.25% hemicellulose, and 3–4% pectin, together with some water soluble materials. This communication on chemical crosslinking of coir is part of our research program on the emerging area of polymer science and technology.

EXPERIMENTAL

Materials and Methods

Coir fibers were purified by soxhelenation with 1 : 1 benzene–ethanol mixture for 72 h followed by washing with ethanol and air drying. Acrylonitrile was purified as reported earlier.²⁶ Chemicals like sodium hydroxide, acetic acid, acetone, ethanol, *p*-phenylene diamine, formaldehyde, phthalic anhydride, acetic anhydride, sulfuric acid, hydrochloric acid, and nitric acid were of analytical grade (BDH Chemicals).

Chemical Modification

Alkali Treatment

Coir fibers were treated with alkali (NaOH, w/v) solution of varying concentrations (2–10%) for 1 h at 35°C with occasional shaking followed by washing with dilute acetic acid and distilled water for 1 week

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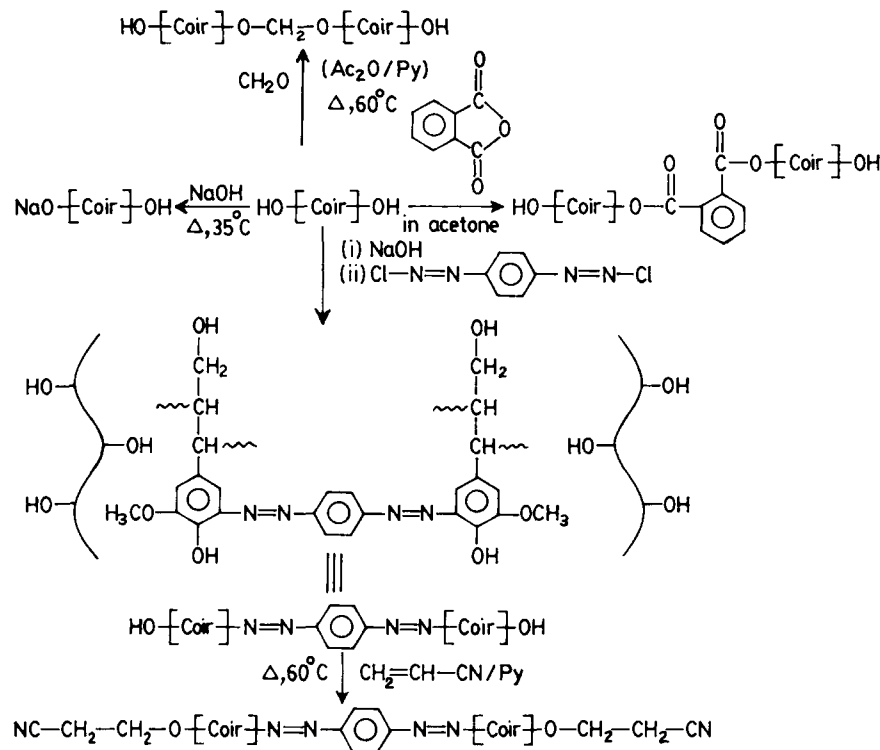


Figure 1 Schematic presentation of chemical modification.

to leach out the absorbed alkali. The material was then air dried.

Crosslinking with Formaldehyde

Coir fiber (1 g) was refluxed at 60°C for 2 h with 20 mL of 40% formaldehyde in the presence of acetic anhydride (20 mL)/pyridine (2 mL) combined catalyst. The fibers were washed with acetone followed by distilled water and air dried.

Crosslinking with *p*-Phenylene Diamine

Coir fiber (1 g) was preswelled with NaOH solution at 35°C for 1 h and then the ice cooled. The fiber was then treated with diazotized *p*-phenylene diamine in ice bath with constant shaking for 0.5 h. The treated fibers were washed thoroughly with dilute acetic acid followed by distilled water to neutral pH and air dried.

Crosslinking with Phthalic Anhydride

Coir fiber (1 g) was refluxed at 60°C for 2 h with 20 mL of 5% phthalic anhydride in acetone in the presence of pyridine as catalyst. The fibers were washed with dilute sodium carbonate, distilled water, and

acetone followed by distilled water to neutral pH and air dried.

Cyanoethylation

Cyanoethylation of formaldehyde and phthalic anhydride crosslinked coir was done by refluxing separately with a mixture of 10 mL of purified acrylonitrile and 10 mL acetone in the presence of pyridine (2 mL) as catalyst at 60°C for various time intervals (0.5–6 h). *para*-Phenylenediamine crosslinked coir was cyanoethylated by refluxing with a mixture of 10 mL of acrylonitrile and 10 mL acetone at 60°C in the absence of catalyst for the same time intervals. After the reaction was completed the fibers were thoroughly washed with acetic acid, methanol, acetone, and distilled water and air dried. All such chemical modifications, are schematically presented in Figure 1.

Testing and Characterization

We observed no significant change in appearance of the fiber upon crosslinking with formaldehyde and phthalic anhydride, but they acquired a dark red color upon crosslinking with *para*-phenylene diamine and a brown yellow color upon alkali treat-

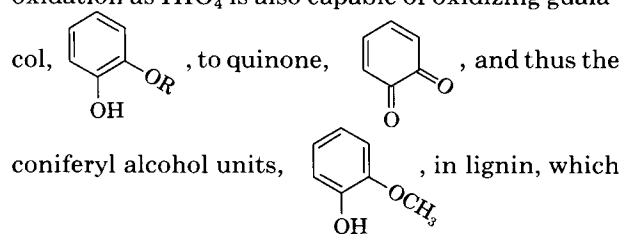
ment. Cyanoethylation of the crosslinked fibers did not impart any coloration onto the fibers. The procedures adopted for affecting the chemical modification were developed by us in this laboratory.

Detection of Nitrogen

Detection of nitrogen through Lassaigne's test²⁷ for diazotized *p*-phenylene diamine crosslinked coir and other crosslinked cyanoethylated coir supports the reaction.

FTIR Spectra

FTIR spectra of the samples were recorded in KBr pellets in a Bruker IFS 66V FTIR spectrometer. The FTIR spectra of the parent and chemically modified coir were analyzed to ascertain whether such crosslinks have truly taken place in the fibers. The spectra of parent and modified coir are shown in Figure 2. The exact position and probable assignment of the peaks are given in Table I. In comparison to parent coir, alkali treated coir (coir-ONa), formaldehyde, *para*-phenylene diamine, and phthalic anhydride crosslinked coir (coir-*c*-CH₂O, coir-*c*-PPDA, coir-*c*-PhA, respectively) showed a reduction on OH stretching intensity and shifting of the peak from 3446.2 to 3421.5, 3431.4, 3481.1, and 3451.0 cm⁻¹, respectively, indicating participation of some free hydroxyl group in the chemical reaction. The point of reaction is probably the phenolic—OH in the lignin components and C₆—OH of the anhydride glucopyranose unit in the cellulose component; and probably does not involve C₂—OH and C₃—OH, as Malapradian oxidation²⁸ with HIO₄ is found to proceed well with modified coir. Consumption of HIO₄ however, cannot dictate the involvement of C₂—C₃ glycolic linkage in the glucose units in the oxidation as HIO₄ is also capable of oxidizing guaiacol,



is structurally analogous to guaiacol, might be suffering oxidation to the quinone structure with HIO₄.^{29,30} This conclusion seems reasonable from the color change of coir from pale yellow to reddish yellow. It is therefore difficult to be sure at this stage of the participation of the C₂—OH and C₃—OH hydroxyl groups in the modification. A weak band at 2849.8 cm⁻¹ in the parent coir, arising from OH

stretching vibration of inter- and intramolecular hydrogen bonded OH groups, is shifted to 2853.4 cm⁻¹ upon treatment with phthalic anhydride, and totally disappears upon reaction with sodium hydroxide, diazotized *para*-phenylene diamine, and formaldehyde, indicating its involvement in the reaction. The medium band at 1739.2 cm⁻¹ due to >C=O stretch in the parent coir upon chemical treatment with the said reagents is only the shift of the wavelength to 1742.0, 1741.7, and 1736.8 cm⁻¹, respectively, in coir-*c*-CH₂O, coir-*c*-PPDA, coir-*c*-PhA, and disappeared in coir-ONa due to gross structural changes during such chemical reactions. The very weak inflection band at 1741.7 cm⁻¹ in the NaOH catalyzed, diazotized *p*-phenylene diamine crosslinked coir is attributed to the surviving >C=O group of the uronic acid residue from the alkali treatment. This is evident from the disappearance of the >C=O band in the pure NaOH treated fiber [Fig. 2(b)]. The weak band at 1642.1 cm⁻¹ is due to absorbed water in the parent coir; it disappeared in CH₂O and phthalic anhydride crosslinked fiber, which in agreement with the moisture regain data shown in Table II. However in *para*-phenylene diamine crosslinked fiber and alkali treated fiber, this band is shifted to a lower wavelength of 1633.8 and 1641.1 cm⁻¹, respectively. Bands at 1609.4 cm⁻¹ (w) and 1512.5 cm⁻¹ (s) in the parent coir due to C—C aromatic stretching vibration of the lignin component shifted to 1612.9 and 1514.6 cm⁻¹ (s) in *para*-phenylene diamine crosslinked fibers. This can probably be attributed to the aromatic π electron being influenced by the extended conjugation with the crosslinked diazo groups. This shifting is evidence that crosslinked diazo has taken place onto the lignin components. A new band at 1487.5 cm⁻¹ in phthalic anhydride crosslinked fiber [Fig. 2(e)] is probably due to contaminated phthalic acid residue in the fiber but not due to —COOH in half-esterified fiber, as corroborated from pH studies. Bands at different places in the FTIR spectra of the parent and modified coir in the region 1464–1050 cm⁻¹ are almost similar and are due to various characteristics of specific groups such as CH₂ bending in glucopyranose of cellulose, OH inplane bending, aliphatic C—H bending, interaction between O—H bending and C—O stretching, asymmetric C—O—C stretching, asymmetric in plane ring stretching, and C—O/C—C stretching vibrations as indicated on Table I. A weak band at 960.7 cm⁻¹ (—CH₂ wagging) in the parent coir [Fig. 2(a)] disappeared on chemical treatment and is probably due to the change of molecular orientation

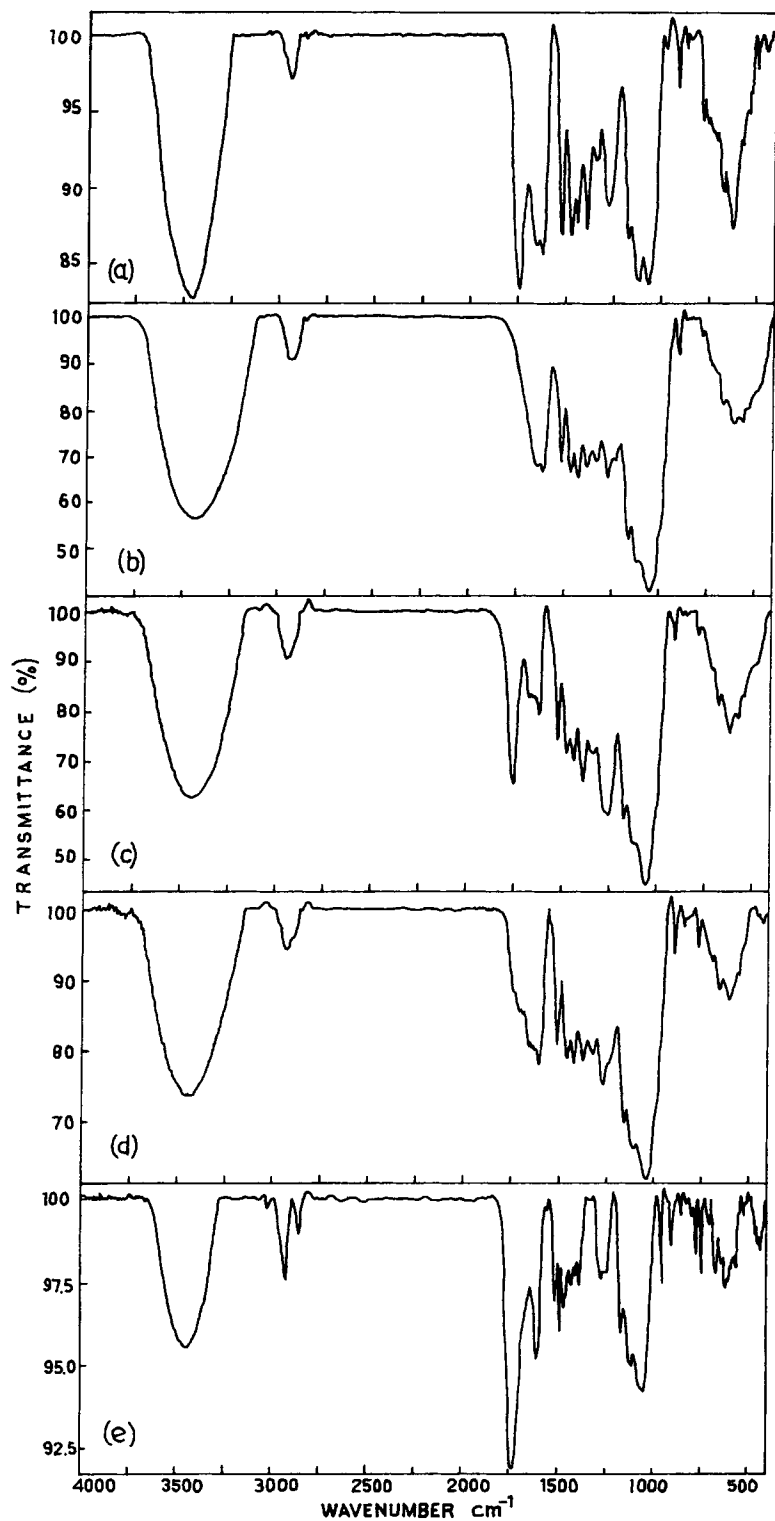


Figure 2 FTIR spectra of coir: (a) parent-coir, (b) coir-ON α , (c) coir-*c*-CH₂O, (d) coirc-PPDA, (e) coir-*c*-PhA.

Table I FTIR Spectra of Parent and Chemically Modified Coir Absorbance (cm⁻¹)

Parent Coir	Coir-ONa	Coir-c-CH ₂ O	Coir-c-PPDA	Coir-c-PhA	Possible Assignment
3446.2	3421.5	3431.4	3481.1	3451.0	O—H Str. Vib.
2928.5	2926.7	2936.7	2934.4	2925.3	C—H Str. vib. of cellulose/hemicellulose
2849.8	—	—	—	2853.2	O—H Str. vib. of inter- and intramolecular H-bonded in cellulose/hemicellulose/lignin making the entire structure a network chelate
1739.2	—	1742.0	1741.7	1736.8	C=O Str. vibr. of 4-methylol glucuronoxylan of hemicellulose
1642.1	1641.1	—	1633.8	—	Water absorption of crystalline region
1609.4	1607.6	1607.0	1612.9	1607.7	Aromatic C=C str. vib. of lignin component
1512.5	1511.0	1511.5	1514.6	1513.1	—
—	—	—	—	1487.5	Phthalic acid str. vib.
1464.4	1464.4	1464.5	1464.1	1465.3	CH ₂ bending vib. of glucopyranose residue
1428.2	1425.3	1426.9	1426.1	1426.8	O—H in plane (scissoring) bending
1382.7	1375.5	1376.7	1382.0	1383.1	Aliphatic C—H bending vib.
1335.7	1330.2	1321.2	1324.2	—	Interaction between O—H bending and C—O str.
1269.7	1270.4	—	1273.0	1270.6	—
1162.6	1162.7	1163.3	1164.1	1164.7	Asymmetric C—O—C str.
1107.0	1107.9	1116.2	1107.9	—	Asymmetric in phase ring stretching
1059.5	1047.8	1049.2	1047.4	1049.8	C—O/C—C str. vib.
960.7	—	—	—	—	Wagging (—CH ₂ —) _n str. vib.
895.6	895.9	896.4	895.8	895.6	β-glucosidic linkage
826.8	833.0	833.0	—	—	Two adjacent aromatic. C—H bending vib. of lignin
851.9	771.4	769.9	851.8	852.2	C—H out of plane vib. of polyaromatic str.
770.6	—	—	771.1	770.8	—
667.2	—	667.2	665.5	666.0	Out of plane bending vib. of intermolecular H-bonded OH group
617.4	607.3	606.0	616.9	616.4	—
520.6	—	—	435.3	525.3	Torsional vib. of pyranose ring

Str. vib., stretching vibration.

Table II Percentage Moisture Regain of Parent and Chemically Modified Coir

Coir-ONa		Coir-c-CH ₂ O		Coir-c-PPDA		Coir-c-PhA	
NaOH (w/v) (%)	Moisture Regain (%)	Time of CE in (h)	Moisture Regain (%)	Time of CE (h)	Moisture Regain (%)	Time of CE (h)	Moisture Regain (%)
0	16.87	0.00	4.08	0.00	16.05	0.00	5.73
2	16.92	1.00	4.12	0.50	13.00	0.50	4.93
4	17.70	2.00	4.00	1.00	12.63	1.00	4.89
6	18.52	3.00	3.98	2.00	12.03	2.00	4.82
8	19.25	4.00	3.92	3.00	11.30	3.00	4.75
10	20.13	6.00	3.92	4.00	10.90	4.00	4.58
				6.00	10.53	6.00	4.18

of the complex polymer. The medium band at 895.6 cm^{-1} due to β -glucosidic linkage in the parent coir, underwent shifting to a longer wave number accompanied with an increase in intensity in the modified fibers. This shift relates to the rotation of glucose residue around the glucosidic bond³¹ and indicates the transition from the parent fiber to the chemically modified fiber. The bands at and beyond 667.2 cm^{-1} (Fig. 2) corroborate clearly with the findings of Blackwell et al.³²

pH Determination

The pH of all the samples in distilled water was measured by using a Systronics-324 pH meter standardized with a buffer of pH 4 and 9. The pH value of all samples except the phthalic anhydride crosslinked fiber was ~ 6.5 and for coir-phthalic anhydride it was ~ 3.75 . The latter sample upon repeated dialysis with deionized water yielded a pH value of 6.4, indicating phthalic acid entanglement with the crosslinked fibers, which were leached out by water. This phthalic acid contamination was also indicated in FTIR spectra of coir crosslinked with phthalic anhydride, imparting a new band at 1487.5 cm^{-1} .

Physical and Chemical Behavior

Percent Moisture Regain (Extent of Hydrophobicity)

About 0.2 g of each of the modified coir were placed separately in previously weighed bottles. The bottles were kept in an oven at $50\text{--}60^\circ\text{C}$ until a constant weight was obtained. The oven dry samples were then kept in an artificial humidity chamber for 1 week. The bottles were weighed at intervals until constant weights were obtained:

% moisture regain

$$= \frac{\text{eq}^m \text{ wt of fibers} - \text{oven dry wt}}{\text{oven dry weight}} .$$

Percent of moisture regain of coir, alkali-treated coir, coir crosslinked with formaldehyde, *para*-phenylene diamine, and phthalic anhydride, and also of the crosslinked coir cyanoethylated for various time intervals are shown in Table II. The data in the table shows that, except for alkali treated coir, the reduction in percent moisture regain is significant and as such for formaldehyde crosslinked fibers has 4.08% of moisture regain; for phthalic anhydride crosslinked it was 5.75% in comparison to parent coir

with 16.87% moisture content. On cyanoethylation of the formaldehyde and phthalic anhydride crosslinked fibers, the moisture regain was lowered from 4.08 to 3.92% and 5.73 to 4.13%, respectively. *para*-Phenylene diamine crosslinked fiber did not show good reduction in the extent of moisture regain, indicating very low degree of crosslinking. This was expected from the structure of the lignin component in the coir, where the coupling point on the conferyl alcohol unit is extremely low and also sterically hindered. However cyanoethylation of this crosslinked fiber led to reduction of moisture regain to 10.53%. The extent of hydrophobicity with formaldehyde and phthalic anhydride crosslinked coir and their cyanoethylated derivative demonstrates their utility as good reinforcements for light weight, low cost composites.

Tensile Strength

The tensile strength of the parent and chemically modified fibers were determined using a KMI tensile tester. The speed of the testing machine was set at 12.7 Nm. The load scale range was adjusted to be adequate for the estimated breaking load of the specimen under test. The jaws were set at the effective gauge length of approximately $254 \pm 1\text{ mm}$. The specimen axis was placed on the grip with an imaginary line joining the points of attachment of the grips to the machine. Then the machine was set to zero. The deflection measuring device was set up and the recorder was started. The ultimate breaking loads were recorded.³³ The results of the tensile strength (kg/cm^2) are presented in Table III. The results of the tensile data showed that treatment of coir with 2% NaOH, under the condition as mentioned earlier, significantly increases its tensile strength but follows depletion with an increase in the concentration of alkali. This is similar to that

Table III Tensile Strength of Parent and Chemically Modified Coir

Sample	Tensile Strength (kg/cm^2)
Parent coir	130.00
Coir-ONa (2%)	161.00
Coir-ONa (8%)	155.00
Coir-ONa (10%)	152.00
Coir- <i>c</i> -CH ₂ O	193.00
Coir- <i>c</i> -PPDA	201.00
Coir- <i>c</i> -PhA	180.00

Table IV Effect of Chemical Behavior of Parent and Chemically Modified Coir

Sample	Percentage Solubility					
	H ₂ SO ₄	HCl	NaOH	NH ₄ OH	NaCl	H ₂ O ₂
Coir	9.97	10.07	11.73	9.47	4.57	14.22
Coir-ONa	14.02	13.97	9.52	2.34	8.20	11.25
Coir-c-CH ₂ O	7.92	7.68	8.12	4.21	2.78	11.21
Coir-c-PPDA	8.47	8.05	7.74	5.72	1.00	15.12
Coir-c-PhA	5.62	4.73	5.82	3.86	2.15	13.05

reported by Kulkarni et al.³ For other chemically modified fibers the increase in tensile strength is significant compared to parent coir. The enhancement may be attributed to chain stiffening of the component polymers in the coir imparted by the introduction of different groups onto the fiber backbones.

Chemical Behavior (Solubility %)

The behavior of parent and modified coir toward H₂SO₄, HCl, NaOH, NH₄OH, NaCl, and H₂O₂ was tested by determining the percent of solubility. For this purpose samples were immersed separately in aqueous solution (0.1M) of the reagents for 2 h at 60°C using a fiber-liquor ratio 1 : 100. The method adopted was similar to that of Leveau et al.³⁴ The results of solubility are recorded in Table IV. The data in Table IV indicate that except with NaCl, phthalic anhydride crosslinked coir had medium resistance to chemical damage followed by CH₂O and PPDA coupled crosslinked fiber. Thus chemical modification of coir either involving the OH groups and/or aromatic ring points impart resistance to attack by common chemical reagents.

CONCLUSION

The results of these studies are reasonably clear that through simple organic reactions with inexpensive reagents, it is possible to enhance the extent of hydrophobicity, mechanical strength, and chemical inertness of an abundant lignocellulosic coir. The described coirs can be used as excellent reinforcing materials for low cost composites.

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