

FTIR Spectra and Physico-Chemical Behavior of Vinyl Ester Participated Transesterification and Curing of Jute

R. K. SAMAL, S. ACHARYA, M. MOHANTY, M. C. RAY

Macromolecular Research Laboratory, Department of Chemistry, Ravenshaw College, Cuttack- 753 003 Orissa, India

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ABSTRACT: In this article we report the transesterification of jute with *n*-Butylacrylate (BA) under appropriate condition using NaOH, Pyridine (Py), and a Pyridine–acetone mixture as a catalyst. The modified vinylog jute was subsequently cured with benzoylperoxide (BPO) in acetone at 50–60°C. The parent and chemically modified jute were characterized by FTIR spectra. The percent moisture regain, mechanical strength, and behavior to common chemical reagents of the parent and modified fibers have also been tested. Transesterification and curing of jute lowered the percentage of moisture regain, imparted mechanical strength, and resistance to common chemical reagents. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 575–581, 2001

Key words: chemical behavior; FTIR spectra; mechanical strength; jute fiber; transesterification

INTRODUCTION

Chemical modification of lignocellulosic/agrowaste fibers are currently being undertaken to make them suitable reinforcing candidates in composites for low-strength applications. This is aimed at the partial replacement of costly and pollution-causing fibers like glass, carbon, borosilicate, etc. Some reports on jute^{1–4} and coir^{5–7} are available. From this laboratory, we have previously commented that most of the reports prior to our work perhaps did not stand up to commercial success due to involvement of expensive chemical reagents and a cumbersome process of modification. As the availability of jute in India is profuse, so it is relevant, important, and also economically profitable for our country to make it an industrially acceptable reinforcing material. In our laboratory we are applying conventional

methods with our own specification using cheap chemicals to modify jute,^{8,9} coir,^{10–13} and PALF^{14–17} for use as a good reinforcement in developing light-weight low-cost composites. This article shows our efforts in this emerging field of polymer research.

EXPERIMENTAL

Materials and Methods

Jute fibers were purified by soxhlet extraction with 1:1 benzene–ethanol mixture for 72 h, followed by washing with acetone, ethanol, and air dried. Butylacrylate was purified as reported earlier.¹⁸ Other chemicals like acetic acid, sodium hydroxide, methanol, acetone, pyridine, sulphuric acid, hydrochloric acid, sodium chloride, benzoylperoxide, etc., were of analytical grade (Merck Chemicals), and were used as such.

Methods of Chemical Modification

Alkali Treatment of Jute (Jute–ONa)

The purified jute fibers were treated with aqueous sodium hydroxide (2% w/v) solution for 1 h at

Correspondence to: R. K. Samal.

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35°C with occasional shaking followed by washing with dilute acetic acid and distilled water for a week to leach out the absorbed alkali. The materials were then air dried.

Transesterification of Jute with Butylacrylate

Using 0.4% NaOH as a Catalyst (Jute-BA/NaOH)

Transesterification of the parent jute (1 g) was conducted under reflux with butylacrylate (20 mL) at 60°C for various time intervals (1 to 8 h) using 0.4% NaOH (20 mL) solution as a catalyst. The transesterified fibers were then washed with methanol, dilute acetic acid, followed by acetone and distilled water. The materials were then air dried.

Using Pyridine as a Catalyst (Jute-BA/Py)

Direct transesterification of jute was carried out by refluxing the jute (1 g) with butylacrylate (15 mL) using pyridine (6 mL) as a catalyst at 60°C for various time intervals (1 to 8 h). The transesterified fibers were then washed with methanol, dilute acetic acid, followed by acetone and distilled water. The materials were then air dried.

Using a Pyridine-Acetone Mixture as a Catalyst (Jute-BA/Py-acetone)

The transesterification of jute was also carried out by refluxing the jute (1 g) with butylacrylate (10 mL) and pyridine (4 mL) mixture as a catalyst at 60°C for various time intervals (1 to 8 h). The transesterified fibers were then washed with methanol, dilute acetic acid, followed by acetone and distilled water. The materials were then air dried.

Curing of Transesterified Jute with Benzoylperoxide

Curing of butylacrylate transesterified jute (0.4 g) was done under reflux with 10 mL of 0.1 M BPO in acetone 40 mL at 60°C for 2 h. The treated fibers were then washed with acetone, dilute acetic acid, followed by distilled water. The material were then air dried. Schematic presentation of various chemical modification of jute are given in Figure 1.

FTIR Spectroscopy

The FTIR spectra of the samples were recorded in KBr pellets in a Bruker IFS 66V FTIR spectrophotometer.

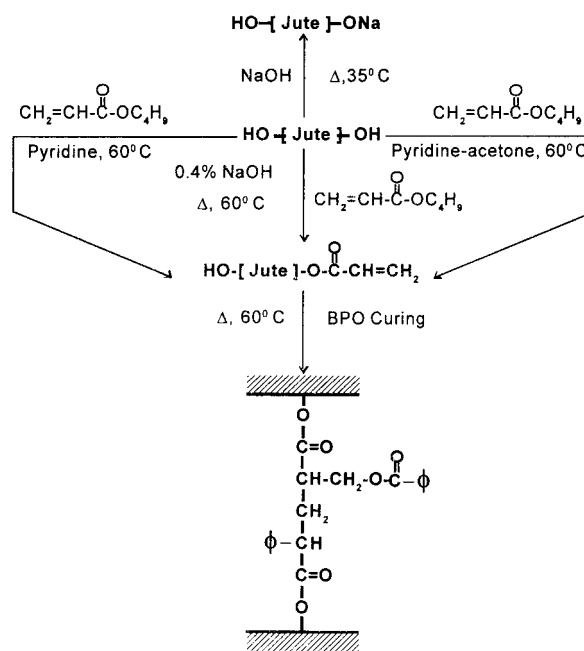


Figure 1 Schematic presentation of various chemical modification of jute.

pH Measurement

The pH of the parent and chemically modified jute was measured in deionized water by using a Systronics 324 pH meter standardized with buffer of pH 4 and 9. For this, the samples were immersed in deionized water using the sample-liquor ratio of 1:100.

RESULTS AND DISCUSSION

We observed no significant change in the appearance of the fibers after transesterification with BA/Py-acetone, BA/Py, and curing with BPO of these transesterified fibers; but the fibers acquired a whitish color after transesterification with BA/0.4% NaOH and curing with BPO.

FTIR Spectra

The FTIR spectra of parent, transesterified, and BPO-cured jute are shown in Figure 2. The exact position and probable assignments of the bands are given in Table I.

In comparison to parent jute, alkali-treated jute (jute-ONa), transesterified jute i.e., jute-BA/Py, jute-BA/0.4% NaOH, jute-BA/Py-acetone, and curing of transesterified jute, i.e., jute-BA/

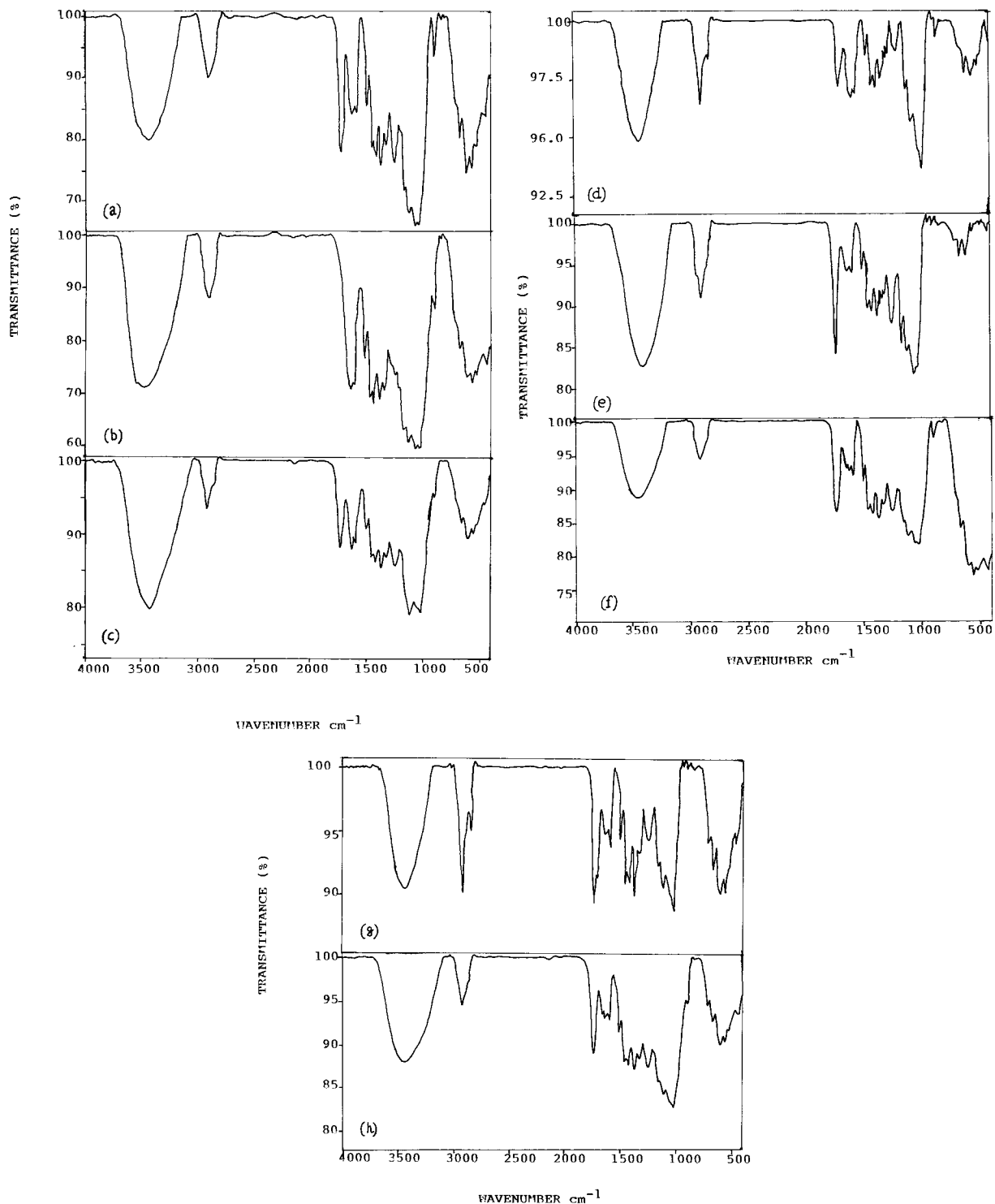


Figure 2 FTIR spectra of parent and chemically modified jute. (a) parent jute; (b) jute-ONa; (c) jute-BA/Py; (d) jute-BA/NaOH; (e) jute-BA/Py-acetone; (f) jute-BA(Py)-C-BPO; (g) jute-BA(NaOH)-C-BPO; and (h) jute-BA(Py-acetone)-C-BPO.

(Py)-C-BPO, jute-BA (0.4% NaOH)-C-BPO, jute-BA(Py-acetone)-C-BPO showed a reduction of OH stretching intensity and shifting of the

peak position from 3449.1 cm^{-1} to 3466.4 cm^{-1} , 3433.3 cm^{-1} , 3449.7 cm^{-1} , 3427.4 cm^{-1} , 3461.7 cm^{-1} , 3445.0 cm^{-1} , and 3437.2 cm^{-1} , respec-

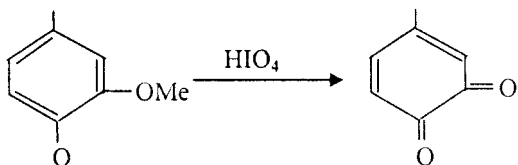
TABLE I FTIR Spectral Data of Parent and Chemically Modified Jute (Absorbance in cm^{-1})

Jute	Jute-ONa	Jute-BA/Py	Jute-BA/0.4% NaOH	Jute-BA/Py-Acetone	Jute-BA(Py)-C-BPO	Jute-BA(0.4% NaOH)-C-BPO	Jute-BA(Py)-Acetone-C-BPO	Possible Assignment
3449.2	3466.4	3433.3	3449.7	3427.4	3461.7	3445.0	3437.2	OH-stretching vibration
2918	2915.2	2923.2	2922.9	2924.1	2920.5	2923.2	2922.4	
2734.2	—	—	—	—	—	—	—	H-bonded
1739.9	—	1738.3	1740.1	1736.8	1739.8	1742.9	1740.3	C=O stretching
—	—	—	—	—	1652.4	1656.6	1651.8	C=C stretching vibration of phenyl nucleus from BPO
1641.2	1637.7	1634.5	1632.6	1642.1	1640.4	—	1640.8	Absorbed water
1597.5	1599.5	1596.3	1595.1	1595.9	1596.2	1595.9	1597.5	Aromatic C=C stretching
1506.1	1506.9	1506.1	1505.9	1505.5	1506.0	1506.1	1506.5	
1463.1	1463.5	1461.5	1462.4	1462.2	1462.9	1464.1	1461.6	—CH ₂ bending (glucopyranose)
1429.4	1429.2	1427.9	1427.4	1427.8	1429.1	1430.2	1430.0	O—H in plane bending vibration
1380.3	1374.9	1376.0	1376.9	1375.4	1374.5	1382.8	1376.8	C—H (aliphatic) bending
—	—	1327.0	1327.3	1327.2	—	—	—	C—C stretching vibration of acrylate moiety
1335.0	1336.1	—	1335.5	1333.9	1335.4	1336.9	1333.5	Interaction between O—H bending and C—O stretching
1250.8	1235.5	1248.2	1239.7	1247.7	1249.2	1248.2	1251.1	
1160	1160.6	—	1157.2	1162.3	—	1157.7	—	C—O—C assymmetric stretching
1114.3	1115.7	1122.2	1115.3	1114.4	1113.8	1115.2	1114.9	Assymmetric in phase ring stretching
1055.0	1060.0	—	—	1060.9	—	—	—	C—O/C—C stretching
1024.4	1025.1	1022.8	1021.6	—	1024.3	1020.5	1024.0	β -glucosidic linkage
894.3	896.6	896.3	895.8	894.8	894.6	894.7	894.9	
833.4	833.4	—	—	834.6	835.0	834.2	830.7	Two adjacent aromatic C—H bending
—	—	—	—	—	—	698.2	700.1	Five adjacent aromatic hydrogen
668.5	666.9	666.9	668.9	667.7	667.5	669.1	669.1	Out plane bending vibration of intermolecular H-bonded O—H group
607.5	606.5	614.4	607.0	610.0	597.0	608.3	606.7	Torsional vibration of pyranose ring
560.1	558.2	559.4	558.9	559.8	559.0	559.6	559.8	
—	518.6	463.5	463.3	520.1	520.1	528.4	435.8	
—	433.4	—	449.8	433.5	433.5	466.4	—	

tively, indicated the participation of some free hydroxyl group in these chemical reaction.

The point of reaction is probably phenolic—OH in the lignin components and C₆—OH of the glucopyranose unit in the cellulose component, but may not be C₂—OH and C₃—OH, as Malapardian oxidation¹⁹ with HIO₄ is found to be positive with modified jute. However, consumption of HIO₄ by

jute cannot be taken as a authentic stand of non-involvement of the C₂—C₃ glycolic linkage of the glucopyranose unit in the cellulose component in the chemical modification, because the HIO₄ is a well-patented oxidizer to cause easy oxidation of guaiacol (*o*-methoxyphenol) to *O*-quinones,^{20,21} and such moiety is also present in the lignin component of jute.



It is thus difficult at this stage to sketch any positive opinion about noninvolvement of C₂—OH and C₃—OH groups in the chemical reaction.

A weak band at 2734.2 cm⁻¹ in parent jute arises from the O—H stretching vibration of the inter- and intramolecular hydrogen OH group in jute, and this almost disappears in all such chemical reactions, indicating its involvement in this reaction. Strong and sharp bands at 1739.9 cm⁻¹ due to a C=O stretch in parent jute disappeared in jute—ONa; however, in jute—BA/Py, jute—BA/0.4% NaOH, jute—BA/Py—acetone, jute—BA(Py)—C-BPO, jute—BA(0.4% NaOH)—C-BPO, and jute—BA(Py—acetone)—C-BPO have only shifted the C=O stretch to 1738.3 cm⁻¹, 1740.1 cm⁻¹, 1736.8 cm⁻¹, 1742.9 cm⁻¹, and 1740.3 cm⁻¹, respectively, due to a gross structural change during such chemical reactions. The disappearance of the C=O band in alkali-treated fiber (jute—ONa) is probably due to transformation of the uronic acid residue in the hemicellulose component in the jute to an interlocked network that suffers reversion upon subsequent chemical treatment. A new band of weak intensities appear at 1652.4 cm⁻¹, 1656.6 cm⁻¹, and 1651.8 cm⁻¹ in the FTIR spectra of jute—BA(Py)—C-BPO, jute—BA(0.4% NaOH)—C-BPO, and jute—BA(Py—acetone)—C-BPO, respectively. This is due to the C=C stretching vibration of the phenyl nucleus incorporated through curing of the transesterified jute with BPO. A weak band at 1641.2 cm⁻¹ due to absorbed water in the parent jute disappeared in jute—BA(0.4% NaOH)—C-BPO upon transesterification and curing; however, in jute—BA/Py and jute—BA/0.4% NaOH, this band is shifted to lower wavelengths of 1634.5 cm⁻¹ and 1632.6 cm⁻¹, respectively. Very weak bands at 1327.0 cm⁻¹, 1327.3 cm⁻¹, and 1327.2 cm⁻¹ in jute—BA/Py, jute—BA/NaOH, and jute—BA/Py—acetone, respectively, are due to the C—C stretching vibration of acrylate moiety incorporated through transesterification. This also supports transesterification of jute under the present conditions. Other bands in the region of 1157 cm⁻¹ to 1020 cm⁻¹ are almost similar for all the samples, and are due to asymmetric C—O—C stretching, asymmetric in phase stretching, and C—O/C=O stretching vibration

TABLE II Percentage Moisture Regain of Parent and Chemically Modified Jute

% of NaOH Treatment (w/v)	Jute—ONa		BA—Jute/Py		BA—Jute/0.4% NaOH		BA—Jute/Acetone—Py		Transesterified Jute Curing with Benzoyl Peroxide (BPO)		
	Time of T.E. in Hours	% of Moisture Regain	Time of T.E. in Hours	% of Moisture Regain	Time of T.E. in Hours	% of Moisture Regain	Time of T.E. in Hours	% of Moisture Regain	Time of Curing in Hours	Curing of the T.E. Jute	% of Moisture Regain
0	1	22.3	1	25.4	1	22.7	1	22.7	1	Jute—BA/Py	14.2
2	2	21.7	2	24.6	2	22.1	2	22.1	2		
5	4	20.4	4	23.7	4	20.4	4	20.4	2 h	Jute—BA/NaOH	18.6
10	6	17.4	6	22.3	6	19.3	6	19.3		Jute—BA/Py—Acetone	13.2
	8	15.6	8	20.8	8	18.1	8	18.1			

TABLE III Mechanical Strength of Parent and Modified Jute

Sample	Strength in Kgf/g
Parent Jute	28
Jute-ONa	46
Jute-BA/Py	29
Jute-BA/NaOH	30
Jute-BA/Py-Acetone	32
Jute-BA(Py)-C-BPO	31
Jute-BA(NaOH)-C-BPO	33
Jute-BA(Py-acetone)-C-BPO	34

(Table I), which are effected to in significant extent by chemical reactions.

The medium band at 894.3 cm^{-1} due to β -glucosidic linkage in parent jute underwent shifts to higher wave numbers and an increase in intensity in the modified fiber relates to the rotation of glucose residue around the glucosidic bond.²² New peaks at 698.2 cm^{-1} and 700.1 cm^{-1} in the FTIR spectra of jute-BA-0.4% NaOH-C-BPO and jute-BA/Py-acetone-C-BPO, respectively, may be due to the five adjacent H-atoms of the aromatic nucleus, indicating introduction of a monosubstituted benzene onto jute arising from curing with BPO. The bands at and beyond 668.5 cm^{-1} in FTIR spectra of parent and modified jute clearly corroborate the findings of Blackwell et al.²³

pH Determination

The pH value of all the samples except the alkali-treated fiber were 6.8, and for jute-ONa, it was 8.2.

PHYSICO-CHEMICAL BEHAVIOR

Percent Moisture Regain (Extent of Hydrophobicity)

About 0.2 g of parent jute and each of the modified jute were placed separately in previously weighed

bottles. The bottles were kept in an oven at 60°C until a constant weight was obtained. The oven-dry samples were kept in an artificial humidity chamber (RH = 80%) for a week until constant weights were obtained.

percent moisture regain

$$= \frac{(\text{Equilibrium wt of the fiber}) - (\text{oven dry wt})}{\text{oven dry wt}}$$

$\times 100$

The data in Table II on the extent of moisture regain shows that the reduction in percent moisture regain is significant in all modified fibers. The extent of hydrophobicity of the various samples follows the order jute-BA(Py-acetone)-C-BPO > jute-BA(Py)-C-BPO > jute-BA/Py > jute-BA/Py-acetone > jute-BA(0.4% NaOH)-C-BPO > jute-BA/0.4% NaOH > jute > jute-ONa. This order shows that jute-BA(Py-acetone)-C-BPO, jute-BA(Py)-C-BPO, and jute-BA/Py are good samples for use as reinforcement.

Mechanical Strength

The mechanical strength of the parent and modified jute were determined using a fiber-breaking strength measuring machine, Good Brand & Co. Ltd, UK. The results of the mechanical strength (kgf/g) are presented in Table III. The result of the mechanical strength data indicates that all the modified fibers have shown good mechanical strength compared to parent fibers. Especially, the alkali-treated fibers showed a significant increase of mechanical strength. The enhancement may be attributed to chain stiffening of the com-

TABLE IV Percentage Solubility of Parent and Modified Jute

Sample	Percentage Solubility					
	H ₂ SO ₄	HCl	NaOH	NH ₄ OH	NaCl	H ₂ O ₂
Parent Jute	7.02	5	18	4.08	4.54	17.03
Jute-ONa	10.2	9	15.8	3.5	6.8	12.16
Jute-BA/Py	5.42	4.75	11.21	3.93	4.1	14.3
Jute-BA/NaOH	4.98	3.81	10.3	3.1	4.02	11.02
Jute-BA/Py-acetone	5.13	4.16	10.8	3.63	4.31	12.67
Jute-BA(Py)-C-BPO	4.78	3.24	8.96	3.01	3.83	10.4
Jute-BA(NaOH)-C-BPO	3.71	2.41	6.04	2.27	2.77	10.8
Jute-BA(Py-acetone)-C-BPO	4.7	2.73	7.37	2.84	2.83	9.7

ponent polymer in jute as a net consequence of the increase hydrogen bonding between OH and ester groups in the neighboring chain.

Chemical Behavior

The behavior of parent, transesterified, and cured jute towards H_2SO_4 , HCl, NaOH, NH_4OH , NaCl, and H_2O_2 was tested by determining the percent of solubility. For this purpose, the samples were immersed separately in aqueous solution (0.1 M) of the reagents for 2 h at 60°C by using a fiber-liquor ratio of 1:100. The method adopted was similar to that of Leaveau et al.²⁴ The result of solubility are recorded in Table IV. The data in Table IV indicate that, among the transesterified samples, the jute-BA/0.4% NaOH has better resistance to chemical damage except that for H_2O_2 . However, BPO-cured transesterified fiber has developed comparatively more resistance to chemical damage. Among all the samples, jute-BA(0.4% NaOH)-C-BPO has remarkable resistance to the chemical reagents except that for H_2O_2 .

CONCLUSION

The results of these studies established that significant hydrophobicity, improved mechanical strength, and resistance to common chemical reagents may be imparted to jute through a simple chemical route involving transesterification and/or curing with the use of inexpensive chemical reagents. The merit of the method may be adopted in large scale for developing ideal reinforcing candidates for fiber reinforced plastic (FRP) for low-strength applications.

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REFERENCES

1. Monto, S. J.; Sugerma, G. *Polym Plast Technol Eng* 1979, 13, 115.
2. Mukherjea, R. N.; Pal, S. K.; Sanyal, S. K. *J Appl Polym Sci* 1983, 28.
3. Varma, I. K.; Anantha Krishna, S. R.; Krishnamoorthy, S. *Text Res J* 1988, 58, 486.
4. Som, N. C.; Mukherjee, A. K. *I J Text Res* 1989, 14(2) 80.
5. Varma, D. S.; Varma, M.; Varma, I. K. *Text Res J* 1984, 54, 827.
6. Varma, D. S.; Varma, M.; Varma, I. K. *J Reinfor Plast Compo* 1985, 4, 419.
7. Varma, D. S.; Varma, M.; Varma, I. K. *Thermochem Acta* 1986, 108, 1999.
8. Samal, R. K.; Mohanty, M.; Panda, B. B. *J Polym Mater* 1995, 12, 235.
9. Samal, R. K.; Mohanty, M.; Panda, B. B.; Rout, S. K. *Ind J Fiber Text Res* 1997, 22, 195.
10. Samal, R. K.; Panda, B. B.; Mohanty, M.; Rout, S. K. *Macromolecular Current Trends*; Allied Publishers: Trivandrum, 1995, p. 36, Vol. I.
11. Samal, R. K.; Rout, S. K.; Panda, B. B.; Mohanty, M. *J Polym Mater* 1995, 12, 229.
12. Samal, R. K.; Rout, S. K.; Panda, B. B.; Mohanty, M. *J Appl Polym Sci* 1995, 58, 745.
13. Samal, R. K.; Rout, S. K.; Panda, B. B.; Senapati, B. K. *J Appl Polym Sci* 1997, 64, 2283.
14. Samal, R. K.; Ray, M. C. *J Polym Mater* 1996, 13, 201.
15. Samal, R. K.; Ray, M. C. *J Appl Polym Sci* 1997, 64, 2119.
16. Samal, R. K.; Ray, M. C. *J Polym Mater* 1997, 14, 183.
17. Samal, R. K.; Ray, M. C. *J Polym Mater* 1998, 15, 271.
18. Giri, G. Ph.D. Thesis; Utkal University, India (1990).
19. Malaparde, L. *Comp Rend Act* 1928, 186, 382.
20. Adler, E.; Hemstarn, S. *Acta Chem Scand* 1955, 9, 505.
21. Adler, E.; Dahler, J.; Westin, G. *Acta Chem Scand* 1960, 14, 1580.
22. Higgins, H. G.; Goldsmith, V.; Mukherjee, A. N. *J Polym Sci* 1958, 32, 57.
23. Blackwell, J.; Kalpak, F. J.; Garden, K. H. *Tappi* 1978, 61, 71.
24. Leaveau, M.; Caillet, M.; Demonhart, N. *Bull Inst Text Fr* 1960, 90, 7.