

Infrared absorption study on UF- and MF-treated jute fabrics

M N Amin

Department of Chemistry, Bangladesh Jute Research Institute, Dhaka 1207, Bangladesh

and

S S Reddy

Chemistry Division, Jute Technological Research Laboratories, 12, Regent Park, Calcutta 700 040, India

Received 29 October 1990; revised received 13 March 1991; accepted 1 May 1991

The infrared spectra of UF- and MF-treated jute fabrics have been studied to know the effect of crosslinking agents on different frequencies. The amide I frequency of carbonyl group in UF-treated sample and amide II band for N-H deformation in UF- and MF-treated samples are well resolved. A group of bands in the range of $1200-1050\text{ cm}^{-1}$, mainly due to ether linkage, is distinctly observed.

Keywords: Infrared absorption, Jute fabric, Melamine formaldehyde, Urea formaldehyde

1 Introduction

In earlier work¹⁻⁴, crosslinking of cotton, linen and viscose with different resins was found to impart improvement in physical properties such as crease resistance, dimensional stability, handle and drape. However, information on the effect of resins on jute is relatively scarce. Das and Ghosh⁵ made some preliminary observation on the strength and wrinkle recovery properties of jute fabric on prolonged treatment with formaldehyde in the presence of magnesium chloride, citric acid, and a combination of magnesium chloride and citric acid as catalysts at room temperature. Amin *et al.*⁶ reported improvement in crease resistance and shrinkage resistance and reduction in moisture regain of jute fabric on treatment with urea formaldehyde (UF) and melamine formaldehyde (MF) catalyzed by magnesium chloride hexahydrate in pad-dry-cure process. Som *et al.*⁷⁻⁹ reported the wrinkle resistance and tensile strength retention of plain weave jute fabrics on treatment with UF, MF, dimethylolethylene urea (DMEU) and dimethylol dihydroxyethylene urea (DMDHEU) in presence of various inorganic salt catalyst systems. Amin *et al.*¹⁰ reported the effect of MF resin on the properties of jute such as crease resistance (dry and wet), reduction in moisture regain, insolubility in cuprammonium hydroxide solution, tensile strength, abrasion resistance and flexural rigidity. Stevens and Smith¹¹ observed that crease recovery increased curvilinearly with increase in degree of substitution and the breaking strength and

tearing strength decreased linearly with increase in dry crease recovery.

The infrared spectra of resin-treated cotton fabrics have been studied extensively in order to know the effect of hydrogen bonding on physical properties including resilience of cotton. Stevens and Smith¹¹ reported that hydrogen bonding of cellulose with substituents on the resin is not significant in producing physical changes. Benerito¹² found that dry wrinkle recovery usually increases when C₆ hydroxyls are bonded with resin. In this case, the intermolecular hydrogen bonds in the 101 and 101 planes are broken to react. When the intermolecular hydrogen bonds associated with C₆ hydroxyls to C₂ hydroxyls are broken to react with resin, the intensity of the band at 1640 cm^{-1} (adsorbed H₂O) decreases in the crosslinked cotton having high dry wrinkle resistance¹².

The information on the effect of resin on jute fabrics by IR studies is relatively scarce. Hence, the present work was initiated to study the changes in IR absorption of different groups in untreated, H₂O₂-bleached and UF- and MF-treated jute fabrics.

2 Materials and Methods

2.1 Fabric

Jute carpet backing cloth made out of *Corchorus olitorius* variety, hereinafter referred to as untreated fabric, was successively desized, scoured, partially delignified and bleached using diastase, sodium

carbonate, sodium chlorite and hydrogen peroxide respectively as per the methods reported earlier¹⁰. The chemical composition of the untreated fabric (α -cellulose 63.3%, pentosan 14.0%, lignin 14.2%, fat 0.6%, pectin 0.2%, acetyl content 0.7%, and ash content 1.14%) and H_2O_2 -bleached jute fabric (α -cellulose 72.14%, pentosan 12.7%, lignin 7.2%, fat 0.1%, pectin 0.2%, acetyl content 0.7%, and ash content 1.01%) determined by the standard methods was also reported in the same communication¹⁰.

2.2 Preparation of UF and MF Precondensates

Precondensates of UF and MF resins were prepared as reported earlier⁶ using urea and formaldehyde in the molar ratio of 1:1.6 for UF precondensate and melamine and formaldehyde in the molar ratio of 1:3 for MF precondensate.

2.3 Treatment of Fabric

The solutions of precondensates (UF and MF) of desired concentration were separately mixed with a softening agent (Turpex NP of Ciba Geigy, 10 g/l) and brought to weakly acidic condition (pH 6-6.9), followed by the addition of magnesium chloride hexahydrate (10% owf, BDH LR grade). Two separate samples of H_2O_2 -bleached jute fabric were immersed separately in the above liquors (material-to-liquor ratio, 1:10), squeezed to a wet pick-up of 90-100%, dried (110°C, 4 min), cured (140°C, 4 min) in a stenter, cooled (24h), washed successively in a soap solution (0.2%) at 40-50°C and cold water, and air dried.

2.4 Infrared Spectra

Infrared spectra of untreated, bleached, UF- and MF-treated jute fabrics were obtained on a Perkin Elmer Infracord 137 using KBr pellet.

3 Results and Discussion

The infrared spectra of untreated and treated jute fabrics are shown in Fig. 1. The approximate positions and probable assignments of the bands are given in Table 1.

3.1 3500-2800 cm^{-1}

The strong broad band around 3380 cm^{-1} in the untreated sample is due to the hydrogen bonded O-H stretching. On H_2O_2 bleaching and resin treatment, it is shifted to higher region and placed at 3450 and 3400 cm^{-1} respectively. It is assumed that the intermolecular hydrogen bonds in native cellulose are disrupted to give higher frequency for modified cellulose¹³. The more shift on H_2O_2 treatment to that on resin treatment may be explained on the basis that H_2O_2 , a mild oxidizing agent, might be

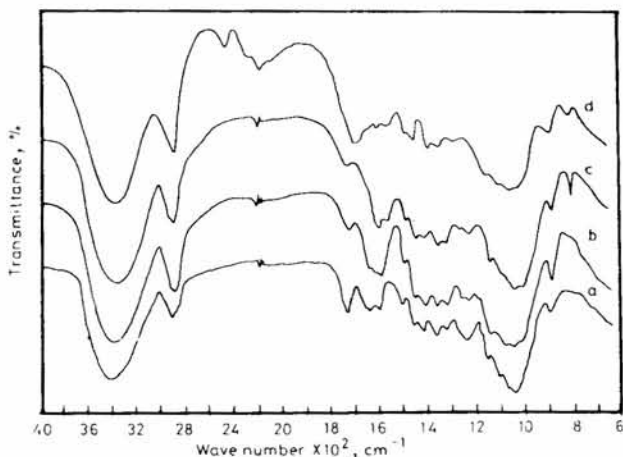


Fig. 1—Infrared spectra of jute fabric: (a) Untreated, (b) H_2O_2 -bleached, (c) MF-treated, and (d) UF-treated

able to break some of the intermolecular hydrogen bonds in cellulose I crystal lattice to give higher shift for free hydroxyl groups near 3450 cm^{-1} . However, in resin-treated samples, more hydroxyl groups are bonded to resin so that free hydroxyls are less as compared to that in the case of H_2O_2 treatment.

The strong band near 2970 cm^{-1} is assigned to C-H stretching vibrations. This frequency is lowered to 2900 cm^{-1} on bleaching or resin treatment. The weak bands near 2870 and 2940 cm^{-1} can be attributed to CH symmetrical and asymmetrical stretching^{14,15}. These bands are not clearly resolved on resin treatment.

3.2 1800-1400 cm^{-1}

The strong band at 1740 cm^{-1} in the spectra of untreated sample is due to carbonyl group of 4-O-methylolglucuronoxylan of the hemicellulose, which is also present along with cellulose and lignin in jute. Its intensity is reduced on treatment. The weak broad band at 1640 cm^{-1} is assigned for absorbed water¹⁶ on cellulose. This band is not seen on resin treatment. It seems that this band might have coupled with the amide I of the UF resin to give strong absorptions near 1660 cm^{-1} . The two aromatic vibrational modes at 1595 and 1505 cm^{-1} are due to lignin and their intensity is lowered on bleaching. The intensity of the peak at 1460 cm^{-1} in the untreated sample increased on resin treatment with a higher shift. Liang and Marchessault^{15,16} ascribed this band to OH in plane bending vibrations.

The strong bands at 1660, 1560 and 1550 cm^{-1} in the resin-treated samples are due to crosslinking agents. It has been reported¹⁷ that in simple N-mono-substituted amides, the amide I band appears at 1640 cm^{-1} . However, electrophilic substitution on nitrogen can give rise to an increase in this frequen-

Table 1—Infrared spectra of resin-treated jute fabrics

Untreated	Frequency, cm^{-1}			Possible assignment
	H_2O_2 -bleached	UF-treated	MF-treated	
3380(s)	3450(s)	3400(s)	3400(s)	O-H stretching
2920(s)	2900(s)	2900(s)	2900(s)	C-H stretching
1740(s)	1730(s)	1730(w)	1730(b)	C=O stretching of hemicellulose
1640(s)	1640(m)	—	—	absorbed water
—	—	1660(s)	—	amide I (C=O of UF resin)
—	—	1550(w)	1560(m)	amide II (N-H deformation)
1595(s)	1595(m)	1595(w)	1595(w)	aromatic (lignin)
1505(s)	1505(s)	1505(w)	1505(w)	aromatic (lignin)
1460(w)	1460(s)	1465(w)	1465(m)	O-H in plane bending
1430(m)	1425(m)	1430(m)	1430(m)	CH_2 bending
1380(s)	1375(m)	1380(m)	1375(s)	C-H bending
1240(s)	—	—	—	C-O stretching mode
—	1260(m)	1260(w)	1260(w)	C-O-C bond/C-H deformation
—	1230(m)	1210(m)	1230(m)	OH deformation
1160(s)	1160(s)	1160(m)	1160(m)	asymmetric (bridge) C-O-C stretching
1110(m)	1110(w)	1110(m)	1110(m)	asymmetric in-phase ring stretching
1060(m)	1060(b)	1060(w)	1060(b)	C-O stretching/C-C stretching
1025(w)	1020(w)	—	—	C-O stretching/C-C stretching
900(m)	897(s)	898(m)	898(s)	β -glucosidic linkage

Relative intensities: s—Strong, w—Weak, b—Broad, m—Medium

cy up to 1680 cm^{-1} . In UF-treated sample, the strong band at 1660 cm^{-1} may be assigned to amide I which has strong carbonyl characteristic. However, this band is not resolved in MF-treated sample as there is no carbonyl group in MF resin. The weak and medium bands at 1560 and 1550 cm^{-1} may be assigned to amide II. The assignment of these bands to amide II has been the subject of much controversy. The amide I band has obviously strong carbonyl characteristics whereas amide II would arise from N-H deformation mode¹⁷.

3.3 1400-1200 cm^{-1}

The bands in the crystalline region 1420 - 1300 cm^{-1} are resolved clearly in the spectra of UF- and MF-treated samples, whereas in the spectra of H_2O_2 bleached sample, this region shows weak bands. The strong band near 1240 cm^{-1} in the untreated sample is due to C-O stretching. On treatment with resin or H_2O_2 or alkali¹⁸, this band disappears and instead two new peaks appear at 1260 and 1230 cm^{-1} . The origin of these two bands are not known clearly. However, these are assumed to be due to C-H bending and O-H deformation in cellulose II which formed due to transition from cellulose I on chemical treatment.

3.4 1200-900 cm^{-1}

The bands in the range 1200 - 1050 cm^{-1} are mainly due to ether linkage. Liang and Marchessault^{15,16} assigned the band at 1160 cm^{-1} to C-O-C asymmetrical stretching. The medium peak at 1110 cm^{-1} is attributed to in-phase ring stretching. The bands in the region 1100 - 1000 cm^{-1} are mainly due to C-O stretching or bending vibrations. Higgins *et al.*¹⁹ assumed that these bands might arise due to coupled C-O stretching with C-C stretching frequency. The sharp band at 895 cm^{-1} in the untreated sample is a characteristic of β -glucosidic linkage in cellulose¹⁵⁻¹⁷. Its intensity is increased on bleaching or resin treatment.

It is assumed that the clear resolution of these bands in UF- and MF-treated samples shows that the cellulose is crosslinked with resin molecule via their methylol groups. If we assume the structure shown in Fig. 2 for UF crosslinked cellulose where one of the methylol groups is bonded with cellulose, the remaining hydroxyl groups attached to the carbon atom alpha to the secondary nitrogen would behave as aldol hydroxyl, especially under acidic condition or heat treatment during curing. Under these conditions, it loses water molecule giving rise to a carbonium ion ($^+\text{CH}_2$) which is stabilized by reson-

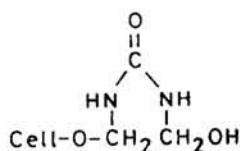
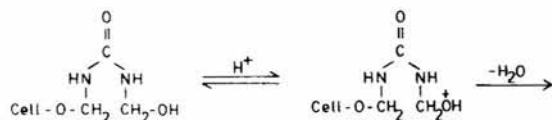
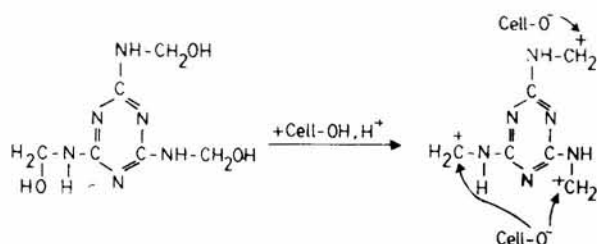


Fig. 2—Cellulose crosslinking with UF resin molecule


 Scheme 1—Stabilization of UF-crosslinked cellulose to give N-H deformation band for 1550 cm^{-1} frequency


Scheme 2—Possible reacting sites for cellulose in MF resin

ance. The probable mechanism is shown in Scheme 1. The decrease in OH absorption in MF-treated sample indicates that the degree of crosslinking is more in this case as more of its hydroxyl groups are involved in crosslinking. The probable sites for bonding α -cellulose with resin are shown in Scheme 2. It is observed that MF resin molecules have three reactive sites to crosslink with cellulose.

For the quantitative study of the infrared absorption, the IR band ratio was calculated using the following equation²⁰

IR band ratio

$$= \frac{\text{Absorption of C=O stretching} \times \text{Absorption of C-H stretching}}{\text{Absorption of O-H stretching}}$$

and the values are given in Table 2. It is observed that the IR band ratio for UF-treated fabric is higher than that for MF-treated sample. The increase in ratio over that for control (untreated) sample shows a decrease in OH absorption which is due to crosslinking. These results conform to the findings of Bandel²¹ who also observed a decrease in OH absorption due to resin treatment. Further, the resin-

Table 2—Infrared absorption values of certain frequencies at different treatments

Type of jute fabric	O-H stretching	C-H stretching	C=O stretching	IR band ratio
Untreated	1.96	1.24	1.18	0.74
H ₂ O ₂ -bleached	7.90	2.00	0.93	0.24
UF-treated	5.00	2.09	2.00	0.84
MF-treated	4.74	1.73	1.12	0.41

treated fabrics show that the IR band ratio increases with resin add-on.

Acknowledgement

The authors wish to express their thanks and gratitude to the Bangladesh Jute Research Institute (BJRI) and Jute Technological Research Laboratories (JTRL) for extending laboratory facilities to carry out the investigation. One of the authors (MNA) is particularly indebted to Bangladesh Agricultural Research Council (BARC) for the award of a fellowship under IDA credit, facilitating him to work with JTRL scientists.

References

- 1 Marsh J T, *An introduction to textile finishing*, 2nd edn (Chapman & Hall, London), 1966.
- 2 Hall A J, *Textile finishing* (Heywood, London) 1966.
- 3 *Manual of textile finishing* (BASF, Ludwigshafen, Germany), 1973.
- 4 Garner W, *Textile laboratory manual*, Vol. II, 2nd edn (Heywood, London) 1966, 95.
- 5 Das P C & Ghosh U K, *J Text Assoc*, 37 (1976) 58.
- 6 Amin M N, Mian A J & Bhuiyan A M, *Bangladesh Pat* 10,01,945 (29 December 1985).
- 7 Som N C, Bagchi A & Mukherjee A K, *Indian J Text Res*, 12 (1987) 78, 126.
- 8 Som N C, Bagchi A & Mukherjee A K, *Indian J Text Res*, 14 (1989) 45, 80, 164.
- 9 Som N C, Bagchi A & Mukherjee A K, *Indian J Technol*, 25 (1987) 674.
- 10 Amin M N, Bhuiyan A M & Mian A J, *J Text Inst*, 81 (1990) 167.
- 11 Stevens C J & Smith B F, *Text Res J*, 40 (1970) 749.
- 12 Benerito R R, *Text Res J*, 38 (1968) 279.
- 13 Liang C Y, in *Instrumental analysis of cotton cellulose and modified cotton cellulose*, edited by R T O'Connor (Marcel Dekker Inc., New York, USA) 1972, 60-90.
- 14 Liang C Y & Marchessault R H, *J Polym Sci*, 37 (1954) 385.
- 15 Marchessault R H & Liang C Y, *J Polym Sci*, 43 (1960) 71.
- 16 Liang C Y & Marchessault R H, *J Polym Sci*, 39 (1954) 269.
- 17 Bellamy L J, *The infrared spectra of complex molecules* (Metsuen, London) 1954, 209-219.
- 18 Sao K P, Methew M D, Jain A K & Ray P K, *Cellul Chem Technol*, 21 (1987) 17.
- 19 Higgins H G, Stewart C M & Harrington K J, *J Polym Sci*, 51 (1961) 59.
- 20 Patel S B, Kulshreshtha A K & Mehta P C, *J Appl Polym Sci*, 13 (1974) 2623.
- 21 Bandel W, *Melliand Textilber Int*, 39 (1958) 204.