

# Modification of Jute by Acrylic Acid in the Presence of $\text{Na}_3\text{PO}_4$ and $\text{K}_2\text{S}_2\text{O}_8$ as Catalysts Under Thermal Treatment

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Received 20 December 1996; accepted 2 August 1997

**ABSTRACT:** Jute fabric was modified using acrylic acid (AA) as the finishing agent in the presence of  $\text{K}_2\text{S}_2\text{O}_8$  and  $\text{Na}_3\text{PO}_4$  catalysts separately or in selected combinations, employing a pad-dry-cure technique. Treatment with 10% acrylic acid at 30°C and at pH 7 produced optimum effects: a batching time of 45–60 min at 30°C, followed by drying of the batched fabric at 95°C for 5 min and curing of the dried fabric at 140°C for 5 min produced most balanced improvements in the textile related properties.  $\text{Na}_3\text{PO}_4$  catalyst allowed esterification of AA with cellulosic, hemicellulosic, and lignin constituents of jute, and  $\text{K}_2\text{S}_2\text{O}_8$  catalyst allowed radical polymerization of free acrylic acid or jute-bound acrylic acid moieties; the said processes ultimately lead to some degree of crosslinking of the chain polymers of jute. Examination of the surface morphology of untreated and treated jute fabrics by scanning electron microscopy revealed a good degree of masking effect on the unit cells of jute and intercellular regions by a cohesive film of polyacrylic acid or its salts, particularly when  $\text{K}_2\text{S}_2\text{O}_8$  was used either alone or in combination with  $\text{Na}_3\text{PO}_4$  as catalyst. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 63–74, 1998

**Key words:** acrylic acid finished jute; improved jute textile; esterification; crosslinking; acrylic-grafted jute

## INTRODUCTION

Since the commencement of industrial production of jute textiles in 1832, jute grew in acceptance and use as a packaging material for grains and many other food items and industrial products.<sup>1–3</sup> Use of jute fabric as primary and secondary backing material in carpets grew in popularity and gained wide acceptance at a later stage.<sup>3–5</sup> However, since about the mid-1950s, jute goods started suffering drastic market losses in developed countries for many reasons, including the spread of mechanized bulk handling of cereals and for growing stiff com-

petition from synthetic fibers or fiber-forming polymers (polyethylene and polypropylene). The synthetic substitute appeared more advantageous with respect to strength, impact resistance, rot resistance, lightness, and a favorable production cost profile; processing flexibility and diverse application potential of the synthetics also severely eroded the profitability of the jute industry and appeared to threaten menacingly the long standing and high-profile jute industry.

But the situation has changed considerably in recent years. The escalating price of petroleum products and energy intensive nature of the synthetic fibers, coupled with their lack of amenability to biodegradation, have drawn renewed interest in agro and plant fibers such as jute. Such fibers are not only renewable, but products from them can also be made abundantly available now at a favorable cost. Moreover, biodegradability of

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*Journal of Applied Polymer Science*, Vol. 68, 63–74 (1998)

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CCC 0021-8995/98/010063-12

**Table I** Different Property Parameters of Scoured and Bleached Jute Fabric Treated with AA (10% on Weight of Fabric) Under Different Conditions: Treated Fabric Dried for 5 min at 95°C and Cured for 5 min at 140°C

Catalyst <sup>a</sup>		Batching Time at 30°C (min)	Application pH	Weight Gain (%)	—COOH gr in meq/100 g	Ester Value	Tenacity (N/cm)	Elongation at Break (%)	Abrasion Resistance (No. of Cycle)	WRA (W + F) (deg)
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Na <sub>3</sub> PO <sub>4</sub>									
Effect of variation of batching time										
+	+	0	7	6.78	28.84	11.41	100.6	6.41	45	152
+	+	15	7	7.24	27.39	16.83	98.2	7.83	47	188
+	+	30	7	8.02	25.61	21.61	87.2	8.84	49	218
+	+	45	7	8.73	23.67	24.82	80.3	9.40	56	238
+	+	60	7	8.96	27.72	22.61	81.7	10.1	58	243
—	+	0	7	6.52	12.61	10.36	98.8	6.23	47	145
—	+	45	7	7.09	27.21	12.89	100.0	6.26	46	158
+	—	45	7	5.21	33.32	6.82	117.7	6.31	64	176
Effect of variation of pH										
+	+	45	5	8.61	24.89	23.84	46.1	6.67	29	219
+	+	45	7	8.73	23.67	24.82	80.3	9.4	56	238
+	+	45	8	8.81	29.21	72.21	106.5	8.47	51	168
+	+	45	10	9.26	31.67	10.56	111.21	8.35	57	154
Only bleached jute										
—	—	—	—	—	10.27	4.83	103.9	5.86	51	143

<sup>a</sup> K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> = 0.5% and Na<sub>3</sub>PO<sub>4</sub> = 15% on weight of jute fabric.

jute enhances its widespread acceptability from environmental considerations. However, capitalization of this renewed interest in jute and jute textile items necessitates planned efforts for (1) improvement in the quality of the traditional jute textiles and, more importantly, for (2) commercially viable and technically attractive developments regarding nontraditional and value-added application for jute to ensure a higher return to the jute processing industry and to the jute growers.

Among the different nontraditional applications envisaged for jute, decorative, and furnishing fabrics, soft luggage, nonwovens, geotextiles and jute-reinforced plastics (JRP), are rated high in importance. Exploitation of jute in these application areas necessitates improvements in various properties of related fibers and textiles. There remains ample scope for balanced improvements in strength, wrinkle recovery and drapability, light fastness (for bleached and dyed jute), fiber shedding, fire resistance, and abrasion resistance. Improved rot resistance, lower moisture absorption, and enhanced compatibility or wettability of jute fiber with synthetic resins are desired for production of jute-reinforced composites.<sup>6,7</sup> The present work relates to modification of jute fiber by reaction with acrylic acid (AA), leading to notable esterification, controlled degree of crosslinking of jute, and graft copolymerization of AA on the fiber substrate.

## EXPERIMENTAL

### Materials

#### *Fabric and Yarn*

Plain weave, 100% jute fabric with 63 ends/dm, 64 picks/dm, 191 tex warp, 194 tex weft, and an average area density of 262 g/m<sup>2</sup> was used for the present study. 100% jute yarn having an average linear density of 192 tex was used.

#### *Textile Finishing Resin, Acrylic Monomers, and Other Chemicals*

Textile-grade 1,3-dimethylol, 4,5-dihydroxyethylene urea (DMDHEU) obtained from Ahura Chemicals Ltd. (Ahuramine-YX), India, was used. Commercial-grade AA, acrylonitrile (AN), methacrylic acid (MAA), and methyl methacrylate (MMA) monomers, obtained locally in Calcutta, were used without any treatment or purifi-

cation. All other chemicals (E. Merck, India) used were of laboratory reagent grade.

### Methods

#### *Scouring*

Scouring of jute fabric was performed<sup>8</sup> using a solution containing 2 g/L of sodium carbonate and 1 g/L of a nonionic detergent at a fabric-to-liquor ratio of 1 : 20 (w/v) at 60°C for 30 min, whereafter, the fabric was washed with water and dried in air.

#### *Bleaching*

Bleaching of jute fabric was performed<sup>9</sup> in aqueous media using a solution containing 0.5% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), 1.66% sodium silicate, 0.42% trisodium phosphate (Na<sub>3</sub>PO<sub>4</sub>), 0.08% sodium hydroxide, and 0.08% nonionic detergent in a laboratory jigger machine at a fabric-to-liquor ratio of 1 : 6 (w/v) for 1 h at 80°C. After bleaching, the fabric was washed with distilled water, neutralized with dilute acetic acid, and finally washed with distilled water until the wash liquor was neutral.

#### *Dyeing*

Bleached fabric and those finished with acrylic monomer system were dyed<sup>8</sup> using Bismark Brown (CI Basic Brown 331) at 4% shade in lab open bath beaker dyeing equipment at 80°C for 1.5 h under stirring condition; pH of the dye bath was adjusted at 4. After completion of dyeing, the fabrics were washed with distilled water and dried in air.

### Application of Polymer or Resin Finishes on Jute

#### *Acrylic Finish*

Presoaking of scoured and bleached jute fabric with a potassium persulphate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) solution of known concentration and subsequent application of aqueous acrylic monomer formulations on the presoaked jute fabric were performed separately by a padding technique<sup>8,10-13</sup> in a laboratory two-bowl padding mangle (two-dip-two-nip). After each of two successive dippings in the acrylic formulation, the pressure between the squeezing rollers was adjusted to enable a wet pick up of 100%. The aqueous acrylic monomer formulations contained only AA or mixtures of AA with methacrylic acid (MAA), methyl methacry-

late (MMA), or acrylonitrile (AN). The monomer solutions were usually neutralized to pH 7 by the addition of a required dose of sodium carbonate. The aqueous formulation also contained a known dose of  $\text{Na}_3\text{PO}_4$  as the esterification catalyst. The padded, squeezed fabrics were allowed to stand at 30°C for different time periods (known as batching time) before they were subjected to drying in an oven at 95°C for 5 min. The dried fabrics were then oven-cured at 140°C for 5 min.

#### **DMDHEU Resin Finish**

In the case of the DMDHEU resin finish,<sup>8</sup> the fabric was likewise padded with the aqueous resin containing 12% DMDHEU and 4%  $\text{MgCl}_2$  under controlled squeeze pressure in order to allow a wet pick-up of 100%. The resin treated fabric was then dried at 95°C for 5 min and subsequently cured at 140°C for 5 min.

The jute fabrics treated with acrylic monomers and DMDHEU resin were soap-washed following ISO-II<sup>14</sup> and then washed with water and dried in air.

#### **Determination of Moisture Regain and Weight Gain**

Moisture regain of jute fabrics was determined following a standard procedure.<sup>15</sup>

For the determination of weight gain upon different finishing treatments, the fabric samples treated with only AA and mixtures of AA and MAA, AA and MMA, and AA and AN were first soap-washed; the fabrics were then extracted under reflux in a water bath for 8–10 h using water, a methanol–water mixture, tetrahydrofuran, and dimethylformamide (DMF), respectively, in order to ensure removal of unreacted monomers and of polymeric acrylic moieties remaining unbound with the chain molecules of jute sample. The extracted fabric samples were then oven-dried.

#### **Tensile Properties**

Tenacity and elongation at break of different fabric samples were measured according to a method<sup>8,16</sup> prescribed by IS: 1969–1968 using a Zwick 1445 CRT Universal Tensile Testing Machine. The results obtained were based on an average of 10 tests in the warp direction of each sample. The test strip specimens were ravelled to a size of 50 × 20 mm between the jaws of the machine, and the tests

were performed<sup>8,16</sup> with a traverse speed of 100 mm/min at a pretension of 0.5*N*.

#### **Determination of Wrinkle Recovery Angle**

Dry wrinkle recovery angle (warp + weft) of selected fabric samples was determined according to a method prescribed by ASTM-D-1295-67 using a SASMIRA Wrinkle Recovery Tester with a specimen size of 25 × 200 mm.

#### **Measurement of Fabric Stiffness (Bending Length)**

Fabric stiffness as expressed in terms of bending length was measured according to IS: 6490-1971 (Cantilever Test) in a SASMIRA Stiffness Tester with a specimen size of 25 × 200 mm.

#### **Determination of Abrasion Resistance**

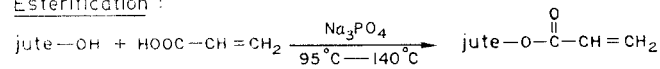
Comparative evaluation of accelerated abrasion resistance of selected fabrics was done in an electronic abrading instrument (Crockmeter) using a standard (IS: 715) paper abrader for a certain wear following AATCC-93-974. The abrasion resistance of the fabric samples was given by digital display of the number of cycles of accelerated abrasion corresponding to the appearance of the wear (first appearance of a hole on the fabric by wear and tear of the yarns).

#### **Measurement of Dyeability, Whiteness Index, and Specular Reflectance**

In order to determine dyeability, the *K/S* value of the treated and untreated fabrics dyed with a basic dye were examined in a Macbeth 2020+ reflectance spectrophotometer interfaced with a computer. The reflectance values (*R*) of the dyed fabric at the wavelength of maximum absorption ( $\lambda_{\text{max}} = 540 \text{ nm}$ ) were converted to the corresponding *K/S* value using the following Kubelka–Munk equation<sup>14</sup>:  $(K/S) = [(1 - R)^2/2R]$ , where *K* is the absorption coefficient, and *S* is the scattering coefficient.

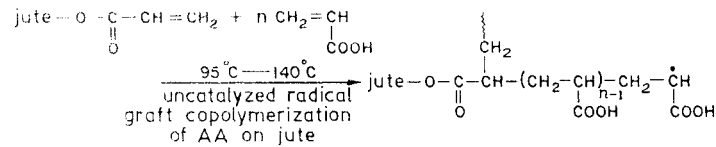
The whiteness index (WI) in the Hunterlab scale of the selected fabric samples was obtained following a standard approach and procedure<sup>17</sup> (ASTM E 313-1976/1973) with the help of Macbeth 2020+ reflectance spectrophotometer. Specular reflectance (surface gloss) of selected fabrics (surface reflectance at 45°) was also measured using the said spectrophotometer.

1. a) Esterification :

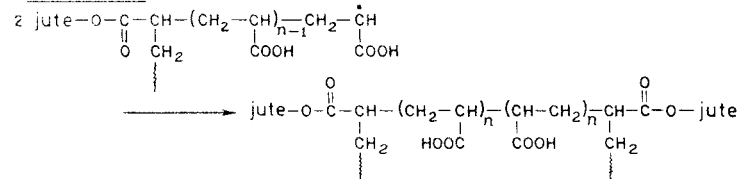


1. b) Uncatalyzed thermal free radical polymerization of AA leading to (i) grafting and (ii) crosslinking :

(i) Grafting :

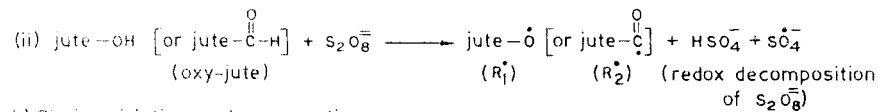
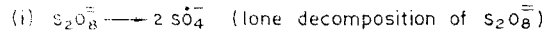


(ii) Crosslinking :

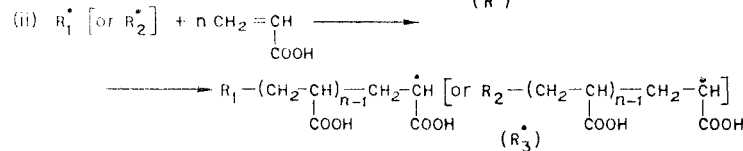


2. Persulphate induced free radical graft copolymerization (30°C–140°C) :

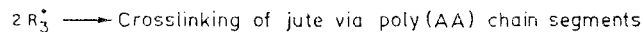
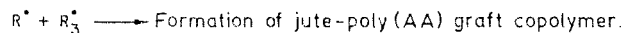
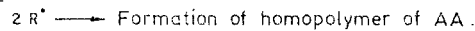
a) Radical generation :



b) Chain initiation and propagation :



c) Chain termination :



**Scheme 1**

### Measurement of Fiber Shedding

Fiber shedding level of the jute fabrics was estimated<sup>18</sup> by measuring the weight loss in mg on abrading a fixed area of a selected fabric sample of 10 cm length with a stretched piece of the corresponding fabric on a drum for a fixed number of cycles using an electronically controlled standard abrading instrument (SDL-Crockmeter).

### Measurement of Uster Hairiness Index

Uster hairiness index of the selected jute yarns (250 m long) were measured by an USTER-3 Uni-

versal Hairiness Tester. Tests were performed at a speed of 50 m/min.

### Determination of Acid Value and Ester Value

Determination of —COOH group content and ester value of selected jute samples were made following the methods described elsewhere.<sup>8,19</sup> The fabric samples were made (metallic) cation free by dipping in dilute HCl for 2 h and subsequently made HCl-free by washing with CO<sub>2</sub>-free distilled water prior to the acid value and ester value determination.

**Table II Effect of AA Treatment At pH 7 on Scoured and Bleached Jute: Fabric Dried At 95°C for 5 min and Cured at 140°C for 5 min**

Bleached Jute Treated With	Weight Gain (%)	Basic Dye Uptake (K/S)	WRA (W + F) in Degrees	Tenacity (N/cm)	Abrasion Resistance (No. of Cycle)	Whiteness Index Hunterlab Scale
None	—	12.13	143	103.9	51	59.23
2% AA	1.602	14.38	181	100.8	41	59.31
4% AA	3.29	18.36	192	92.47	46	59.47
8% AA	6.84	21.87	220	81.04	50	59.26
10% AA	8.73	23.13	231	80.26	56	59.82
12% AA	10.54	24.56	234	75.95	59	59.76

For AA treatment,  $\text{Na}_3\text{PO}_4$  content was 1.5 times the content of AA, and the fabric was presoaked with 0.5%  $\text{K}_2\text{S}_2\text{O}_8$ .

### Scanning Electron Microscopy

The surface morphology of jute fibers taken from treated and untreated jute fabrics was studied in a Hitachi scanning electron microscope (Model S340). The test fibers were coated with gold–palladium alloy using a sputter coater, and observations were made at an operating voltage of 18–20 kV.

### Infrared Spectroscopy

Infrared (IR) spectra of unmodified and selectively modified jute samples were obtained following the KBr pellet technique as detailed elsewhere<sup>20</sup> using Shimadzu IR 440 spectrophotometer. The dried fiber samples were crushed to a size finer than 20 mesh before pelletizing with KBr. The test KBr pellets contained about 1% powdered fiber.

## RESULTS AND DISCUSSION

Use of free AA for treatment of jute under the experimental conditions caused severe acid degra-

dation of the fibers and the development of brittleness with drastic drop in the tenacity of the treated fabrics (Table I). All subsequent applications of AA were therefore done by maintaining the pH of the aqueous solutions of the monomers at 7 by neutralizing the acid with sodium carbonate under stirring. Preliminary studies indicated (data not shown) that drying at 95°C and curing at 140°C produced optimum effects; property improvements of the AA-finished jute fabric are shown in Table I.

### Role of Dual Catalyst System for Acrylic Acid Application

It would be helpful if we consider at the outset the mechanism of modification of jute with AA under the influence of  $\text{Na}_3\text{PO}_4$  used as the esterification catalyst and  $\text{K}_2\text{S}_2\text{O}_8$  as the catalyst to induce free radical graft copolymerization of AA on jute. The following sequence of reactions would be expected to take place, ultimately leading to notable changes in the chemical nature of jute during the overall process.  $\text{Na}_3\text{PO}_4$  is known to be an efficient ester-

**Table III Effect of Treatment of AA With or Without MAA, MMA, or AN on Scoured and Bleached Jute**

Treatment	Weight Gain (%)	WRA (W + F) (deg)	Tenacity (N/cm)	Abrasion Resistance (No. of Cycles)	Bending Length (cm)	Whiteness Index (Hunterlab Scale)
None	—	143	103.9	51	3.8	59.23
5% AA + 5% MA	7.26	190	97.07	59	2.6	59.16
5% AA + 5% AN	5.37	166	99.41	60	3.0	59.21
5% AA + 5% MMA	5.85	188	96.66	59	2.8	59.60
10% AA	8.73	238	80.26	56	2.6	59.82

For monomer treatments, the fabric was presoaked with 0.5%  $\text{K}_2\text{S}_2\text{O}_8$ , and the  $\text{Na}_3\text{PO}_4$  content was 1.5 times the monomer content.

Table IV Comparison of Properties of AA-Finished Jute and Conventional DMDHEU-Finished Jute Fabrics

Type of Finish	WRA (W + F) (deg)	Bending Length (cm)	Abrasion Resistance (No. of Cycle)	Tenacity (N/cm)	Elongation at Break (%)	Fiber Shedding (mg)	Uster Hairiness Index	Moisture Regain (%)	Light Fastness Fastness Rating <sup>a</sup>
None	143	3.8	51	103.9	5.87	34.6	11.26	16.32	1
10% AA finished	238	2.6	56	80.26	9.4	9.4	5.6	19.21	3
12% DMDHEU finished	246	4.3	36	66.28	4.32	36	11.8	9.82	1

<sup>a</sup>Fabric dyed with a basic dye (CI Basic 331).

fication catalyst,<sup>8</sup> and reaction 1(a) in Scheme 1, producing AA ester of jute, would be the direct consequence of its catalytic action. However, the AA ester of jute may then react with the excess AA, leading to thermal polymerization of the monomeric acid as revealed by eq. 1(b) (i) in Scheme 1 and to subsequent crosslinking of jute as shown by eq. 1(b) (ii). Direct consequence of esterification under the influence of Na<sub>3</sub>PO<sub>4</sub> is therefore unlikely to enhance —COOH group content of jute, even though it would lead to enhancement in the ester value of the product. However, uncatalyzed thermal polymerization of AA, ultimately leading to grafting and crosslinking [Scheme 1's eq. 1(b)] potentially occurs in addition to persulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>)-induced free radical polymerization of AA [Scheme 1, eqs. 2(a)–(c)].

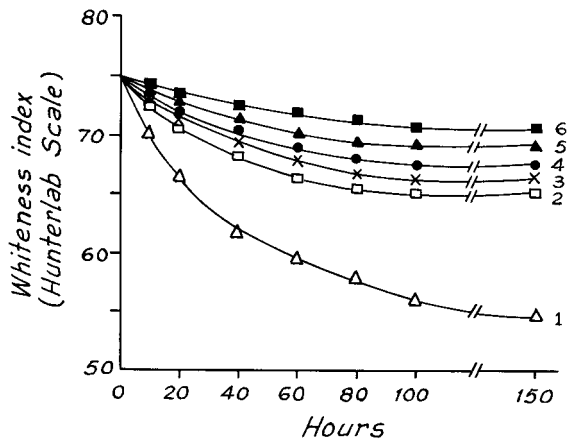
The thermal graft copolymerization and crosslinking would cause measurable enhancements in the —COOH content of the product, from which removal of the unbound (not chemically bound to jute) monomeric and polymeric AA was ensured by solvent extractions.

On the other hand, direct influence of the free radical catalyst, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, would cause substantial enhancements in the —COOH content of the modified jute as a consequence of graft copolymerization without enhancement in the ester value. However, some purely thermal esterification involving OH groups in the chain molecules of jute and AA during the curing process, even in the total absence of the esterification catalyst Na<sub>3</sub>PO<sub>4</sub>, cannot be altogether precluded. Any enhancement in the ester value of the AA-modified jute in the absence of the esterification catalyst should thus be taken as a consequence of this thermal esterification.

Under the influence of the two catalysts taken together (Na<sub>3</sub>PO<sub>4</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) for the curing of jute, all the reactions shown and discussed above are likely to take place simultaneously or successively, leading to weight gain for the fiber and enhancement in its —COOH group content and ester value. Moreover, additional reactions leading to further esterification and complex network formation (due to limited establishment of ester linkages between the carboxylic (—COOH) groups of a polycarboxylic chain bound to a particular jute molecule and alcoholic (—OH) groups of the same or other neighboring jute molecules) may also take place.

#### Effect of Variation of Batching Time

Relevant results are shown in Table I. In each experiment, the AA dose level was maintained at



**Figure 1** Resistance to photoyellowing of scoured and bleached jute fabric: (1) untreated fabric (WI-75) and fabric treated with (2) AA + AN, (3) AA + MAA, (4) AA + MMA, (5) citric acid, and (6) AA.

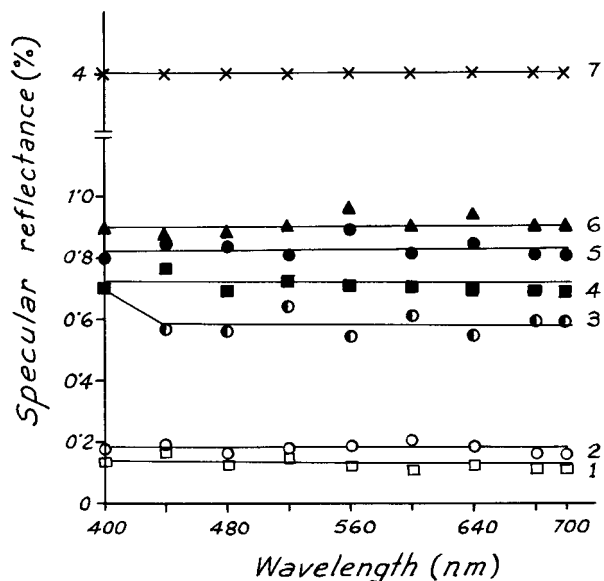
10% (w/w). For batching at room temperature (30°C) for 0–60 min under the dual catalyst system and subsequent drying by heating at 95°C for 5 min, followed by curing at 140°C for 5 min, there is an increase in the weight gain, abrasion resistance, and wrinkle recovery angle (WRA) of the fabric; on the other hand, the tenacity value decreased with an increase in the batching time. The drop in tenacity between finished jute fabrics having 0 and 60 min batching time at 30°C, however, was  $\leq 20\%$ . Batching for an extended time distinctly favors a higher incorporation of AA moieties on jute by  $K_2S_2O_8$ -induced graft copolymerization.

The carboxylic content appears to drop and the ester value tends to increase as the batching time is increased from 0 to 45 min. There is little likelihood of the establishment of ester linkages at ambient temperatures over the different periods of batching. Initial graft copolymerization or homopolymerization of AA to increasing extents over increasing batching time periods at ambient temperature (30°C) and further polymerization of free AA and bound AA moieties during the drying period at 95°C cause an overall change in environment and proximity of the hydroxyl groups of jute and carboxyl groups of the unbound or jute-bound AA or polyacrylic acid moieties in a manner that finally causes an enhanced degree of esterification during curing at 140°C under the influence of the  $Na_3PO_4$  catalyst.

The esterification reaction that assumes more prominence at the high processing temperature in the final stage (140°C) appears to be somewhat

dependant on the initial batching time. A higher batching time favors improved transformation of the grafted-on AA or polyacrylic acid units to ester moieties at the high curing temperature (140°C) under the influence of the esterification catalyst in the final stages of processing.

This may well explain the trends of change in the acid value and ester value with a change in batching time, as shown in Table I. However, beyond an optimum period (45 min) of batching, the initial accumulation of polyacrylic acid on jute fabric by grafting and some crosslinking of jute become very high indeed prior to heating at the curing temperature (140°C); the trends of change in the carboxyl content and ester value get significantly perturbed on curing in the subsequent step, even though the tenacity value, abrasion resistance, and WRA of the fabrics remain at the same level or are slightly improved (Table I) due to favorable curing or crosslinking effect. In the absence of  $Na_3PO_4$ , the esterification catalyst, simple persulphate action expectedly leads to limited graft copolymerization and little esterification over the optimum batching period at 30°C. Subsequent thermal curing ultimately produces a finished fabric having much enhanced carboxyl content and poor ester value for which the observed tenacity value is even higher than that of the untreated (bleached)

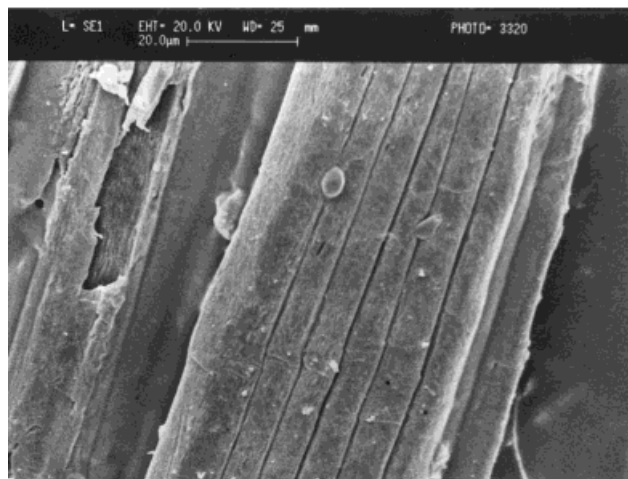


**Figure 2** Specular reflectance of jute fabric: (1) scoured fabric, (2) scoured and bleached fabric, and fabric (2) treated with (3) AA + MAA, (4) AA + MMA, (5) AA + AN, (6) AA, and (7) white ceramic tile.

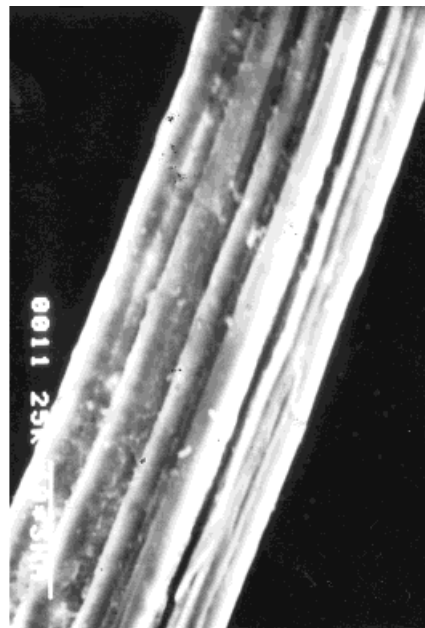


jute; the abrasion resistance is also the highest for this finished fabric, even though the improvement in the WRA is not high enough. Data in Table I clearly show that retention or improvements in the functional group pattern and

weight gain, as well as the textile related properties, are optimal on the pad-dry curing of bleached jute with AA at pH 7 under the influence of the dual catalyst system following a batching time of 45–60 min.



Micrograph-A



Micrograph-B

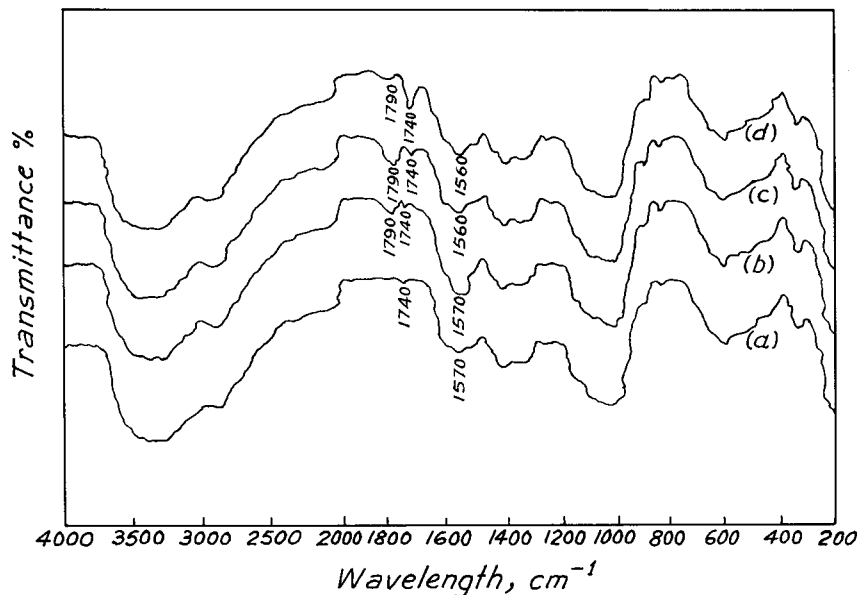


Micrograph-C



Micrograph-D

**Figure 3** Scanning electron micrographs of (A) scoured and bleached jute fiber ( $\times 1800$ ) and of the same modified with AA in the presence of (B)  $\text{Na}_3\text{PO}_4$  only ( $\times 2400$ ), (C)  $\text{K}_2\text{S}_2\text{O}_8$  only ( $\times 2400$ ), and (D) a dual catalyst ( $\text{K}_2\text{S}_2\text{O}_8$  and  $\text{Na}_3\text{PO}_4$ ) system ( $\times 2500$ ).



**Figure 4** Infrared spectra of (a) scoured and bleached jute and of the same modified with AA in the presence of (b)  $K_2S_2O_8$ , (c)  $Na_3PO_4$ , and the (d) dual catalyst ( $K_2S_2O_8$  and  $Na_3PO_4$ ) system.

### Effect of Variation of pH

Table I also shows the effect of variation of pH of the AA finishing formulation on the properties of the finished fabrics; relevant data clearly indicate that under neutral condition (pH 7), optimum grafting and esterification, leading to much improved WRA, abrasion resistance, and substantial weight gain, are achieved with nearly 80% retention of tenacity of the initial fabric. Under a slightly alkaline condition (pH 8, 10), improvement in the WRA is only marginal or poor, even though the improvement in abrasion resistance is notable, and there is even 5–10% enhancement in the tenacity of the finished fabric. A slightly acidic condition (pH 5) results in poor retention of tenacity (<45%) and abrasion resistance (<30%) despite substantial weight gain much as a consequence of weakening of the fiber in the fabric by acid attack. PH 7 apparently provides the most optimum condition for the finishing process (Table I).

### Optimum Application Level of Acrylic Acid

Table II shows the effect of application of different quantities of AA under the influence of the dual catalyst system at pH 7. Data in Table II clearly indicate that optimum weight gain and balance of textile related properties for the finished fabric

are obtained for application of 10% AA. The finished jute fabric, so obtained, also shows a substantial enhancement in the dye uptake ( $K/S$ ) value using a basic dye (Table II).

Table III shows the effect of using MAA, AN, and MMA separately with AA in equal weight proportions (for a total quantity of monomer at 10%) under the optimal conditions of fabric finish. Tenacity retention and abrasion resistance for the three different copolymer-based finished products are higher than those achieved with a product finished with AA only under comparable conditions. The product finished with AA only shows the highest WRA. The binary monomer systems apparently provide improved polymeric films and fewer crosslinkages via initial esterification with higher formation of leachable homopolymers or lower weight gain.

A comparison between AA-finished and DMD-HEU-finished jute fabrics against the unfinished jute fabric with respect to their property parameters (Table IV) clearly indicates that AA produces much desired improvements in the fabric quality; AA specifically imparts a lower order of stiffness (bending length), a higher abrasion resistance with higher retention of strength, improved resilience and fiber shedding quality, high moisture regain, and light fastness rating (for fabric dyed with a basic dye) and, at the same time, it exhibits much lower hairiness.

It was a common observation that the whiteness index of bleached jute practically remained undiminished on an AA finish but it suffered some lowering on finishing with DMDHEU for nearly comparable improvements in the WRA.

### Photoyellowing of Jute

The AA treatment protects the bleached jute fiber against extensive photoyellowing (Fig. 1) and, in this regard, it is even better than the product provided by the polyfunctional acid (citric acid), which is incapable of providing a protective polymeric film. Products based on treatment with AA and another monomer (MAA, MMA, or AN) in equal weight proportions are characterized by lower resistance to photoyellowing compared to those provided by the simple AA treatment. Figure 2 provides information about the relative rating of scoured jute, bleached jute, and differently finished bleached jute fabrics with the acrylic monomer system with respect to surface gloss or specular reflectance at 45°. It is clear from the specular reflectance data that AA-based finished products from bleached jute attain substantially improved gloss; the order of improvement of gloss with acrylic monomer based finishes is AA > (AA + AN) > (AA + MMA) > (AA + MAA). Higher specular reflectance is indicative of deposition of smoother and more cohesive film on the fabric (fiber) surface with wide coverage on completion of the finishing process.

### Scanning Electron Microscopy

Scanning electron micrographs of bleached jute with or without modification with AA are shown in Figure 3.

The micrograph in Figure 3(A) for simple bleached jute fiber clearly shows its multicellular structure with the distinct presence of an intercellular region between neighboring unit cells. An AA finish on jute using Na<sub>3</sub>PO<sub>4</sub> only as the esterification catalyst brings about some change in the surface morphology [Fig. 3(B)] where a developing masking effect due to the presence of esterified AA moieties and also due to limited formation of films of polyacrylic acid (grafted to the jute fiber) consequent to the thermal polymerization of AA during short period of curing at 140°C are distinctly visible. The masking effect is, however, much more intense with a cohesive film cover due to large-scale growth of film forming polyacrylic acid, presumably grafted to the fiber wherever the

radical polymerization catalyst K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> has been used in the absence or presence of the esterification catalyst Na<sub>3</sub>PO<sub>4</sub>, [Fig. 3(C) and (D), respectively]. Due to the dual catalyst (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> + Na<sub>3</sub>PO<sub>4</sub>) effect, surface deposition appears to be somewhat higher in Figure 3(D). The results of surface reflectance (specular reflectance, as shown in Fig. 2) are also in consistence with the results of scanning electron microscopy (SEM), which again match well with the mechanism outlined.

### Infrared Analysis

Figure 4 shows the IR spectra for (a) bleached jute and for bleached jute treated with AA in presence of (b) K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, (c) Na<sub>3</sub>PO<sub>4</sub>, and (d) K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and Na<sub>3</sub>PO<sub>4</sub>. A broad absorption band over 3500–3000 cm<sup>-1</sup>, characteristic of hydrogen-bonded O—H stretching vibration, is common to all the spectra. Other notable absorption bands in the regions of 1560–1570 cm<sup>-1</sup> and at 1740 cm<sup>-1</sup>, appearing in different intensities, are characteristic of carboxylate (anion) and ester stretching vibrations, respectively. The AA finish of jute in the presence of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> [Fig. 4(b)] results in the appearance of a new weak absorption band at 1790 cm<sup>-1</sup>, characteristic of vinyl ester stretching, and an intensification of the absorption band at 1570 cm<sup>-1</sup> for the carboxylate anion. AA finish in the presence of the esterification catalyst (Na<sub>3</sub>PO<sub>4</sub>) only, however, results in an intensification of the absorption band at 1790 cm<sup>-1</sup> for vinyl ester stretching consequent to incorporation of AA moieties in the fiber by esterification; weak and medium absorption bands at 1740 and 1560 cm<sup>-1</sup> for ester stretching and carboxylate anion stretching, respectively, appear in the said spectrum. However, the AA finish on jute under the dual catalyst (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> + Na<sub>3</sub>PO<sub>4</sub>) system expectedly results in substantial weakening of the 1790 cm<sup>-1</sup> (vinyl ester) band with sharp intensification of the band at 1740 cm<sup>-1</sup> (due to ester stretching) with good retention of the band corresponding to 1560 cm<sup>-1</sup> for carboxylate (anion) stretching.

### CONCLUSIONS

The appropriate AA finish on scoured and bleached jute fabric renders the fabric suited for many diverse applications, such as furnishing, upholstery, draperies, soft luggage, and blended tex-

tiles for apparels, in view of certain property advantages imparted. The major property advantages that can be derived from AA finishes by following a pad-dry-cure process under the catalytic influence of  $\text{Na}_3\text{PO}_4$  and  $\text{K}_2\text{S}_2\text{O}_8$  are substantial improvements in (1) tex value, (2) the WRA, (3) surface gloss or reflectance, (4) flexibility, (5) whiteness index, (6) light fastness rating, (7) abrasion resistance, (8) moisture regain, (9) basic dye uptake, and (10) resistance to photoyellowing. The AA finished jute fabric also shows nearly 80% retention of tenacity with substantial gain in elongation at break, much subdued fiber-shedding character, and lower hairiness index.

Mechanistic considerations, IR spectroscopy, and SEM analysis and also specular reflectance data indicate that the property improvements are the direct consequence of esterification of jute, grafting of film-forming poly(acrylic acid) on jute, and notable crosslinking of the jute fiber by long segments of poly(acrylic acid).

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