

# Studies of Acetylation of Jute Using Simplified Procedure and Its Characterization

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**ABSTRACT:** Dried and defatted jute fibers were acetylated for different time and temperature in the absence of catalyst and solvent. Extent of acetylation were measured by weight percent gain (WPG). These values were compared with the standard method of acetylation using a cosolvent (pyridine) system. The characterization of acetylated fibers was performed by FTIR, DSC, TGA, and SEM studies. The maximum WPG was 18.0 for an acetic anhydride–pyridine system at 120°C for 4 h whereas using only acetic anhydride WPG was 12.3 at the same reaction condition. Thermal stability of acetylated jute was found to be higher than the untreated jute. SEM studies were carried out to investigate the fiber surface morphology. FTIR studies also produced evidence for acetylation. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1517–1523, 1997

**Key words:** jute; fibrils; acetylation; infrared spectra; thermal stability

## INTRODUCTION

Jute, like other natural fibers, is hygroscopic and exhibits a tendency to be in moisture equilibrium with the relative humidity of the surrounding atmosphere, either by taking up moisture from or giving out moisture to the atmosphere. This aspect is important in textiles in regard to their ability to transfer water vapor from the human body.<sup>1</sup> However, for applications like composites, this aspect is detrimental insofar as its dimensional stability is concerned.

There is a growing interest in natural fiber based composites, mainly due to their high spe-

cific modulus,<sup>2</sup> light weight, low cost, and resistance to deforestation in addition to the other usual advantages. Moreover, natural fibers possess fairly reactive cell walls that allow modification on the surface. Other potential advantages over man-made fibers include reduced tool wear and safer handling and working conditions. In addition to these technical advantages, there are also the significant environmental advantages of using fibers that come from a continually renewable resources and utilize atmospheric CO<sub>2</sub>. The superiority of jute composite for the application of rotor blades is explained elsewhere.<sup>3</sup>

Unfortunately, factors like dimensional stability limit the use of jute composites due to swelling and shrinkage in moist and dry atmospheres, respectively. This is due to adsorption of water molecules with the other polar groups such as (—OH), (—CO), (—COOH), (—CH<sub>2</sub>OH), (—NH<sub>2</sub>), (—CONH<sub>2</sub>), and (—NH) present in the cell wall of the jute fiber. To increase the scope

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of its utilization, modification of the fiber is essential. Acetylation, methylation, cyanoethylation, etc., are such methods. Jute contains 21–23% hemicellulose, 13–14% lignin, and 61–64% cellulose. Taking advantage of the plentiful hydroxyl groups present in the different constituents, acetylation of jute using acetic anhydride and concentrated  $H_2SO_4$  as catalyst and solvent was carried out by Gopal et al.<sup>4</sup> and Callow and Speakman<sup>5</sup> following preparation of cellulose triacetate from activated cotton linters by a heterogeneous fibrous process.<sup>6</sup> Acetylation of jute fabric and X-ray studies on the acetylated jute fabric were reported by Roy<sup>7</sup> using acetic acid–perchloric acid and acetic anhydride. Infrared studies on jute and acetylated jute were also done by Gopal et al.<sup>4</sup>

All the above acetylation systems are still confined in the laboratory due to factors such as solvent and catalyst recovery, which greatly complicates the process and makes it commercially unappealing. Previous studies in this area highlighted the benefits of using a solvent free, catalyst free acetylation method<sup>8</sup> and its effect on strength, rot resistance, hydrophobicity, and abrasion resistance was studied by Mona et al.<sup>9</sup> and Callow.<sup>10</sup>

The aim of this work was to study the effect of a solvent free, catalyst free acetylation system on jute fiber at different times and temperatures and to compare this with a cosolvent system. FTIR analysis was performed to investigate the reaction. TGA and DSC analysis were carried out to study the thermal behavior of acetylated jute fiber and to compare it with the control. Electron micrographs were also taken to study the surface characteristics. The use of this acetylated jute fiber to develop dimensionally stable jute composites will be communicated in the future.

## EXPERIMENTAL

### Acetylation

#### Materials

The materials used were: chopped jute fiber (25–30 mm) W2; corchorus capsularies collected from IJIRA (India); acetic anhydride (BP Chemicals), AR grade; pyridine (E. Merck), GR grade. The solvents and reagents were used without further purification.

#### Methods

Jute fibers were defatted by using mixed solvents such as toluene : industrial methylated spirit

(IM) : acetone at 4 : 1 : 1 (v/v) for 4 h in a Soxhlet apparatus. Defatted fibers were oven dried for 24 h at 105°C. About 1 g fiber was acetylated using 50 mL of acetic anhydride alone and a mixture of 25 mL acetic anhydride and 25 mL pyridine in a hard glass test tube for 1, 2, 3, and 4 h each at 60, 80, 100, and 120°C. The test tube was closed by a rubber cork immediately after the addition of the reagents. After acetylation the sample was washed with distilled water repeatedly to remove unreacted reagent. Acetylated jute fibers were then oven dried at 105°C for 24 h. The weight percent gain (WPG) due to acetylation was calculated based on oven dried unreacted fiber.

### FTIR

Infrared spectra of the raw and acetylated jute fibers were recorded from dismembrated samples (2%) in KBr pellets by a Cygnus 100 Mattson FTIR spectrophotometer.

### Thermal Characterization

TGA and DSC analysis were carried out using a Mettler TG 50 and DSC 25 module attached to a Mettler TC 11 4000 thermal analyzer. All the measurements were made under nitrogen flow (150 mL/min) keeping a constant heating rate (10°C/min) and using an alumina crucible with a pin hole. All the figures were computer generated using an Epson model PC AX2 attached to the TC 11 4000 system.

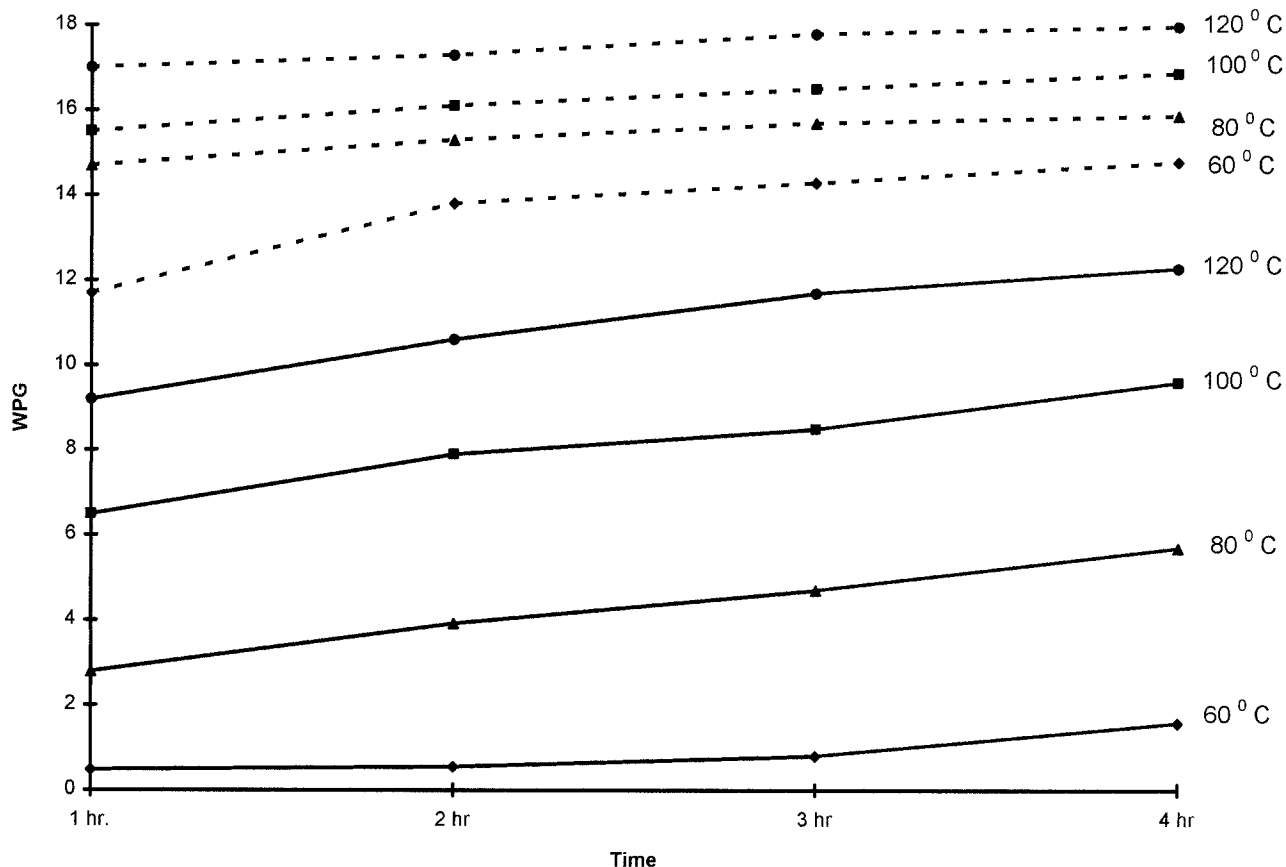
### SEM

The fiber samples were coated with a thin layer of a gold–palladium alloy using a sputter coater. SEM micrographs were taken using a Cambridge S 250 Model.

## RESULTS AND DISCUSSION

### Acetylation

From the above studies it was found that the maximum WPG was 18.0 for the acetic anhydride–pyridine system at 120°C for 4 h whereas using only acetic anhydride WPG was 12.3 at the same reaction condition. With a rise in temperature and time WPG increased and it is shown in Figure 1. Because acetylation depends on moisture con-



**Figure 1** WPG vs. time at 60, 80, 100, and 120°C: (—) with acetic anhydride alone; (- - -) with acetic anhydride and pyridine.

tent,<sup>11</sup> in all the experiments oven dried jute fibers were used. At higher temperature and longer reaction time, acetic anhydride was able to swell the fiber, making reactive chemical sites more accessible to and therefore, enhancing the reaction rate. The highest weight gain was obtained from samples with pyridine as cosolvent. This may be attributed to appreciable swelling that allowed acetic anhydride to react with the hydroxyl groups. Acetylated fiber was found to be brighter and lighter in color. This may be attributed to the process that removed some extractives, thus giving light colored fibers.

#### FTIR

Infrared spectra of raw and acetylated jute fibers are shown in Figure 2. The infrared band assignment for raw jute fibers are also shown in Table I. Acetylation of jute fibers decreased the peak area at about  $3450\text{ cm}^{-1}$ , indicating protection of

some free hydroxyl groups by acetyl groups. The band intensity of control fibers at  $1740\text{ cm}^{-1}$  (15.53%),  $1357\text{ cm}^{-1}$  (15.04%), and  $1235\text{ cm}^{-1}$  (14.04%) increased and shifted to higher values in the acetylated fibers of  $1751\text{ cm}^{-1}$  (19.20%),  $1375\text{ cm}^{-1}$  (20.41%), and  $1241\text{ cm}^{-1}$  (19.23%), respectively, thereby providing evidence for successful acetylation.

#### Thermal Characterization

Jute fibers and acetylated jute fibers were subjected to derivative thermogravimetric (DTG) and DSC analysis in an  $\text{N}_2$  atmosphere to determine their thermal nature. The DTG curve of jute fibers (Fig. 3) gives an initial peak below  $100^\circ\text{C}$  due to loss of moisture. After this peak the curve exhibits two decomposition steps. The first decomposition peak (shoulder) at  $301.0^\circ\text{C}$  is due to hemicellulose (wt loss 10.4%) and the second peak at  $361.0^\circ\text{C}$  is due to  $\alpha$ -cellulose decomposition (wt loss

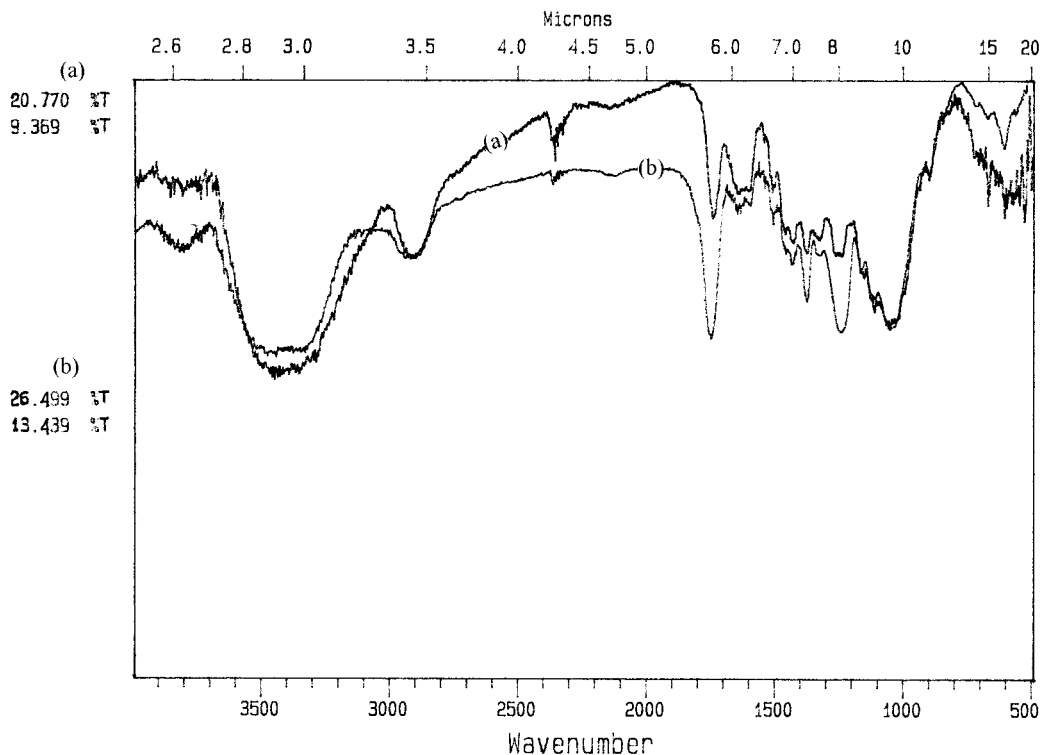


Figure 2 FTIR spectra of (a) untreated jute and (b) acetylated jute.

Table I Infrared Band Assignment for Raw Jute Fibers

Frequency (cm <sup>-1</sup> )	Assignment
3200–3600	OH stretching
2905	CH <sub>2</sub> and CH <sub>3</sub> stretching
1740	Carbonyl (C=O) Stretching of carboxylic acid or ester
1650	H—O—H bending of absorbed water
1616	Benzene ring stretching (lignin)
1500	Benzene ring stretching (lignin)
1440	CH <sub>2</sub> bending in lignin
1411	CH <sub>2</sub> and CH <sub>3</sub> bending
1357	CH <sub>3</sub> bending
1320	CH <sub>2</sub> wagging (lignin)
1235	C—O stretching of acetyl (lignin)
1150	C—O—C antisymmetric bridge stretching in cellulose and hemicellulose
1110	O—H association in cellulose and hemicellulose
1028	C—O stretching in cellulose, hemicellulose, and lignin
879	$\beta$ -Glucosidic linkage
600	Out of plant OH bending

66.3%). In the acetylated jute fibers (Fig. 4) the shoulder due to hemicellulose decomposition is missing and weight loss at the major degradation step (373.0°C) increases to 87.2%. This may mean that the stability of hemicellulose has been increased during acetylation. The main decomposition temperature increases from 363.0 to 373.0°C, which indicates that the thermal stability of the acetylated jute fibers is higher than that of the untreated specimen. Weight loss due to moisture desorption of acetylated jute fibers is negligible as compared to jute fibers. For acetylated jute fibers the residue left at 650.0°C (9.4%) is less than that of untreated material (14.1%), which indicates that the acetylated material is lost with volatile products and does not contribute to char formation. So it is expected that the jute composites based on acetylated jute would have slightly better thermal stability than the control.

A DSC thermogram of jute fibers (Fig. 5) in an N<sub>2</sub> atmosphere gives a peak below 100°C due to moisture desorption (11.8%). The decomposition is mainly governed by the endothermic peak at 363°C, which is attributed to  $\alpha$ -cellulose decomposition.<sup>12</sup> For acetylated jute fibers (Fig. 6) the moisture content at the first peak is very low

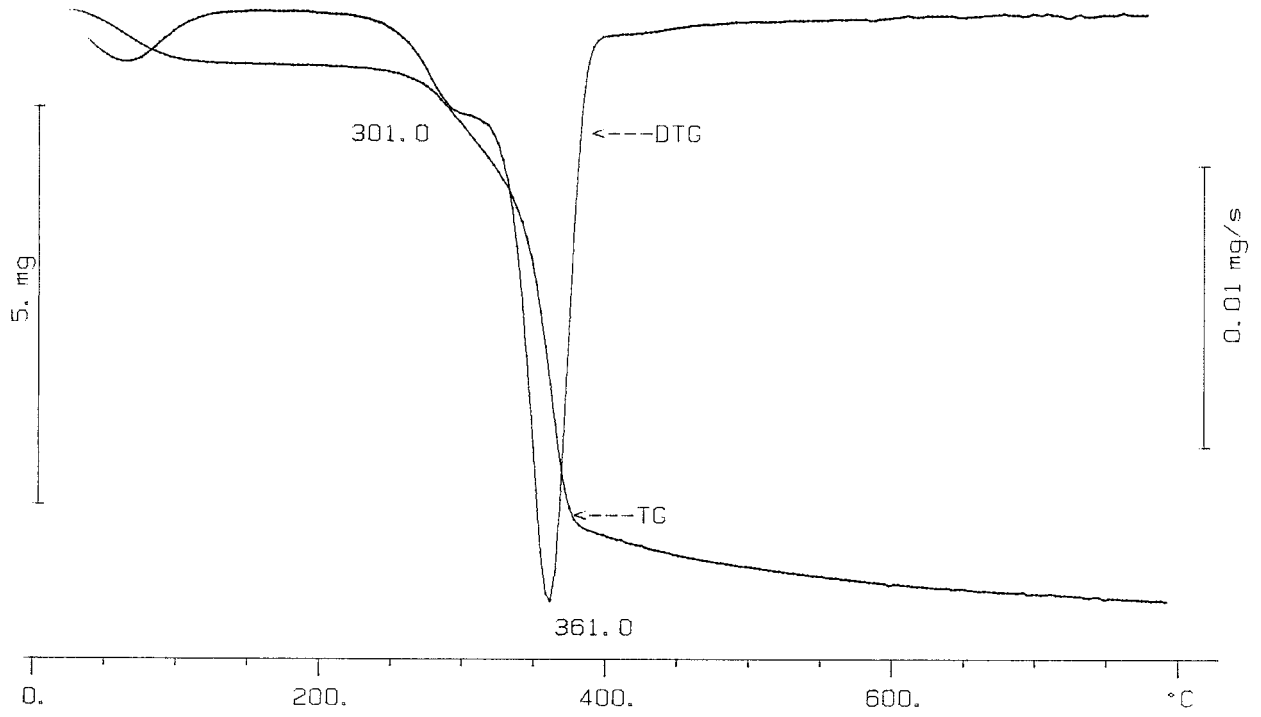


Figure 3 DTG curve of untreated jute.

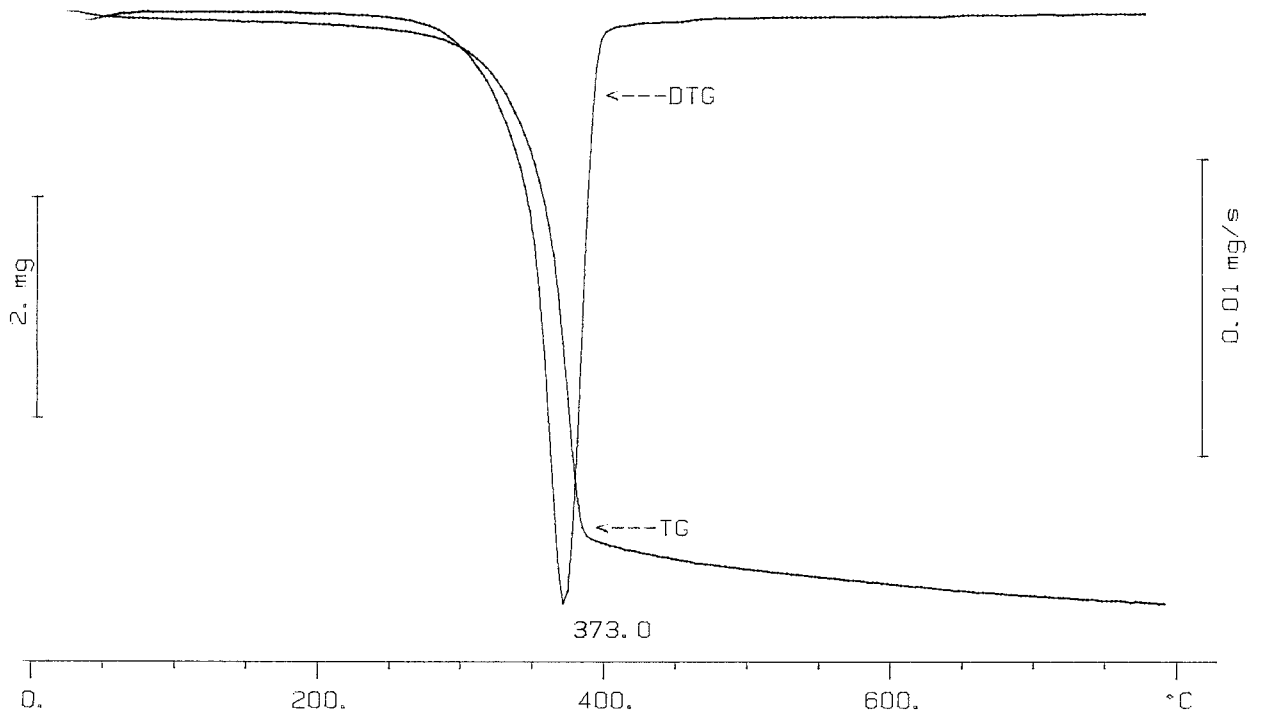
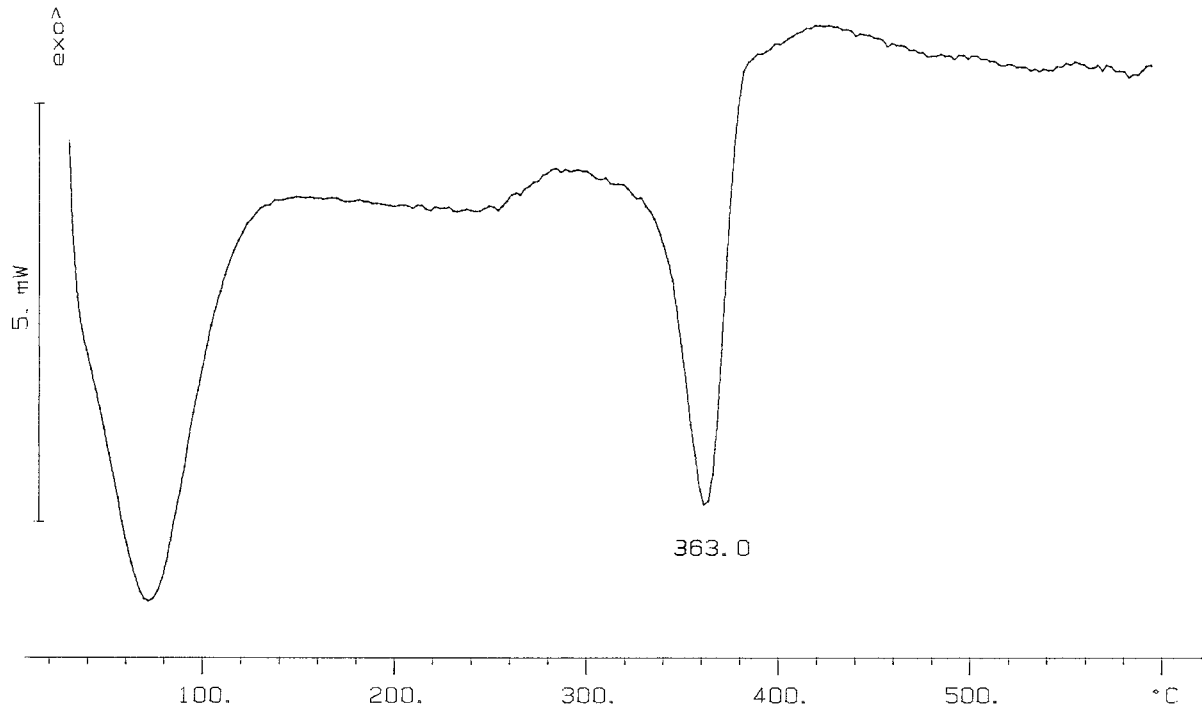
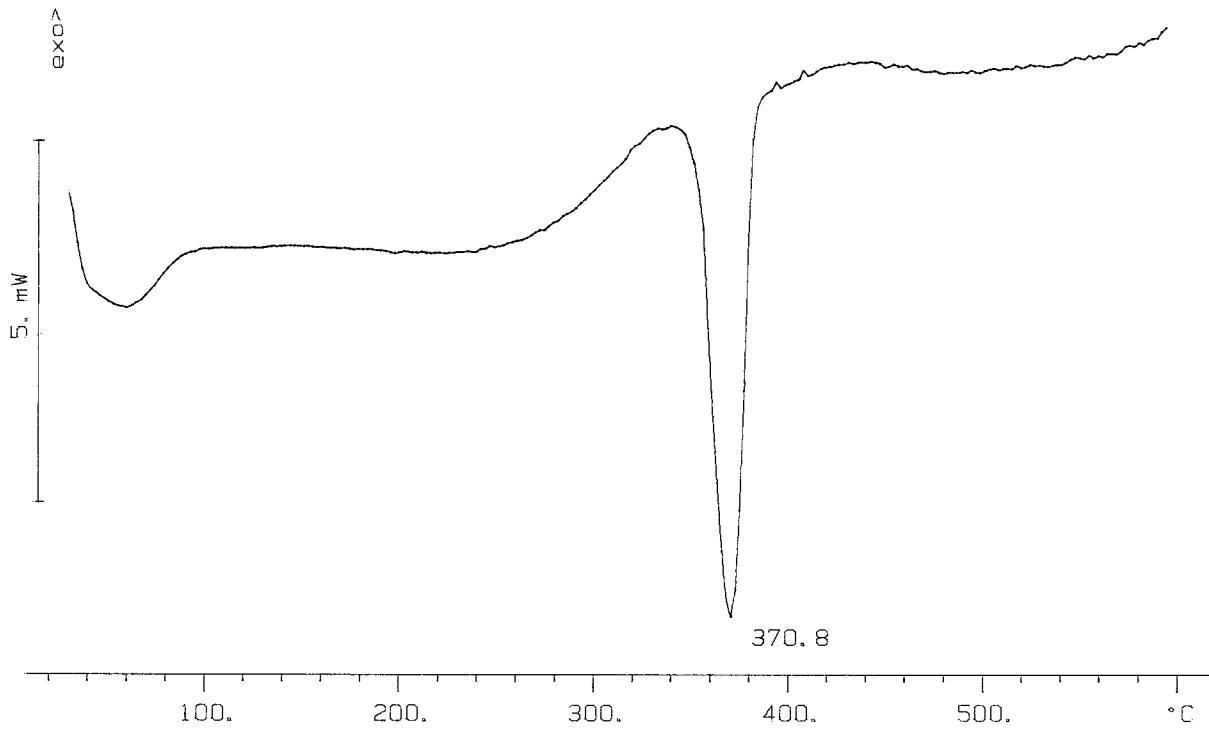


Figure 4 DTG curve of acetylated jute.



**Figure 5** DSC thermogram of untreated jute.



**Figure 6** DSC thermogram of acetylated jute.

(1.6%) and the main decomposition peak is shifted to a higher value (370.8°C), which indicates that the thermal stability of acetylated jute fibers increases. The moisture contents were measured following the method described elsewhere.<sup>13</sup>

### SEM Study

Scanning electron micrographs of untreated and acetylated jute fibers are shown in Figures 7 and 8. Acetylation has covered the gaps between the fibrils and ultimately smooths the surface of the fiber. These actions may be due to the bulking action of the acetyl group bonded to the cell wall polymers and may help in reducing swelling in water when these treated fiber are used in making composites.<sup>14</sup>

### CONCLUSION

The maximum WPG found was 18.0 for the acetic anhydride–pyridine system at 120°C for 4 h whereas using only acetic anhydride WPG was 12.3 at the same reaction condition. The thermal stability of acetylated jute was found to be higher than the untreated jute. From the SEM studies it was evident that the gaps between the fibrils had been covered after acetylation. FTIR studies also produced evidence for acetylation.



**Figure 7** Scanning electron micrograph of untreated jute. Original magnification  $\times 300$ .



**Figure 8** Scanning electron micrograph of acetylated jute. Original magnification  $\times 300$ .

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