Improvement of Functional Properties of Jute-Based Composite by Acrylonitrile Pretreatment

A. K. SAHA,[1] S. DAS,[1] R. K. BASAK,[1] D. BHATTA,[2] B. C. MITRA[3]

[1] Indian Jute Industries' Research Association, 17 Taratola Road, Calcutta - 7000 88, India

[2] P. G. Department of Chemistry, Utkal University, Bhubaneswar-751004, India

[3] National Institute of Research on Jute and Allied Fibre Technology, 12 Regent Park, Calcutta-700040, India

ABSTRACT: Cyanoethylation of jute fiber in the form of nonwoven fabric was successfully achieved using an acrylonitrile monomer which is said to react with the hydroxyl groups of fiber constituents. The degrees of cyanoethylation to different extents were undertaken by varying the reaction time. An IR study showed that extent of cyanoethylation increases with increase of the reaction time. Cyanoethylated fibers thus obtained were further treated with unsaturated polyester resin to obtain modified fiber composites. These composites have been found to be tolerant against cold and boiling water where water absorption and thickness swelling are much reduced compared to those of unmodified fiber composite. It is also observed that the moisture content of the modified fiber composites is remarkably reduced. Cyclic tests reveal that use of cyanoethylated fiber leads to improvement of the dimensional stability of the fiber composites. The mechanical properties of the modified fiber composites improved remarkably due to better bonding at the fiber–matrix interface and this effect is more pronounced with a higher degree of cyanoethylation. A scanning electron micrograph of the fractured surfaces of cyanoethylated jute composite showed excellent retention of resin on broken fiber ends, whereas the unmodified composite showed uncoated fibers and holes in the matrix. DSC data demonstrated that the moisture content of the composites reduces with increase of the cyanoethylation. Both TG and DSC thermograms showed an additional peak due to decomposition of cyanoethyl group which is shifted to a higher value with the extent of cyanoethylation. However, the cellulose degradation temperature remained almost the same. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 495–506, 2000

Key words: jute fiber; cyanoethylation; unsaturated polyester resin; composite; dimensional stability

INTRODUCTION

The performance and properties of fiber-filled polymer composites[1–6] are governed by the properties of the components and by the nature of interface between the matrix and the fiber. The strength of the interfacial bond between the fiber and matrix plays an important role in determining the strength of the composite. Because of unsatisfactory adhesion[7,8] between the fiber and matrix, a composite, made from jute fiber and unsaturated polyester resin, does not produce sufficient strength and modulus. Again, composites prepared from jute fiber[9–14] encounter dimen-


Table I Nitrogen Contents of Untreated and Treated Jute Nonwoven Fabrics

Sample	Reaction Time for Cyanoethylation (h)	Nitrogen Content (%)
Untreated jute nonwoven fabric	Nil	0.29
Cyanoethylated nonwoven fabric	1	4.17
Cyanoethylated nonwoven fabric	2	4.27
Cyanoethylated nonwoven fabric	3	4.45
Cyanoethylated nonwoven fabric	4	4.73
Cyanoethylated nonwoven fabric	5	5.08

sional changes during consumer use. Owing to its hydrophilic nature, jute fiber takes up moisture from the surroundings during humid conditions or when it is in direct contact with water. Due to the absorption of moisture, fiber molecules are pushed apart by the absorbed water molecules and swelling takes place which alters the dimen-

sion of the former, resulting in a change in the dimension of the ultimate composite.

Jute is known to be a lignocellulosic fiber comprising α-cellulose, hemicellulose, and lignin. It is believed that jute fiber has a semicrystalline structure and α-cellulose predominantly forms the crystalline region, whereas lignin and hemi-
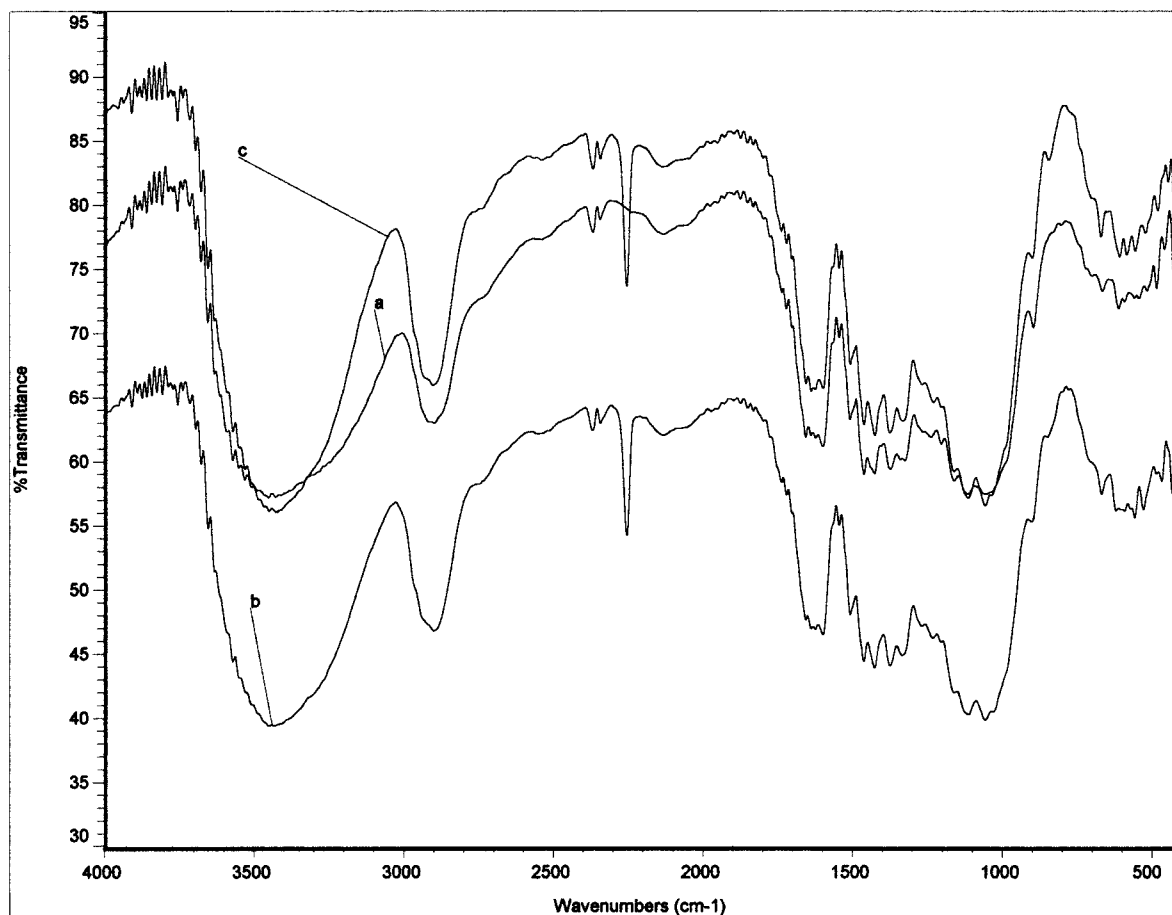
Figure 1 Infrared spectra of (a) untreated jute fiber, (b) cyanoethylated jute fiber, reaction time 2 h, and (c) cyanoethylated jute fiber, reaction time 3 h.

Table II   Equilibrium Moisture Contents of Composites

Sample	Moisture Content (%) at Different RH		
	32	65	90
Control	4.85	8.43	10.70
MJC-1	2.83	4.76	7.84
MJC-2	2.49	4.67	6.56
MJC-3	2.41	4.56	6.38
MJC-4	2.27	4.31	5.99
MJC-5	2.14	4.26	5.87

MJC-1 denotes composite made from jute fiber, cyanoethylated at 1 h.

cellulose exist in an amorphous region. Although the more accessible hemicellulose is mainly responsible for high moisture regain of jute, the hydroxyl groups present on the surface of the crystalline region and the lignin also take part in the moisture absorption. These hydroxyl groups are the active centers to attract water molecules to form hydrogen bonds between the hydroxyl groups and water molecules. Various methods are known to minimize the proneness of agro fiber-based composites to a change of dimension with the changing relative humidity of the atmosphere in which the composite materials are exposed. These include restriction of moisture access by using surface finishes, impregnation of the vinyl type of monomers and subsequent polymerization, and the blocking of moisture-attracting groups by prospective chemical modification. Effort has been made in the present work to develop a property enhanced jute-based polyester composite where both the mechanical properties and dimensional stability will be improved by minimizing its limitation through effective chemical modification of the fiber.

EXPERIMENTAL

Materials and Chemicals

General-purpose unsaturated polyester resin (USP) was obtained from M/S Ruia Chemicals
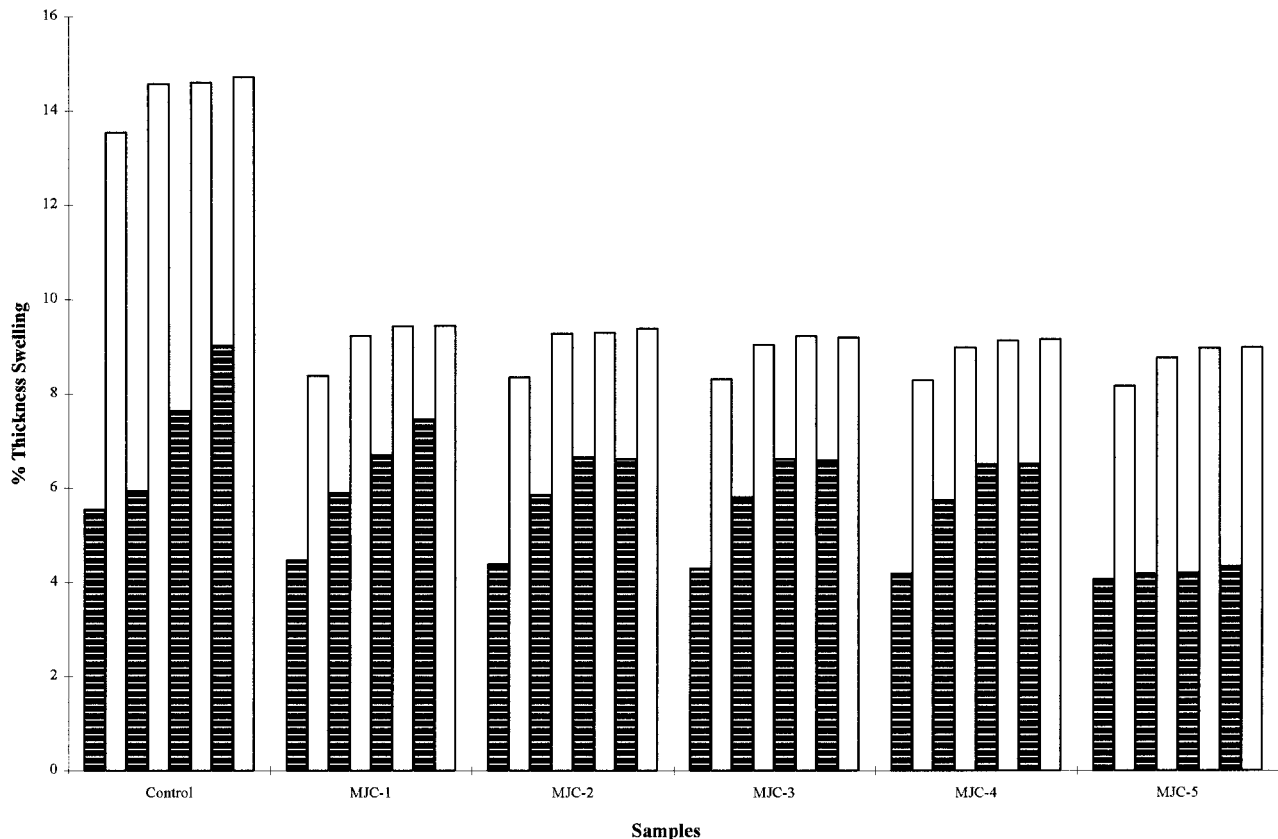
Figure 2   Effect of cyclic change of relative humidity between 30 and 90% on dimension (percent thickness swelling) of composites.

Table III   Water Absorption and Thickness Swelling of Composites at 24°C

Sample	Water Absorption (%)		Thickness Swelling (%)	
	2 h	24 h	2 h	24 h
Control	24.96	49.76	24.68	31.94
MJC-1	5.86	13.60	3.98	11.88
MJC-2	5.09	8.02	3.76	11.19
MJC-3	4.96	6.98	3.21	10.58
MJC-4	4.62	5.45	2.95	10.36
MJC-5	3.99	5.24	2.62	9.21

Pvt. Ltd. (Calcutta, India), which was based on orthophthalic anhydride, maleic anhydride, 1,2-propylene glycol, and styrene. The styrene content was about 35%. Uniaxially oriented jute-based needle punched nonwoven fabric (750 gm/cm^2) was procured from M/S Birla Corp. Ltd. Laboratory (Calcutta, India) reagent-grade acrylonitrile of S. D. Fine Chemicals (Mumbai, India) was used in this study without further purification.

Cyanoethylation of Jute Nonwoven Fabric and Fabrication of Composite Sheet

Cyanoethylation of jute nonwoven fabrics as well as fabrication of composite sheets were carried out by adopting the procedure reported earlier.[15,16]

Testing Procedure

The nitrogen content of the cyanoethylated jute nonwoven was estimated by the Kjeldahl method. The water-absorption property both at room temperature and boiling conditions was determined by ASTM D 570-81 method. The tensile properties were determined in accordance with ASTM D 638M-84 at a crosshead speed of 5 mm/min, whereas the flexural test of the specimens was measured as per ASTM D 790M-84 at a crosshead speed of 0.5 mm/min. The tensile-fracture surfaces of the composite samples were studied using a scanning electron microscope (Hitachi scanning electron microscope, Model S-415 A) operated at 25 keV.

TGA and DSC analyses were carried out using a Mettler TG 50 and a DSC 25 module attached to a Mettler TC 11 4000 thermal analyzer. All measurements were made under a nitrogen flow (100 mL/min), keeping a constant heating rate (10°C/min) and using an alumina crucible with a pin hole.

RESULTS AND DISCUSSION

Cyanoethylation of the jute fiber was carried out for dual purposes: first, to reduce the hygroscopicity of the jute fiber and at the same time the bulking of the fiber cell wall, and, second, for improving the compatibility with the polyester resin. The evidence of cyanoethylation of the fiber was provided by estimating the nitrogen contents of the fibers which increased with increasing reaction time. Data on the nitrogen contents of fibers (in the form of felt), cyanoethylated to different extents, are incorporated in Table I.

Infrared spectra[17,18] (Fig. 1) show that a varying amount of the cyanoethyl group was introduced with polymer chains of the jute constituents. All five pretreated samples show a prominent band at 2240 cm^{-1} due to a C≡N stretching vibration which is not exhibited in the untreated jute sample. Moreover, the intensity of the C≡N stretching band is increased with increasing time of the reaction. All the samples indicate a strong band at around 3380 cm^{-1} due to —OH stretching, which is distinctly weaker in cyanoethylated samples compared to the untreated one. The decrease in intensity of the —OH stretching band in the case of acrylonitrile pretreated jute samples may be attributed to chemical interaction with the acrylonitrile through —OH groups of the jute constituents.
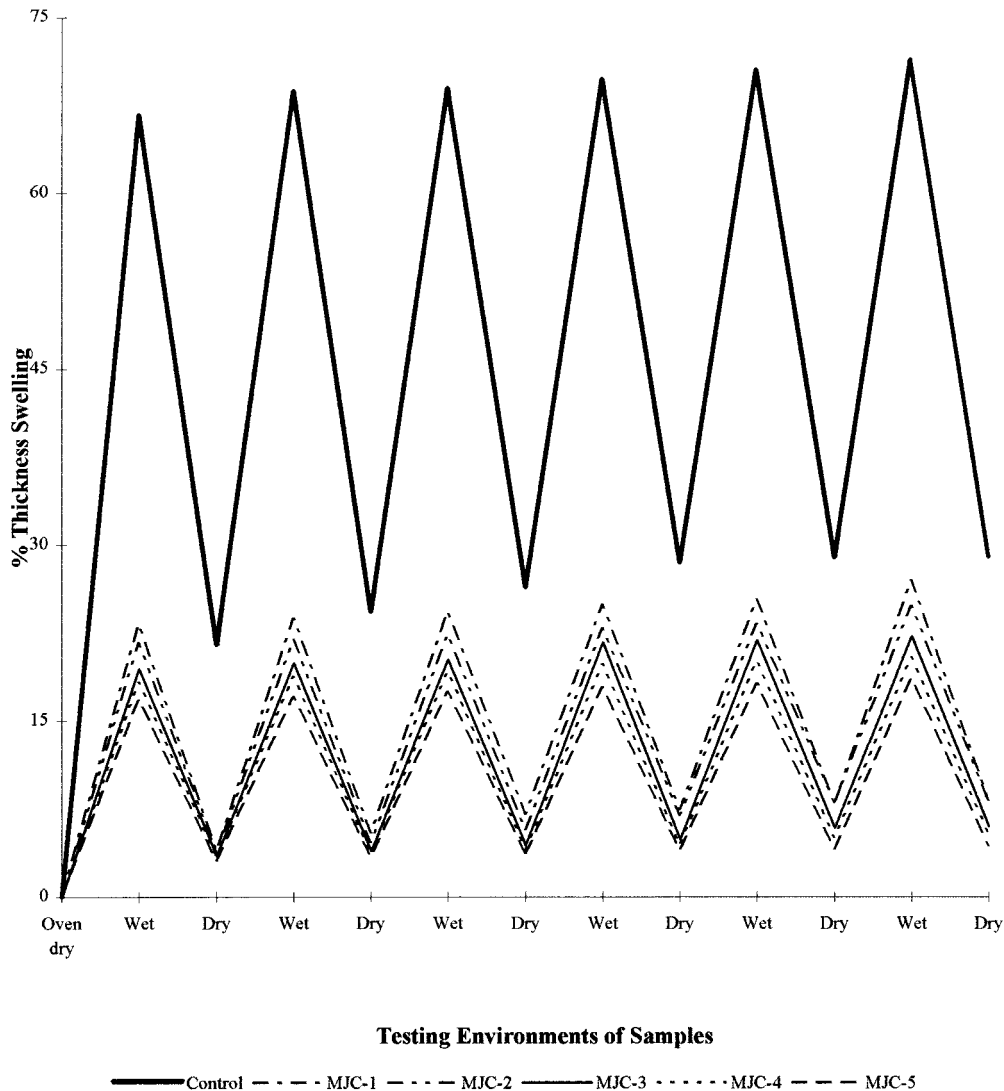
Composites, made from cyanoethylated jute and unsaturated polyester resin, were tested for equilibrium moisture contents at three different relative humidities, that is, 32, 65, and 90% at

Table IV   Water Absorption and Thickness Swelling of Composites at Boiling Condition

Sample	Water Absorption (%)		Thickness Swelling (%)	
	0.5 h	2 h	0.5 h	2 h
Control	42.37	48.09	62.31	66.67
MJC-1	9.58	14.06	16.34	23.32
MJC-2	8.26	13.59	14.21	21.76
MJC-3	8.01	13.07	13.56	19.47
MJC-4	7.39	12.46	12.97	18.35
MJC-5	7.11	11.08	11.25	16.89
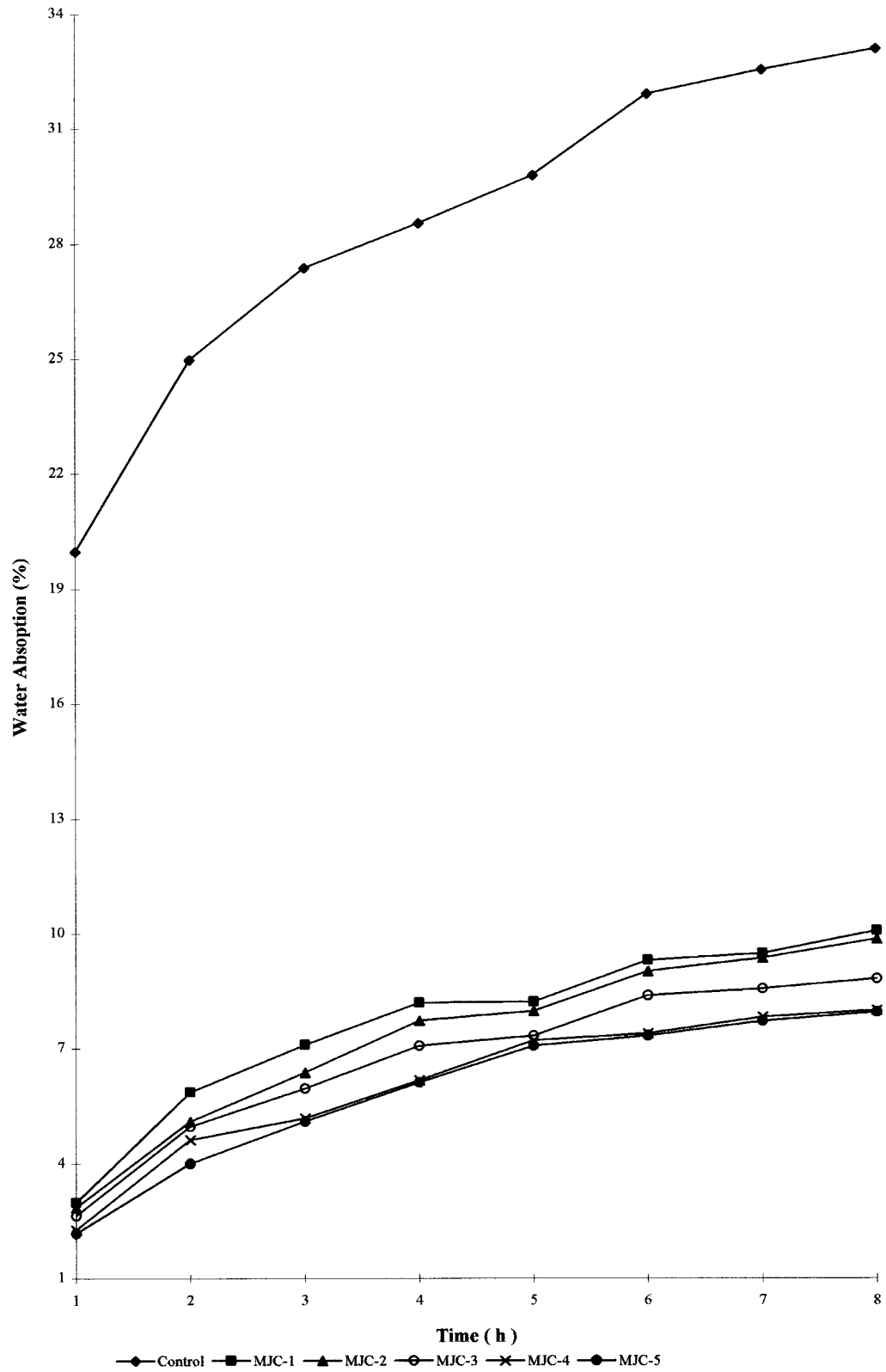
**Figure 3**   Rate of water absorption of composites at room temperature.

Figure 4 Changes in thickness in repeated water-soaking test of composites made from cyanoethylated jute fiber.

30°C, and the results obtained were compared with those of the untreated jute using the same resin composition depicted in Table II. The data indicate that cyanoethylation reduces the moisture content significantly and the equilibrium moisture content decreases as the level of cyanoethylation is increased. In 30–90% relative humidity cyclic tests (Fig. 2), the thickness swellings are found to reduce with increasing level of cyanoethylation. The control sample swells to a maximum of 14.72% in thickness at 90% humidity, but under identical conditions, the cyanoethylated sample shows only 9.01%. It is also observed in the case of the control composite that, after completion of each cycle, the sample does not re-

vert to its original thickness and an increase in thickness over the preceding dimension is observed. But in the case of the treated samples, the above phenomenon is significantly reduced and almost disappeared for MJC-5.

Water absorption and thickness swelling were determined by dipping the samples in water at 24°C for 2 and 24 h and the data are presented in Table III. The values obtained using boiling water are shown in Table IV. It is evident from the data that water absorption and thickness swelling decrease with increase in the extent of the cyanoethylation of jute fibers. The control sample, that is, the composite made from the untreated jute, absorbs 24.96 and 49.76% water when it is dipped

a

□ Flex. Str. ▧ Flex. Str. after boiling

b

□ Flex. Mod. ▧ Flex. Mod. after boiling
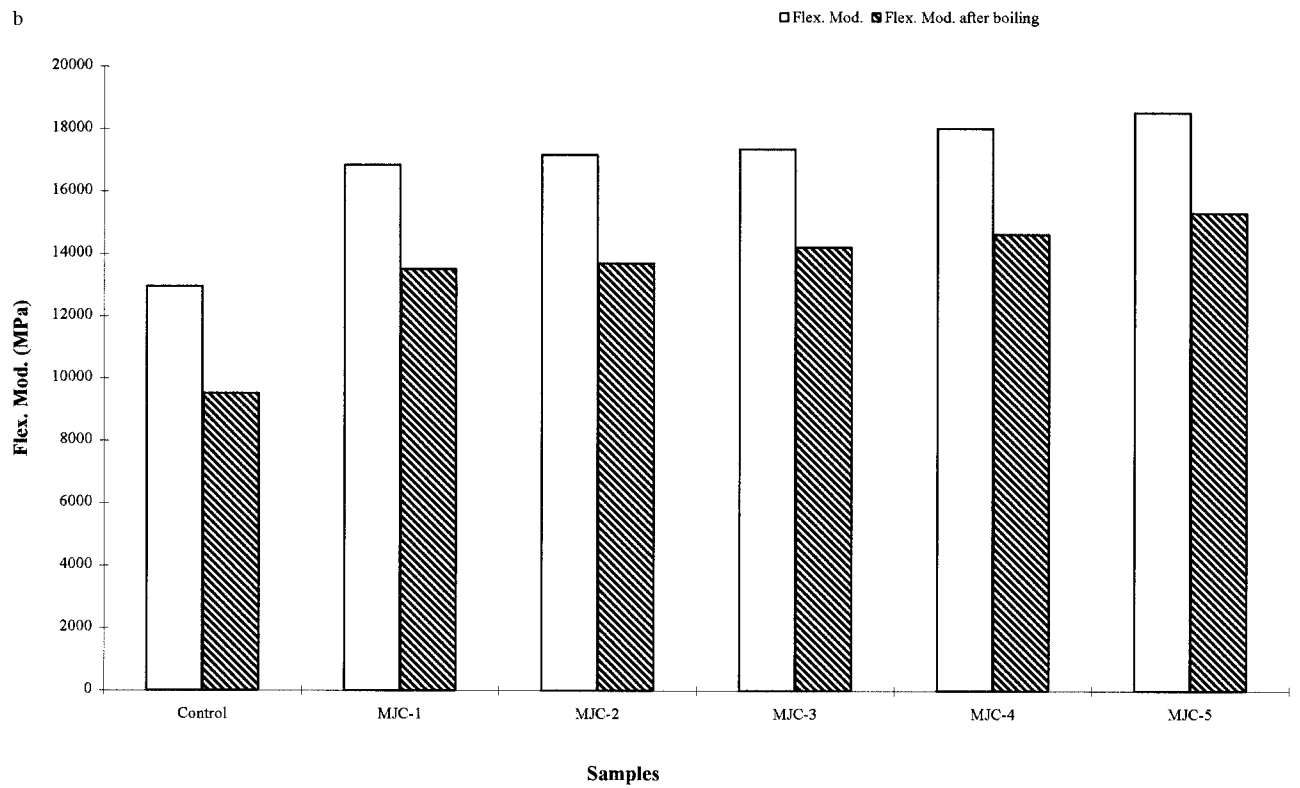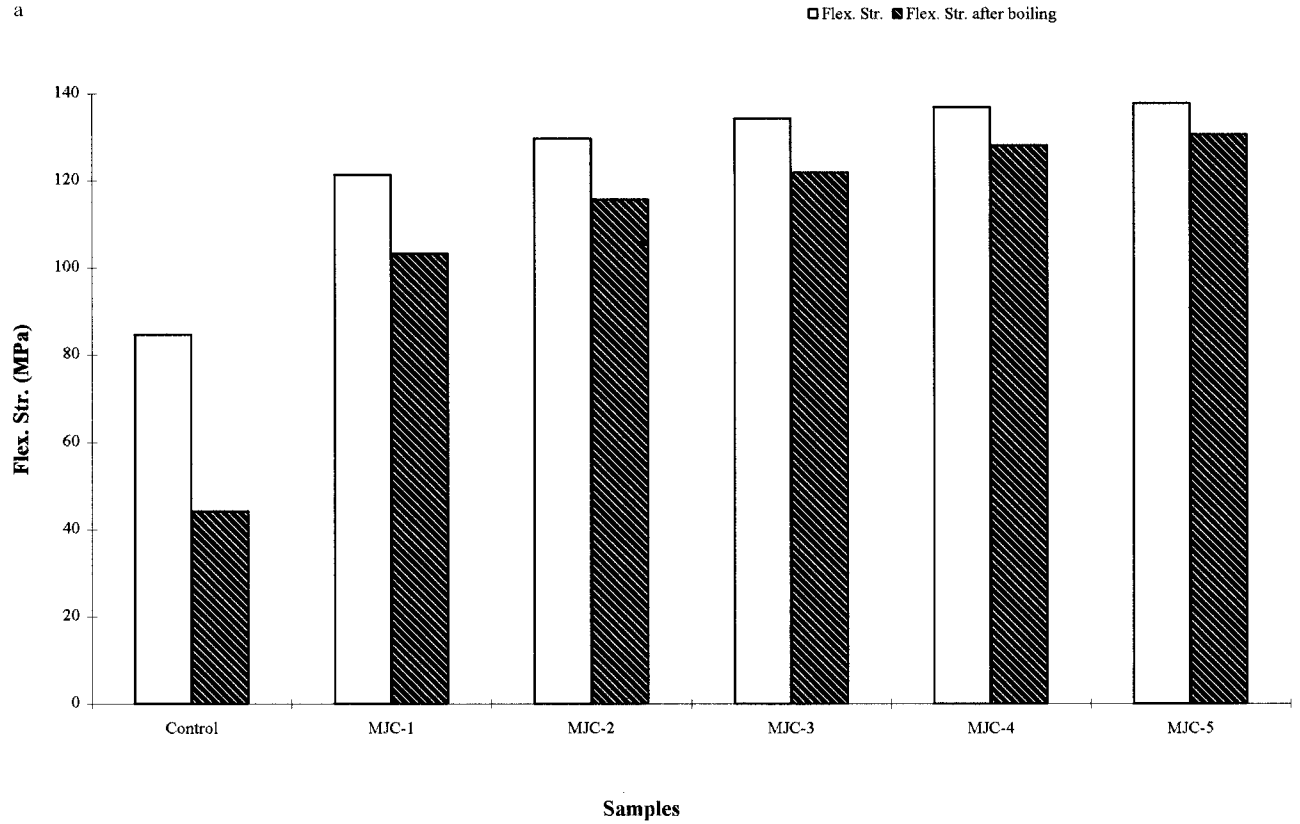
Figure 5 (a) Effect of boiling water on the retention of flexural strength of the composites. (b) Effect of boiling water on the retention of flexural modulus of the composites.

Table V   Mechanical Properties of Composites

| Sample	Dry Tensile Strength (MPa)	Wet Tensile Strength (MPa)	Dry Flexural Strength (MPa)	Wet Flexural Strength (MPa)	Dry Flexural Modulus (MPa)	Wet Flexural Modulus (MPa)
Control	74.24	25.89	84.81	40.21	12,970	6750
MJC-1	89.96	48.83	121.39	76.99	16,050	14,840
MJC-2	99.59	56.65	129.73	88.61	17,630	15,250
MJC-3	104.76	60.38	134.36	95.93	17,980	16,740
MJC-4	108.60	63.03	136.90	100.6	18,050	17,260
MJC-5	109.32	67.33	137.87	101.76	18,080	17,430

in water for 2 and 24 h, respectively, whereas it swells in thickness to the extent of 24.68 and 31.94%, respectively. On the contrary, the modified samples absorb water to the extent of 5.86–3.99% and 13.60–5.24% in 2 and 24 h of the water-soaking tests, respectively. But they show thickness swelling to the extent of 3.98–2.62% and 11.88–9.21% in 2 and 24 h in the water soaking test, respectively. A similar trend, in respect to the water absorption as well as to the thickness swelling, was also observed when the experiments were conducted in boiling water for both 0.5 and 2 h. The rate of water absorption by the composites (Fig. 3) is also drastically reduced by cyanoethylation.

Specimens were subjected to an 8-h exposure cycle[19] consisting of 2 h of wetting in boiling water and 6 h of drying at 105°C, which was repeated six times for a total of 48 h. The results of the repeated 2-h boiling water/oven-drying test show (Fig. 4) that the swelling decreases with increase in the level of cyanoethylation. There is a 71.39% increase in thickness during the six-cycle test in

the case of the control sample, but the cyanoethylated sample (MJC-5) swells less than 19%.

The effect of boiling water on the retention of the flexural strength and modulus of the composites was studied by dipping them in boiling water for 1 h, which is exhibited in Figure 5. It is clearly seen from the figure that the cyanoethylated jute nonwoven produces stronger and superior water-resistant composites than does the untreated jute. It is also seen that the water-resistance property improves with increasing extent of cyanoethylation. The control sample suffered a loss in flexural strength to the extent of 48%, whereas the composite, made from cyanoethylated felt (MJC-5), suffered a loss of 5% only.

Another important aspect of pretreatment of the fiber with acrylonitrile and composites made therefrom is the remarkable gain of mechanical properties compared to that made from untreated jute fiber. The strength and modulus values of different samples, as changed by the different level of cyanoethylation of fiber, are illustrated in Table V. It is clearly seen that the flexural and
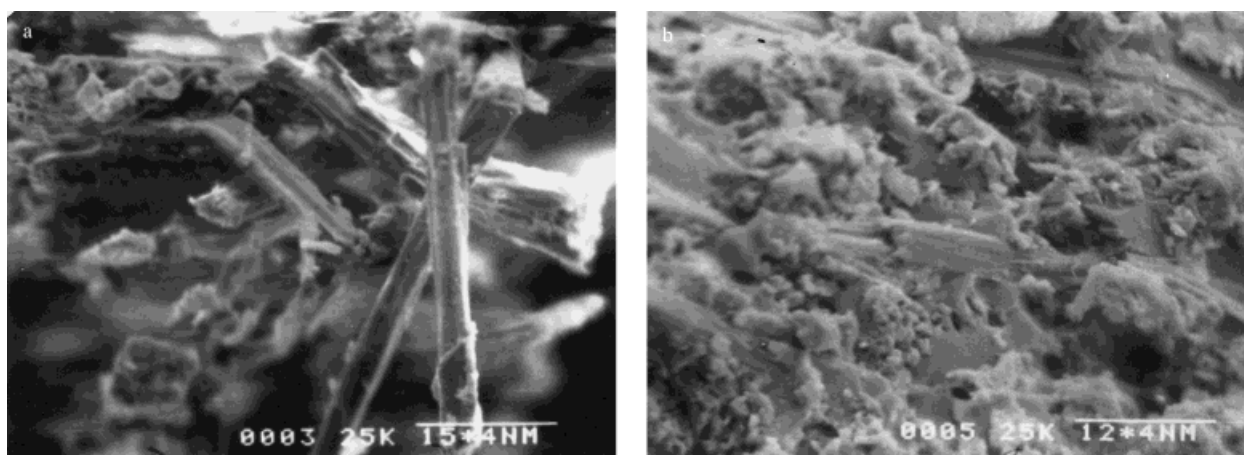
Figure 6   Scanning electron micrographs (200×) of tensile fracture surfaces of (a) unmodified and (b) cyanoethylated jute–polyester composite.

the tensile strength increases with the extent of cyanoethylation and reaches the maximum at 5-h reaction time. Cyanoethylation of jute, prior to composite fabrication, caused improvements in the dry flexural strength and modulus by 62 and 39%, respectively. Moreover, a gain in flexural strength and modulus, in a wet condition, are 153 and 158%, respectively.

Scanning electron micrographs[20] of fractured surfaces of both the unmodified and the chemically modified jute–polyester composite are shown in the Figure 6. The latter shows excellent retention of the resin on broken fiber ends, whereas the former shows uncoated fibers and holes in the matrix.

Figure 7 shows TG and DTG thermograms of the jute and jute composites. In the DTG curve of jute fiber (Table VI), the first peak below 100°C is due to evaporation of moisture and the shoulder peak at 279.7°C is due to decomposition of hemicellulose, whereas the peak at 345.0°C is due to cellulose decomposition.[9,21–23] Weight loss at this decomposition step is maximum (65.6%). The composite MJC-1, obtained from cyanoethylated (reaction time 1 h) jute and unsaturated polyester resin, shows an additional peak at 297.7°C (Table VI). The hemicellulose peak merged with this new peak. As the treatment time with acrylonitrile increases from 1 to 5 h, the peak temperature at this degradation step gradually increases. The weight loss at this degradation stage also increases gradually with increase in the reaction time. Table I shows that the level of cyanoethylation increases with increasing reaction time. So, this new peak in the temperature range 299.7–310.0°C is believed to be the degradation of the cyanoethyl group. Char left at 550°C is almost the same. The peak temperature due to cellulose decomposition does not change abruptly with increasing time of the reaction.

The DSC curve (Fig. 8, Table VII) of jute fiber shows an endothermic peak below 100°C due to the evaporation of moisture. The exothermic peak at 315.1°C is due to hemicellulose decomposition and the endothermic peak at 379.0°C is due to cellulose decomposition.[9,21,22,24] The first peak shows 11.8% moisture content, which is measured by the DSC technique.[25] In the case of composite materials, the moisture content gradually decreases with the increase in the extent of the cyanoethylation of jute. This is due to blocking of the moisture attracting hydroxyl groups by chemical modification. A new endothermic peak appeared just before the cellulose decomposition
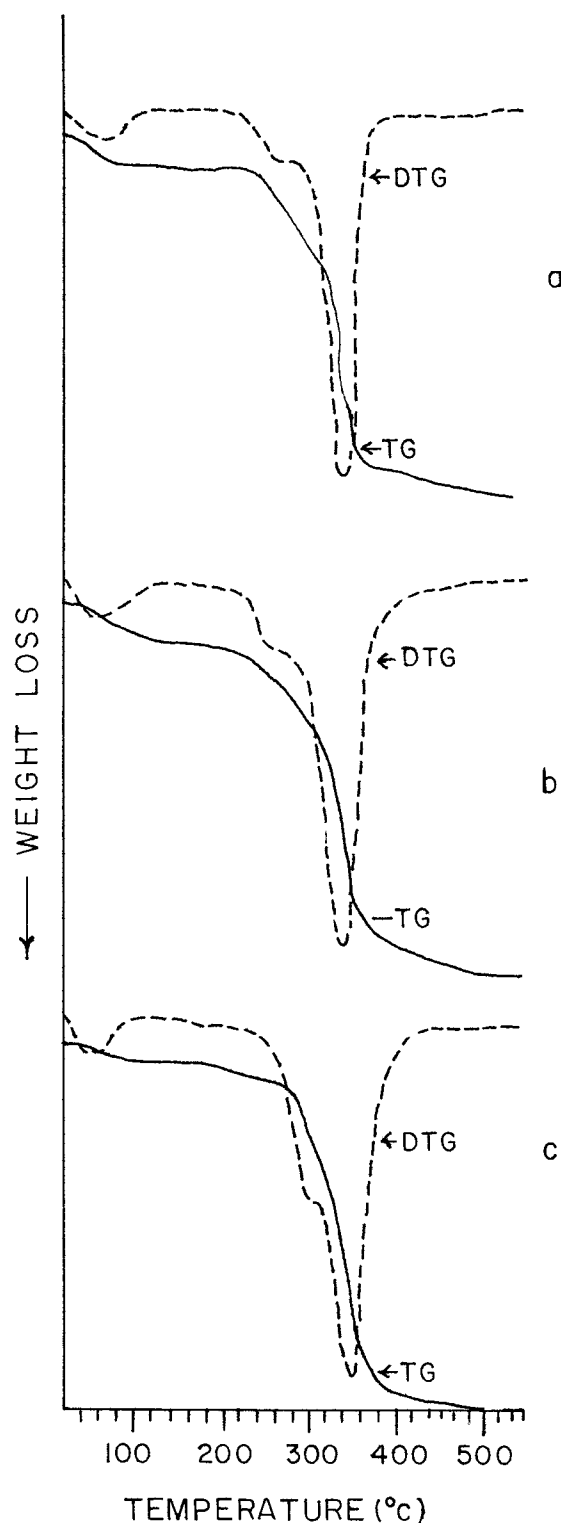
Figure 7   TG and DTG thermograms of (a) jute fiber, (b) untreated jute composite (control), and (c) cyanoethylated jute composite (MJC3) in nitrogen atmosphere.

Table VI   Results of Derivative TG Analysis of Jute and Jute Composites in Nitrogen Atmosphere

Sample	Peak Temperature (°C)	Weight Loss (%)	Residual at 550°C (%)
Jute fiber	67.7	8.41	
	279.7	10.01	15.68
	345.0	65.60	
Untreated jute composite (control)	62.3	7.76	
	268.8	8.81	18.66
	339.7	64.70	
MJC-1	54.3	4.84	
	299.7	14.63	13.17
	345.0	67.22	
MJC-2	59.7	4.03	
	301.0	21.26	14.85
	345.0	59.63	
MJC-3	62.3	4.90	
	307.0	22.85	13.69
	345.0	58.48	
MJC-4	51.7	4.88	
	308.5	24.65	13.24
	347.7	57.18	
MJC-5	54.3	4.2	
	310.0	27.71	11.89
	345.0	56.37	

peak. This new endothermic peak gradually shifted to a higher value from 318.0 to 329.6°C as the extent of cyanoethylation increased. The hemicellulose peak probably merged with this new peak. In the case of the composite made from untreated jute, this new peak is absent. Hence, this new endothermic peak of the composite made from treated jute may be due to the decomposition of cyanoethyl groups. This new peak also appeared in the case of cotton when it was cyanoethylated.[26] The change in peak temperature due to cellulose decomposition of the jute composite is very small.

CONCLUSIONS

- The moisture regain, water absorption, and thickness swelling of the jute fiber-based composite are significantly reduced when cyanoethylated fiber is used.
- The rate of water absorption of the composite decreases with increase in the level of cyanoethylation of the fiber.
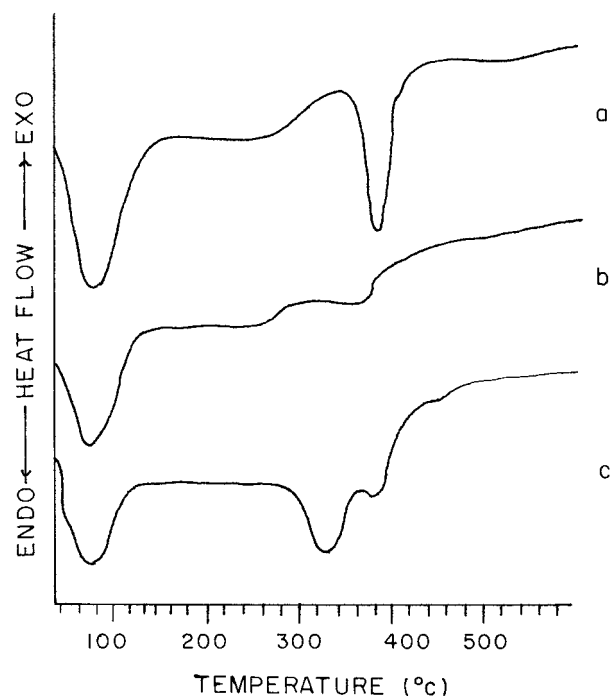
Figure 8   DSC thermograms of (a) jute fiber, (b) untreated jute composite (control), and (c) cyanoethylated jute composite (MJC3) in nitrogen atmosphere.

Table VII   Results of DSC of Jute and Jute Composite in Nitrogen Atmosphere

Sample	Peak Temperature (°C)	Moisture Content (%)	Nature of Peak
Jute fiber	74.4	11.8	endo
	315.1		exo
	379.0		endo
Untreated jute composite (control)	70.5	8.1	endo
	293.0		exo
	361.0		endo
MJC-1	66.4	6.8	endo
	318.0		endo
	375.0		endo
MJC-2	63.8	6.2	endo
	319.1		endo
	375.0		endo
MJC-3	67.9	5.8	endo
	323.0		endo
	377.0		endo
MJC-4	70.5	5.4	endo
	323.0		endo
	378.8		endo
MJC-5	59.2	4.7	endo
	329.6		endo
	380.1		endo

- It appears from the cyclic test that the dimensional stability of the composite is remarkably improved due to cyanoethylation of the jute fiber.
- A significant improvement on the tensile and the flexural properties of the jute–polyester composite in dry as well as wet conditions is observed due to use of the cyanoethylated fiber.
- The scanning electron micrographs of the fractured surface of the samples reveal improved bonding at the interface between the cyanoethylated fiber and the polyester resin.
- Thermal study shows that the initial thermal decomposition temperature is shifted to a higher value while the final decomposition temperature remains unaltered due to cyanoethylation of the fiber.

REFERENCES

1. Owlabi, O.; Czvikovszky, T.; Kovaes, I. J Appl Polym Sci 1985, 30, 1827.
2. Belmars, H.; Barrera, A. Ind Eng Chem Prod Res Dev 1981, 20, 555.
3. Usmani, A. M.; Ball, G. L. J Elastom Plast 1980, 12, 18.
4. Setua, D. K.; De, S. K. Rubb Chem Technol 1983, 56, 808.
5. Murty, V. M.; De, S. K. Rubb Chem Technol 1983, 55, 287.
6. Salyer, I. O.; Usmani, A. M. Ind Eng Chem Prod Res Dev 1982, 21, 17.
7. Mukherjee, R. N.; Pal, S. K.; Sanyal, S. K. J Appl Polym Sci 1983, 28, 3029.
8. Chand, N.; Rohatgi, P. K.; Satyanarayana, K. G. In International Encyclopedia of Composites; Stuart, M. L., Ed.; V. C. H.: Weinheim, Germany, 1991; Vol. 4, p 9.
9. Mitra, B. C.; Basak, R. K.; Sarkar, M. J Appl Polym Sci 1998, 67, 1093.
10. Philip, A. R. Reinforc Plast 1964, 8, 306.
11. Philip, A. R. Eng Mater Des 1965, 8, 475.

12. Bhatnagar, S. S.; Khan, G. A. R.; Verman, L. C. Ind Patents 28 281, 28 427, 1926.
13. Sridhar, M. K.; Basavasrajappa, G.; Kasturi, S. G.; Balasubramanian, N. Indian J Text Res 1982, 787.
14. Shah, A. N.; Lakkad, S. C. Fibre Sci Technol 1981, 15, 41.
15. Saha, A. K.; Das, S.; Bhatta, D.; Mitra, B. C. J Appl Polym Sci 1999, 71, 1505.
16. Saha, A. K.; Mitra, B. C. J Appl Polym Sci 1996, 62, 733.
17. Amin, M. N.; Reddy, S. C. Indian J Text Res 1991, 16, 185.
18. Conner, R. T. O.; Duper, E. F.; Mecall, E. R. Text Res J 1958, 28, 542.
19. Hon, D. N. S.; Shiraishi, N. In Wood and Cellulosic Chemistry; Marcel Dekker: New York, Basel, 1991; Part III, Chapter 15, p 749.
20. Hartlein, R. C. Ind Eng Chem Prod Res Dev 1971, 10, 92.
21. Basak, R. K.; Saha, S. G.; Sarkar, A. K.; Saha, M.; Das, N. N.; Mukherjee, A. K. Text Res J 1993, 63, 658.
22. Pandey, S. N.; Dey, A.; Mathew, M. D. Text Res J 1993, 63(3), 143.
23. Bhaduri, S. K.; Mathew, M. D.; Dey, A.; Pandey, S. N. Cellulose Chem Technol 1994, 28, 595.
24. Bhaduri, S. K.; Mathew, M. D.; Dey, A.; Pandey, S. N. Cellulose Chem Technol 1994, 28, 391.
25. Widmann, G.; Riesen, R. In Thermal Analysis: Terms, Methods and Applications; Oehme, F.; Huthig, A., Eds.; Verlag: Heidelberg, 1987.
26. Mac Kenzie, R. C. In Differential Thermal Analysis; Academic: London, New York, 1972; Vol. 2, pp 437.