

Characterization of Grafted Jute Fiber by Optical and Scanning Electron Microscopy

S. K. KUNDU,* P. K. RAY, S. K. SEN, and S. K. BHADURI

Jute Technological Research Laboratories, Indian Council of Agricultural Research,
12, Regent Park, Calcutta 700 040, India

SYNOPSIS

Raw and partially delignified jute fibers were grafted with acrylonitrile and methyl methacrylate monomers, using the redox system of initiation with ceric ammonium sulfate. Grafting was also carried out in a mixed monomer system with acrylonitrile and methyl methacrylate monomers in different proportions. The optimum grafting condition depends on the duration of grafting treatment and proportion of grafting monomers. The monomers entered the fiber matrix with high add-on and, at still higher graft add-ons, the ultimate fibers suffered disintegration. The surfaces were increasingly covered with grafted materials and longitudinal cracks developed on the fiber surface with higher add-on. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Work on the grafting of cellulosic material by vinyl monomers has been going on for a long time.¹⁻⁷ The materials include cotton,^{1,2} rayon,³ and other synthetic fibers.⁴⁻⁷ Some work, on the grafting of jute by vinyl monomers, has also been reported.^{8,9} No work, however, has been reported on the changes in surface topology of grafted jute fibers. The present work was undertaken in order to examine the gradual changes in surface topology, brought about by the grafting of acrylonitrile and methyl methacrylate monomers.

It is known that grafting takes place in two ways, that is, by interaction of the monomer at the surface of the cellulosic substrate, or at random within the cellulose molecule. With the cellulosic fibers, grafting takes place both in the amorphous region and on the surface of the oriented regions (crystallites) in the fiber. Surface grafting may lead to different effects on the properties than those effects produced by volumetric grafts that are located throughout the fiber. To improve the resistance of the cellulosic fiber against abrasion, or to make fibers hydrophobic, one

may resort to surface grafting. But to impart a wool-like appearance and properties, or to alter the dyeing properties of fibers, the grafting should be carried out internally and not superficially.

The morphology of cellulosic graft copolymers depends on the method of producing the graft, the experimental conditions of grafting, the nature of the substrate, and the type of monomer used.^{10,11} Various graft polymers have been studied by light microscopy in order to determine the location of graft polymers. Cotton fibers, when grafted with propiolactone,¹² showed that the fibers are swollen and round after a weight increase of 35% due to grafting. With increased grafting, the fibers swell so much that they crack. This shows that grafting takes place inside the fiber, rather than on its surface.

Thejappa and Pandey¹³ grafted styrene onto cotton. They observed, by transmission electron microscopy, that grafts are uniformly distributed throughout the cross section of the fibers, and the usual layering of the cells in the cotton fiber is completely masked when compared with untreated cotton samples.

Kaizermann et al.¹⁴ examined microscopically the transverse section of polyacrylonitrile-grafted cotton and rayon fabrics. They observed that the fibers were almost completely penetrated by polymer deposits, although the polymer appeared to be greater near

* To whom correspondence should be addressed.

Table I Graft Add-Ons of Acrylonitrile Monomer on Raw Jute

Time of Reaction (h)	Graft Add-Ons (%)
2	14.8
3	20.4
4	21.9

the surface. Hebeish¹⁵ observed that the mechanism of grafting onto different cellulosic materials cannot be compared, as the grafting onto hydrocellulose was found to be more a surface phenomenon, while grafting onto swollen cotton and viscose took place inside the fiber.

Iwakura et al.¹⁶ observed a cross section of cellulose, grafted with glycidyl methacrylate (GMA) after dyeing on an acid dye in the presence of pyridine. They observed that, when initiated by Ce^{IV} ions, the grafting of GMA starts from the surface of the fiber and progresses towards the center, as the grafting ratio is increased. On the other hand, grafting starts in the core of the fiber with the redox graft polymerization of the $Fe^{II}-H_2O_2$ -cellulose system.

EXPERIMENTAL

Sample Preparation

C. olitorius (tossa jute), used in this study, was dewaxed by soxhleting with an alcohol-benzene mixture (1:1, v/v). The temperature under the soxhlet apparatus was adjusted so that siphoning occurred within a 2 to 3 min interval. Each sample was treated for 8 h. The extracted fibers were next rinsed with alcohol (to remove adhering benzene from the fi-

Table II Graft Add-Ons of Acrylonitrile Monomer on Bleached Jute

Time of Reaction (h)	Graft Add-Ons (%)
1	17.8
2	20.8
3	27.4
4	29.0
5	30.3

Table III Graft Add-Ons of Methyl Methacrylate Monomer on Raw Jute

Time of Reaction (h)	Graft Add-Ons (%)
1	15.7
2	18.9
3	20.4
4	23.1
5	23.9

bers), and then were washed several times with distilled water, to remove other reaction products. The estimation of lignin was done by the TAPPI standard, according to which 15 mL of cold (12–15°C), 72% sulfuric acid was added to 1 gm of an oven-dry sample. This dissolved the carbohydrates, leaving an insoluble residue of lignin. The mass of this insoluble lignin was determined and the percentage was determined.

A part of the dewaxed jute was then bleached by 0.5% volume aqueous hydrogen peroxide solution at 80°C for 2 h. The lignin content of the raw dewaxed jute was found to be 12%, while that of bleached jute was only 8%.

The redox system of grafting was employed to graft the raw dewaxed and bleached jute fiber. Acrylonitrile, methyl methacrylate, and a mixture of methyl methacrylate and acrylonitrile in different proportions (in a mixed monomer system) were taken in the present study. Ceric ammonium sulfate in 1% sulfuric acid was taken as the initiator. The grafting reaction was carried out in an inert (nitrogen) atmosphere at 40°C. The only parameter that was varied in the grafting reaction was the time of reaction; with increasing time, the graft add-ons increased. The graft add-ons of different grafted jute are given in Tables I–VI.

Table IV Graft Add-Ons of Methyl Methacrylate Monomer on Bleached Jute

Time of Reaction (h)	Graft Add-Ons (%)
1	17.8
2	20.6
3	24.7
4	26.2
5	26.9

Table V Graft Add-Ons of Acrylonitrile and Methyl Methacrylate Monomer (in Mixed Monomer System) on Raw Jute^a

MMA : AN	Graft Add-Ons (%)
100 : 0	8.0
75 : 25	9.2
50 : 50	20.0
25 : 75	10.6
0 : 100	8.0

^a Time of reaction: 4 h.

It was noted that, in the case of both acrylonitrile and methyl methacrylate monomers, the add-ons leveled off at 4 h grafting.

In the mixed monomer system, acrylonitrile and methyl methacrylate were taken in different proportions from 100 : 0 to 0 : 100. As was observed, at 4 h of grafting, the graft add-on leveled off in cases of both acrylonitrile and methyl methacrylate monomers taken individually, so in the mixed monomer system, all the grafting reactions were in progress for 4 h. It was observed that in both the case of raw and of bleached jute fibers, the proportions of acrylonitrile and methyl methacrylate at 50 : 50 yielded the highest add-on.

Examination of Cross Sections

The cross sections of raw and grafted jute were determined using an optical microscope with the following arrangements:

The grafted and raw fiber samples were introduced through small holes in thin aluminum plates, and were shaved off from both sides. The cross sections of the fiber samples were then examined in a projection microscope in transmission mode. The

Table VI Graft Add-Ons of Acrylonitrile and Methyl Methacrylate Monomer (in Mixed Monomer System) on Bleached Jute^a

MMA : AN	Graft Add-Ons (%)
100 : 0	26.0
75 : 25	28.4
50 : 50	31.8
25 : 75	30.0
0 : 100	24.0

^a Time of reaction: 4 h.

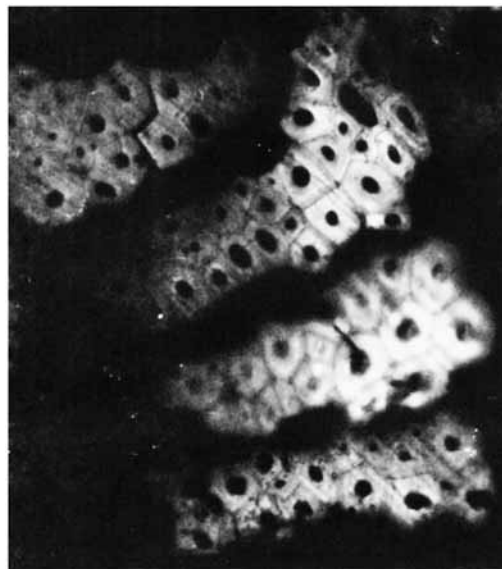


Figure 1 Cross section of raw bleached tossa jute.

photomicrographs of transverse sections of differently grafted tossa jute fibers, as well as raw fibers, are shown in Figures 1-5.

Examination of Surface Topology

The surface topology of raw jute and differently grafted jute fibers was examined under a scanning

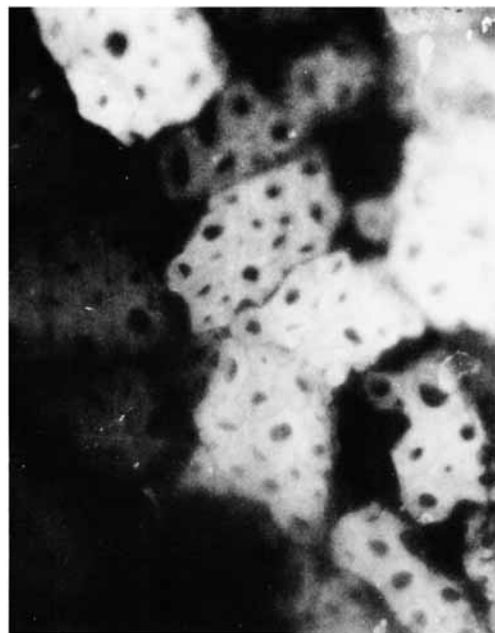


Figure 2 Cross section of 9.2% grafted tossa jute (MMA:AN = 75:25).

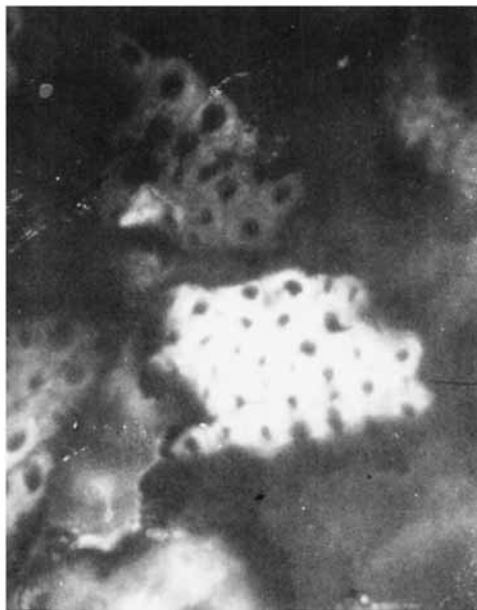


Figure 3 Cross section of AN grafted tossa jute (23% add on).

electron microscope. For this purpose, the fiber samples were coated with a thin film (20 nm) of gold in a sputter coater. The coated samples were then examined under an Hitachi S-430 scanning electron microscope at an operating voltage of 15 to 20 KV.

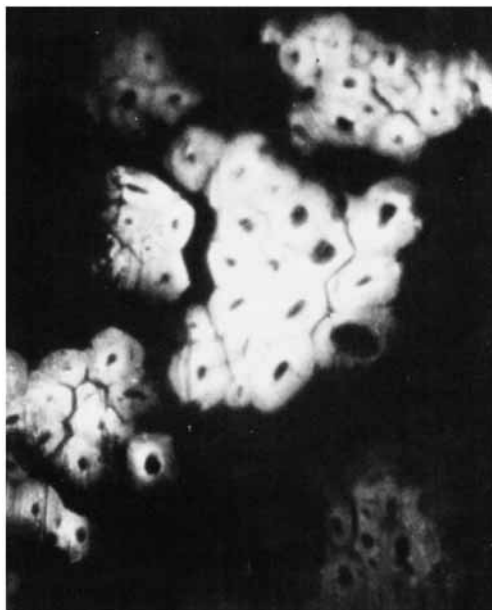


Figure 4 Cross section of MMA grafted tossa jute (31% add on).

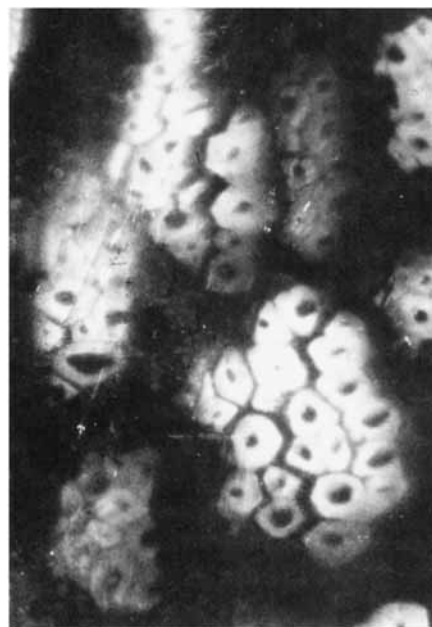


Figure 5 Cross section of MMA grafted bleached tossa jute (31.8% add on).

The scanning electron microphotographs of raw and grafted jute fibers are shown in Figures 6–11.

RESULTS AND DISCUSSION

The optical microphotographs of transverse sections of raw and grafted jute fibers are shown in Figures 1–5. When compared to cross sections of raw jute (Fig. 1), it was noted that when acrylonitrile was grafted onto it, at 9% and 23% (Figs. 2 and 3), the

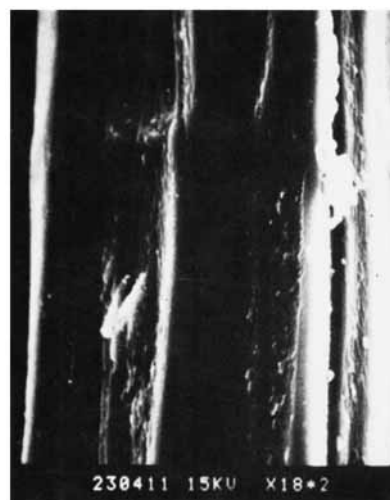


Figure 6 Electron microphotograph of raw bleached tossa jute.

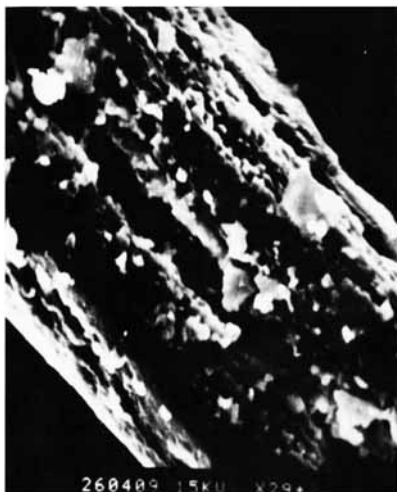


Figure 7 Electron microphotograph of 21.9% AN grafted tossa jute.

lumen size was diminished. This is possibly due to the fact that, with the increase of graft add-on, some of the grafted molecules enter the fiber matrix, causing the lumen size to be reduced.

At high graft add-on of methyl methacrylate monomer, it was noted that, when bleached jute was grafted with add-on of 31%, the pressure, due to excessive grafted materials inside the fiber matrix, caused the cells to disintegrate (Fig. 4). In the case of a mixed monomer system (MMA : AN = 50 : 50), with a graft add-on of 30%, the cells also showed signs of disintegration (Fig. 5).

The scanning electron microphotographs of raw



Figure 9 Electron microphotograph of 30.3% MMA grafted tossa jute.

and grafted jute are shown in Figures 6–10. It was observed that in the case of acrylonitrile grafted jute fibers, with an increase of graft add-on, the fiber surface was found to be covered with grafted polymer to a higher degree and the surface features of the fiber were not visible (Figs. 6 and 7). Thejappa and Pandey¹³ observed similar features in polystyrene-grafted cotton.

In case of methyl methacrylate grafting, it was noted that at 23% add-on, due to the pressure of grafting materials, longitudinal cracks developed on the fiber surface (Fig. 8). At still higher add-on (30.3%) of methyl methacrylate, there was more ac-



Figure 8 Electron microphotograph of 23.1% MMA grafted tossa jute.

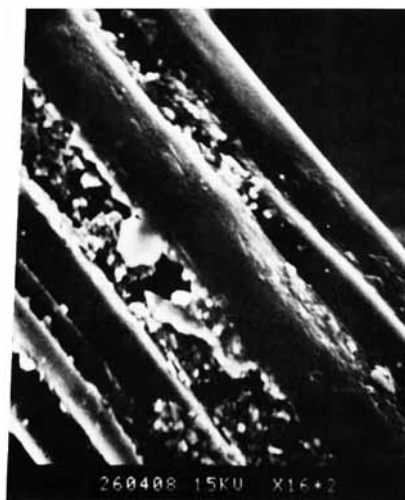


Figure 10 Electron microphotograph of 8% grafted tossa jute (MMA:AN = 100:0).



Figure 11 Electron microphotograph of 31.8% grafted tossa jute (MMA:AN = 50:50).

cumulation of polymers on the fiber surface and more cracks developed (Fig. 9).

Scanning electron microscopic examination of jute fibers, grafted with a mixed monomer system of methyl methacrylate and acrylonitrile at a low add-on of 8% of grafted materials (MMA : AN = 100 : 0) (Fig. 10), revealed that the fiber surface had a deposit of grafted materials. But, at high add-on (31.8%) (MMA : AN = 50 : 50) (Fig. 11), longitudinal as well as transverse cracks developed on the fiber surface.

The authors thank Dr. S. N. Pandey, Director, Jute Technological Research Laboratories, for his keen interest in the work and for permitting the publication these results.

Thanks are due to the Indian Council of Agricultural Research for providing work facilities.

REFERENCES

1. J. C. Arthur, Jr., *J. Macromol Sci. Chem. A*, **10**, 653 (1976).
2. J. P. Kennedy and A. Vidal, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 1765 (1975).
3. R. J. Ambrose and J. J. Newell, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 2129 (1979).
4. G. Rausing and S. Sunner, *Tappi*, **45**, 203A (1962).
5. J. L. Garnett, *Radiat. Phys. Chem.*, **14**, 79 (1979).
6. V. Y. Kabanov and R. E. Aliev, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 1255 (1979).
7. A. Chapiro, *J. Polym. Sci. Symp.*, **56**, 431 (1976).
8. M. M. Huque, Md. Mahmood Habibuddin, and A. J. Mian, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 1447 (1980).
9. J. Erdebji, E. Szkely, and A. Haman, *Papripon*, **23**, 212 (1979).
10. M. L. Rollins, A. M. Cannizzaro, F. A. Blouin, and J. C. Arthur, Jr., *J. Appl. Polym. Sci.*, **12**, 71 (1968).
11. R. W. Liggett, J. L. Hoffmann, and A. C. Tanquary, *American Dyestuff Repr.*, **58**, 25 (1969).
12. R. M. Reinhardt, J. D. Reid, and G. C. Daul, *Textile Res. J.*, **26**, 1 (1956).
13. N. Thejappa and S. N. Pandey, *J. Appl. Polym. Sci.*, **27**, 2307 (1982).
14. S. Kaizermann, G. Mino, and L. F. Meinfeld, *Textile Res. J.*, **32**, 136 (1962).
15. A. Hebeish, Ph.D. Thesis, Gujarat University, 1967.
16. Y. Iwakura, T. Kurosaki, K. Uno, and Y. Imai, *J. Polym. Sci.*, **C4**, 673 (1964).

Received April 23, 1992

Accepted October 5, 1992