Polyacrylonitrile (PAN)-Grafted Jute Fibres: Some Physical and Chemical Properties and Morphology

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SYNOPSIS

Grafting of polyacrylonitrile (PAN) on (dewaxed and bleached) jute fibres was done by aqueous polymerization of acrylonitrile (AN) in the presence of the fiber samples employing a sodium periodate (IO_4^-) and copper sulfate (Cu^{2+}) combination as the initiator. Effect of PAN grafting to different extents on X-ray crystallinity, tensile properties, thermal behavior, whiteness index, dyeability, light-fastness rating, and moisture regain properties of the fiber samples were studied and analyzed. Their rot resistance, determined by a standard soil burial test, were also examined and compared. Twenty to thirty percent PAN-grafting was found to impart a most desirable balance of physical properties including fiber strength and modulus, moisture regain, whiteness index, and light-fastness rating. PAN grafting also makes the otherwise nonresistant jute fiber significantly rot-resistant. Morphology of the different fiber samples as studied and compared using scanning electron microscopy indicates that PAN grafting occurs on surfaces and intercellular regions as well as within the lumens of the multicellular jute fibers.

INTRODUCTION

Jute, a lignocellulosic bast fiber, is grown extensively in India and some neighboring countries. As an agricultural product, jute is renewable and, therefore, its long-term application prospect is secured and bright despite the fact that the fiber has been facing stiff competition from its synthetic counterparts in its traditional field of application, viz., in the area of packaging. While the economy of the major jute-growing countries and the fate of thousands of jute growing families in countries such as India are being threatened potentially by the synthetics in view of their favorable production economy and the status of the technology at the current stage, attempts to improve the economic and technology status of jute fiber production and processing are being made on a continuous basis not only to mitigate the challenge it faces, but also to expand and diversify its application.

Properties of jute can be modified and tailored to different degrees by its chemical modifications including graft copolymerization with a vinyl monomer under selective, controlled conditions.[1-6] The multicellular and multiconstituent nature[7,8] of jute, however, poses some problems in modifying it by graft copolymerization. The selection of catalysts or initiator systems, in this context, is critical in keeping the proneness of oxidative and hydrolytic degradations of jute in view.

The present article reports changes and improvements in the consequential physical properties, dyeability characteristics, thermal response, and morphological features of jute fiber as a result of graft copolymerization in aqueous medium under specified conditions using a Cu^{2+} — IO_4^- combination as the initiator and acrylonitrile (AN) as the vinyl monomer.

EXPERIMENTAL

Pretreatments of Jute Fiber/Fabric

Dewaxing

Raw jute fiber (*Corchorus olitorius*) obtained locally was dewaxed by extracting with an ethanol–benzene

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Table I Effect of PAN Grafting[a] on Properties and Fine Structure of Defatted Jute (DJ) and Bleached Jute (BJ)

			IO_4^--treated Fiber		Grafted Fiber, % Grafting									
					10%		20%		25%		30%		40%
Properties	DJ	BJ	DJ	BJ	DJ	BJ	DJ	BJ	DJ	BJ	DJ	BJ	DJ
Specific stress (cN tex^{-1})	38.4	36.3	32.2	33.1	42.4	34.7	42.1	36.3	41.5	37.4	38.5	39.1	29.6
Breaking extension (%)	1.75	1.68	1.38	1.40	1.79	1.63	1.62	1.70	1.56	1.72	1.53	1.74	1.42
Initial modulus (cN tex^{-1})	2194	2161	2333	2364	2369	2122	2599	2135	2600	2174	2503	2247	2084
Moisture regain (%)	13.4	—	—	—	12.2	—	11.2	—	10.4	—	9.9	—	8.9
Retention of specific stress (%) after 21 days of SSBT	Nil	—	—	—	48.0	—	50.0	—	54.0	—	56.0	—	—
X-ray crystallinity (%)[b]	58.1	—	57.6	—	50.9 (56.5)	—	46.0 (57.5)	—	—	—	40.0 (57.1)	—	—
Direct dye uptake (%)	—	38.0	—	—	—	48.0	—	52.0	—	55.0	—	60.0	—
Basic dye uptake (%)	—	90.0	—	—	—	84.0	—	79.0	—	77.0	—	73.0	—
Whiteness index	32.0	61.0	—	40.0	—	52.0	—	56.0	—	60.0	—	63.0	—
Light-fastness rating	—	1–2	—	1	—	2–3	—	3–4	—	4	—	5	—

[a] Grafting was done at 50°C for 1 h using an aqueous [IO_4^-] (0.005 mol L^{-1}) and [Cu^{2+}] (0.001 mol L^{-1}) combination as the initiator; fiber-to-liquor ratio: 1 : 50 (w/w); concentration of AN was varied from 4 to 15% (v/v) to effect different degrees of grafting.

[b] Nos. within and without parentheses indicate % crystallinity value of the grafted fibers calculated on the basis of jute (DJ) content and on the overall basis, respectively.

mixture (1 : 2 v/v) under reflux for 6 h; this was followed by washing with ethanol and distilled water in succession, drying in air, and, finally, under vacuum at 40°C to obtain dewaxed jute (DJ).

Scouring

Jute fabric (300 g/m^{-2}) was scoured by treating with a 2% nonionic detergent solution at 70°C for 1 h using a fabric–liquor ratio of 1 : 50 (w/w). The scoured fabric was then washed successively with hot and cold distilled water and dried in air.

Bleaching

DJ or scoured jute fabric was also selectively bleached using 1 vol aqueous solution of H_2O_2 containing 1% Na-silicate and 0.5% Na-orthophosphate at 70°C for 2 h, maintaining a fiber-to-liquor ratio of 1 : 20 (w/w) at pH 10–11. This was followed by washing with distilled water, treatment with 1% acetic acid solution, and washing again with distilled water until free from acid. The bleached jute (BJ) was then dried in air.

Graft Copolymerization

Aqueous graft copolymerization of AN on DJ or BJ fiber/fabric was done using a sodium periodate (0.005 mol L^{-1})–copper sulfate (0.001 mol L^{-1}) combination as the initiator[9] and purified AN as the monomer at 50°C for 1 h using a fiber-liquor ratio of 1 : 50 (w/w) under a nitrogen atmosphere; concentration of AN was varied (4–12% v/v) to obtain jute with different degrees of % grafting. Polyacrylonitrile (PAN)-grafted fiber samples were then successively washed with dilute (0.01*N*) HCl and distilled water and dried. The dried samples were then extracted with dimethylformamide (DMF) at 50°C over an extended time period (72 h) to ensure removal of associated PAN homopolymer. The extracted PAN-grafted jute samples were then dried at 40°C under vacuum. PAN homopolymer from selected DMF extracts was recovered by precipitation with methanol and drying under vacuum.

X-ray Crystallinity

X-ray crystallinity values of finely powdered and vacuum-dried samples of DJ and PAN-grafted DJ were determined directly on a Philips electronic X-ray diffractometer (Model 1700) using a PW 1710 computation system.

Scanning Electron Microscopy

The surface morphologies of a Au–Pd alloy-coated DJ and of selected PAN-grafted DJ were examined using a Hitachi scanning electron microscope (Model S430) at a working distance of 10 mm and an operating voltage of 10–15 kV.

Thermal Analysis

Thermal analysis of DJ, PAN-grafted DJ, and PAN homopolymer formed during graft copolymerization was done by thermogravimetry (TG) using a Mettler TA 4000 system and by differential scanning calorimetry (DSC) using a DuPont Model 9900 thermal analyzer under a nitrogen atmosphere, maintaining a heating rate of $10 \pm 1°C\ min^{-1}$ and a sample weight of 10 ± 2 mg in each case.

Physical and Mechanical Properties

Tensile properties of DJ/BJ and PAN-grafted DJ/BJ fibers, conditioned at $25 \pm 2°C$ and 65% relative humidity for 72 h, were determined on an Instron universal testing machine (Model 1148). A test length of 10 mm and a crosshead speed of 5 mm min^{-1} were employed, and an average of 50 tests has been reported for each sample.[10]

The average linear density (tex) of the conditioned fibers were determined by weighing 50 fibers, each of 5 cm length. Moisture regain of different DJ and PAN-grafted DJ samples were determined following ASTM D-2495-75.[11] The brightness index of scoured, bleached, and PAN-grafted jute fabrics were determined by measuring the percentage reflectance in a photovolt reflectance meter (EEL, UK) using magnesium oxide as the reference material.[12,13] Light-fastness of BJ and PAN-grafted BJ samples were examined in a Weather-O-meter (Atlas Electric Corp., USA) by exposing the samples to a Xenon arc lamp at 40°C following standard procedures.[14]

Dyeability

Dyeability (dye uptake %) of BJ and PAN-grafted BJ samples were determined spectrophotometrically (Shimadzu UV-3000) using the dyes C.I. Direct Yellow 12 and C.I. Basic Green 4, following standard procedures.[15]

Rot Resistance

Rot resistance has been expressed as percentage of tensile strength retained after subjecting the fibers to a standard soil burial test for 21 days at $30 \pm 2°C$ in an incubator.[16]

RESULTS

Results of the studies relating to X-ray crystallinity, physical and mechanical properties, thermal behavior, rot resistance, moisture regain and dyeability, whiteness index, and light-fastness rating of jute fibers/fabrics (defatted or bleached) and variability of these properties on different degrees of PAN grafting on jute are given in Table I and Figures 1–4.

X-ray Crystallinity

The crystallinity value of defatted jute (DJ) was found to be about 58% (Table I). The PAN-grafted jute fibers (% grafting in the range of 10–30%) apparently exhibit an overall degree of crystallinity lower than that of DJ, much as a consequence of the incorporation of the amorphous PAN as grafted-on chains in the fiber. However, when the degree of crystallinity is calculated on the basis of the weight of the jute component in the grafted fiber in each case, little difference in crystallinity (%) between the grafted and the ungrafted fiber is indicated. Thus, it appears that the grafted (amorphous) chains of PAN find their location and anchorage in the amorphous regions of the jute fiber and they are indicated to penetrate little in the crystalline zones. The fine structure of the jute fiber thus remains mostly unaffected on PAN grafting.

Tensile Properties

For evaluation of the effect of PAN grafting on the tensile properties of jute fiber, both DJ and BJ were used for grafting using IO_4^-—Cu^{2+} combination as the aqueous initiator at 50°C for 1 h. Tensile properties of the said fibers were also measured after treating them with aqueous IO_4^- only for 1 h at 50°C in the absence of the monomer, keeping the reaction conditions otherwise comparable in order to evaluate to what extent the oxidative attack of IO_4^- only would affect the fiber. Treatment of jute fibers with IO_4^- only causes lowering in tenacity or specific stress by about 8 and 16% and lowering in breaking extension (BE) by about 16 and 20% for bleached jute (BJ) and dewaxed jute (DJ), respectively, in a manner resulting in a measurable gain in the initial modulus (IM) in each case. PAN grafting on DJ using an IO_4^-—Cu^{2+} combination to the extent of 10–25% grafting, however, effects improvement in tenacity by about 8–10% and this is associated with

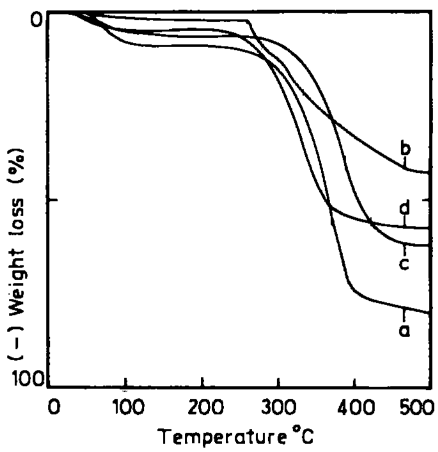


Figure 1 Thermogravimetry (weight loss % vs. temperature): (a) DJ; (b) PAN homopolymer; (c) 25% PAN-grafted DJ; (d) 50% PAN-grafted DJ. Heating rate 10°C min^{-1}; sample weight, 10 ± 2 mg; tests carried out under flowing nitrogen.

a lowering in BE in a manner resulting in about 8–20% improvement in the IM of the fiber (Table I). For BJ, small, measurable improvements in tenacity are observed only at a relatively high level of % grafting (> 20%), whereas BE and IM values remain almost unaltered for the range of % grafting studied (up to 25–30%) (Table I). For PAN-grafted DJ, improvement in tenacity tends to follow a falling trend on increase in % grafting despite a significant initial improvement over ungrafted DJ. Improvement in tenacity and IM values with simultaneous lowering in BE values of the fibers are apparently caused by filling up of voids in the lumens and particularly in the intercellular matrix regions of the multicellular jute fiber that are filled partly with the amorphous lignin and hemicellulose constituents. Filling up of voids by the grafted-on PAN in the intercellular regions thus results in stiffening of the matrix as well as improved cementing action, leading to more efficient transfer of stress between the ultimate cells. Possible filling up of the lumens of the ultimate cells of the fibers by the grafted-on PAN is likely to impart a homogenesing effect again by elimination or reduction of voids, thereby causing effective improvements in ability to bear stress.

Differences in tensile behavior of PAN-grafted DJ and BJ as detailed above, though intriguing at first sight, are not entirely unexpected. H_2O_2 bleaching of DJ under alkaline condition as practiced in this study is accompanied by about 7% loss in weight and splitting of many of the relatively coarser DJ fibers, resulting in a drop in the linear density value from 3.05 to 2.70 tex. Thus, BJ has a larger specific surface area than that of DJ[17] and the former is weaker, too. Hence, to effect improvement in strength of BJ by the mechanism discussed above, higher graft add-on is required just to account for the additional surface area caused by bleaching. Besides, BJ being an oxidized substrate, the nature of the graft copolymerization reaction with reference to distribution of location and the degree of polymerization of the grafted-on polymer chains using BJ might be different from those obtained using DJ. These factors possibly account for the differences in the tensile behaviour of ungrafted and PAN-grafted DJ and BJ.

Moisture Regain and Rot Resistance

From the relevant data presented in Table I, it is observed that the moisture regain value of DJ decreases on PAN grafting; the higher the % grafting, the lower the moisture regain value. This is expected in view of the prominent hydrophobicity of PAN.

Jute is highly prone to microbial degradation, causing loss of strength. Rot resistance of jute improves on PAN grafting (Table I). The level of rot resistance, as expected, increases with increase in % grafting. The presence of PAN inhibits microbial

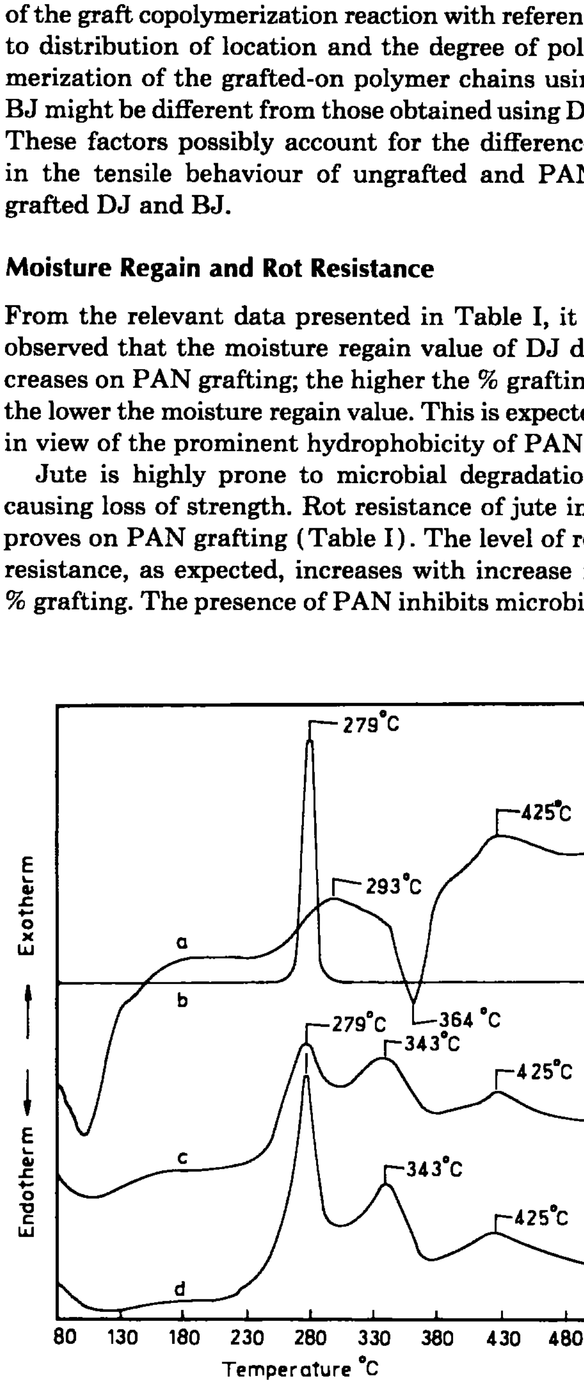


Figure 2 DSC thermograms, under flowing nitrogen: (a) DJ; (b) PAN homopolymer; (c) 25% PAN-grafted DJ; (d) 50% PAN-grafted DJ. Heating rate 10°C min^{-1}; sample weight, 10 ± 2 mg.

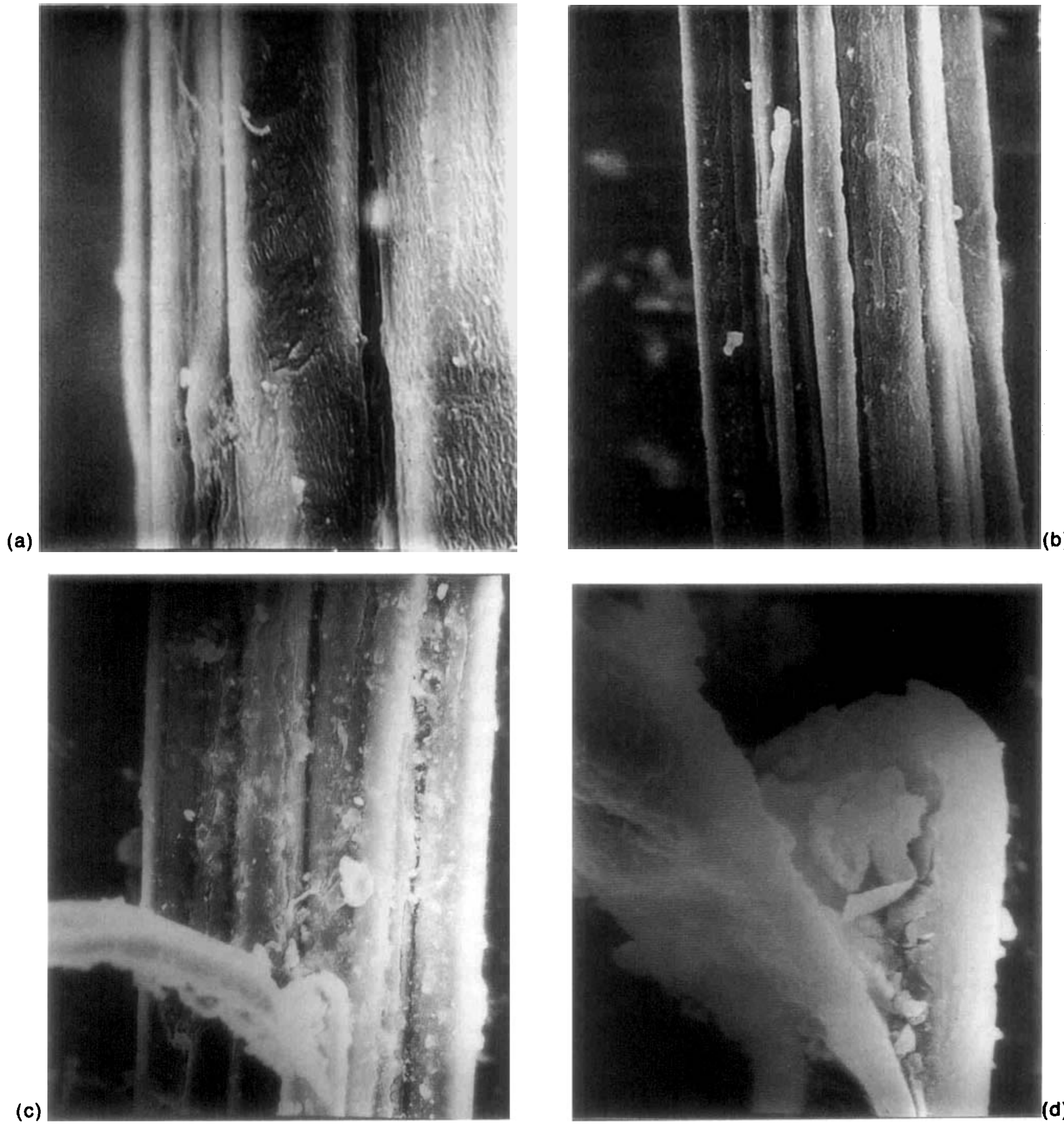
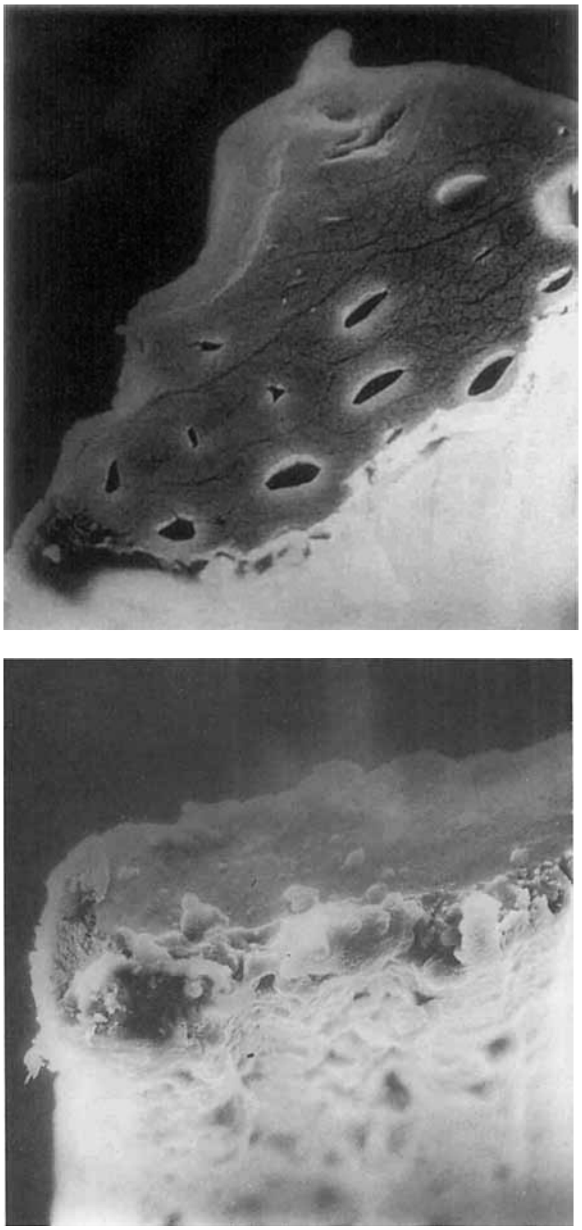


Figure 3 SEM micrographs showing surface morphology of $NaIO_4$-treated DJ and PAN-grafted DJ of different degrees of grafting: (a) $NaIO_4$-treated DJ (×1800); (b) 15% PAN-grafted DJ (×1000); (c) 25% PAN-grafted DJ (×1000); (d) torn out part of PAN-grafted DJ fiber [as in micrograph (c)] magnified (×3800).

growth, and as a result, it is observed that for a graft level of 10% even after 21 days of standard soil burial the grafted fiber retains about 48% of its original strength compared to the total loss of strength (zero retention of strength) suffered by the ungrafted jute.

Whiteness Index and Light Fastness

From the results given in Table I, it is observed that on PAN grafting the whiteness index value of BJ initially suffers unfavorably, but continues to im-



(a)

(b)

Figure 4 SEM micrographs showing the morphology of transverse sections of (a) DJ fiber (×2000), showing voids corresponding to the lumens in the ultimate cells and (b) 30% PAN-grafted DJ fiber (×2000) showing growth/deposition of grafted-on PAN both on the fiber surface and inside the lumens as well causing a good degree of a masking effect and elimination of voids.

prove with increase in % grafting, such that for a % grafting ≥ 25%, the whiteness index becomes comparable with or even better than that of BJ. The decrease in the whiteness index at a low level of % grafting appears to be the result of the action of the initiator system, particularly of IO_4^- on BJ, which is clearly evident from a very low whiteness index value of the initiator (IO_4^-)-treated BJ sample. A slight browning of jute on IO_4^- treatment consequent to formation of quinonoid structures in the lignin moieties[9,18] causes the initial drop in the whiteness index. The pale brown surface, however, becomes progressively masked by the deposition of the grafted-on (white) PAN as the % grafting increases, thus leading to progressive improvement in the whiteness index subsequently.

Masking of the surface of the jute fiber (here, BJ) with the grafted-on PAN, which is far more resistant to light[12,19,20] than jute itself, also results in improvement in light fastness of the grafted jute. The masking effect of grafted-on PAN is apparent on examination of the SEM micrographs of the ungrafted and PAN grafted jute fibers shown later (Figs. 3 and 4). The light-fastness rating increases from 1 to 2 for BJ to as high as 5 for 30% PAN grafting on BJ (Table I).

Dyeability

From the results given in Table I, it is apparent that although BJ exhibits a dye uptake value of about 38% with respect to the direct dye, films of PAN homopolymer extracted out with DMF from the gross products of graft copolymerization exhibit an average dye uptake value as high as 75%. However, with the basic dye, while BJ exhibits a dye uptake value of about 90%, PAN shows practically no affinity for the dye under comparable conditions. Consequently, PAN grafting improves and impairs dyeability of BJ with respect to direct dye and basic dye, respectively, showing correspondingly increasing and decreasing trends in the dye-uptake values with increase in % grafting.

Disproportionate (i.e., more than the weighted average) increase in direct dye uptake and a similar decrease (less than the weighted average) in basic dye uptake on PAN grafting on BJ may be accounted for in part by the following considerations: Grafting results in an increase in specific surface area of BJ due to (i) incorporation of relatively low-density PAN (specific gravity 1.10) on BJ (specific gravity 1.50) and (ii) splitting of some BJ fibers by the hydrolytic action of the grafting medium. The splitting is evidenced by the trends of changes in the linear density (tex) values of the grafted fibers; the tex values showing changes not commensurate with % grafting (tex values of BJ, 10% PAN-grafted BJ, and 25% PAN-grafted BJ being 2.70, 2.64, and 3.01, respectively).

Thermogravimetric (TG) Analysis

TG curves of selected fiber samples (DJ and 25% and 50% PAN-grafted DJ) and PAN homopolymer (powder) are shown in Figure 1. Three distinct zones can be identified in the TG curves of the fiber samples, grafted or ungrafted. The initial zone corresponds to small loss in weight due to evaporation of absorbed water. The middle zone is associated with a sharp loss in weight after onset of the thermal decomposition process (onset temperature, T_1), and the third and final zone appears after the thermal decomposition subsides and a more or less steady weight retention for the carbonized residue is indicated.

PAN grafting on DJ improves its thermal stability, T_1, increasing from 215°C for DJ to 280°C for 25% PAN-grafted DJ and to 230°C for 50% PAN-grafted DJ. Weight retention at 500°C also improves on PAN grafting, the weight retention value increasing from 19% for DJ to about 38–43% for PAN-grafted fibers (25–50% grafting). This is expected in view of relatively high weight retention (~ 60%) for PAN under comparable conditions. Observation of a lowering in T_1 value of the fiber after an initial significant improvement in its value with increase in % grafting runs parallel to the observation of a relatively sharp falling trend in mechanical properties (modulus and tenacity) of the PAN-grafted DJ beyond 25–30% grafting. It appears that increasing PAN grafting beyond the 25–30% range results in increasing accumulation of internal stresses and strains due to uneven filling of microvoids by and surface deposition of the grafted-on PAN, causing the highly grafted fibers to be increasingly stress-sensitive (both mechanical and thermal) and, hence, less resistant.

DSC Analysis

DSC curves of the above four samples (Fig. 2) show an weak endothermic peak around 100°C due to evaporation of water. The DSC curve of jute is characterized by two weak exothermic peaks around 293 and 425°C assigned to hemicellulose and lignin decompositions, respectively, and a strong endotherm around 364°C due to decomposition of the cellulose constituent.[21,22] The DSC curve of PAN shows a strong and sharp exotherm around 279°C. PAN grafting brings about significant changes in the decomposition pattern of DJ. An exotherm corresponding to decomposition of PAN appears around 279°C. As a consequence of two successive and overlapping exothermic decompositions corresponding to the decomposition of PAN (279°C) and of hemicellulose (293°C), the liberated and accumulated heat apparently more than compensates for the heat absorbed during the endothermic decomposition of the cellulose components of the PAN-grafted DJ that follows, the net result being the appearance of a relatively broad exotherm over the zone 317–375°C with positioning of its peak around 343°C, and the normal endothermic peak for cellulose decomposition at 364°C virtually fails to show up as a consequence. The exotherm around 425°C due to lignin decomposition, however, remains mostly unaffected in each grafted fiber sample.

Study of Surface Morphology of DJ and PAN-grafted DJ by Scanning Electron Microscopy

Scanning electron micrographs (Figs. 3 and 4) of DJ, of $NaIO_4$-treated DJ, and of (Cu^{2+} — IO_4^-)-initiated PAN-grafted DJ fiber samples reveal that on grafting of PAN the surface of the DJ fiber becomes masked with the grafted-on polymer [Fig. 3, micrographs (b) and (c)] and the masking effect is more prominent with higher % grafting. Large-scale deposition of the grafted polymers can be seen on the fiber surface as well as in the intercellular regions of the jute fiber (Fig. 3). The micrograph of the 25% PAN-grafted DJ reveals deposition of the grafted-on PAN inside the lumen of the ultimate cells [Fig. 3, micrographs (c) and (d)], indicating that the grafted-on PAN is located not only on the fiber surface and the intercellular regions but also in the void zones deep inside the fiber structure including the lumens. This is also clearly evidenced by a comparison of the micrographs of transverse sections of a sample of DJ fiber and of a 30% PAN-grafted DJ fiber [Fig. 4, micrographs (a) and (b)].

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REFERENCES

1. I. M. Trivedi and P. C. Mehta, *Cellulose Chem. Technol.*, **7**, 401 (1973).
2. N. Y. Abou-Zeid, A. Higazy, and A. Hebeish, *Angew. Makromol. Chem.*, **121**, 69 (1984).
3. P. Ghosh, A. R. Bandopadhyay, and S. Das, *J. Macromol. Sci. Chem. A*, **19**, 1165 (1983).
4. M. Misra, A. K. Mohanty, and B. C. Singh, *J. Appl. Polym. Sci.*, **33**, 2809 (1987).

5. P. Ghosh, S. Biswas, and C. Datta, *J. Mater. Sci.*, **24**, 205 (1989).
6. S. Moharana and S. S. Tripathy, *J. Appl. Polym. Sci.*, **42**, 1001 (1991).
7. B. C. Kundu, K. C. Basak, and P. B. Sarkar, in *Jute in India*, Indian Central Jute Committee, Calcutta, India, 1959, p. 40.
8. S. G. Barker, *J. Text. Inst.*, **30**, 273 (1939).
9. P. K. Ganguly, PhD Thesis, Calcutta University, 1992.
10. S. Samajpati, A. Majumdar, and P. C. Dasgupta, *Text. Res. J.*, **49**, 8 (1979).
11. American Society for Testing Material, Part 33, Philadelphia, Pennsylvania, 1976, pp. 496–502.
12. A. B. Sengupta and T. Radhakrishnan, in *New Ways to Produce Textiles*, The Textile Institute, Manchester, UK, 1972, p. 112.
13. R. S. Hunter, in *Measurement of Appearance*, Interscience, New York, 1975, p. 174.
14. *Standard Methods for the Determination of the Colourfastness of Textiles*, The Society of Dyers and Colourists, London, 1962, pp. 57, 109.
15. H. C. Giles, in *Laboratory Course in Dyeing*, Society of Dyers and Colourists, London, 1971, p. 76.
16. Bureau of Indian Standards, I.S. 1623 (1960).
17. M. M. Roy, R. R. Mukherjee, and M. K. Sen, *J. Text. Inst.*, **41**, T249 (1950).
18. E. Adler, I. Falkehag, and B. Smith, *Acta. Chem. Scand.*, **16**, 529 (1962).
19. C. W. Davis and P. Shapiro, in *Encyclopedia of Polymer Science and Technology*, H. F. Mark and N. G. Gaylord, eds., Interscience, New York, 1964, Vol. I, p. 355.
20. H. J. Callow and J. B. Speakman, *J. Soc. Dyers Colorists*, **65**, 758 (1949).
21. M. V. Ramiah, *J. Appl. Polym. Sci.*, **14**, 1323 (1970).
22. I. K. Verma, S. R. Ananthakrishnan, and S. Krishnamurthy, *Text. Res. J.*, **58**, 486 (1987).

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