Preparation, Characterization, and Properties of Unbleached, Bleached, and Grafted Pulps from JRC-321 Variety Jute Fiber

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ABSTRACT: Graft copolymerization onto jute pulps opened the door to new concepts in pulp and paper research. Jute pulp from the JRC-321 variety white jute fiber was prepared by the alkaline sulfite pulping process. The pulp obtained was bleached by the chlorination, extraction, and hypochlorite sequence technique to remove excess lignin for making bright and good quality paper. Special attention was focused on the graft copolymerization of acrylamide monomer onto the unbleached and bleached pulps by the use of a complex initiating system: Cu(II)/glycine/$KHSO_5$ in aqueous solution. It was found that percentage grafting was high in the case of bleached pulp. The grafted pulps so obtained were characterized by FTIR and their thermal behavior was characterized by TGA. Their mechanical properties such as tensile strength, percentage elongation, and tenacity were measured and compared. The physical properties such as rot-resistance and water-retention capacity of the grafted and the ungrafted pulps were determined. The effect of the percentage grafting variation on the above mentioned properties was examined. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1963–1969, 2002

Key words: jute pulp; bleaching; graft copolymerization; TGA; tensile strength; water retention; rot resistance

INTRODUCTION

Jute has been utilized as a low-cost material for pulp and paper making for a number of years. It was proven that the jute fiber of the white variety is finer than the tossa variety and out of various white varieties, fiber from JRC-321 is the finest variety known today. The extensive research and development activity in the field of graft copolymerization of natural and synthetic fibers with vinyl monomer has been studied since the early days.[1–6] The purpose of grafting of vinyl monomers onto cellulose and wool fibers, in most of the reports,[7–10] is to produce synthetic fibers with improved properties. In addition, the graft copolymerization of vinyl monomers onto jute fibers has been reported,[11–14] which are very important to the manufacture of good quality fabrics, white paper, and board with/without bleaching. However, except for one or two reports on grafting onto cellulose pulp, reports on grafting onto jute pulp are scanty.

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Potassium monopersulfate ($KHSO_5$) under the influence of some metal-salt/complexing-agent couples effectively initiates vinyl polymerization and graft polymerization onto cellulose and jute fibers.[15–17] At present, we have used a simple, novel, nonconventional complex initiating system: Cu(II)/glycine/$KHSO_5$/H_2O for graft copolymerization. This system[18] has already been shown to be a success for the emulsion polymerization of acrylonitrile. The present investigation has opened the door to the new concepts in grafting onto unbleached and bleached pulps with special reference to their mechanical and physical properties. These novel synthetic materials prepared by low-cost technique with improved properties may shed light on their commercial use as superabsorbents and bright, good quality paper.

EXPERIMENTAL

Materials

Acrylamide (AM) monomer (Merck, Germany) was purified by recrystallization from acetone and dried at room temperature under vacuum. A 4-mol dm^{-3} stock solution of the monomer in triple-distilled water was used. Potassium monopersulfate was a gift sample from DuPont, USA and was used without purification. A stock solution 12.9×10^{-2} mol dm^{-3} of the initiator was used for all experiments and the strength of stock solution was determined iodometrically. All other reagents were of British Drug House analytic reagent (AR) grade and used after purification by standard methods.

Methods

Pulping

White jute fiber JRC-321 variety was used specifically for preparing jute pulp by alkaline sulfite process. The pulp was prepared from white jute fiber JRC-321 of raw material on a 10-L-capacity electrically heated rotatory digester. The pulping conditions were as described under the following: Total chemicals as Na_2O was 9.8%, liquor to fiber ratio was 4 : 1. The cooking cycle employed at (a) time from room temperature to 100°C was 45 min, (b) time from 100° to 160°C was 1 h, and (c) time for cooking at 160°C was 2 h 45 min.

Bleaching of the Pulp

Bleaching of the pulp[19] was done by the standard CEH (chlorination, extraction, and hypochlorite) sequence technique with total chlorine consumption of 7.26%. Chlorination of the pulp was carried out with 3.72% chlorine at 5% consistency for 60 min at room temperature. The pH was maintained at 2–3 during the chlorination process. After chlorination, the above pulp was treated with 2% NaOH for 45 min at 50–60°C. Then the pulp was washed until free of alkali. The alkali-washed pulp was treated with 1.5% sodium hypochlorite for 50 min at 40–50°C.

Grafting onto the Pulp

Graft copolymerization reaction was carried out in a constant shaking temperature bath with an accuracy of 0.1°C, under oxygen-free nitrogen atmosphere. Both the bleached and the unbleached jute pulps were first soaked with appropriate quantities of monomer AM and other reagents were taken in a reaction vessel and deaerated by oxygen-free nitrogen gas. The known quantity of $KHSO_5$ was injected through a rubber tube after proper thermal equilibrium. After a specific time interval, each reaction was arrested by quenching the vessel in ice-cold water, followed by addition of ammonium ferrous sulfate solution which spontaneously consumed unreacted $KHSO_5$.[20] The homopolymer polyacrylamide was removed by repeated washing with warm water, until the extract gave no precipitation with methanol. The grafted jute pulp was washed repeatedly in conductivity water and dried to a constant weight.

Characterization and Properties

Infrared Spectra

To confirm the graft copolymer formation, IR spectroscopy was performed. The IR spectra of the raw jute, jute pulps, and acrylamide-grafted pulps in the form of KBr pellets were recorded in the model Paragon-500 FTIR of Perkin–Elmer.

Thermogravimetric Analysis (TGA)

TGA was conducted by using a Shimadzu DTA-500 system. It was carried out in air from room temperature to 800°C at a heating rate of 10°C/min.

Tensile Properties

The tensile strength of the raw jute fiber, unbleached, bleached, and grafted pulps were determined through determination of stiffness at break following the method of Haque and Habibud-

Table I Variation of Percentage Grafting with AM of Raw Jute, Unbleached, and Bleached Pulps, at [$KHSO_5$] = 12.9 × 10^{-3} mol dm^{-3}, [Cu(II)] = 20.0 × 10^{-3} mol dm^{-3}, [Gly] = 20.0 × 10^{-3} mol dm^{-3}, jute/jute pulp = 0.15 g at 45°C for 3 h

	% Grafting		
[AM] (mol dm^{-3})	Raw Jute Fiber	Unbleached Pulp	Bleached Pulp
0.1	15.4	30.2	40.4
0.2	18.8	36.4	49.8
0.4	24.5	50.8	62.2
0.6	34.2	61.4	70.5
0.8	42.2	67.4	78.9
1.0	38.2	50.8	67.4
1.2	28.4	32.2	52.8

dowla.[21] The stiffness at break was determined from the value of tenacity and elongation at break by using the following relationship:

Stiffness at break

= (tenacity at break/elongation at break) × 100

The tenacity was expressed as g/den. After conditioning the samples, they were combed and the fiber aggregates of uniform length were taken and weight and length were determined. The tensile strength was determined by means of a Dutrons tensile tester, Brand-20 Kgf capacity.

Water Retention and Rot-Resistance Properties

The ungrafted pulp and grafted pulp samples were subjected to the evaluation of their water-retention and rot-resistance properties as per the standard techniques explained in the discussion.

RESULTS AND DISCUSSION

Graft copolymerization of acrylamide onto chemically modified jute (i.e., the jute pulp both unbleached and bleached instead of using pure raw jute) was done with a view to increase graft percentage and it was found to be correct. The results in Table I indicated that graft percentage increased in pulps because of a decrease in the percentage of lignin content in the pulp that was already reported by Kubota and Ogiwara,[22] where the effect of lignin on grafting of methyl methacrylate on cellulose by ceric ion was studied.

The grafting reaction is initiated by potassium monopersulfate either alone or in the presence of Cu(II)/glycine chelate complex. The enhancement of percentage grafting in the presence of *in situ* developed complex may be attributed to their effectiveness in causing fast decomposition of $KHSO_5$ to form primary radicals ($OH^{\bullet}$, $SO_4^{-\bullet}$, $HSO_3^{\bullet}$, $HSO_4^{\bullet}$) which attack jute pulp to generate the macromolecule radical that initiates grafting. In such a reaction, negligible formation of homopolymer is noticed. The mechanism of grafting is proposed as reported elsewhere.[27]

We, therefore, used the Cu(II)/glycine/$KHSO_5$ complex system in the study of graft copolymerization of acrylamide onto jute pulp, at varying reaction parameters. The optimum condition of grafting with maximum grafting percentage (unbleached 67.4% and bleached 78.9%) is at the concentrations of AM, 0.8 mol dm^{-3}; $KHSO_5$, 32.2 × 10^{-3} mol dm^{-3}; Cu(II)SO_4, 2.0 × 10^{-3} mol dm^{-3}; glycine, 2.0 × 10^{-3} mol dm^{-3}; and jute pulp, 0.15 g at 45°C. Again, it is reported that on increasing the solvent composition of both acetic acid and methanol in the reaction medium, the graft percentage and rate of grafting decrease.

Grafting Mechanism

1. Formation of primary radicals (Initiation)

(a) $$\mathrm{Cu(II)} + \mathrm{glycine} \overset{\beta}{\leftrightharpoons} \mathrm{complex}$$

(b) $$\mathrm{Complex} + HSO_5^- \overset{K_d}{\rightleftharpoons} SO_4^{-\bullet} + H_2O + \mathrm{Cu(I)} - \mathrm{complex}$$

$$\mathrm{Complex} + HSO_5^- \leftrightharpoons {}^{\bullet} \; {}^{\bullet}OH + HSO_4^{\bullet} + \mathrm{Cu(I)} - \mathrm{complex}$$

$$\mathrm{Complex} + HSO_5^- \leftrightharpoons HSO_3^{\bullet} + O_2 + \mathrm{Cu(I)} - \mathrm{complex}$$

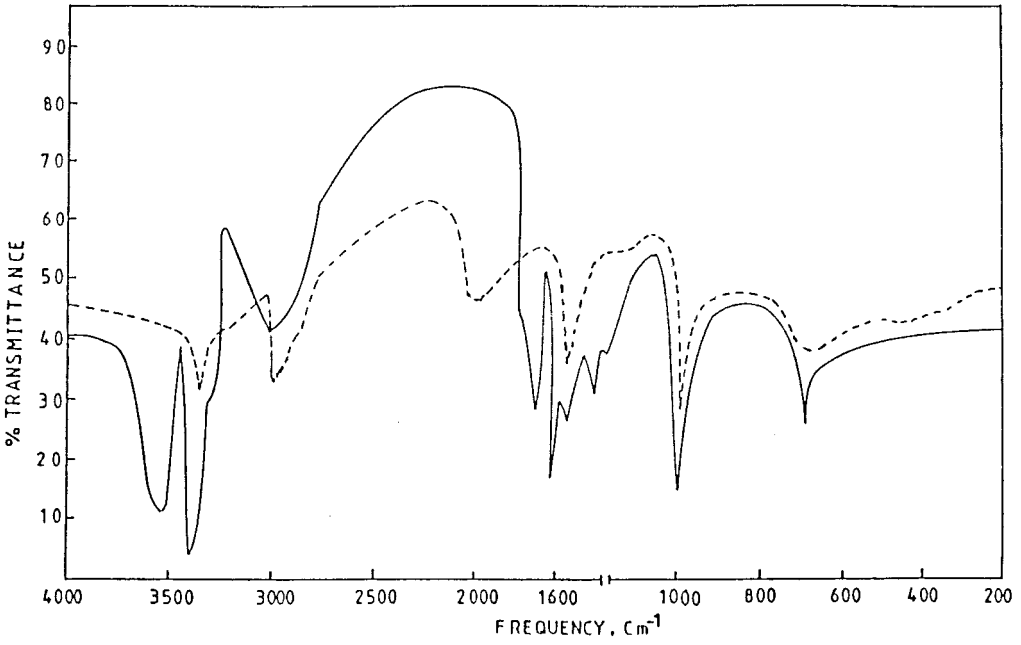

Figure 1 IR spectra of bleached jute pulp (----) and pulp-*g*-PAM (—).

(c) $R^{\bullet} + JH \rightarrow J^{\bullet} + RH (R^{\bullet} \equiv {}^{\bullet}OH, HSO_4^{\bullet}, SO_4^{-\bullet}$ and $HSO_3^{\bullet})$

$$J^{\bullet} + M \xrightarrow{K_i} JM^{\bullet}$$

2. Propagation

$$JM_1^{\bullet} + M \xrightarrow{K_p} JM_2^{\bullet}$$

$$JM_{n-1}^{\bullet} + M \xrightarrow{K_p} JM_n^{\bullet}$$

3. Termination

$$JM_n^{\bullet} + JM_m^{\bullet} \xrightarrow{K_{t1}} \text{graft copolymer}$$

$$JM_n^{\bullet} + \text{Cu(II)} - \text{complex} \xrightarrow{K_{t2}} \text{graft copolymer} + \text{Cu(I)} - \text{complex}$$

$$RM_n^{\bullet} + \text{Cu(II)} \xrightarrow{K_{t3}} \text{Graft copolymer} + \text{Cu(I)} + H^+$$

4. Oxidation

$$J^{\bullet} + HSO_5^- \xrightarrow{K_o} \text{oxidation products}$$

Characterization

Acrylamide-grafted jute pulps were characterized by the following methods.

IR Analysis

IR spectroscopy was a valuable tool of identifying graft copolymerization reaction, which is used to establish the evidence of grafting,[23–25] to ensure complete removal of ungrafted products, and to determine the functional grouping of the grafted sample.

From Figure 1 it was observed that the ungrafted unbleached and bleached pulps similar to parent jute fiber showed the characteristic broad absorption bands at 3400 cm^{-1} for free —OH band of O—H stretching vibration and 1040 cm^{-1}

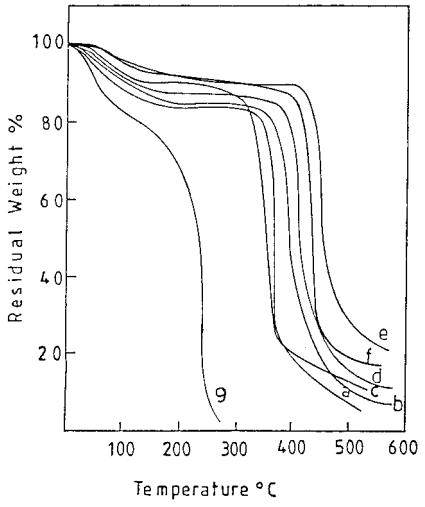

Figure 2 TG curves of (a) raw jute fiber; (b) unbleached pulp; (c) bleached pulp; (d) raw jute-*g*-PAM (42.2%); (e) unbleached pulp-*g*-PAM (67.4%); (f) bleached pulp-*g*-PAM (78.9%); (g) PAM.

for C—O stretching vibration. In addition to that extra peak, asymmetric and symmetric N—H stretching vibrations at 3520 and 3400 cm^{-1}, respectively, were observed in unbleached and bleached-grafted samples. Again, peak at 1690 cm^{-1} is due to >C═O stretching vibration in amide and 705 cm^{-1} for C—N stretching of primary amide, thereby indicating the occurrence of grafting of acrylamide onto both unbleached and bleached jute pulps. There was no significant difference in spectral patterns of unbleached and bleached grafted samples, except a slight difference in lignin absorbance.

Thermal Analysis

The thermal behavior of ungrafted jute pulps and grafted pulps were studied by comparing their primary thermograms (TGA curves). Primary thermograms of parent jute fiber, jute-*g*-PAM, jute unbleached pulp, bleached pulp, unbleached pulp-*g*-PAM, and bleached pulp-*g*-PAM are shown in Figure 2. The temperature of decomposition, T_D, is very much influenced by the percentage of grafting as shown in the case of one category of grafted sample (i.e., unbleached pulp-*g*-PAM sample).

For the above sample, the T_D values of 410°, 452°, 466°, 473°, 486°C for grafting of 30.2, 36.4, 50.8, 61.4, and 67.4%, respectively, indicated that the T_D increases on increasing percentage grafting.

The TGA curves (Fig. 2) of the various samples indicated that the T_D's of unbleached (386°C) and bleached pulps (372°C) are slightly higher than that of parent jute fiber (350°C). However, the T_D values increased significantly in the case of grafted pulps (unbleached-*g*-PAM, 486°C and bleached-*g*-PAM, 453°C), indicating higher thermal stability of the graft copolymers over the base fiber and pulps. Hence, the grafted samples become moderately thermally stable.

Mechanical Properties

Tensile Strength

The strength of the grafted, bleached, unbleached pulps, and the original jute fibers were evaluated

Table II Effect of Graft Percentage on Tensile Properties of Acrylamide-*g*-Jute Pulps

Sample	% Grafting	Elongation at Break (BL %)	Tenacity (gm/den)	Tensile Strength
Raw jute fiber	0	0.63	0.079	36.3
Unbleached pulp-*g*-PAM	0	0.62	0.142	44.5
	30.2	0.58	0.098	49.0
	36.4	0.54	0.125	52.4
	50.8	0.24	0.315	58.3
	61.4	0.20	0.356	61.5
	67.4	0.32	0.398	64.2
Bleached pulp-*g*-PAM	0	0.65	0.107	39.8
	40.4	0.63	0.218	50.7
	49.8	0.58	0.263	52.6
	62.2	0.50	0.340	58.7
	70.5	0.43	0.392	62.2
	78.9	0.27	0.421	64.8

Table III Water Retention of Acrylamide-Grafted Pulps at Various Grafting Percentages

Bleached Pulp-*g*-PAM		Unbleached Pulp-*g*-PAM	
% Grafting	Water Retention (g/g)	% Grafting	Water Retention (g/g)
0	10	0	8
40.4	27	30.2	19
49.8	33	36.4	22
62.2	42	50.8	28
70.5	48	61.4	32
78.9	51	67.4	35

and presented in Table II. It was observed that the tensile strength does not significantly decrease in the case of unbleached and bleached pulps than that of virgin jute fiber. However, in the case of pulp-*g*-PAM samples, the strength increases slightly, which is an added advantage. The disadvantage of the decrease in strength properties of the ungrafted pulps, due to the loss of the binding and strength material, lignin, is overcome by grafting of PAM onto pulps. Further studies showed that the above properties increased with an increase in percentage grafting. Similar effects were observed for elongation and tenacity of grafted and ungrafted pulp samples.

Physical Properties

Water Retention

The water retention properties of dry jute pulp and pulp-*g*-PAM samples were determined by the methods reported by Ranby and Gadda.[26] The results are given in Table III. A prominent increase in water retention is noticed for grafted and ungrafted pulps in comparison to raw jute fibers. This remarkable high water absorption and retention capacity of the grafted pulps opened the door to their use as commercial superabsorbents in diapers and sanitary napkins. Again, the water retention increases on increasing the percentage grafting with the hydrophilic monomer, acrylamide. This property is enhanced by the samples when hydrolyzed with dil. NaOH. This result is in accordance with the result of grafted acrylamide onto cotton–cellulose fiber by Sahoo et al.[27]

Rot Resistance

The rot resistance of the ungrafted and grafted pulps was determined as per Mino et al.[28] Acrylamide-grafted jute pulp did not significantly improve the fabric properties as observed from their rot- and mildew-resistance behavior. The results of a 2 week soil burial test on fabric are recorded in Table IV. The results showed that the ungrafted and grafted jute pulps afforded comparatively little protection to bacterial attack of the pulp. However, the ungrafted pulps showed bet-

Table IV Rot Resistance Values of Unbleached and Bleached Jute Pulps and Their Grafted Samples at Various Grafting Percentages

Sample	% Grafting	Initial Tensile Strength (dyn/cm^2)	Tensile Strength (dyn/cm^2) after 2 Weeks of Burial	% Strength Retain
Raw jute	0	35.3	3.0	8.2
Unbleached pulp-*g*-PAM	0	44.5	4.8	10.7
	30.2	49.0	2.5	5.1
	36.4	52.4	3.4	6.4
	50.8	58.3	3.6	6.2
	61.4	61.5	4.6	7.4
	67.4	64.2	4.7	7.3
Bleached pulp-*g*-PAM	0	39.8	4.6	11.5
	40.4	50.2	2.2	4.3
	49.8	52.8	3.3	6.2
	62.2	58.8	3.8	6.4
	70.5	62.1	4.5	7.2
	78.9	64.8	4.7	7.2

ter rot-resistance behavior than their grafted counterparts.

CONCLUSION

The methods are described in detail and the results are presented which demonstrate the effectiveness of the approach in developing a deeper understanding of chemistry as well as critical thinking skills. The ungrafted bleached pulps exhibited higher grafting percentage over the unbleached pulps, because of low lignin contents as revealed by permanganate number. The grafted pulps exhibited higher thermal stability, water retention capacity, and tensile properties over the ungrafted pulps and raw jute fiber, due to copolymerization of the hydrophilic monomer, acrylamide. However, the rot-resistance studies indicated that because of the chemical modification of raw jute fiber via pulping, bleaching, and grafting, the synthetic samples lose their protection to bacterial attack under soil.

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