CATIONIC DYEABLE ANTIBACTERIAL JUTE OBTAINED THROUGH GRAFTING

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In the current study, jute fabric was grafted with acrylic acid (AA) using potassium persulfate (KPS) as an initiator. The graft polymerization parameters were optimized in terms of temperature, time, initiator and monomer concentrations. The grafted product was characterized using FTIR and TGA and further evaluated for moisture regain and yellowness index properties. The ungrafted and grafted fabrics were then dyed using cationic dyes. In order to get cationic dyed antibacterial jute, the dyed jute was treated with copper sulfate and the effect of the treatment on the obtained shade, fastness and antibacterial activity was studied. Grafted jute showed distinct improvement in colour value and fastness properties. The copper sulfate treatment of dyed jute imparted efficient antibacterial activity to jute against both gram positive and gram negative bacteria with negligible influence on appearance.

Keywords: jute, grafting, dyeing, cationic dyes, Cu salt treatment, antibacterial activity

INTRODUCTION

Renewable resources are gaining increasingimportance in our modern society due to their positive effects on agriculture, environment and economy.[1] Biopolymers are renewable raw materials and are widely accepted because of the limited existing quantities of fossil supplies and the recent environment conservation regulations. In this regard, cellulose rich biomass acquires enormous significance as chemical feedstock, since it consists of cellulose, hemicelluloses and lignin, which are biopolymers containing many functional groups suitable for chemical derivatization.[2]

Known as the 'golden fibre' due to its golden and silky shine, jute is an abundant natural fiber occupying the second place in terms of world production levels of cellulosic fibers. Jute is ligno-cellulosic and is a coarser variety of bast fibre. It has some inherent advantages, namely agro-renewability, biodegradability, good tensile strength and modulus, high moisture regain and good dyebility. Due to its eco-friendly and biodegradable nature, the demand for jute fiber is rising day by day.[3-6]

However, certain inherent defects can also be associated with jute, such as poor antimicrobial properties, loss of strength and yellowing upon exposure to light, as well as poor colour fastness properties.

These defects determine the replacement of jute with synthetic materials. Considering the need to use environment-friendly products, eliminating the inherent defects of jute would bring back into the forefront its use in a number of important textile applications and would thus reduce the dependence on non-biodegradablesynthetic materials. One of the ways of making jute fit for proper use is the modification of jute by graft co-polymerization using synthetic monomers to combine some of the advantages of synthetic products with those of jute.

Graft copolymerization of various vinyl monomers onto cellulose is a process that attempts to combine synthetic polymers with cellulose, to produce a material with the best properties of both. In graft copolymerization, side chain grafts with functional groups are covalently attached to a main chain of a polymer backbone to form a branched copolymer.[7]

By chemical modification of cellulose through graft copolymerization with synthetic monomers many different properties, including water absorbency, elasticity, ion exchange capabilities, thermal resistance and resistance to microbiological attack can be improved.[8]

Researchers studied the effect of jute grade, blending with other fibers, pretreatment regime, enzymatic treatment, as well as type of dye for attaining high performance dyeing with high value-added potential applications. [9]

Ibrahim *et al.* reported the functionalization of jute fibre in order to improve its dyeability and functional properties. [10]

Cationic dyes are known for high tinctorial values and brilliancy of shades. However, cationic dyes have no affinity for cellulosic fibres and they require mordants to dye cotton. They produce attractive, bright and highly intensive coloured effects, but with very low fastness to wet treatments and light.[11]

Even though raw jute shows some dyeability towards cationic dyes, due to the presence of hemicellulose in it, the inferior fastness properties of such dyeing is always a question. Even though a number of attempts to improve the dyeability of jute fibres have been reported,[12-16]studies aiming to improve cationic dyeability and impart antibacterial performance are scarce.

In the current work, the modification of jute has been carried out by graft co-polymerisation using acrylic acid as monomer. The improvement in cationic dyeability of jute on grafting has been explored. The possibility of preparing antibacterial cationic dyed jute by applying copper sulfate has also been studied.

EXPERIMENTAL

Materials

Jute fabric previously scoured and bleached was used as substrate for grafting. Cationic dyes were supplied by Clariant (India) limited. All other chemicals used were of laboratory grade.

Grafting of jute fabric

The grafting reaction was carried out in a three-necked flask provided with nitrogen inlet and thermometer pocket. In a typical reaction, the fabric (of known weight) was placed in a flask containing distilled water maintaining a material to liquor ratio of 1:50. After the desired temperature was reached, the required quantity of potassium persulfate (KPS) initiator (on weight of jute fabric) was added followed by addition of required quantity of acrylic acid (AA) (w/w ratio of jute) 10 min after the addition of initiator. The reaction was continued under nitrogen atmosphere for the desired time with constant stirring. After completion of the reaction, the grafted fabric was then washed with boiling water, to remove the homopolymers of acrylic acid, until constant weight was reached. The graft add-on was calculated using the formula:

$$Graft\ add\ on\ (\%) = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and $W_2$are the weight of ungrafted and grafted fabrics.

Characterization of grafted product

The analysis of jute-graft-AA was done by the methods described below.

FTIR analysis

The FTIR spectra of original and grafted samples were recorded using an FTIR spectrophotometer (Shimadzu 8400s, Japan) using the ATR sampling technique by recording 45 scans in %T mode in the range of 4000-600cm^{-1}.

Thermo gravimetric analysis (TGA)

The thermograms of grafted and ungrafted jute cellulose fabric samples were recorded using aluminum pansin the temperature range 30-500 °C and under inert N_2 atmosphere at a flow rate of 50ml/min (Shimadzu, Japan).

Measurement of textile properties

Moisture regain

The moisture regain was determined by the vacuum dessicator method with sodium nitrite to give 65% RH at 21± 1 °C.[17] The samples were treated with 1%NaOH for 3h and then measured again for moisture regain analysis.

Yellowness index

The samples were evaluated for yellowness by determining the E-313 yellowness index using Spectraflash SF 300 (Datacolor International, U.S.A.).

Dyeing with cationic dyes

The ungrafted and grafted jute fabrics were dyed with cationic dyes, namely Methylene Blue (C.I. Basic Blue 9) and Coacryl Red (C.I. Basic Red 14). The dyebath was set with 2% (owf) acetic acid and dye solution (0.5% owf) maintaining a material to liquor ratio of 1:30 and it was heated upto 90 °Cat a heating rate of 2.5 °C/min. Dyeing was continued at 90 °C for 30 min. The fabric samples were then washed with cold water followed by soaping treatment using Auxipon NP (nonionic soap) at 60 °C for 30 min. Finally, they were given a cold wash.

Simultaneous two bath dyeing and metal treatment

The optimum grafted sample was dyed with cationic dye (Methylene blue) using 0.25% shade, soaped and then treated with 0.5% $CuSO_4$(owf). The fabric was then washed with cold water and dried.

Analysis of dyed fabrics

Colourvalue by reflectance method

The dyed samples were evaluated for the depth of colour by the reflectance method using a 10degree observer. The K/S values were determined using the expression:

$$\frac{K}{S}=\frac{(1-R)^2}{2R}$$

where R is the reflectance at complete opacity; K is the absorption coefficient; S is the scattering coefficient.

Washing fastness (ISO-II)

Evaluation of colour fastness to washing was carried out using ISO II methods.[18]

Rubbing fastness

Evaluation of colour fastness to rubbing (dry and wet) was carried out using a "crock-meter" with 10 strokes of rubbing.

Light fastness

The colour fastness to light was carried out using ISO 105/B02 test methods.

Determination of antimicrobial activities of dyed fabrics

The antibacterial activity of the dyed fabrics was estimated by AATCC Test Method 100-2004.[19]The reduction in number of bacterial colonies formed with respect to the untreated control sample was estimated by using the following equation:

$$R=\frac{100(B-A)}{B}$$

Where R = % reduction in bacterial count; A = the number of bacterial colonies recovered from the inoculated treated test specimen swatches in the jar incubated for 24 h contact period; B = the number of bacterial colonies recovered from the inoculated untreated control test specimen swatches in the jar immediately after inoculation (at "0" contact time).

RESULTS AND DISCUSSION

Evidence of grafting

The jute fabric grafted with acrylic acid was characterized in order to validate grafting. The FTIR spectrum of grafted fabric (Figure 1), when compared with that of the ungrafted fabric, clearly indicated the peak for –COOH group at 1712 cm^{-1}, which is due to the introduction of polyacrylic acid graft chain onto the jute backbone.

Figure 2 shows the thermogram of ungrafted and grafted jute samples. In the initial stage, weight loss values of both samples were of 8.21% and 10.0% at 250 °C, respectively. Between 250 °C to 350 °C, drastic decomposition of the samples resulted in a significant weight loss, which was of 50.71% for ungrafted and 51.07% for grafted jute fabric at 350 °C. However, beyond 350 °C, the loss in weight was slowed down and finally at 450 °C, the weight loss values observed were 92.14% for ungrafted and 79.50% for grafted jute, respectively. This clearly indicates the relatively higher thermal stability of the grafted jute sample, as compared to that of the ungrafted jute. This could be attributed to the formation of a side chain network as a result of grafting of acrylic acid onto the jute backbone, increasing its molecular weight.

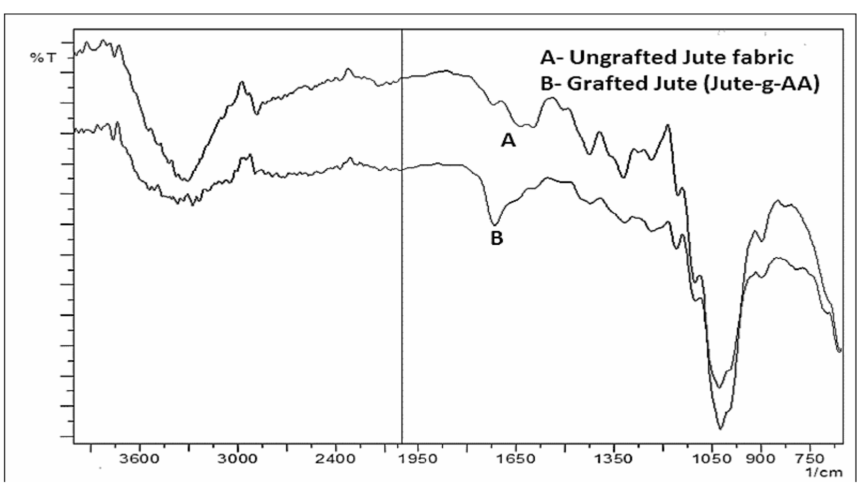

Figure 1: FTIR spectra of ungrafted (A) and grafted jute (B)

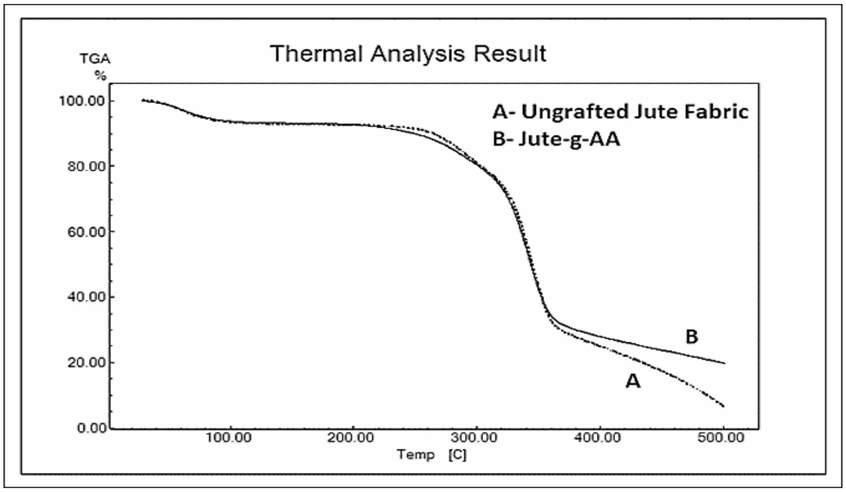

Figure 2: TGA of ungrafted and grafted jute

Optimization of grafting parameters

The effect of various parameters on the graft add-on of acrylic acid onto jute fabric was studied and the results are summarized in Table 1. With an increase in temperature from 60 °C to 70 °C, graft add-on increased, while beyond 70 °C further increase in temperature resulted in a decrease in graft add-on. The increase in graft add-on with temperature is explained by the higher rate of dissociation of initiator, as well as by the diffusion and mobility of monomer from the aqueous phase to the cellulose phase.[2] With an increase in temperature beyond 70 °C, the radical termination reaction might be accelerated, leading to a decrease in graft add-on and an increase in the extent of homopolymerization. This may be possibly due to a recombination of the growing homopolymer chain radicals,whichis possible at higher temperatures.

An increase in graft add-on with grafting time from 1 h to 2 h was observed. It may be attributed to the increase in the number of grafting sites in the initial stages of the reaction due to the higher amount of initiator participating in the formation of reactive sites on the cellulose backbone. However after 2h, there was no significant change in graft add-on.

The increase in the concentration of potassium persulfate from 4% to 5% resulted in increased graft add-on. However, any increase in the concentration beyond 5% resulted in a decrease in graft add-on values. The initial increase in graft add-on with the increase in the concentration of KPS may be due to the increase in the number of radicals generated. It is well known that high initiator concentrations lead to short chain polymers, therefore it can be expected that a higher concentration of KPS might result in decreasing graft add-on.[20]Also higher initiator concentration may also lead to more homopolymer formation, bringing down the concentration of reactive monomer available for grafting.

Graft add-on increased significantly initially with increasing the monomer to fibre ratio from 0.5:1 to 1:1 and then slightly from 1:1 to 1.5:1. This is because of the higher initial availability of monomer for grafting. At higher concentration, homopolymer formation is dominant compared to grafting, causing only a slight increase in graft add-on. However, the efficiency of grafting is decreased. Hence, the 1:1 ratio was found to be optimum for grafting.

Effect of grafting on textile properties of jute

The results in Table 2 indicate the increased moisture regain with an increase in graft add-on, giving an 8.24% increase in moisture regain for the optimum grafted sample (with a graft add-on of 5.88%), when compared with that of the ungrafted sample. This enhancement in moisture regain was due to the introduction of polyacrylic acid in the molecular structure of the cellulose substrate during grafting. The grafting of a hydrophilic monomer like acrylic acid imparts hydrophilicity to the grafted substrates. Since jute is inherently hydrophilic, the extent of hydrophilicity imparted, as indicated by the moisture regain values, was of lower order. The yellowness index was found to be increasing with graft add-on, showing an obvious decrease in whiteness, which may the combined effect of the introduction of the graft chain of polyacrylic acid, ester formation during grafting and the treatment of jute at higher temperature for sufficiently long time.

Table 1
Optimization of grafting parameters

Sr. No.	Monomer:substrate	Initiator concentration (%owf)	Time (h)	Temperature (°C)	Graft add-on (%)
Effect of temperature					
1	1.0 : 1.0	5	2	60	2.34
2	1.0 :1.0	5	2	70	5.88
3	1.0 : 1.0	5	2	80	4.62
Effect of time					
1	1.0 : 1.0	5	1	70	2.68
2	1.0 : 1.0	5	2	70	5.88
3	1.0 :1.0	5	3	70	5.85
4	1.0 : 1.0	5	4	70	5.80
Effect of initiator concentration					
1	1.0 : 1.0	4	2	70	3.28
2	1.0 :1.0	5	2	70	5.88
3	1.0 : 1.0	6	2	70	4.62
Effect of monomer concentration					
1	0.5:1.0	5	2	70	2.48
2	1.0:1.0	5	2	70	5.88
3	1.5:1.0	5	2	70	5.96

Table 2
Effect of grafting on textile properties

Sr. No.	Graft add-on (%)	Moisture regain (%)	Increase in moisture regain over ungrafted (%)	Yellowness index
1	Ungrafted	14.20	0	45.11
2	2.34	14.82	4.04	57.77
3	3.28	15.17	6.80	58.74
4	4.62	15.27	7.56	58.96
5	5.88	15.37	8.24	59.99

Effect of grafting on cationic dyeing of jute

Grafting of jute with acrylic acid is another tool for making cellulose anionic and hence cationic dyeable, as carboxyl groups introduced as a result of grafting act as sites for attachment of cationic dye molecules. The results in Table 3 indicate an increase in colour strength, for both cationic dyes with the increase in graft add-on (%) and hence with the increase in the carboxyl content of grafted jute. With a graft add-on of 5.88%, the increase in colour strength, compared to that of ungrafted jute, was 91.27% for methylene blue and 73.49% for coacryl red C4G. The shades were found to be quite even all along the fabric,which can be an advantage when grafting substrates are in the form of fabric compared to other forms of substrates.

The fastness properties of the dyed samples were also improved for the grafted-dyed jute, as compared to that of ungrafted-dyed jute irrespective of the dye. Cationic dyes are known for inferior fastness properties on cellulose and hence the improvement in the fastness properties for the grafted product may be attributed to the increase in the carboxyl groups, which provide better attachment to the sites for dye molecules and hence offer resistance to removal through washing or rubbing. The improvement in light fastness was due to the larger amount of dye being adsorbed on the fibre, as compared to when the graft copolymer was absent. The dyed jute fabric with optimum graft add-on showed improvement in light fastness by 3 grades and in rubbing fastnessby 1 to 2 grades.

Effect of metal treatment on undyed and dyed grafted jute fabrics

The treatment with copper sulfate was carried out on various jute fabrics for assessing changes in the shade and antibacterial efficacy (the results are summarized in Table 4). The results indicate a substantial change in the colour value of ungrafted jute after the treatment with copper sulphate. However, the change in appearance of methylene blue dyed jute after treatment was minimal. The fastness remained unaffected after the treatment with copper sulfate.

Imparting of antibacterial functionality seemed to be dependent upon the metal treatment along with the attachment of metal ions to substrates, so that they are not removed after washing. The ungrafted-treated jute showed lower bacterial reduction, which may be due to lower adsorption of copper ions in the absence of suitable attachment points on the backbone.

Table 3
Effect of grafting on colour strength (K/S) of cationic dyed jute

Sr. No.	Graft add-on (%)	K/S	Increase in K/S to ungrafted standard (%)	Fastness properties		
				Wash	Rubbing	Light
Dye: Methylene Blue						
1	Ungrafted	27.083	N/A	3	1-2	2
2	2.34	35.672	31.34	4	2-3	4
3	3.28	40.268	48.68	3-4	2-3	4
4	4.62	40.906	51.03	3-4	3	4
5	5.88	51.803	91.27	3-4	3	5
Dye: Coracryl Red C4G Supra						
1	Ungrafted	2.679	N/A	2	1-2	2
2	2.34	3.911	45.98	4	2-3	4
3	3.28	4.469	66.81	4	3	4
4	4.62	4.582	71.03	4	3	4
5	5.88	4.648	73.49	4	3	5

Table 4
Effect of grafting on treatment of jute with copper sulfate

Sr. No.	Sample	K/S	L*	a*	b*
1	Ungrafted	1.5807	69.917	3.917	20.253
2	Undyed grafted treated	1.6346	67.769	-4.632	15.889
3	Dyed grafted untreated	35.134	38.064	57.252	26.814
4	Dyed grafted treated	35.132	46.745	57.252	-3.687

Table 5
Antibacterial activity of $CuSO_4$ treated jute

Sample	Antimicrobial activity (%)	
	S.aureus	*E. coli*
Ungrafted untreated	4.82	5.18
Ungrafted treated	31.53	31.10
Grafted treated	95.90	96.58
Grafted dyed untreated	55.50	57.65
Grafted dyed treated	99.10	99.50

A similar treatment on grafted jute showed efficient bacterial reduction of both *S. aureus* and *E. coli* bacteria. The cationic dyed jute also displayed some antibacterial activity, which was further enhanced after the treatment with copper sulfate. Similar observations were reported by researchers in the case of plasma treated linen fabric and acrylic acid-polyethylene glycol adduct containing cellulosic fabrics.[21,22] The grafted-dyed-treated jute showed the highest bacterial reduction among all the substrates studied, which was of 99.10% for *S. aureus* and 99.50% for *E. coli* bacteria.

CONCLUSION

Jute fabric was successfully grafted with acrylic acid using KPS initiator. The optimum conditions found on the basis of the present work were 70 °C asgrafting temperature, 2 h time; 5% KPS concentration and 1:1 monomer:fibre ratio. The grafted product showed improvement in moisture regain with development of yellowness. The grafted product showed an increase in the colour strength of cationic dyeing with distinct improvement in all fastness properties. The two bath treatment of dyeing and treatment with copper sulfate imparted efficient antibacterial property to the jute fabric.

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