GRAFTING OF BAMBOO RAYON WITH ACRYLIC ACID AND ITS EFFECT ON CATIONIC DYEING

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Bamboo is considered to be an important biopolymer source with useful applications in various fields, including the textile industry. In the present study, the bamboo rayon fabric has been grafted with acrylic acid using potassium persulfate (KPS) as an initiator. The graft copolymerization parameters were optimized in terms of temperature, time, initiator concentration and monomer concentration. The grafted product was characterized by FTIR, TGA and SEM analyses, and was further evaluated as to properties like moisture regain and yellowness index. The ungrafted and grafted fabrics were then dyed using cationic dyes. The colour strength increased with an increase in the carboxyl content of the grafted product. The dyed samples showed a distinct improvement in fastness properties.

Keywords: bamboo rayon, grafting, dyeing, cationic dyes

INTRODUCTION

Renewable resources are of increasing interest in our modern society, due to their positive effects on agriculture, environment and economy.[1] Being renewable raw materials, biopolymers are gaining considerable importance, given the limited quantity of existing fossil supplies and the recent environment conservation regulations. In this context, 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] Bamboo, a lignocellulosic material, is an abundant natural resource in some parts of the world.[3] Belonging to the *Poaceae* grass family, bamboo is a renewable resource capable of producing a much higher amount of biomass per unit area and time, as compared to timber species.[4] It has been reported that pulp obtained from Cizhu bamboo shows 51% cellulose content, which is similar to the yield of hardwoods (42-51%) and slightly higher than that of softwoods (39-43%).[5] Of the regenerated cellulosic fibres, Lyocell (solvent-spun fibre) has the highest tenacity in both dry and wet states, due to a higher degree of crystallinity and molecular orientation, compared to bamboo and viscose rayon fibres. Moreover, as there are a number of voids in the cross section of bamboo and viscose rayon fibres, they have a higher moisture absorption capacity.[6-7]

Graft copolymerization of various vinyl monomers onto cellulose is a process attempting to combine synthetic polymers with cellulose, in order to produce materials presenting 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.[8] By the 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.[9]

Although grafting of vinyl monomers onto cellulose[10-15] and lignocellulosic materials,[8,16-20] using different initiators, has been extensively investigated by researchers, the information concerning grafted bamboo is rather scarce in the literature. Grafting of methyl methacrylate[21-24] and acrylonitrile[2-3,25] on bamboo was earlier studied by researchers. A comparative study of cellulose methyl methacrylate graft copolymer, using different cellulose sources, like cotton, bamboo and viscose rayon, has been also reported.[26] Grafting of bamboo fibre with different acrylates,[27] a mixture of acrylic acid and acrylamide,[28] has been also carried out. Superabsorbent resin was prepared by grafting bamboo pulp with acrylamide.[29]

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 colour effects, but with very low fastness to wet treatments and light.[30] Hence, grafting of cellulose with acrylic acid is already used as a preparatory technique for dyeing[30-33] or printing[30] of cationic dyes on cellulosic substrates.

In the present work, bamboo rayon (regenerated bamboo cellulose) fabric was grafted with acrylic acid using potassium persulfate as an initiator and the parameters of grafting were optimized. The grafted products were characterized and cationic dyeing of bamboo rayon, otherwise impossible without premordanting, was carried out. This was followed by the evaluation of colour strength and fastness properties. Grafting with acrylic acid enabled a multifold increase in colour strength, with improvements in the fastness properties of cationically dyed bamboo rayon.

EXPERIMENTAL

Materials

Bamboo rayon fibres were converted into yarn (30 count). The yarn was knitted to make fabric, which was then scoured and used for grafting. All chemicals used were of a laboratory grade. The cationic dyes used were supplied by Clariant India Ltd.

Methods

Grafting of bamboo rayon 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 the flask containing distilled water, maintaining a material-to-liquor ratio of 1:20. After the desired temperature was reached, the required quantity of potassium persulfate (KPS) initiator (on weight of bamboo rayon) was added, followed by the addition of a required quantity of acrylic acid (AA) (w/w ratio of bamboo rayon) 10 min after the addition of initiator. The reaction was continued under nitrogen atmosphere, for the desired time under constant stirring. After the completion of the reaction, the grafted fabric was 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:

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

where W_1 and W_2 are, respectively, the weight of the ungrafted and that of the grafted fabrics.

Characterization of grafted product

The analysis of AA-grafted bamboo rayon was done by the methods described below.

FTIR Analysis

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

Thermogravimetric Analysis (TGA)

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

Scanning Electron Microscopy (SEM)

The analysis of the morphology of the dried and of the grafted bamboo rayons was carried out using a scanning electron microscope (Jeol JSM 6380LA JEOL, Japan).

Carboxyl content

The carboxyl content was determined by the method reported in the literature.[34]

Measurement of textile properties

Moisture regain

Moisture regain was determined by the vacuum dessicator method with sodium nitrite, to obtain 65% RH at 21±1 °C.[35] The samples were treated with 1% NaOH for 3 h and then the moisture regain was measured again.

Yellowness index

The samples were evaluated as to 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 bamboo rayon fabrics were dyed with cationic dyes, and namely Methylene blue (CI Basic Blue 9) and Rhodamine B (CI Basic Violet 10). The dye bath was prepared with 2% owf acetic acid and 0.5% owf dye solution, maintaining a material-to-liquor ratio of 1:30, heated up to 90 °C with 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 using Auxipon NP (nonionic soap) at 60 °C for 30 min. Finally, the products were cold washed.

Analysis of dyed fabrics

Colour assessment by reflectance method

The dyed samples were evaluated for the depth of colour by the reflectance method using a 10 degree observer. The absorbance of the dyed samples was measured on Spectraflash SF 300 (Datacolor International, U.S.A.) equipped with reflectance accessories. The K/S values were determined using the expression:

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

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

Washing fastness (ISO-II)

The evaluation of colour fastness to washing was carried out using ISO II methods.[36]

Rubbing fastness

The 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 determined by ISO 105/B02 test methods.

RESULTS AND DISCUSSION

Evidence of grafting

The bamboo rayon fabric grafted with acrylic acid has been characterized in order to validate grafting. The FTIR spectrum of the grafted fabric (Figure 1), when compared to that of the ungrafted fabric, clearly indicates the peak for the –COOH group at 1710.74 cm^{-1}, which is due to the introduction of polyacrylic acid graft onto the bamboo rayon backbone.

Figure 2 shows the thermogram of the ungrafted and grafted bamboo rayon samples. In the initial stage, weight loss values of both samples were of 9.5% and 12.0% at 250 °C, respectively. Between 250 and 350 °C, the drastic decomposition of the samples resulted in a significant weight loss – of 59.22% for ungrafted and 56.2% for grafted bamboo rayon fabric at 350 °C. However, beyond 350 °C the weight loss slowed down and, finally, at 450 °C, reached values of 96.81% for ungrafted and 90.13% for grafted bamboo rayon, respectively. This clearly indicates that the grafted sample showed relatively higher thermal stability, as compared to that of the ungrafted bamboo rayon. This could be attributed to the formation of a side chain network as a result of acrylic acid grafting onto the cellulose backbone, which increased molecular weight.

The SEM micrograph of modified bamboo rayon (Fig. 3b) clearly shows a surface deposition, which is absent in the non-modified substrate (Fig. 3a). This further confirms the presence of grafted acrylic acid on the cellulose backbone.

The carboxyl content values (Table 2) of the representative samples indicate an increase in the carboxyl content values after grafting, which further confirms the grafting of acrylic acid onto the bamboo rayon.

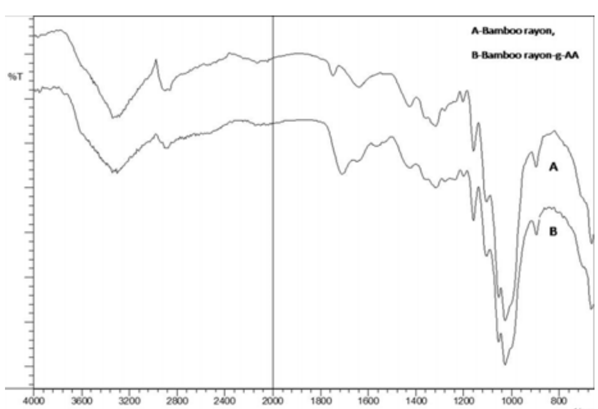


Figure 1: FTIR spectra of ungrafted and grafted bamboo rayon samples

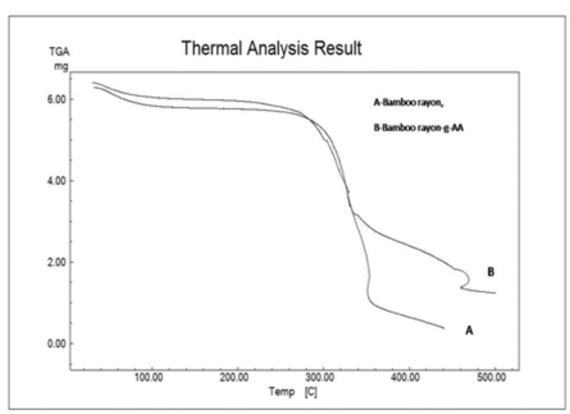
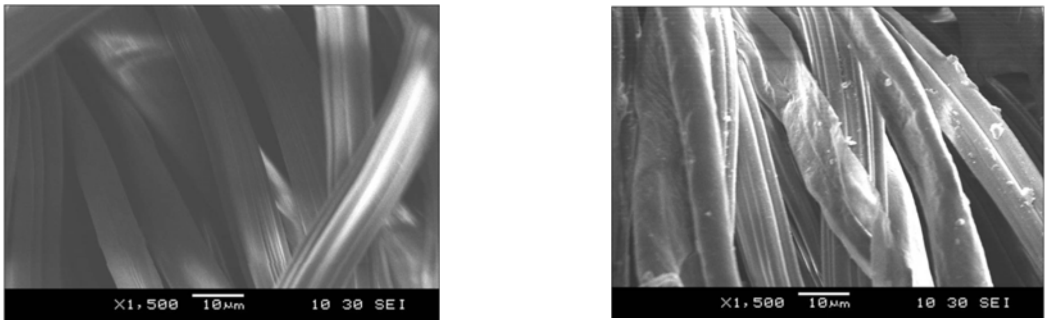


Figure 2: TGA of ungrafted and grafted bamboo rayon samples



(a) (b)

Figure 3: SEM micrographs of ungrafted (a) and of grafted (b) bamboo rayon samples

Optimization of grafting parameters

The effect of various parameters on the graft add-on of acrylic acid onto the bamboo rayon backbone has been summarized in Table 1. With an increase in temperature from 40 °C to 60 °C, the graft add-on increased, while beyond 60 °C, any further increase in temperature resulted in the decrease of graft add-on. The increase in graft add-on with temperature is explained by the higher rate of initiator dissociation, as well as by the diffusion and mobility of the monomer from the aqueous phase to the cellulose phase.[2] With an increase in temperature beyond 60 °C, the radical termination reaction might be accelerated, leading to a decrease in graft add-on and also to an increase in the extent of homopolymerization. This may be possibly due to the recombination of increasing homopolymer chain radicals, which is possible at higher temperatures.

An increase in graft add-on with grafting time ranging from 1 to 3 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 3 h, there was no further significant increase in graft add-on.

The results listed in Table 1 indicate an increase in graft add-on with the increase in potassium persulfate concentration, which may be due to the increase in the number of radicals generated. A further increase in initiator concentration decreased graft add-on possibly due to homopolymer formation, which occurred simultaneously, causes a reduction in the concentration of available monomer for grafting. 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 a decreasing graft add-on.[10]

Table 1
Effect of different parameters on grafting

Sr. No.	Monomer:Substrate (W:W)	Temperature (°C)	Time (h)	Initiator concentration (%)	Graft add-on (%)
Effect of temperature					
A	1:1	40	3	1.5	2.13
B	1:1	50	3	1.5	7.93
C	1:1	60	3	1.5	14.85
D	1:1	70	3	1.5	11.64
E	1:1	80	3	1.5	11.10
Effect of time					
A	1:1	60	1	1.5	8.12
B	1:1	60	2	1.5	11.23
C	1:1	60	3	1.5	14.85
D	1:1	60	4	1.5	14.92
Effect of initiator					
A	1:1	60	3	0.5	5.26
B	1:1	60	3	1.0	11.24
C	1:1	60	3	1.5	14.85

D	1:1	60	3	2.0	12.81
E	1:1	60	3	2.5	9.89
Effect of monomer ratio					
A	0.5:1	60	3	1.5	10.52
B	1:1	60	3	1.5	14.85
C	2:1	60	3	1.5	14.96

Table 2
Effect of grafting on textile properties

Sr. No.	Graft add-on (%)	Carboxyl content (meq/100 g)	Moisture regain (%)	Increase in moisture regain over control (%)	Yellowness index
1	0.0	4.0	11.11 (*11.2)	0.0 (*0.81)	15.58
2	2.13	25.2	11.30 (*12.03)	1.71 (*8.28)	17.23
3	7.93	84.96	12.64 (*15.5)	13.77 (*39.51)	19.04
4	14.85	140.2	13.51 (*18.7)	21.60 (*68.32)	25.45
5	11.64	129.5	13.12 (*17.6)	18.09 (*58.42)	23.49
6	11.10	126.64	12.95 (*17.3)	16.56 (*55.72)	22.31

*Represents moisture regain values of caustically treated products

Graft add-on was initially found to be increasing significantly with increasing the 0.5:1 monomer-to-fibre ratio to 1:1, and then from 1:1 to 2:1. This is explained by the initially higher availability of the monomer for grafting, while at a higher concentration, the homopolymer formation is dominant compared to grafting, causing only a slight increase in graft add-on. However, the efficiency of grafting is decreased. Hence, a 1:1 ratio was found to be the optimum one for grafting.

Effect of grafting on textile properties of bamboo rayon

The results in Table 2 indicate that the moisture regain increased with the increase in graft add-on, determining a 21.6% increase in moisture regain for the optimum grafted sample, compared to that of the ungrafted sample. This enhancement in moisture regain was due to the introduction of polyacrylic acid into the molecular structure of the cellulose substrate during grafting. The carboxyl content was also increased with the increase in graft add-on, resulting in an increased hydrophillicity of the grafted sample. The moisture regain of the grafted product was further increased after the treatment with sodium hydroxide, which formed a corresponding salt, showing a 68.32% increase for the sample with the optimum graft add-on, compared to that of the ungrafted sample. The sodium carboxylate group had a much higher moisture absorption capacity than the protonated carboxylic group,[10] hence an enhancement has been recorded. The yellowness index was found to be increasing with graft add-on, showing an obvious decrease in whiteness, which may be due to the increase in the carboxyl content of the product.

Effect of grafting on cationic dyeing of bamboo rayon

Cationic dyeing of cellulose is generally done by premordanting it with tannic acid, as cellulose lacks the groups required for the attachment of cationic dye molecules. Grafting of cellulose with acrylic acid is another technique for making cellulose anionic and, hence, cationic dyeable, as the carboxyl groups introduced as a result of grafting act as sites for the attachment of cationic dye molecules. The results in Table 3 indicate an increase in colour strength, for both dyes, found for increasing graft add-on and carboxyl content of the grafted bamboo rayon. With a graft add-on of 14.85%, the increase in colour strength, compared to that of ungrafted bamboo rayon, was of 659.96% for Methylene blue, and of 828.98% for Rhodamine B dyes. The shades were found to be even along the fabric, which may be an additional advantage of grafting fabric substrates, compared to other types of substrates.

The fastness properties of the dyed samples were also found to improve for both dyes. Cationic dyes are known for inferior fastness properties on cellulose; hence the improvement in fastness properties of the grafted product may be attributed to the increase in the content of carboxyl groups, which provides a better attachment of dye molecules to the sites, offering resistance against removal through washing or rubbing. The improvement in light fastness is due to a larger amount of dye being adsorbed onto the fibre, as compared to the experiment with no graft copolymer. The samples with the optimum graft add-on showed a 3 grade improvement in light fastness and a 1-2 grade improvement in rubbing fastness.

Table 3
Effect of grafting on dyeing properties

Sr. No.	Graft add-on (%)	K/S	Washing fastness		Rubbing fastness		Light fastness
			C*	S*	Dry	Wet	
Dye used – Methylene Blue, 0.5% shade							
1	0.0	2.28	2	1-2	2	2	1
2	2.13	3.90	2-3	2	2-3	2	2
3	7.93	5.86	3	3	2-3	2-3	3
4	14.85	17.36	4	4	3-4	3	4
5	11.64	11.16	4	3-4	3	3	3
6	11.10	10.33	4	3-4	3	3	3
Dye used – Rhodamine B, 0.5% shade							
1	0.0	2.10	2-3	1-2	2	1-2	1
2	2.13	4.31	2-3	2	2-3	2	3
3	7.93	10.58	3	2-3	2-3	2-3	3
4	14.85	19.51	4	3-4	3-4	3	4
5	11.64	17.82	4	3-4	3	2-3	4
6	11.10	14.82	4	3-4	3	2-3	3

*C – change in shade; S – staining

CONCLUSIONS

Bamboo rayon fabric has been successfully grafted with acrylic acid using a KPS initiator. The optimum conditions worked out on the basis of the present work are the following: grafting temperature – 60 °C, grafting time – 3 h, KPS concentration – 1.5%, monomer:fibre ratio – 1:1. The grafted product showed an improvement in moisture regain, which was further enhanced especially when the samples were treated with NaOH after grafting. Therefore, better comfort properties can be expected for such fabrics. The grafted product showed a multifold increase in the colour strength of cationic dyeing, with a distinct improvement in all fastness properties.

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