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Antibacterial and acid and cationic dyeable bamboo cellulose (rayon) fabric on grafting

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ABSTRACT

Bamboo is considered to be important biopolymer with useful applications in various fields including textiles. In the current study bamboo rayon fabric was grafted with a mixture of acrylic acid and acrylamide using potassium persulfate (KPS) as an initiator. The graft copolymerization parameters were optimized in terms of acrylic acid to acrylamide ratio, temperature, time, initiator concentration and monomer concentration. The grafted product was characterized using FTIR, TGA and SEM and further evaluated for properties like moisture regain and yellowness index. The ungrafted and grafted fabrics were then dyed using cationic and acid dyes. The grafted material showed improved dyeability towards both acid and cationic dyes with improvement in fastness properties. Ag^+ ions adsorbed on grafted fabric, through treatment with $AgNO_3$, were reduced into $Ag^{(0)}$ nanoparticles. Such fabric showed excellent antibacterial properties against both gram positive and gram-negative bacteria with durability of 50 washes.

1. Introduction

Renewable resources are of importance in our modern society because of their positive effects on agriculture, environment and economy (Kumar & Singh, 2008). Biopolymers being renewable raw materials, are gaining considerable importance 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 to chemical derivatization (Khullar, Varshney, Naithani, & Soni, 2008). Bamboo, a lignocellulosic material, is an abundant natural resource in some parts of the world (Lin, Wu, Tan, & Tai, 1982). Bamboo belonging to the grass family Poaceae is an abundant renewable natural resource capable of production of maximum biomass per unit area and time as compared to counterpart timber species (Sharma, Varshney, Chauhan, Naithani, & Soni, 2009).

Graft copolymerization of various vinyl monomers onto cellulose is a process in which attempts have been made to combine synthetic polymers with cellulose, to produce material with 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 branched copolymer (Zheng et al., 2010). 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 (Mcdowall, Gupta, & Stannett, 1984). Grafting of polymers by mixtures of vinyl monomers is important since different types of polymer chains containing various functional groups can be introduced into the polymer structure. The synergistic effect during graft copolymerization of mixed vinyl monomers is very important, since it varies from one mixture to another and determines the extent of grafting yield from each feed monomer (El-Salmawi, El-Naggar, Said, & Zahran, 1997). Graft copolymerization of binary mixtures of vinyl monomers onto different polymeric materials has been reported in the literature (Celik & Sacak, 1996; Coskun, Sacak, & Karakisla, 2005; El-Salmawi et al., 1997; Hegazy, El-Gammal, Khalil, & Mabrouk, 2006; Lokhande & Teli, 1984; Singha & Rana, 2012). Although the grafting of vinyl monomers onto cellulose (Kumar, Naithani, & Pandey, 2011; Littunen et al., 2011; Liu & Sun, 2008; Mondal, Uraki, Ubukata, & Itoyama, 2008) and lignocellulosic materials (Hsu & Pan, 2007; Zheng et al., 2010) using different initiators has been extensively investigated by researchers, information concerning grafted bamboo is rather scarce in the literature. Some information regarding grafting of bamboo is available in the literatures (Khullar et al., 2008; Lin, Lin, & Hsu, 1980; Lin, Lin, & Hu, 1981; Lin et al., 1982; Liu, Wu, & Chen, 2007; Sun, Wang, Huang, Xu, & Ren, 2006; Wan et al., 2011).

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

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attractive, bright and highly intensive colored effects but with very low fastness to wet treatments and light (El-Zairy, 1990). Hence grafting of cellulose with acrylic acid is already used as a tool for dyeing (Ghosh & Das, 1998; Ghosh & Das, 2000; Hebeish, Refai, Zahran, & Ali, 1996) or printing (El-Zairy, 1990) of cationic dyes on cellulosic substrates. Grafting of bamboo rayon with acrylic acid and it's cationic dyeability is earlier reported from our laboratory (Teli & Sheikh, in press). Normally acid dyes do not dye cellulose and hence by grafting bamboo rayon with acrylamide, such a possibility can be explored. Such grafted material can serve as a best platform for the attachment of silver nanoparticles to impart durable and broad spectrum antibacterial properties.

In the current work, bamboo rayon (regenerated bamboo cellulose) fabric was grafted with binary mixture of acrylic acid and acrylamide using potassium persulfate as an initiator and the parameters of grafting were optimized. The grafted products were characterized and dyeing behavior of grafted bamboo rayon towards cationic and acid dyes was studied. The immobilization of silver nanoparticles on grafted bamboo rayon was also attempted and the modified material was tested for its application in antibacterial products.

2. Materials and methods

2.1. Materials

Bamboo rayon fibres were converted into yarn (30 count). The yarn was knitted to make fabric (single jersey) which was scoured and used for grafting. All chemicals used were of laboratory grade. Cationic dyes used were supplied by Clariant India Ltd. Acid dyes used were supplied by Amritlal Dyes India Ltd.

2.2. Methods

2.2.1. 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 flask containing distilled water maintaining material to liquor ratio 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 addition of required quantity of monomers (w/w ratio of bamboo rayon) after 10 min of addition of initiator. The reaction was continued under nitrogen atmosphere for the desired time with constant stirring. After completion of reaction, the grafted fabric was then washed with hot water several times, to remove the homopolymers, till the constant weight was reached. The graft add-on was calculated using the formulae

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

$$\text{Graft efficiency}\quad(\%) = \frac{W_2 - W_1}{W_3} \times 100$$

where W_1, W_2 and W_3 were the weight of ungrafted fabric, grafted fabric and monomer taken initially for grafting respectively. Characterization of grafted product

Analysis of grafted bamboo rayon was done by the following methods.

2.2.2. FTIR analysis

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

2.2.2.1. Thermo gravimetric analysis (TGA). The thermograms of grafted and ungrafted bamboo rayon fabric sample were recorded using aluminum pan between temperature range 30–500 °C and under inert atmosphere of N_2 at a flow rate of 50 ml/min (Shimadzu, Japan).

2.2.2.2. Scanning electron microscopy (SEM). Analysis of the morphology of dried bamboo rayon and grafted bamboo rayon was carried out using scanning electron microscope (FEI Quanta 200, Netherlands).

2.2.3. Measurement of textile properties

2.2.3.1. Moisture regain. The moisture regain was determined by the vacuum dessicator method with sodium nitrite to give 65% RH at 21 ± 1 °C (Hebeish et al., 1983). The samples were treated with 1% NaOH for 3 h and again measured for moisture regain analysis.

2.2.3.2. Yellowness index. Samples were evaluated for yellowness by determining the E-313 yellowness index using Spectraflash SF 300 (Datacolor International, USA).

2.2.4. Dyeing with cationic dyes

The ungrafted and grafted bamboo rayon fabrics were dyed with cationic dyes namely Methylene Blue (C.I. Basic Blue 9) and Rhodamine B (C I Basic Violet 10). The dyebath was set with acetic acid (2% on weight of fabric) and dye solution (0.5% on weight of fabric) maintaining material to liquor ratio as 1:30 (pH 4.2 ± 0.05) and it was 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 treatment using Auxipon NP (nonionic soap) at 60 °C for 30 min. Finally they were given cold wash.

2.2.5. Dyeing with acid dyes

The ungrafted and grafted bamboo rayon fabrics were dyed with acid dyes namely Acid brill. Green VS conc. supra (C.I.Acid Green 16) and Acid mill Navy blue RNX (C I Acid Blue 13). The liquor was made up with ammonium sulfate 2% on weight of fabric (pH 6.75 ± 0.05). The fabric was entered at 40 °C and run continuously as the liquor was raised to boil over a period of 45 min. Dyeing was continued for 45 min at boil. The fabric samples were then washed with cold water followed by soaping treatment using Auxipon NP (nonionic soap) at 60 °C for 20 min. Finally samples were washed with cold water.

2.2.6. Analysis of dyed fabrics

2.2.6.1. Color value by reflectance method. The dyed samples were evaluated for the depth of color by reflectance method using 10° observer. The absorbance of the dyed samples was measured on Spectraflash SF 300 (Datacolor International, USA) equipped with reflectance accessories. The *K*/*S* values were determined using expression:

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

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

2.2.6.2. Washing fastness (ISO-II). Evaluation of color fastness to washing was carried out using ISO II methods (Trotmann, 1984).

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

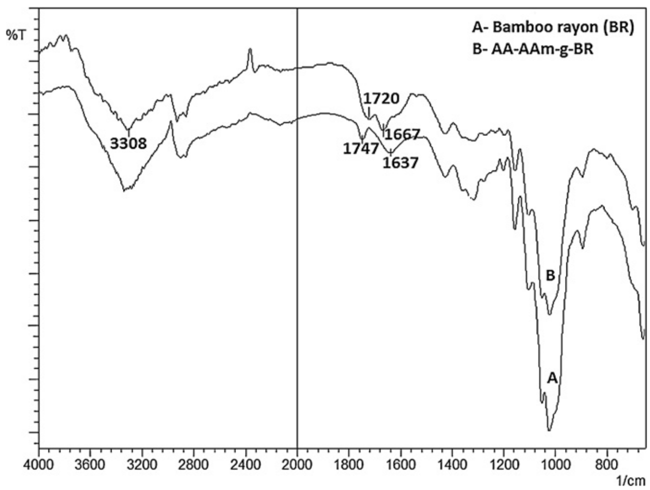

Fig. 1. FTIR spectra of ungrafted and grafted bamboo rayon.

2.2.6.4. Light fastness. The color fastness to light was carried out using ISO 105/B02 test methods.

2.2.7. Preparation of nano-Ag loaded grafted bamboo rayon fabric

A dry preweighed piece of grafted undyed fabric (AA-AAm-g-BR) was equilibrated in distilled water for 2 h. Thereafter the swollen fabric was put in an aqueous solution of $AgNO_3$, prepared by dissolving $AgNO_3$ (0.25% on weight of fabric) in double distilled water, maintaining material to liquor ratio 1:30 for 2 h. The Ag ions present in the fabric were reduced to Ag nanoparticles by putting the fabric in 0.66 mM sodium borohydride solution at 30 °C for 24 h. The resulting dark brown color of the grafted fabric indicated the formation of Ag nanoparticles within the polymer network part of the grafted fabric. Finally the fabric was rinsed with distilled water for 2 min and put in dust free chamber at 40 °C until it gained constant weight (Gupta, Bajpai, & Bajpai, 2008). The silver nanoparticle containing grafted bamboo rayon was designated as nanoAg.AA-AAm-g-BR.

2.2.8. Antibacterial testing

The antibacterial activity of the treated fabrics was estimated by AATCC Test Method 100-2004 (AATCC technical manual, 2007).

3. Results and discussion

3.1. Evidence of grafting

The bamboo rayon fabric grafted with mixture of monomers was characterized in order to validate grafting. The FTIR spectrum of grafted fabric (refer Fig. 1) when compared with that of the ungrafted fabric clearly indicated the peaks at 1720 cm^{-1} and 3308 cm^{-1} which are due to introduction of —COOH and $—NH_2$ group which is due to introduction of graft side chains on to bamboo rayon backbone.

Fig. 2 shows the thermogram of ungrafted and optimum grafted bamboo rayon samples. In the initial stage weight loss values of both samples were 9.5% and 10.45% at 250 °C, respectively. Between 250 °C and 350 °C, the drastic decomposition of the samples resulted in to significant weight loss which was 59.22% for ungrafted and 34.98% for grafted bamboo rayon fabric at 350 °C and finally at 450 °C, weight loss values observed were 96.81% for ungrafted and 80.5% for grafted bamboo rayon, respectively. This clearly indicates that the grafted sample showed relatively higher thermal stability as compared to that of ungrafted bamboo rayon. This could be attributed to the formation of side chain network as a result of grafting mixture of monomers onto cellulose backbone increasing molecular weight.

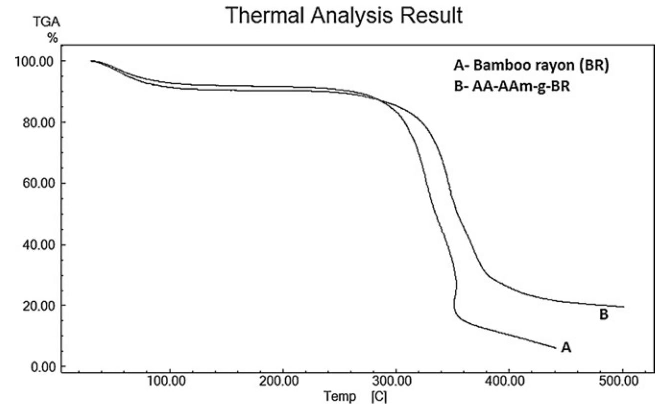

Fig. 2. TGA of ungrafted and grafted bamboo rayon.

SEM micrograph (refer Fig. 3) of modified bamboo rayon clearly shows a surface deposition, which is absent in unmodified substrate. This further confirms the presence of grafted acrylic acid and acrylamide grafted chains on cellulose backbone.

3.2. Optimization of grafting parameters

The effect of various parameters on graft add-on of monomers onto bamboo rayon backbone has been summarized in Table 1. The results in Table 1 clearly indicate the enhanced graft add-on when using binary mixture of acrylic acid (AA) and acrylamide (AAm) as compared to individual monomers keeping the total monomer available constant (1:0.5 ratio of fibre to monomer). The graft add-on increased as acrylic acid was gradually replaced by acrylamide in the blend.

During the grafting of AAm–AA binary mixtures onto bamboo rayon fabric, the synergistic influence has been witnessed giving enhanced grafting. Obviously, it indicates that the rate of grafting is enhanced at the expense of the rate and the extent of homopolymer formation, resulting in the increase in the efficiency of grafting. This also implies that AAm and AA monomer molecules are present in solution with some kind of association between the two, which increases or decreases depending upon their relative proportion in the bath. Obviously, it is maximum, when they are present in 50:50 ratio. It is, therefore, possible that the AAm and AA monomer molecules form a labile complex, and the extent of its formation will be the highest, when the monomers are present in equal proportion. The complex formation seems to have considerable influence in changing the rates of reaction during the grafting process: (i) due to the complex formation mobility of the reacting species in the solution is reduced, thereby retarding the rate of homopolymerization; (ii) when one monomer molecule diffuses inside the fiber structure, it automatically carries another monomer molecule present in the complex, thus increasing the monomer concentration in the fibre phase-a very favorable situation for higher graft-copolymer formation; (iii) when the monomer molecule reacts with the free radical on the backbone of the cellulose, the chain propagation is enhanced due to the complex, and, hence, a higher amount of monomer molecules is utilized resulting in the synergistic influence. Similar contentions have been supported in the literature on grafting studies with reference to polyester and lignocellulosic substrates, respectively (Lokhande & Teli, 1984; Teli & Sheikh, 2011).

With increase in temperature from 40 °C to 65 °C, graft add-on increased while beyond 65 °C, further increase in temperature resulted in decrease in graft add-on. The increase in graft add-on

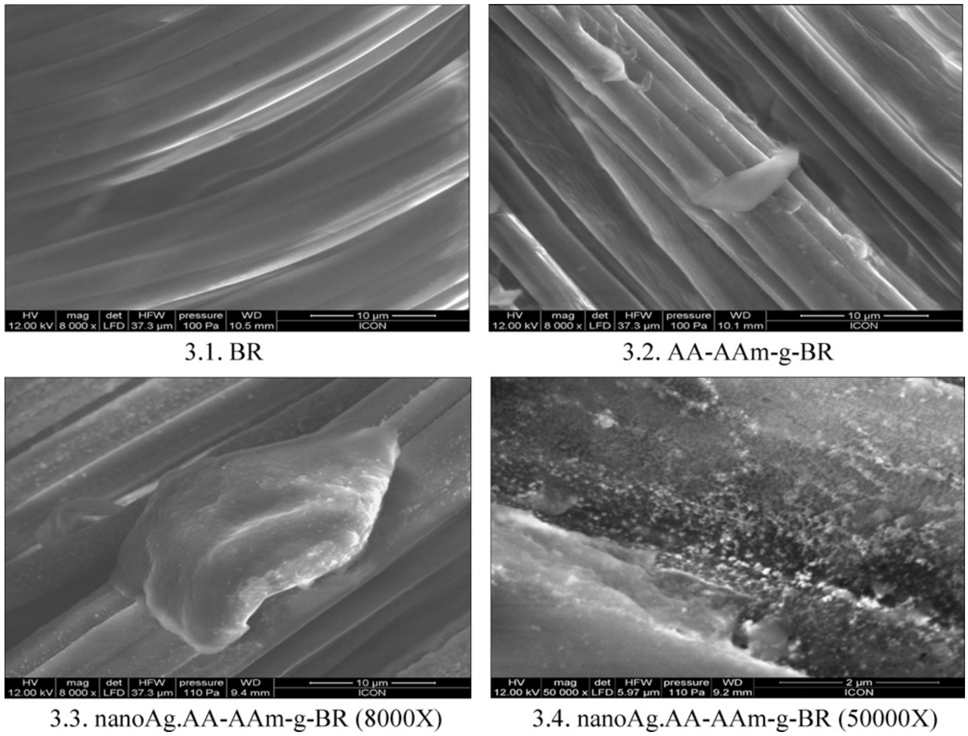

Fig. 3. SEM photographs of ungrafted (BR), grafted (AA-AAm-g-BR) and silver nanoparticles containing grafted bamboo rayon (nanoAg.AA-AAm-g-BR).

with temperature is because of higher rate of dissociation of initiator as well as the diffusion and mobility of monomer from aqueous phase to cellulose phase (Khullar et al., 2008). With increase in temperature beyond 65 °C, the radical termination reaction might be accelerated, leading to decrease in graft add-on.

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

Results in Table 1 indicate the increase in graft add-on with increase in potassium persulfate concentration which may be due to increase in the number of radicals generated. A further increase in initiator concentration decreased the graft add-on possibly due to homopolymer formation which occurs simultaneously, causing

Table 1
Effect of different parameters on graft properties.

Sr. No.	AA:AAm (w/w)	Monomer:substrate (w/w)	Temp. (°C)	Time (h)	Initiator conc. (%)	Graft add-on[a] (%)	Graft efficiency[a] (%)
1. Effect of blend composition							
A	1:0	0.5:1	65	2.0	2.0	14.55	29.1
B	0.75:0.25	0.5:1	65	2.0	2.0	18.32	36.64
C	0.5:0.5	0.5:1	65	2.0	2.0	25.05	50.1
D	0.25:0.75	0.5:1	65	2.0	2.0	22.1	44.2
E	0:1	0.5:1	65	2.0	2.0	16.08	32.16
2. Effect of temperature							
A	0.5:0.5	0.5:1	40	2.0	2.0	7.55	15.1
B	0.5:0.5	0.5:1	50	2.0	2.0	12.89	25.78
C	0.5:0.5	0.5:1	60	2.0	2.0	22.74	45.48
D	0.5:0.5	0.5:1	65	2.0	2.0	25.05	50.1
E	0.5:0.5	0.5:1	70	2.0	2.0	21.82	43.64
3. Effect of time							
A	0.5:0.5	0.5:1	65	1.0	2.0	15.12	30.24
B	0.5:0.5	0.5:1	65	2.0	2.0	25.05	50.1
C	0.5:0.5	0.5:1	65	3.0	2.0	25.10	50.2
D	0.5:0.5	0.5:1	65	4.0	2.0	25.23	50.46
4. Effect of initiator							
A	0.5:0.5	0.5:1	65	2.0	0.5	8.06	16.16
B	0.5:0.5	0.5:1	65	2.0	1.0	15.16	30.32
C	0.5:0.5	0.5:1	65	2.0	1.5	22.20	44.4
D	0.5:0.5	0.5:1	65	2.0	2.0	25.05	50.1
E	0.5:0.5	0.5:1	65	2.0	2.5	20.68	41.36
5. Effect of monomer ratio							
A	0.5:0.5	0.25:1	65	2.0	2.0	14.51	58.04
B	0.5:0.5	0.5:1	65	2.0	2.0	25.05	50.1
C	0.5:0.5	0.75:1	65	2.0	2.0	25.15	33.53

[a] Represents average value of 3 determinations, standard deviation (%) range ±0.98–1.4.

Table 2
Effect of grating on textile properties.

Sr. No.	Graft add-on (%)	Moisture regain[a] (%)	Increase in Moisture regain over control (%)	Yellowness index[b]
1	0.0	11.11 (11.2)[c]	0 (0.81)[c]	15.68
2	7.55	13.10 (17.43)[c]	17.91 (56.88)[c]	18.38
3	12.89	14.82 (19.5)[c]	33.39 (75.51)[c]	18.72
4	21.82	16.21 (19.8)[c]	45.90 (78.21)[c]	19.47
5	22.74	16.82 (20.1)[c]	51.39 (80.92)[c]	21.54
6	25.05	17.10 (20.53)[c]	53.91 (84.78)[c]	21.95

[a] Represents average value of 3 determinations, standard deviation (%) range ±0.4–0.99.
[b] Represents average value of 3 determinations, standard deviation (%) range ±0.46–1.01.
[c] Represents moisture regain values of caustic treated products.

Table 3
Effect of grafting on cationic dyeability of bamboo rayon.

Sr. no.	Graft add-on (%)	*K*/*S*[a]	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	7.55	5.94	3	3	2–3	2–3	3
3	12.89	7.77	3–4	3	3	2–3	3
4	21.52	17.45	4	4	3–4	3	5
5	22.74	17.61	4	4	3–4	3	5
6	25.05	17.71	4	4	3–4	3	5
Dye used – Rhodamine B, 0.5% shade							
1	0.0	2.10	2–3	1–2	2	1–2	1
2	7.55	10.15	4	3–4	3	3	3
3	12.89	11.11	4	3–4	3	3	4
4	21.52	20.19	4	4	4	3	5
5	22.74	21.64	4	4	4	3–4	5
6	25.05	22.71	4	4	4	3–4	5

C* – change in shade; S* – staining.
[a] Represents average value of 3 determinations, standard deviation (%) range ±0.9–1.44.

reduction in 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 decreasing graft add-on (Mondal et al., 2008).

The graft add-on was found to be increasing significantly initially with increasing monomer to fibre ratio 0.25:1 to 0.5:1 and then slightly from 0.5:1 to 0.75:1. This is because of more availability of monomer for grafting initially, while at higher concentration, the homopolymer formation is dominant compared to grafting causing only slight increase in graft add-on. However efficiency of grafting decreased for optimum graft add-on. Hence 0.5:1 ratio was found to be optimum for grafting.

3.3. Effect of grafting on textile properties of bamboo rayon

Results in Table 2 indicate that the moisture regain increased with increase in graft add-on giving 53.91% increase in moisture regain for optimum grafted sample (graft add-on 25.05%) when compared with that of ungrafted sample. This enhancement in moisture regain was due to the introduction of hydrophilic copolymers of acrylic acid and acrylamide in molecular structure of cellulose substrate during grafting. The moisture regain of grafted product was further increased after treatment with sodium hydroxide showing 84.78% increase for sample with optimum graft add-on (25.05%) over that of ungrafted sample. This may be attributed to conversion of $-CONH_2$ groups to $-COOH$ and $-COONa$ groups after saponification. The absorbency behavior may be interpreted by postulating that the collaborative absorbent effect of–$CONH_2$, $-COONa$, and $-COOH$ groups is superior to that of single $-CO\ NH_2$, $-COONa$, and $-COOH$ groups (Wu, Wei, Lin, & Lin, 2003).

The yellowness index was found to be increasing with graft add-on showing obvious decrease in whiteness, which may be due to increase in grafted copolymer content of the product, which covers the surface of the fabric to certain extent.

3.4. Effect of grafting on dyeing properties of bamboo rayon

Results in Table 3 indicate the increase in color strength, for both the cationic dyes, was found with increase in graft add-on. With graft add-on of 25.05%, the increase in color strength, compared to that of ungrafted bamboo rayon, was 676.75% for Methylene Blue and 981.43% for Rhodamine B dyes.

It is to be noted that the ungrafted bamboo rayon gave faint coloration (very low *K*/*S* values), since the rayon may have hardly few $-COOH$ groups and whatever cationic coloration was possible, may be attributed to accessibility of the rayon to hold the dye with Vander walls forces. However, the grafted samples showed enhanced dyeing. This is clearly due to electrostatic bonding between dye cations and anionic sites in bamboo rayon containing acrylic acid grafts.

The fastness properties of the dyed samples were also found to be improved for both the dyes. Generally improvement in fastness properties for grafted product may be attributed to stronger salt linkages existing between carboxyl groups of acrylic acid grafts and dye cations offering resistance to removal in washing or rubbing. The fastness of the grade 4 thus clearly indicates very good shades with highly improved depths. Improvement in light fastness is due to higher amount of dye being adsorbed on the modified fibre as compared to that on ungrafted. The samples with optimum graft add-on (25.05%) showed 2–4 grade improvement in light fastness and 1–2 grade improvement in rubbing fastness.

Results in Table 4 indicate the increase in color depth (*K*/*S* values), for both the acid dyes with increase in graft add-on of modified bamboo rayon. With graft add-on of 25.05%, the increase in color depth was 111.35% for Acid green 16 and 120.61% for Acid blue 13,

Table 4
Effect of grafting on acid dyeability of bamboo rayon.

Sr. no.	Graft add-on (%)	*K/S*[a]	Washing fastness		Rubbing fastness		Light fastness
			C*	S*	Dry	Wet	
Dye used – Acid brill. Green VS conc. Supra, 0.5% shade							
1	0.0	0.208	2	3	2	2	3
2	7.55	0.3097	3	3–4	3–4	3–4	4
3	12.89	0.3459	3	4	4	3–4	4
4	21.52	0.3849	3	4	4	3–4	4
5	22.74	0.4144	3–4	4	4	3–4	4
6	25.05	0.4396	3–4	4	4	3–4	5
Dye used – Acid mill Navy blue RNX, 0.5% shade							
1	0.0	0.718	2	3	2–3	2	2
2	7.55	0.9408	3–4	3	3–4	3	3
3	12.89	0.9664	3–4	3	3–4	3	4
4	21.52	1.0259	3–4	3	3–4	3	4
5	22.74	1.2767	4	3–4	4	3–4	4
6	25.05	1.584	4	4	4	3–4	5

C* – change in shade; S* – staining.
[a] Represents average value of 3 determinations, standard deviation (%) range ±1.19–1.47.

as compared to that of ungrafted bamboo rayon. The fastness properties of the dyed samples were also found to be improved for both the dyes.

The initial dyeability seen in case of ungrafted bamboo rayon is due to H-bonding and Vander walls forces, as a result of accessibility of the dye in the fibre. However, enhancement in dyeability with acid dye in acidic pH, may be attributed to $-CONH_2$ groups incorporated due to acrylamide grafting, which get protonated to $-CONH_3^+$ and hence cause electrostatic attraction for acid dye anions. It is because of this reason, not only enhancement in acid dyeability was deserved, but also the improvement in fastness properties.

Improvement in light fastness is due to higher amount of dye being adsorbed on the grafted fibre, as compared to that on ungrafted fibre. The samples with optimum graft add-on showed 1–3 grade improvement in light fastness and 1–2 grade improvement in rubbing fastness.

3.5. Preparation and antibacterial activity of silver nanoparticles loaded bamboo rayon fabric

When grafted bamboo rayon sample was put in water, it swells to some extent due to the hydrophilic nature of monomers as well as backbone polymer and the presence of charged $-COO^-$ groups along the macromolecular chains as a result of ionization of acrylic acid moieties in the network. The grafted fabric was further treated with $AgNO_3$, where the adsorption of silver ions takes place and this adsorption mechanism can be viewed as the complexation of the Ag with carboxyl groups of the grafted samples. Finally when the swollen fabric containing Ag^+ ions was put in sodium borohydride solution, the ions are reduced to $Ag^{(0)}$ nanoparticles, and distributed almost uniformly throughout the network (Gupta et al., 2008).

SEM figures clearly indicate the presence of silver nanoparticles on the surface of the modified fabric which was visible even at a low magnification. The grafted polymer networks were also visible in the SEM photographs. The nanoAg.AA-AAm-g-BR showed typical brown color development which also indicates the formation of silver nanoparticles in the grafted fabric.

The quantitative antibacterial assessment was made using AATCC-100(2004) test method and the results are presented in Table 5. The results indicate the excellent antibacterial activity of the nanoAg.AA-AAm-g-BR samples. The bamboo rayon fabric showed no antibacterial activity against both *Staphylococcus aureus* and *Escherichia coli* as reported by some researchers (Qin, Chen, Zhang, Zhang, & Liu, 2010). The nanoAg.AAAAm-g-BR showed reduction of *S. aureus* which was 100% in case of freshly modified fabric which was subsequently reduced with number of washes and showed 91.74% bacterial reduction even after 50 washes. The results clearly indicate, the stronger holding of silver nanoparticles by bamboo rayon fabric grafted with AA and AAm, since grafting with such monomers resulted in introduction of $-COOH$ and $-CONH_2$ groups in the grafted side chain on the bamboo rayon backbone which leads to better interaction of such substrates with silver nanoparticles. In case of *E. coli*, the reduction was 100% for unwashed fabrics which again subsequently reduced with number of washes and showed 97.19% bacterial reduction after 50 washes. These results clearly indicate the better immobilization of silver nanoparticles using such kind of grafted fabrics. Development of brown color can be considered as limiting factor, but since the color development on the fabric was found to be even across the dimensions, it can be used for colored fabric. The results found were very encouraging as far as end uses like hospital textiles are concerned.

Table 5
Antibacterial properties and durability of the silver nanoparticles containing products (nanoAg.AA-AM-g-BR).

Sr. no.	No. of washes	Bacterial reduction[a] (%)	
		S. aureus	*E. coli*
1	0	100	100
2	5	100	100
3	10	98.54	100
4	20	97.57	99.43
5	50	91.74	97.19

[a] Represents average value of 3 determinations, standard deviation (%) range ±0.44–1.11.

4. Conclusion

Bamboo rayon fabric was successfully grafted with acrylic acid-acrylamide mixture using KPS initiator. The optimum conditions worked out on the basis of present work were as follows: grafting temperature, 60 °C; grafting time, 2 h; KPS concentration, 2%; monomer:fibre ratio, 0.5:1. The grafted product showed improvement in moisture regains which was further enhanced especially when the samples were treated with NaOH after grafting. The grafted product showed multifold increase in color strength of cationic and acid dyeing with distinct improvement in all kinds of fastness properties. The silver nanoparticles immobilized grafted bamboo rayon showed excellent and durable antibacterial activities against both gram positive and gram-negative bacteria.

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