STUDY OF GRAFTED SILVER NANOPARTICLE CONTAINING DURABLE ANTIBACTERIAL BAMBOO RAYON

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In the current study, the bamboo rayon fabric was grafted with acrylic acid using potassium persulfate as an initiator and further treated with silver nitrate followed by borohydride reduction. The modified product was characterized using FTIR, TGA and SEM. The characteristic brown colour developed after reduction was measured spectrophotometrically. The grafted bamboo rayon with nanosilver was then evaluated for antibacterial activity against both gram-positive and gram-negative bacteria and the durability of their antibacterial activity after washing. The product showed antibacterial activity against both types of bacteria, which was found to be durable until 50 washes.

Keywords: bamboo rayon, grafting, nanosilver, antibacterial

INTRODUCTION

Textiles, especially those made of natural fibers, are an excellent medium for the growth of microorganisms when the basic requirements for their growth, such as nutrients, moisture, oxygen, and appropriate temperature, are present. The large surface area and ability to retain moisture of textiles also assist the growth of microorganisms on the fabric.[1] The growth of microorganisms on textiles inflicts a range of unwanted effects not only on the textile itself, but also on the wearer. These effects include the generation of unpleasant odor, stains, discoloration in the fabric, a reduction in fabric mechanical strength and an increased likelihood of contamination.[2]

Like a house, a hospital contains an immense amount of textiles with the added threat of high volumes of traffic. Because of the constant flow of people, especially those with infectious diseases, many researchers have focused on creating finishes specifically for hospital use. The majority of these microorganisms are passed from person to person by various textiles.[3] During the last two decades, workers have reported some bacteria with resistance to antibiotics, such as methicillin originating from *Penicillium notatum*. One of the most well known bacteria with resistance to antibiotics is methicillin resistant *Staphylococcus aureus* (MRSA), which causes infections in patients with low disease resistance.

The number of patients infected with MRSA is reported to be increasing. Infection of patients in hospital is spread by MRSA through the clothes and/or hands of medical personnel. To avoid these infections, it is indispensable to provide clothing with antibacterial activity to be used in the hospital.[4]

In the last few decades, with the increase in new antimicrobial fibre technologies and the growing awareness about cleaner surroundings and healthy lifestyle, a range of textile products based on synthetic antimicrobial agents, such as triclosan, metal and their salts, organometallics, phenols and quaternary ammonium compounds, have been developed and quite a few are also available commercially.[5] Although some other metals, such as copper, zinc, and cobalt, have attracted attention as effective antimicrobial agents for textiles, silver is by far the most widely used in general textiles as well as in wound dressings. Silver has been known to be a disinfectant for many years and is being used in many forms for the treatment of infectious diseases. It has broad spectrum antibacterial activity, while exhibiting low toxicity towards mammalian cells. Silver is innocuous to human skin owing to its nontoxic nature, and this makes it a safe antiseptic material to be used on clothing or other textile products.[6] Silver nanoparticles are potent and broad spectrum antibacterial agents with activity against diverse species within both gram-positive and gram-negative bacteria. They show good antibacterial property with their large surface area to volume ratio, which provide a better contact with the microorganism.[7]

Bamboo, a lignocellulosic material, is an abundant natural resource in some parts of the world.[8] Bamboo belonging to the Poaceae grass family is an abundant renewable natural resource capable of production of maximum biomass per unit area and time, as compared to counterpart timber species.[9] Bamboo pulp fibre is widely applied in textile industry to produce dry goods. Generally, bamboo pulp fibre loses the antibacterial property present inherently in bamboo resulting from the treatment with alkali in the processing.[10]

Modification of natural or synthetic polymers is carried out with an aim of imparting specific properties to the product. Desirable and targeted properties can be imparted to the natural and synthetic polymers through graft copolymerization in order to meet the requirement of specialized applications.[11] Chemical grafting is one of the popular methods for modifying the structure and properties of biopolymers.[12] 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.[13]

The grafting of various textile fibres with different monomers using different initiators has been reported in literature.[14-17] The grafting used as a tool to bind the metal ions and to immobilize metal particles to various fibres to make them antibacterial was attempted by some researchers.[18-20] However, very little work is reported on modification of bamboo rayon. Grafting of bamboo rayon with acrylic acid,[21] acrylamide[22] were earlier reported by researchers from our laboratory. The grafting of bamboo rayon with a binary mixture of acrylic acid and acrylamide followed by immobilization of silver nanoparticles and the antibacterial activity of modified fabric were also reported.[23] In the current work, bamboo rayon fabric was grafted with acrylic acid followed by deployment of silver nanoparticles. The modified material was tested for its application in antibacterial products.

EXPERIMENTAL

Materials

Bamboo rayon fibres were converted into yarn (30 count). The yarn was knitted to make fabric, which was scoured and used for grafting. All chemicals used were of laboratory grade.

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, bamboo rayon fabric (of known weight) was placed in a flask containing distilled water, maintaining a material to liquor ratio of 1:20. After the desired temperature (60 °C) was reached, 1.5% (on weight of fabric, owf) of potassium persulfate (KPS) initiator was added followed by the addition of acrylic acid (1:1 owf) 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 washed with boiling water, to remove the homopolymer of acrylic acid until a 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, respectively.

Preparation of nano-Ag loaded grafted bamboo rayon fabric

A dry preweighed piece of grafted fabric was equilibrated in distilled water for 2 h. Thereafter the soaked fabric was put in an aqueous solution of $AgNO_3$ prepared by dissolving 0.25% owf $AgNO_3$ in double-distilled water, maintaining a material to liquor ratio of 1:30 for 2 h. The Ag^+ ions present in the fabric were reduced to Ag^0 nanoparticles by putting the fabric in 0.66 mM sodium borohydride solution at 30 °C for 24 h. The resulting dark brown colour 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 a dust-free chamber at 40 °C, until it gained constant weight.[20] The silver nanoparticle containing grafted bamboo rayon was designated as nanoAg.AA-g-BR.

Characterization of modified fabric

The analysis of unmodified and modified fabric samples was done by the methods listed below.

FTIR analysis

The FTIR spectra of the 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 4000-600 cm^{-1}.

Thermogravimetric analysis (TGA)

The thermograms were recorded using an aluminum pan in the temperature range from 30 to 500 °C and under inert atmosphere of N_2, at a flow rate of 50 ml/min (Shimadzu, Japan).

Scanning electron microscopy (SEM)

The analysis of the morphology was carried out using scanning electron microscope (FEI Quanta 200, The Netherlands).

Colour value by reflectance method

The typical brown colour developed on the silver treated grafted bamboo rayon fabric after borohydride reduction was measured on a Spectraflash SF 300 (Datacolor International, U.S.A.) equipped with reflectance accessories. 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 coefficient.

Antibacterial testing (AATCC 147)

One loopful of the diluted inoculum was streaked to an agar plate. The test specimen was gently pressed transversely across the agar surface, which was incubated at 37 °C for 24 h. The incubated plate was examined for the interruption of growth along the streaks of inoculum beneath the specimen and for a clear zone of inhibition beyond its edge. The average width of a zone of inhibition along a streak on either side of the test specimen was calculated using the following equation:

$$W = \frac{T-D}{2}$$

where T is the width of test specimen and clear zone in mm; and
D is the width of test specimen in mm.

Antibacterial testing (AATCC 100)

The antibacterial activity of the treated fabrics was estimated by AATCC Test Method 100-2004.[24]

Durability of antimicrobial activity

The durability to laundering was measured using conditions as per ISO 105-CO6-1M test methods.[25]

RESULTS AND DISCUSSION

Preparation of silver nanoparticle loaded bamboo rayon fabric

When the acrylic acid grafted bamboo rayon sample was put in water, it swelled 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 resulting from the ionization of acrylic acid moieties in the network. The grafted fabric was further treated with $AgNO_3$, where the adsorption of silver ions took place and the absorption mechanism could be viewed as the complexation of the Ag with carboxyl groups of the grafted samples during the adsorption and finally when the swollen fabric containing Ag^+ ions was put in sodium borohydride solution, the ions were reduced to Ag nanoparticles, and distributed almost uniformly throughout the network.[20]

Characterization of modified products

The grafted bamboo rayon fabric was characterized in order to validate grafting. The optimization of the grafting reaction was reported earlier by researchers from our laboratory.[21] The graft add-on (%) was found to be 14.85 with the reaction parameters mentioned in the experimental section. The carboxyl content of the bamboo rayon fabric increased from 4 meq/100 g to 140 meq/100 g, which clearly supports the grafting of acrylic acid on the bamboo backbone. The FTIR spectrum of grafted fabric (Figure 1), when compared with that of the control fabric (ungrafted), clearly indicated the peak for –COOH group at 1710.74 cm^{-1}, which was due to the introduction of polyacrylic acid graft onto the bamboo rayon backbone. In the case of nanoAg.AA-g-BR, the peaks became broad with strong intensity, which confirmed the immobilization of silver nanoparticles on grafted bamboo rayon.

Figure 2 shows the thermograms of ungrafted and nanoAg.AA-g-BR samples. In the initial stage, the weight loss values of the samples were of 9.5% and 9.78% at 250 °C, respectively. Between 250 °C and 350 °C, the drastic decomposition of the samples resulted in significant weight loss, which was of 59.22% for ungrafted and 47.04% for nanoAg.AA-g-BR fabrics 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 of 96.81% for ungrafted and 86.41% for nanoAg.AA-g-BR, respectively. This clearly indicates that the nanosilver treated grafted samples showed relatively higher thermal stability, as compared to that of ungrafted bamboo rayon. This could be attributed to the formation of side chain networks, as a result of grafting of acrylic acid onto the cellulose backbone, to the increasing molecular weight and further to the introduction of nanosilver in the polyacrylic acid matrix.

The surface morphology of the nanosilver containing grafted bamboo fabric was studied using SEM analysis. The surfaces of the unmodified and modified fabrics were depicted as SEM images in Figures 3-5. The figures clearly indicate the presence of silver nanoparticles on the surface of the modified fabric, visible even at a low magnification. The grafted polymer networks were also visible in the SEM photographs.

Figure 1: FTIR spectra of fibres

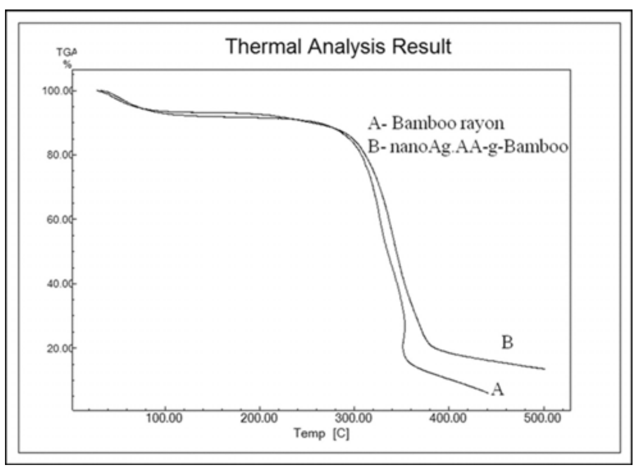

Figure 2: TGA of original and nanosilver containing bamboo rayon

Table 1
Colour values of nano-Ag containing grafted bamboo rayon

Sr. no.	No. of washes	K/S	L*	a*	b*
1	0	3.8544	45.13	2.61	8.55
2	5	3.5634	46.94	2.25	9.30
3	10	3.0034	50.79	2.53	11.5
4	20	2.9997	48.80	2.24	8.50
5	50	2.9844	52.12	2.48	12.17

*CIE colour co-ordinates

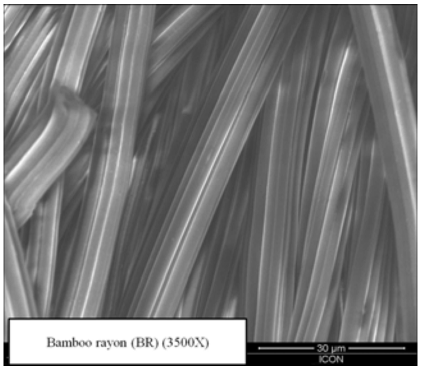

Figure 3: SEM photograph of ungrafted bamboo rayon

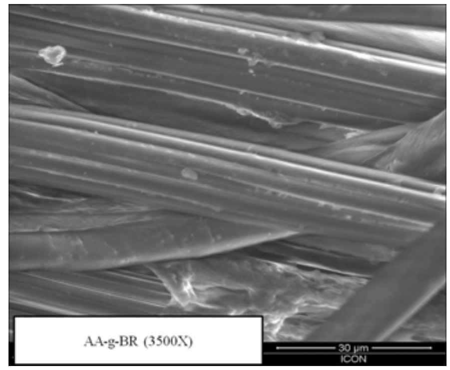

Figure 4: SEM photograph of grafted bamboo rayon (AA-g-BR)

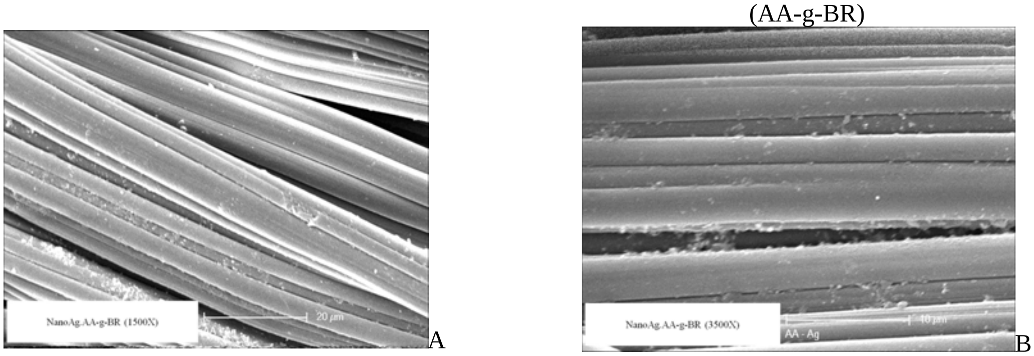

Figure 5: SEM photographs of nanoAg.AA-g-BR (A – 1500X, B – 3500X)

Colour measurement of Ag nanoparticle containing fabrics

The typical brown colour developed on the fabrics due to nano Ag formation was measured and presented in Table 1. The nanoAg.AA-g-BR showed strong absorption at 400 nm, considered as maximum wavelength for the measurement of colour values, which clearly indicated the presence of silver nanoparticles. The colour strength was found to be reducing after subsequent washes, but retained 77.4% of the initial colour value after 50 washes. This can be considered as due to immobilized silver nanoparticles, which are fast to washing even after 50 washes. Since the nanoparticles were distributed almost uniformly throughout the fabric, the brown shade was found to be even and where a dark shade is required, these treatments can be used advantageously.

Antibacterial activity and durability of modified fabrics

The results in Table 2 indicate the antibacterial activity assessment of the nanoAg.AA-g-BR samples, which was conducted using an AATCC 147-2004 method. The average width of an inhibition zone along a streak, on either edge of the test specimen, was calculated as described earlier. When the fabric specimen was placed on top of the bacterial lawn, antimicrobial agents (silver particles) from the fabric diffuse into the media that has bacterial lawn (growth). The nanoAg,AA-g-BR fabric samples showed no bacterial growth under the sample contact area, where as the untreated specimen exhibited considerable bacterial growth. The zones of inhibition for the treated fabrics were 4.5 mm for *S. aureus* and 5.0 mm for *E. coli*, respectively, indicating antibacterial activity while untreated fabric did not exhibit any zone of inhibition. After subsequent washing, the antibacterial activity was reduced and the zone of inhibition after 50 washings was reduced to 2.3 mm for *S. aureus* and 2.9 mm for *E. coli*. Hence it can be concluded that the antibacterial activity was retained for 50 washes against both bacteria.

Since silver nanoparticles were bound in polyacrylic acid side networks, a lower number of Ag^0 will be released in agar media and hence the width of clear zones obtained was found to be lower. The quantitative antibacterial assessment was done using the AATCC-100(2004) test method and the results are presented in Table 3.

While, as reported by some researchers,[10] untreated bamboo rayon fabric shows no antibacterial activity against both *S. aureus* and *E.*

coli, the results of the present study clearly indicate the excellent antibacterial activity of the nanoAg.AA-g-BR samples. The nanoAg.AA-g-BR showed a reduction of *S. aureus*, which was of 98.68% in the case of freshly modified fabric and was subsequently reduced with the number of washes, showing an 84.86% reduction of antibacterial activity even after 50 washes.

Table 2
Antibacterial properties (AATCC 147)

Sr. no.	No. of washes	Growth under specimen		Zone of inhibition (mm)	
		S. aureus	*E. coli*	*S. aureus*	*E. coli*
1	Ungrafted	Yes	Yes	0	0
2	0	No	No	4.5	5.0
3	5	No	No	4.1	4.8
4	10	No	No	3.6	4.1
5	20	No	No	3.0	3.5
6	50	No	No	2.3	2.9

Table 3
Antibacterial properties and durability of the products (AATCC-100)

Sr. no.	No. of washes	Bacterial reduction (%)	
		S. aureus	*E. coli*
1	0	98.68	100
2	5	98.026	100
3	10	96.71	100
4	20	95.39	98.49
5	50	84.86	96.24

The results clearly indicate the stronger holding of silver nanoparticles by bamboo rayon fabric grafted with acrylic acid, since grafting with such monomers resulted in the introduction of the polyacrylic acid side chain on the bamboo rayon backbone, which leads to a better interaction of such substrates with silver nanoparticles. In the case of *E. coli*, the reduction of antibacterial activity was of 100% for unwashed fabrics, which again subsequently reduced with the number of washes, showing 96.24% after 50 washes. These results clearly indicate the better immobilization of silver nanoparticles using this kind of grafted fabrics. The development of brown colour can be considered as a limiting factor, but since the colour development on the fabric was found to be even across the dimensions, it can be used for coloured fabric. The results found are very encouraging as far as end uses, such as hospital textiles, are concerned.

CONCLUSION

The silver nanoparticles were successfully immobilized in the grafted bamboo rayon fabric. The modified fabrics displayed high colour values due to silver nanoparticles and a better retention of the latter. The modified product also displayed antibacterial activity against both gram-positive and gram-negative bacteria, which was durable until 50 washes. The cross-infections occurring in hospitals due to infected clothing can be hence prevented using such modified brown coloured fabrics, such products being a suitable candidate for hospital clothing.

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