Durable Multifunctional Cellulose Using Copper Nanoparticles

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Abstract

In the current work, bamboo rayon fabrics grafted with mixture of acrylic acid and acrylamide (AA.AAm-g-BR) was utilized as a backbone to prepare bamboo rayon-copper nanoparticles composite. The swollen grafted fabric was treated with $CuSO_4$ followed by conversion of Cu^{2+} ions into copper nanoparticles. The modified product was characterized using FTIR, TGA and SEM techniques and then evaluated for antibacterial activity against gram positive and gram negative bacteria. The composite fabric showed antibacterial activity against both types of bacteria which was found to be durable till 50 washes. The modified material also showed improved UV protection because of presence of copper nanoparticles. The modified product can be utilized as protective clothing.

Keywords: Copper nanoparticles, Bamboo rayon, antibacterial, UV protection.

Introduction

In today's consumer driven market, the demand for functional textile materials is increasing. Textile materials made of natural fibres are an excellent medium for the growth of microorganisms because of its large surface area and ability to retain moisture. The growth of microorganisms on the fabric can cause a range of adverse effects like generation of unpleasant odor, stains, discoloration in the fabric, reduction in the tensile strength of the fabric and an increased likelihood of contamination. Apart from this, the UV protection is becoming the desirable property as textiles act as barrier layer between human body and the environment and can protect the same from harmful effect of UV light if finished properly. Bamboo, a lignocellulosic material, 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. 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 due to its treatment with alkali in the processing. 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 [1-4]. Metal and metal oxide nanoparticles are getting momentum in functional modification of textile

materials; however, there is always a question of durability of functional properties on textiles. The grafted fibres especially from hydrophilic monomers can adsorb metal ions from the solution and also swell in contact with water and hence offer suitable backbone to immobilize the nanoparticles and prepare the composite.The deployment of various nanoparticles on grafted bamboo rayon has been reported earlier from our laboratory [5-9]. In the current work knitted bamboo rayon fabric grafted with acrylic acid-acrylamide blend (AA.AAm-g-BR) was utilized as a backbone to prepare the composite of it with copper nanoparticles for imparting multifunctional properties.

Materials and Methods

Materials

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

Methods

The grafting reaction was carried out in a three-necked flask provided with nitrogen inlet and thermometer pocket as per the reported procedure [5].The copper nanoparticle loaded grafted bamboo rayon fabric was prepared by using the procedure mentioned in the literature [8]. Analysis of unmodified and modified fabric samples was done using FTIR (Shimadzu 8400s, Japan), TGA analysis ((Shimadzu, Japan) and Scanning Electron Microscopy (Philips XL 30, Netherlands). The change in appearance of of bamboo rayon fabric after modification was measured on Spectraflash SF 300 (Datacolor International, U.S.A.). The antibacterial activity of the treated fabrics was estimated by AATCC Test Method 100-2004 [10]. The UPF of the composite fabrics was evaluated on the Spectrophotometer Cary UV-VIS 300 (Cary, USA and durability of functional properties to laundering was measured using washing conditions as per ISO 105-CO6-1M test methods [11].

Results and Discussion

Preparation of copper 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 monomer as well as backbone polymer. The grafted fabric was further treated with $CuSO_4$, where the adsorption of copper ions takes place and the adsorption mechanism can be viewed as the complexation of the copper with carboxyl groups of the grafted samples and binding of copper ions with electron rich nitrogen atom of acrylamide. When the swollen fabric containing Cu^{2+} ions was treated with sodium borohydride solution, the ions are converted to $Cu^{(0)}$ nanoparticles, and distributed almost uniformly throughout the network.

Characterization of modified products

The grafted bamboo rayon fabric (AA.AAm-g-BR) was characterized in order to validate grafting. The optimization of the grafting reaction was earlier reported from our laboratory [5]. The add-on (graft yield

%) was found to be 25.05% with the reaction parameters mentioned in the experimental section. 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 indicative of graft side chains of acrylic acid amd acrylamide. There is hardly any change in the FTIR spectra of AA.AAm-g-BR and nanoCu-AA.AAm-g-BR was observed as the nanoparticles were just immobilized on the grafted bamboo rayon and there is no introduction of any functional groups. The similar observations were also made in earlier research using silver and ZnO nanoparticles [5,9].The thermograms of ungrafted, AA.AAm-g-BR and nanoCu.AA.AAm-g-BR samples (refer Fig. 2) indicate that in the initial stage weight loss values of samples were 9.5%, 10.45% and 10.13% at 250^{0}C, respectively. The final weight loss values observed at 450^{0}C were 96.81% for ungrafted, 82.83% for grafted and 67.62% for nanoCu.AA.AAm-g-BR samples. This clearly indicates that the copper nanoparticle containing grafted samples (nanoCu.AA.AAm-g-BR) showed relatively higher thermal stability as compared to that of ungrafted and grafted bamboo rayon. This could be attributed to the formation of side chain network as a result of grafting of vinyl monomers onto cellulose backbone increasing molecular weight and further introduction of copper nanoparticles in the grafted matrix.

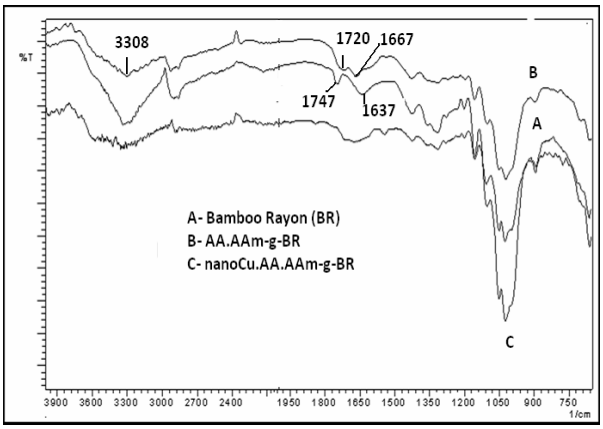


Fig. 1: FTIR spectra of fibres

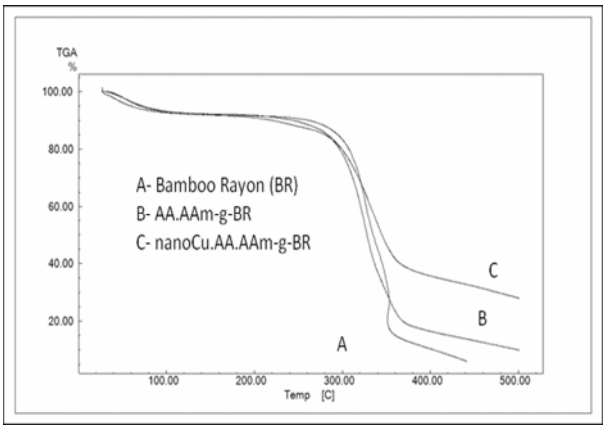


Fig. 2: TGA of fibres

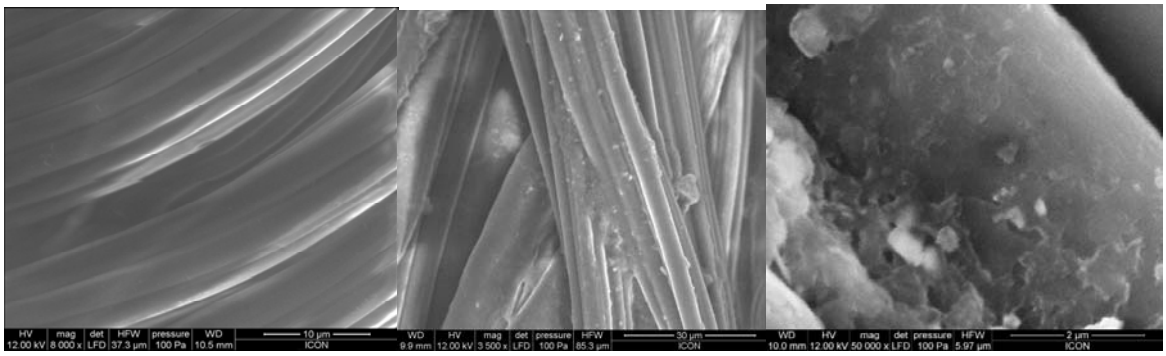
The surface morphology of nanoCu.AA.AAm-g-BR was studied using SEM analysis and the images of the fabric surfaces are shown in Fig. 3 which clearly indicates the presence of copper nanoparticles on the surface of the modified fabric.

Change in appearance of the fabric

The change in appearance of modified fabrics due to copper nanoparticle formation was measured and results are summarized in Table 1. The K/S values are of very small order, indicating the appearance of only slight greenish tinge to the modified bamboo rayon. The colour strength of the tinge was found to be increasing with $CuSO_4$ concentration from 0.25% to 1.0%.

Antibacterial activity and durability of the modified fabrics

The quantitative antibacterial assessment was made using AATCC-100(2004) test method and the results are presented in Tables 1 and 2. The bamboo rayon fabric showed no antibacterial activity against both *S.aureus* and *E.coli* as also reported by some researchers [4].



3a 3b 3c

Fig. 3: SEM photographs of ungrafted bamboo rayon (3a) and copper nanoparticles (3b and 3c) containing grafted bamboo rayon (nanoCu.AA-AAm-g-BR)

The results clearly indicate the excellent antibacterial activity of the nanoCu.AA.AAm-g-BR samples which was found to be improving with increase in concentration of $CuSO_4$. This was quite obvious as the antibacterial action was because of copper nanoparticles which will be in the higher proportion when higher concentration of $CuSO_4$ was taken. However, the antibacterial activity was optimized at 0.5% $CuSO_4$ which showed 100% reduction of both types of bacteria. The unwashed copper nanoparticle containing ungrafted bamboo rayon, showed excellent antibacterial activity. However it was reduced drastically after subsequent washing showing only 50% reduction level after 5 washes.

Table 1Colour values and antibacterial activity of nanoCu.AA.AAm-g-BR

Nature of sample	$CuSO_4$ conc. % (owf)	K/S	L	a*	b*	Bacterial reduction (%)	
						S. aureus	*E. coli*
Ungrafted	0	0.22	82.59	-0.84	8.42	N	N
AA.AAm-g-BR	0.25	0.33	80.36	-4.55	-4.62	99.85	95.55
AA.AAm-g-BR	0.5	0.58	78.63	-12.02	3.17	100	99.11
AA.AAm-g-BR	1.0	0.64	74.24	-0.01	7.76	100	100

N represents negligible bacterial reduction

The nanoCu.AA.AAm-g-BR showed reduction of *S.aureus* from 100% to 80.06% even after 50 washes (refer Table 2). The results clearly indicate the stronger holding of copper nanoparticles by bamboo rayon fabric grafted with acrylic acid-acrylamide blend. This may be attributed to introduction of side

chains of vinyl monomers (AA and AAm) on the bamboo rayon backbone during grafting which leads to better interaction of such substrates with copper nanoparticles. In case of *E.coli* the reduction was from 98.22% for freshly modified to 81.33% after 50 washes. The results emphasize that the antibacterial activity of nanoCu.AA.AAm-g-BR fabric was very intense even with small amount of copper nanoparticles. The excellent fastness to washing is due to antibacterial agent being immobilized.

Table 2 Durability of the antibacterial properties of ungrafted and grafted samples loaded with copper nanoparticles (0.5%)

No. of Washes	Bacterial Reduction(%)			
	Ungrafted		Grafted	
	S. aureus	*E. coli*	*S. aureus*	*E. coli*
0	88.50	82.45	100	98.22
5	43.10	41.75	98.58	96.89
10	17.25	17.10	97.15	95.11
50	-	-	80.06	81.33

The UV protection of the modified fabrics was evaluated and the results are summarized in Table 3. Results clearly indicate the efficient UV protection by the nanoCu.AA.Am-g-BR. In general UPF in excess of 50 was considered to be excellant protection and the modified fabric displayed the UPF in close to 100. The UPF was found to be decreasing with subsequent washing showing the value 45.123 after 20 washes. Hence it can be claimed that the modified fabric could display efficient UV protection till atleast 20 washes.

Table 3 Durability of the ultraviolet protection of nanoCu.AA.AAm-g-BR (0.5%)

No. of Washes	Calculated UPF
0	98.070
5	65.180
10	57.752
20	45.123
30	20.220

Conclusions

The copper nanoparticles were successfully immobilized on the acrylic acid-acrylamide blend grafted bamboo rayon fabric to form bamboo rayon-copper nanoparticle composite. The modified product displayed antibacterial activity against both gram positive and gram negative bacteria which was durable till 50 washes. The composite also displayed efficient UV protection durable till 20 washes.

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