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

M.D. Teli*, Javed Sheikh

Department of Fibres and Textile Processing Technology, Institute of Chemical Technology, Matunga (E), Mumbai 400019, India

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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.
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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

* Corresponding author. Tel.: +91 22 3361 2811; fax: +91 22 3361 1020.
E-mail addresses: mdt9pub@gmail.com, textileudct@yahoo.com (M.D. Teli).

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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.

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