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Extraction of chitosan from shrimp shells waste and application in antibacterial finishing of bamboo rayon

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ABSTRACT

Chitosan can be best utilized as safe antibacterial agent for textiles but there is always a limitation of its durability. The chitin containing shellfish waste is available in huge quantities, but very low quantities are utilized for extraction of high value products like chitosan. In the current work chitosan was extracted from shrimp shells and then used as antibacterial exhaust finishing agent for grafted bamboo rayon. Chitosan bound bamboo rayon was then evaluated for antibacterial activity against both gram positive and gram negative bacteria. The product showed antibacterial activity against both types of bacterias which was durable till 30 washes.

1. Introduction

Huge amounts of crab and shrimp shells have been abandoned as wastes by worldwide seafood companies. This has led to considerable scientific and technological interest in chitin and chitosan as an attempt to use these renewable wastes [1]. Chitosan is a functional, linear polymer that can be derived by the partial deacetylation of chitin. It is the most abundant natural polysaccharide on the earth after cellulose and can be obtained from the exoskeleton of marine crustaceans, such as crabs, lobsters, shrimps and krill [2]. Chitosan comprises copolymers of glucosamine and N-acetyl glucosamine and has a combination of many unique properties such as nontoxicity, biocompatibility, and biodegradability [3]. The antimicrobial ability, coupled with its non-toxicity, biodegradability and biocompatibility, are facilitating chitosan's emerging applications in food science, agriculture, medicine, pharmaceuticals and textiles [4]. Chitosan has been widely used in three areas of textile manufacture, such as the primary production of human-made fibre, textile fibre finishes, and textile auxiliary chemicals [5]. Various applications of chitosan in textiles have already been reported [6–11]. Chitosan is a natural cationic polysaccharides, and is known to suppress the metabolism of bacteria when sticking to the bacterial cell wall [12]. Application of chitosan from different sources and their antimicrobial activities has been reported [13–15]. The different modifications of chitosan and the resulting antimicrobial activity are also reported in literature [16–19].

Since present work consists of application of chitosan on bamboo rayon, it is important to understand this fibre. Bamboo, a lignocellulosic material, is an abundant natural resource in some parts of the world [20]. 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 [21]. Bamboo pulp fibre is widely used in textile industry to produce dry goods. Generally, bamboo pulp fibre loses the antibacterial property inherent in bamboo, due to the treatment of it with alkali during the processing [22]. Functional finishing of bamboo pulp fabric with chitosan in citric acid medium has been reported [23]. Attachment of chitosan to bamboo pulp fabric through controlled oxidation has also been reported recently [24]. 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 [25]. The grafted side chains can act as hook to attach other useful ingredients to the substrate.

Even though chitosan show antibacterial properties, there is always a question of durability of such finishes on textile substrates. Hence in the current work, chitosan was extracted from shrimp shells and the possibility of application of chitosan as durable antibacterial finishing agent for bamboo rayon has been explored using acrylic acid grafting technique onto bamboo rayon. Since such methods could be better used in garment finishing, the possibility of exhaust finishing has been studied.

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2. Materials and methods

2.1. Materials

Shrimp shell waste was obtained from local fish market. Bamboo rayon fibres were converted into yarn (30 count). The yarn was knitted on the circular knitting machine (Bharat Machine works, India) to make fabric (single jersey, gsm-133.28, WPI-36, CPI-38) which was scoured and used for grafting. All chemicals used were of laboratory grade.

2.2. Methods

2.2.1. Preparation of chitosan from shrimp shells

Extraction of chitosan from shrimp shells was performed as per the procedure earlier reported [26]. The raw shrimp shells were washed thoroughly with water, dried under vacuum and then grinded in a mortar with pestle. The shrimp shells powder so obtained was then soaked in 1 M NaOH for 24 h, washed and dried. The shrimp shells powder was then demineralized using 1 M HCl, deproteinized using 1 M NaOH, discoloured using $KMnO_4$ and Oxalic acid to get chitin powder. The chitin obtained was then subjected to deacetylation using 50% NaOH which was repeated to get higher degree of deacetylation in chitosan.

2.2.2. Characterization of chitosan

2.2.2.1. FTIR analysis. The FTIR spectra of shrimp shells, chitin, chitosan and commercial chitosan were recorded using Shimadzu FTIR spectrophotometer using ATR mode of operation and scanning of the FTIR spectrophotometer was carried out from 4000 to 600 cm^{-1}.

2.2.2.2. Estimation of molecular weight of chitosan. The molecular weight of chitosans was determined by measuring the viscosity of 0.05–0.15% chitosan dissolved in 0.5 mol/l acetic acid and 0.2 mol/1 sodium acetate solutions using an Oswald viscometer [27].

2.2.2.3. Estimation of degree of deacetylation. The powder was tested for degree of deacetylation by titration [28].

2.2.2.4. Estimation of nitrogen content. Nitrogen content was estimated by Kjeldahl's Method [29].

2.2.3. 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 flask containing distilled water maintaining material to liquor ratio 1:20. After the desired temperature (60 °C) was reached, 1.5% (on weight of fabric, owf) of potassium persulphate (KPS) initiator was added followed by addition of acrylic acid (1:1 owf) after 10 min of addition of initiator. The reaction was continued under nitrogen atmosphere for 3 h with constant stirring. After completion of reaction, the grafted fabric was washed with boiling water, to remove the homopolymers of acrylic acid, repeatedly till the constant weight was reached. The graft add-on was calculated using the formulae

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

where W_1 and W_2 were the weights of ungrafted and grafted fabrics.

2.2.4. Preparation of chitosan bound grafted bamboo rayon fabric

The grafted bamboo rayon fabric (AA-g-BR) was treated with 5%, 10% and 20% (owf) of chitosan using 1% acetic acid at 60 °C for 30 min. The fabric was squeezed and dried at 100 °C for 4 min. The chitosan bound grafted bamboo rayon was designated as CTS-AA-g-BR.

2.2.5. Characterization of modified fabric

Analysis of unmodified and modified fabric samples was done by the following methods.

2.2.5.1. FTIR analysis. The FTIR spectra of 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}.

2.2.5.2. Thermo gravimetric analysis (TGA). The thermograms were recorded using aluminium pan between temperature range 30–500 °C and under inert atmosphere of N_2 at a flow rate of 50 ml/min (Shimadzu, Japan).

2.2.5.3. Scanning electron microscopy (SEM). Analysis of the morphology was carried out using scanning electron microscope (Philips XL 30, Netherlands).

2.2.6. Measurement of textile properties

2.2.6.1. Moisture regain. The moisture regain was determined by the vacuum desiccator method with sodium nitrite to give 65% RH at 21 ± 1 °C [30].

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

2.2.7. 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. 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 is calculated using the following equation:

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

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

2.2.8. Antibacterial testing (AATCC 100)

The antibacterial activity of the treated fabrics was estimated by AATCC Test Method 100-2004 [31].

2.2.9. Durability of antimicrobial activity

The durability to laundering was measured using washing conditions as per ISO 105-CO6-1M test methods [32].

3. Results and discussion

3.1. Extraction of chitosan from shrimp shells

The nitrogen content at various stages of chitosan preparation was estimated (refer Table 1). The results clearly indicated the decrease in nitrogen content in the case of chitin as the result of treatment on shrimp shells causing deproteinization. This is because the proteins in the shrimp shells along with other nitrogenous materials get removed in the conversion process ofshrimp