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Utilization of chitosan nanoparticles as a green finish in multifunctionalization of cotton textile

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ABSTRACT

Chitosan nanoparticles were synthesized through polymerization of CS at different concentrations with methacrylic acid (MAA) using $K_2S_2O_8$ as initiator. This polymerization gave rise to suspension which was ice-cooled then subjected to severe centrifuging and the supernatant discarded to yield CS nanoparticles. Major characteristics of the so prepared CS nanoparticles namely size/distribution of the particles, their structural features, surface description and thermal stability were examined using DLS, FTIR, SEM and TGA, respectively. When CS nanoparticles were used as a finish for cotton fabrics with a crosslinking agent, the fabric displayed improved dyeability and thermal stability as well as antibacterial activity and UV protection. These latter two functionalities were significantly increased by post treatment of fabric with copper sulfate.

1. Introduction

Nanotechnology occupies nowadays position in most fields of concern, since it allows manipulating matter at the nanoscale level [1,2] and tailoring final product properties.

Chitosan is an attractive highly reactive polymer particularly due to the amino and hydroxyl functional groups present on its chain, such groups include also chemical linking of chitosan to inorganic reinforcing network in hybrid preparation. Moreover, the bio-degradability, non-toxicity and natural abundance of chitosan make it green material which can be easily and economically extracted from marine canning industry byproducts [3–5].

The literature reports several attempts to produce chitosan particles with different particles size, especially at the nanoscale [6,7]. Mostly, the particle sizes obtained are above 175 nm; usually in the range from 175 to 600 nm [8]. Methacrylic acid (MAA) polymerization is a new promising system for producing chitosan nanoparticles [1].

Recently chitosan nanoparticles were investigated for antimicrobial textile applications as chitosan in the nano form is highly active because of the very high surface area to volume ratio and expected to have desirable bioactivity even at very low concentrations [9–11]. Preparation and application of novel chitosan nanoparticles on bioactive polyester fabric to impart enhanced antimicrobial activity at a very low concentration were reported [9]. Also reports [10] studied the effects of chitosan type and nanochitosan concentrations on the anti-bacterial and shrink-proofing properties of the wool fabric; the nanochitosan-treated wool fabric possesses better anti-bacterial and shrink-proofing properties.

Chitosan nanoparticle dispersion solution as a novel multifunctional agent was developed to modify *Antheraea pernyi* silk [11]. The results revealed that the surface of the chitosan-nanoparticle-treated *A. pernyi* silk fiber was rougher than that of bulk chitosan-treated and untreated ones, and a higher specific surface could be achieved. In addition, enhancement in antibacterial activity, breaking strength, and wrinkle-resistance properties of the chitosan-nanoparticle-treated *A. pernyi* silk fabric were also recorded. Previous reports disclosed, additionally that chitosan nanoparticles enhance the dye ability of silk with acid as well as reactive dye [12] and improve the adsorption capacities of many acid dyes [13].

We undertake the present work with a view to synthesize, characterize and utilize chitosan (CS) nanoparticles as a green ecofreindly finish in multifunctionalization of cotton fabric. Our target is to achieve cotton fabrics which can perform several concomitant functions such as improved dye ability and thermal stability as well as antimicrobial activity and UV protection. Further augmentation in the latter two functionalities is envisaged through post treatment of CS nanoparticles finished fabric with copper sulfate. The superiority of CS nanoparticles over bulk chitosan is also verified.

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2. Experimental

2.1. Materials and methods

Chitosan® (CS) 100 (chipro GmbH, Germany), deacetylation >95%, Mw 95 kDa, CS-salt, high aqueous solubility potassium persulfate ($K_2S_2O_8$), methacrylic acid (MAA) and 3-glycidyloxypropyl trimethoxysilane (GPTMS) from Aldrich (St. Louis, USA) were used. Reactive dye was purchased from YORKSHIRE-SARBEN, GmbH, Germany. Acid Red 266 was from Thai Ambica, Thailand.

2.2. Preparation of CS–PMAA nanoparticles

CS–PMAA nanoparticles were obtained by polymerizing MAA in CS solution [1] as described hereafter. Firstly, CS was dissolved in an aqueous MAA solution (0.5%, wt/v) for 12 h under magnetic stirring. The CS concentrations used in synthesis process were 0.2, 0.5, and 0.8 (wt/wt%). Next, 0.2 mmol of $K_2S_2O_8$ was added to the CS–MAA solution under continuous stirring at 70 °C for 1 h, leading to the formation of CS–PMAA nanoparticles, which were then cooled in an ice bath. The suspension was centrifuged for 30 min at 4000 rpm and the supernatant was discarded. The particles were resuspended in millipore water.

2.3. Characterization of chitosan nanoparticles

2.3.1. DLS (dynamic light scattering)

The size of chitosan nanoparticles was measured by dynamic light scattering (DLS), using Zetasizer, Nano-S, produced by Malvern. DLS was used to measure the hydrodynamic diameter and size distribution of the particles.

2.3.2. Morphology study of the nanoparticles

The prepared solutions were analyzed by scanning electron microscopy (SEM), Topcon-Microscope (ATB-55) to investigate morphological changes of the surface structure.

2.3.3. Fourier transform infrared (FTIR)

Infrared spectroscopy of chitosan and chitosan nanoparticles were carried out using ATR-FTIR instrument. The latter was from SHIMADZU, Model IR prestige-21, Germany.

2.3.4. Thermal analysis (TGA)

Thermo gravimetric analysis (TGA) was carried out using PerkinElmer TG-DTA analyzer, model Pyris1, operating under nitrogen atmosphere with initial sample weight of 8 mg. The runs were performed over a temperature range of 50–600 °C at a heating rate of 10 °C/min under a continuous N_2 flow of 100 ml/min.

2.4. Application of bulk chitosan and chitosan nanoparticles on cotton fabrics

The finishing treatment was performed according to the pad-dry-cure method for cotton fabric samples. Bulk chitosan and chitosan nanoparticles at different concentrations of 0.2–0.8% was incorporated in a finishing bath containing 1% GPTMS as a cross linker. In all cases, the treated fabrics were impregnated for 5–10 min and squeezed between rollers to a liquor uptake of 100%. Fixation was effected at 140 °C for 10 min after drying at 80 °C for 3 min; the cured fabrics were then washed, rinsed and finally dried.

2.5. Characterization of chitosan treated cotton fabric

2.5.1. Textile testing and instrumentation analysis

Monitoring the finished fabrics properties was carried out as per the following procedures:

- Ninhydrin test was used for detection of amino groups of chitosan; ninhydrin reacts with the free amino group of chitosan and develops a violet color.
- Color measurements, expressed as *K*/*S*, were carried out using Data color spectrophotometer 3880 (cocos Manual Version 2, 3). The color degree is given according to Berger (light source D65/10).
- Chitosan nanoparticles treated fabrics were examined by scanning electron microscopy (SEM), Topcon-Microscope (ATB-55) to investigate morphological changes of the surface structure.
- Nitrogen content of the treated samples was determined according to Kjeldahl method [14].
- Transmissions of UV radiation were measured according to AS/NZS 4399:1996 – Sun Protective Clothing – Evaluation and Classification using a Cary 50 Solar screen transmission spectrophotometer.

2.5.2. Test organism

Escherichia coli DSMZ 498 and *Micrococcus lutues* ATCC 9341 were used as non-pathogenic substitutes for Gram-negative and Gram-positive bacteria.

2.6. Anionic dyeing of cotton fabric treated with bulk chitosan and chitosan nanoparticles

Dyeing was carried out to clarify the difference in color (*K*/*S*) between cotton fabric having catatonically charged surface active group as a result of treatment with bulk chitosan and those treated with chitosan nanoparticles.

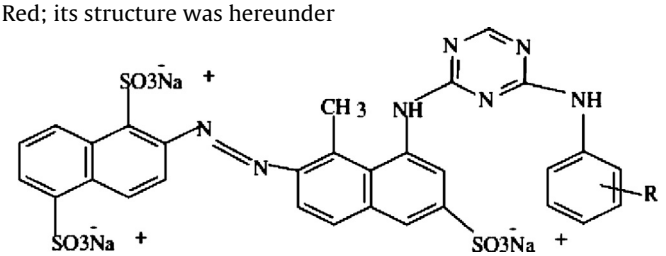
The *K*/*S* value is commonly used to represent the amount of dye fixed or dye content of textile substrates. The *K*/*S* values were determined from the reflectance measurements.

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

where *K*/*S* is the ratio of absorption and scattering coefficient and *R* is the reflectance of the fabric.

2.6.1. Reactive dye

Bulk chitosan and chitosan nanoparticles treated fabric samples were dyed with reactive dye, namely the reactive dyestuff Intracron Red; its structure was hereunder



The dyeing process occurs using the exhaustion method, as follows: the dyeing solution was prepared using a final dye concentration equal to 500 mg/l and material to liquor ratio (MLR) 1:50. The dyeing temperature was increased to 60 °C. The sample was introduced in the dye bath followed by the addition of 50 g/l sodium sulfate; after 20 min, 5 g/l sodium carbonate was added with stirring, then after another 20 min, 40 g/l sodium hydroxide was added and the dyeing process was continued for 50 min. At the end of the dyeing process, the samples were thoroughly washed with hot water and 0.1% Marlipal, then rinsed with cold water and finally