Progress in Organic Coatings 120 (2018) 123–131

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

A green and facile approach to durable antimicrobial coating of cotton with silver nanoparticles, whey protein, and natural tannin

S. Srisod[a], K. Motina[b], T. Inprasit[a], P. Pisitsak[a,*]

[a] Department of Materials and Textile Technology, Faculty of Science and Technology, Thammasat University, Pathum Thani, 12121, Thailand
[b] Department of Biotechnology, Faculty of Science and Technology, Thammasat University, Pathum Thani, 12121, Thailand

ARTICLE INFO

Keywords:
Antimicrobial coating
Cotton
Silver nanoparticle
Tannin
Whey protein
Xylocarpus granatum

ABSTRACT

Antimicrobial cotton textiles were fabricated via green synthesis of silver nanoparticles (AgNPs) from silver nitrate, using whey protein isolate (WPI) as both reducing agent and stabilizer. Natural tannin-rich extract from *Xylocarpus granatum* bark (XGBE) was used to form insoluble complexes with the WPI through hydrogen bonding and hydrophobic forces. Cotton fabrics were coated using one-step padding of the AgNP/WPI/XGBE mixture, followed by air drying. Both WPI and XGBE served as an excellent natural binder for AgNPs with cotton. Transmission electron microcopy showed the AgNPs to be almost spherical, with a mean diameter of 31 nm. Antimicrobial treatment did not significantly alter the original color of the fabrics at low AgNPs loadings. The coated fabrics showed strong and durable antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*, with 99.99% bacterial reduction. Treatment with only 50 ppm of silver nitrate and WPI maintained more than 90% bacterial reduction after 50 washing cycles. In a test of antifungal properties, at least 203 mg silver per kilogram of fabric was required to suppress the growth of *Aspergillus niger*. *In-vitro* cytotoxicity testing demonstrated the antimicrobial treated fabrics to be non-toxic to L929 cells. Antimicrobial treatment did not have significant negative effects on the drapeability and tearing strength of the fabrics. This approach is very attractive in terms of the safety and biocompatibility of the raw materials, the simplicity of the synthesis and the coating process, and the antimicrobial effectiveness of the treated fabrics.

1. Introduction

Due to the modern consumer demand for health and hygiene, the market for antimicrobial textiles has grown over the last few decades [1]. Promising business sectors include, but are not limited to, medical and healthcare products, sport wear, underwear, and military uniforms. Cotton dominates the natural fiber industry due to its natural softness, heat retention, and high hygroscopicity [2]. Unfortunately, cotton fiber is prone to microbial attack. When in contact with the human body, they provide an ideal environment for the growth and multiplication of pathogenic microbes, giving rise to offensive smells, skin infections, allergies, and other related conditions [3]. Deterioration of cotton products can also be in terms of appearance or mechanical integrity.

Silver has found many medical applications since ancient times [4]. Its antimicrobial activity has been attributed to the release of Ag(I) ions from silver nanoparticles (AgNPs) or dissociation of Ag salts (such as $AgNO_3$ or AgCl) upon contact with water. In the case of AgNPs, Ag(I) ions can also be generated from oxidation in the presence of water and oxygen. Although the exact antimicrobial mechanisms of AgNPs are not fully understood, it has been reported that Ag(I) ions or AgNPs of less than 10 nm are capable of penetrating the cells of the microorganisms, deactivating their vital physiological functions [5]. Silver ions are capable of binding with the disulfide (S-S) and sulfhydryl (-SH) groups present in the protein of the cell wall, disrupting their metabolic processes [6]. Binding of Ag(I) ions to DNA prevents the proliferation of bacteria. In the presence of oxygen, silver may accelerate the production of reactive oxygen species (ROS), which are fatal to microbial cells [5].

Coating of textiles with silver salts such as silver nitrate stains the fabric to black-brown upon exposure to air and light, due to an uncontrolled reduction process. The use of more stable AgNPs is therefore recommended for textile applications [7]. Smaller silver particles generally exhibit stronger antibacterial activity [8]. AgNPs are nanoscale clusters of metallic silver atoms, whose exceptional microbial efficiency is due to their high surface-to-volume ratio. They therefore release silver Ag(I) ions more readily than bulk silver. The biocidal activity of AgNPs also initiated at far lower concentrations than that of Ag(I) ions [5]. AgNPs dominate the literature as a robust against bacteria, fungi,

* Corresponding author.
E-mail address: penwisa@tu.ac.th (P. Pisitsak).

https://doi.org/10.1016/j.porgcoat.2018.03.007
Received 25 October 2017; Received in revised form 4 March 2018; Accepted 10 March 2018

and viruses [9,10] and the use of AgNPs in consumer products such as textiles, toothpastes, shampoos, detergents, towels, toys, and humidifiers is becoming widespread [11]. Their properties depend on their shape, structure, size, and size distribution, which are in turn governed by the preparation technique [8].

Metal nanoparticles can be produced by physical or chemical routes. The physical route involves evaporation/condensation and laser ablation, while the chemical route mostly relies on the chemical reduction of metal ions in solution [8]. The most simple and widely used synthesis route for AgNPs is probably the reduction of silver nitrate in aqueous solution, using a reducing agent such as sodium borohydride ($NaBH_4$) or hydrazine. The use of strong reducing agents like $NaBH_4$ allows the formation of AgNPs of smaller size than those prepared using weaker reducing agents [5]. However, there is a movement toward the use of safer and more environmental friendly reducing agents, e.g. polysaccharides, plant extracts, or even microorganisms [8]. Protein also serves as a natural reducing agent for the synthesis of gold nanoparticles from gold salts [12].

To prevent nanoparticle agglomeration, a stabilizer is usually added in the course of preparation. It binds to the nanoparticle surface and improves stability via electrostatic or steric effects. Electrostatic stabilization is achieved by coordination of anions (such as halides, carboxylates, or polyoxoanions) with the particle surface, consequently exerting coulombic repulsion between the approaching nanoparticles. Steric stabilization is realized by the presence of chemical moieties (mostly polymers) that, due to their bulk, prevent agglomeration of the nanoparticles [8]. Previous studies have shown that many natural compounds can act both stabilizer and reducing agent in the synthesis of AgNPs (such as *J.curcas* [13], *Rhodomyrtus tomentosa* extract [14], and hydroxypropyl starch [15]).

Most in situ synthesis methods for AgNPs on cotton require chemical grafting or fabric pretreatment, e.g. with polyacrylamide or chitosan. In-situ synthesis of silver nanoparticles on cotton without the addition of a stabilizer has been reported [2,16–19] and the rougher surface of natural fibers binds more effectively with AgNPs than the smooth surface of synthetic fibers [5]. Some approaches have used alkali treatment to swell the cellulose fibers, promoting the diffusion of positively-charged silver ions into the negatively-charged fiber structure [2,19,20]. Cellulose molecules have been reported to exhibit both reducing and stabilizing effects, enabling the formation of AgNPs directly on the fibers [5,17]. However, all previous studies that did not use additional stabilizer were conducted at high temperatures over long synthesis times, and the low silver loadings that resulted were lost over a relatively small number of washing cycles.

Whey protein constitutes about 20 percent of the milk protein content, and is retained in the serum phase of the cheese making process [21]. The primary whey proteins are beta-lactoglobulin, alpha-lactalbumin, bovine serum albumin, immunoglobulins, and proteose peptones [22]. Whey protein isolate (WPI, > 90%) can produce transparent, flexible, and even edible films. WPI edible films and coating formulations with different functionalities have been demonstrated [23,24]. Pisitsak et al. (2016) successfully utilized WPI and tannin-rich colorant to dye cotton textiles, producing a reddish-brown shade with good color fastness to washing and excellent UV protection properties. It was argued that complexation of tannin with WPI produced durable, water-insoluble coating on the cotton fibers through hydrophobic interactions and hydrogen bonding [25].

In the present study, we hypothesized that WPI would act as both a reducing agent and a stabilizer for AgNPs synthesis, due to its bulk (steric effect) and ionizable groups (electrostatic effect). Given the film-forming abilty of WPI, the protein-crosslinking ability of tannin, and the affinity between silver and protein, it was postulated that WPI and tannin would serve as a natural binder for AgNP coating of cotton fabrics. Their hydrophilic properties would create a moist environment, allowing the release of silver ions and producing antimicrobial activity, while their insolubility in water would improve the washing fastness of the treated fabric.

2. Materials and methods

2.1. Materials

A plain weave cotton fabric (mass per unit area of 155 g/m^2, warp and weft yarn counts of Ne 28 and Ne 34, threads per unit length of 131 ends/cm and 69 picks/cm) was desized with alpha-amylase, then bleached and scoured with 4 g/L of 50% sodium hydroxide, 4 g/L of 50% hydrogen peroxide, and 1 g/L of non-ionic wetting agent at 100 °C for 30 min prior to use. WPI (90%) was obtained in powder form. Tannin-rich extract from *Xylocarpus granatum* bark (designated XGBE) was produced by immersing the bark in water (bark-to-water mass ratio of 1:5) overnight, heating at 80 °C for 1 h, filtering, and then spray drying at 180 °C. This yielded a reddish-brown powder with 74.0% tannin content [25,26].

2.2. Methods

2.2.1. Preparation of antimicrobial coating solutions

Antimicrobial finishing solutions comprising XGBE, WPI, and silver nitrate were prepared in DI water. A clear, reddish brown XGBE solution of 2.5 g/L was separately prepared. WPI powder was dissolved in 250 ml of DI water and silver nitrate of the same weight was added under stirring. The solution changed from colorless to yellowish brown because of the reduction of silver(I) ions to silver nanoparticles. Extra DI water of 215 ml was added to the silver nitrate/WPI solution, followed by 35 ml of the XGBE solution, to obtain a total volume of 500 ml. The mixture was stirred for 15 min, at which time the color became deep reddish brown. All preparation steps were conducted at room temperature, using DI water of pH 10 (adjusted with NaOH). At this pH, the fastest change from colorless to yellow was observed, and no precipitate was produced. This confirmed that the silver nanoparticles had formed most rapidly, and that the mixture had good stability. The final concentrations of silver nitrate and WPI ranged from 50 to 500 ppm (25–250 mg in the 500 ml of reaction mixture), while that of XGBE was fixed at 175 ppm (87.5 mg in 500 ml).

2.2.2. Antimicrobial coating of cotton textiles

Cotton samples (10 g) were immersed in the prepared antimicrobial finishing solution until thoroughly wet. The samples were padded using a padding mangle (Newave Lab. Equipment Co., Ltd.) at a nip pressure of 1.5 kg/cm^2 resulting in 100% wet pickup, followed by air-drying. Removal of excess chemicals was performed by washing with 2 g/L standard soap at 60 °C for 20 min in a lab IR dyeing machine (Starlet DL-6000).

2.2.3. Color parameters of the antimicrobial finished fabrics

The color parameters of the finished cotton fabrics were measured with a spectrophotometer (GretagMacbeth color i5) and reported in terms of CIELab color space with L^* representing brightness (0 = black, 100 = white), a^* corresponding to the red-green coordinate (-ve = green, +ve = red), and b^* to the yellow-blue coordinate (-ve = blue, +ve = yellow). C^* specifies chroma and h° represents hue angle and both parameters can be calculated from the a^* and b^* values. The color strength of the fabric was expressed in terms of K/S, with a greater value indicating greater color strength. Color differences between the untreated and the treated fabrics were represented by ΔE^*. A greater ΔE^* value represented a larger deviation of the sample color from the reference color.

2.2.4. UV–vis spectroscopy

The absorption spectra of silver colloidal solutions were collected using a UV–vis spectrophotometer (Perkin-Elmer Lambda 25). The presence of a surface plasmon resonance peak was used to confirm the