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Silver/waterborne polyurethane-acrylate's antibacterial coating on cotton fabric based on click reaction via ultraviolet radiation

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ABSTRACT

Silver/waterborne polyurethane-acrylate (Ag/WPUA) coating was firstly synthesized by a novel and facile method of combining in-situ reduction and polymerization reactions. Cotton fabrics were pre-treated to introduce −SH groups by the reaction between the $-OC_2H_5$ groups of 3-mercaptopropyltriethoxysilane and −OH groups of cotton fabrics. Then antibacterial finishing of cotton fabric was obtained with Ag/WPUA coating under ultraviolet (UV) radiation where click reaction was taken place between −SH groups and C=C bonds. Ag/WPUA coating was characterized by transmission electron microscopy (TEM), Fourier transforms infrared spectra (FTIR) and X-ray diffraction (XRD). The chemical bonding, antibacterial property, thermal stability and mechanical property of antibacterial cotton were investigated. The results of antibacterial test elucidate that the bacterial reduction was 99.99% for *E. coli* and *S.aureus*, revealing that the finishing on cotton fabrics has excellent antibacterial activity. Furthermore, the antibacterial cotton fabrics still maintains good mechanical properties like breaking strength and thermal stability.

1. Introduction

As the natural fibers, cotton was is widely available due to its excellent performance such as softness, breathability, moisture absorption and wearing comfort properties, etc [1]. Whereas cotton fabric easily was attacked by the microorganism and fungus owing to cotton fibers' large surface area and ability to retain moisture [2]. Therefore, necessary finishes like antibacterial finishing are required on the cotton fabrics to suit modern life and are welcomed by consumers. The antibacterial cotton fabric can be applied to medical linen, surgical clothing, medical curtains, couches, operating tables and other medical textiles. So far, much research has been devoted to these finishes in the textiles field [3].

In terms of antibacterial finishing, antimicrobial agents may be in form of inorganic and organic biological agents. The organic anti-bacterial agent more varieties, such as organic compounds, metal halide, quaternary ammonium salts and diphenyl ethers, organic nitrogen compounds, and so on. But the hydrolysis and drug resistance were inescapable in application. The inorganic agents are Au, Ag, Cu, Zn, Hg, Pb, TiO_2 and ZnO. Considering the hydrolysis and drug resistance from organic antibacterial agents, the inorganic antibacterial agent was more proper to be applied in the home textiles [4]. For example, silver nanoparticles are always introduced to impart antibacterial property as broad antibacterial spectrum and strong permeability [5–9]. But problem with durability is not easily solved as the deposition of metal grain on the fabrics surface strongly depend on the surface conditions of the fibers [10]. Due to the rough surface and porous structure of fabric substrate, it is not only difficult to uniformly deposit silver nanoparticles on the fabrics' surface, but hard to immobilize them as they will be readily washed off during the daily use [11].

Regarding these, the non-formaldehyde resin finishing of UV-curable WPUA was proposed, which could effectively reduced energy consumption, strength losses and formaldehyde emission. As for waterborne polyurethane, the finishing is based on the −NCO groups, which can cross-link with −OH groups of fabrics. Nevertheless, the-NCO groups of WPUA can react with active hydrogen compounds (such as water molecules) [12,13]. Therefore the WPU was capped by sodium bisulfate and methyl ethyl ketone oxime before reacting with the −OH groups of fabrics. But the stability of WPU capped is poorer. In comparison to the conventional WPU, acrylate monomers were utilized to serve as capping agent to obtain the WPUA with excellent stability.

Based on what we discussed above, Ag/WPUA coating is an effective approach to obtain antimicrobial property via UV-curing. As for the present methods of preparing Ag/WPUA coating, one way is to add

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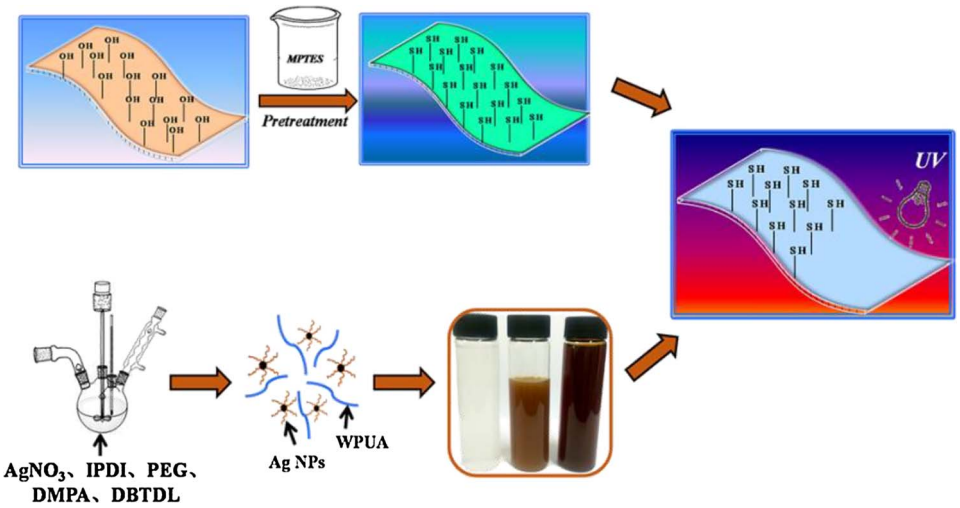

Scheme 1. The preparation process of Ag/WPUA coating and its finishing on cotton fabrics.

silver powders during resin synthesis [14–17], another way is to explore appropriate scaffolds for the stabilization of silver nanoparticles [18–20]. However, the problems are focused on silver nanoparticles aggregation and poor non-durable effect. Hence, our group proposed herein to synthesize Ag/WPUA coating by a novel and facile method as depicted in Scheme 1, which combined in-situ reduction and polymerization reactions. With polyethylene glycol used as reducing and waterborne polyurethane-acrylate acted as stabilizing agents, silver nanoparticles were in situ generated in this system to achieve uniform dispersion. Polyethylene glycol was used as a reducing agent for silver nitrate, alongside its participation as a soft segment in the preparation of carboxylate-containing segmented polyurethane. The carboxylate-functional group in the prepared waterborne polyurethane-acrylate is expected to chemical bond with the silver ions [21]. The method can guarantee the high purity of materials and the steps of preparation were simplified.

Furthermore, we proposed a useful tool of thiol-ene reaction based on click chemistry to graft Ag/WPUA coating onto cotton fabric, which has the characteristics of efficiency, simple and high yield in many fields [22–24]. The reaction between thiol and lack of electronic material (such as acrylate) was described with thiol-ene reaction which caused free radicals. The initiator was emitted, and free radical was formed under the proper temperature or light. 3-mercaptopropyltriethoxysilane was used to pre-treat cotton fabrics. Due to the reaction between $-OC_2H_5$ groups of 3-mercaptopropyltriethoxysilane and −OH groups of cotton, −SH groups were introduced. Then the finishing of cotton fabric was carried out with C═C bonds provided by Ag/WPUA and −SH groups on cotton under UV radiation, with the advantages of energy-saving and environmental protection. The prepared Ag/WPUA were characterized by transmission electron microscopy, Fourier transforms infrared spectra and X-ray diffraction. The resultant cotton fabric was analyzed by antibacterial activity, thermal stability and mechanical property.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$), sodium hydroxide(NaOH), peregal O ($C_{58}H_{118}O_{24}$), isophorone diisocyanate (IPDI), 2,2-bis(hydroxymethyl) propponic acid (DMPA), methyl ethyl ketone (C_4H_8O), polyethylene glycol(PEG, Mw = 600 g/mol)and triethylamine (TEA)were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Dibutyltin dilaurate (DBTDL) and pentaerythritol triacrylate (PETA) were purchased from TCI Shanghai Co., Ltd. 3-mercaptopropyltriethoxysilane (MPTES) were purchased from Addams. Cotton fabrics (basis weight is 143 g/m^2) were obtained from Zhejiang Saintyear Textile Co, Ltd. 2, 2-dimethoxy-2-phenylacetophenone were purchased from Adamas. PEG and DMPA were degassed for 6 h by vacuum up to −0.1 mpa at 100 °C. All the chemicals were used without further purification. Deionized water was used in all experiment processes.

2.2. Treatments

2.2.1. Preparation of silver/waterborne polyurethane-acrylate coating

Synthesis of silver/waterborne polyurethane-acrylate coating was carried out according to the typical method reported in literatures [25–30]. 0.054 mol IPDI, 1 wt%$AgNO_3$, 0.025 mol PEG, 0.023 mol DMPA and 1% DBTDL were charged into a 250 ml four-necked round bottom flask fitted with a mechanical stirrer, thermometer, nitrogen inlet and reflux condenser. The stirring (150 rpm) was carried out at 80 °C for 4 h. In this process, 0.277 mol methyl ethyl ketone was slowly dropped into the system to reduce the viscosity of the reaction mixture. Subsequently, to cap the terminal of −NCO groups of pre-polymer, pentaerythritol triacrylate was added and reacted at 70 °C until the theoretical −NCO content of the pre-polymer got as determined by the dibutyl-amine titration method [31]. When the reaction mixture was cooled to room temperature, the system was neutralized by 0.023 mol TEA at room temperature for 45 min and demonized water was added into the system to obtain silver/waterborne polyurethane-acrylate coating with a solid content of about 50% under vigorous stirring at 5000 rpm for 20 min.

2.2.2. Antibacterial finishing of cotton fabrics

Pre-treatment of the cotton fabric was carried out by 15 g/L sodium hydroxide and 7 g/L peregal O at 70 °C for 30 min. Then 5 wt% MPTES was dissolved in an 80:20 ethanol and water solution at room temperature for 30 min with a mild shaking action. Cotton fabrics were dipped in the MPTES solutions for 3 min and cured at 120 °C for 5 min [32]. In the subsequent process, the cotton fabric was immersed in finishing solution with 1 wt% 2,2-dimethoxy-2-phenylacetophenone and Ag/WPUA coating, which contains various concentration of nano-silver through padding technique (pickup 76.3%), followed by UV radiation for 15 min at room temperature [33]. The cotton treated with Ag/WPU is abbreviated as Ag/WPUA-C_X where X represents the concentration of the $AgNO_3$.