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Novel immobilization of a quaternary ammonium moiety on keratin fibers for medical applications

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ABSTRACT

This paper introduces a new approach for immobilizing a quaternary ammonium moiety on a keratinous substrate for enhanced medical applications. The method involves the generation of thiols by controlled reduction of cystine disulfide bonds in the keratin, followed by reaction with [2-(acryloyloxy)ethyl]trimethylammonium chloride through thiol-ene click chemistry. The modified substrate was characterized with Raman and infrared spectroscopy, and assessed for its antibacterial efficacy and other performance changes. The results have demonstrated that the quaternary ammonium moiety has been effectively attached onto the keratin structure, and the resultant keratin substrate exhibits a multifunctional effect including antibacterial and antistatic properties, improved liquid moisture management property, improved dyeability and a non-leaching characteristic of the treated substrate.

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1. Introduction

Keratin fibers such as wool and cashmere are known as luxury textile materials because of their unique comfort and esthetic properties. They are also excellent materials for medical applications. Medical sheepskin products are now used extensively in hospitals, nursing homes and private homes for the prevention and treatment of pressure sores, bed sores and decubitus ulcers, due to their superior pressure, shear, heat, and moisture dissipation capabilities [1,2]. However, proteins in keratin fibers can harbor bacteria and act as nutrients and energy sources for bacteria under certain conditions, especially at high humidity and in the presence of sweat, soil and other contaminants [3]. The growth of microorganisms on textiles has the potential to inflict a range of unwanted effects on both the textiles and the wearers. Bacteria can discolor and degrade keratin substrates or develop unpleasant odors, reducing their effective lifespan. Moreover, some bacteria can cause cross infections, rashes and discomfort to humans [4,5]. This is especially relevant in medical applications where the textiles are expected to be in prolonged contact with the skin. In addition, people who have pressure sores and decubitus ulcers are often the ones being immunocompromised as well, due to poor circulation, old age, diabetes or other diseases, and so the need for antibacterials is even higher. It is therefore highly desirable to minimize the growth of microbes on textiles during their use and storage.

The commonly used methods of preparing antibacterial fibers and substrates involve attaching an antimicrobial agent to the fiber's surface through absorption or coating or incorporating the agent into the fibers during their extrusion. Many antimicrobial agents have been applied to textile fibers such as silver and other metal compounds, quaternary ammonium compounds, N-halamines, triclosan, polybiguanides and chitosan [3–6]. Among them, quaternary ammonium compounds (QACs) are very potent biocides. The widely accepted antimicrobial mechanism is that QACs destabilize the cytoplasmic membrane, which leads to cell leakage and eventually death [7]. At present, the application of QACs to natural fibers is generally realized through absorption and coating, and the treated fibers and fabrics are often shown to be leachable and less active after washing. As a result, the antimicrobial effect is only temporary [8]. A more sustainable approach is therefore required to immobilize QACs on surfaces by covalent bonding. This is expected to offer long-term antibacterial protection for keratin substrates, and eradicate bacteria by contact killing.

In this investigation, an acrylate monomer bearing a quaternary ammonium moiety [2-(acryloyloxy)ethyl]trimethylammonium chloride (2-AE), was employed to react with the cysteine thiol

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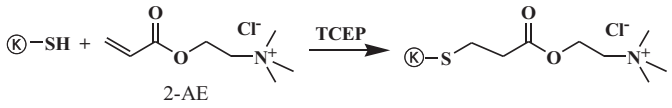

Scheme 1. The reaction of [2-(acryloyloxy)ethyl]trimethylammonium chloride (2-AE) with a cysteine thiol (Ⓚ SH).

residues (Ⓚ SH) in a keratin fiber (where Ⓚ = keratin fiber), in order to immobilize the quaternary ammonium moiety on the fiber through "thiol-ene" click chemistry [9]. The proposed reaction is shown in Scheme 1. The mechanism of this type of reaction is typically referred to as base catalyzed addition of a nucleophile. Alkyl acrylate groups are excellent acceptors, readily accepting the weaker thiol nucleophiles [10].

Wool, as one of the most widely used keratin fibers, was used as a representative keratin substrate in this study. As the cysteine thiol content in a wool fiber is limited, more available reaction sites are required in order to achieve a sufficient density of the immobilized quaternary ammonium moieties on the fiber. Recently, we have reported the controlled reduction of cystine disulfide bonds in wool with tris(2-carboxyethyl)phosphine hydrochloride (TCEP), as an effective way to produce more cysteine thiols in the fibers, while maintaining acceptable fiber mechanical properties [11]. This reductive process was directly adopted for the current study as a pretreatment step before the application of the QAC.

The QAC immobilized wool substrates were characterized by infrared and Raman spectroscopy, and evaluated for their antibacterial efficacy and performance changes in liquid moisture adsorption, surface resistivity and dyeability. The sustantativeness of the treatment was also assessed.

2. Materials and methods

2.1. Materials

A Merino wool plain weave fabric of 190 g/m^2 was used in this study as a representative keratin substrate. Tris(2-carbonxyethyl)phosphine hydrochloride was purchased from Soltec Ventures (Beverly, USA). [2-(Acryloyloxy)ethyl]trimethylammonium chloride solution (80 wt.% in H_2O) was obtained from Aldrich, and the inhibitor was removed prior to use. All the other chemicals were analytic grade reagents and used without further purification.

2.2. Treatments

The pretreatment solution was prepared by dissolving TCEP in a water:ethanol (1:1 v/v) mixture to form a 20 mmol/L TCEP solution, and the pH was adjusted to about 5.0 with a Na_2CO_3/$NaHCO_3$ buffer. Wool fabrics were treated in the TCEP solutions at room temperature for 2 h, where a gentle shaking action was applied using an orbital mixer at a speed of 100 rpm. After the pretreatment, the wool samples were rinsed with deionized water, dried in the air, and stored in sealed plastic bags before being analyzed or used for further treatments.

In the subsequent process, the TCEP pretreated wool fabrics were immersed in a solution containing 10% 2-AE, in the presence of a catalytic amount of TCEP. The pH of the treatment solution was adjusted to 7.0–7.5, and the liquor to goods ratio was 50:1 (v/w). The treatment was carried out at room temperature for 15 h under gentle stirring. After the treatment, the samples were thoroughly rinsed with water and air dried.

To assess the substantiveness of the treatment, the treated samples were also subjected to an accelerated washing test using a Launder-O-Meter, where the fabric samples were washed with 2 g/L Triton X-100 (a nonionic surfactant) at 40 °C for 45 min in the presence of 10 stainless steel balls, followed by thorough rinsing with water.

2.3. Infrared and Raman spectroscopic analyses

Infrared attenuated total reflectance (ATR) spectra were collected from the fabrics using a Perkin Elmer (Beaconsfield, UK) System 2000 Fourier transform infrared spectrometer fitted with single bounce ZnSe Pike Technologies MIRacle ATR accessory (Madison, USA) and mercury cadmium telluride detector. Spectra were collected at 4 cm^{-1} resolution with 64 scans co-added. Spectra obtained from several locations of each treated sample revealed little variability. For comparison purposes, all infrared spectra were normalized on the amide I band at 1635 cm^{-1}.

Raman spectra were obtained at a resolution of 4 cm^{-1} using a Bruker RFS-100 FT-Raman spectrometer (Karlsruhe, Germany) equipped with an Adlas Nd:YAG laser operating at 1.064 μm and a liquid nitrogen cooled germanium diode detector. Fabric samples were held on a mirrored backing, while solids and liquids were held in glass vials. All spectra were collected in 180° backscatter geometry. Data acquisition was performed using Bruker OPUS software (version 3.1). For fabrics, 512 scans were collected at a laser power 500 mW. To improve the signal to noise ratio, three spectra collected from different areas of each fabric were co-averaged to produce a final spectrum for analysis. A Blackman-Harris 3-term apodization function was used.

All spectroscopic data manipulation was carried out using Grams AI software. Fabric spectra were generally normalized on the intensity of the amide I mode at 1654 cm^{-1} as it is not affected by the presence of the monomer in either the unreacted or bound state. All peak intensity comparisons were made at the peak maxima using a consistently defined two point baseline.

2.4. Antibacterial activity test

The antimicrobial activities of the treated and untreated control wool fabrics were tested against the gram-negative bacteria *Escherichia coli* (ATCC 11229). The quantitative procedure for evaluation of degree of antibacterial activity is based on the AATCC test method 100-2004 (the assessment of antibacterial activity on textile materials); and the qualitative evaluation is according to the standard ISO-20645 (textile fabrics – determination of antibacterial activity – agar diffusion plate test).

The antimicrobial efficacy is reported as the percentage of bacteria reduction *R*% which is calculated based on the colony number of live bacteria before and after contact with the test specimen by the equation

$$R\% = 100 \times \frac{B - A}{B},$$

where *A* is the mean colony number of live bacteria recovered from inoculated test specimen swatches incubated over 5 h contact, and *B* is the mean number of bacteria after incubation of the initial culture at the same dilution factor at zero contact time. If $A > B$, no reduction occurs.

For qualitative assessment, round fabric samples (10 mm in diameter) were gently pressed onto agar plates containing the original overnight culture. The plates were incubated at 37 °C for 24 h and the zone of inhibition and interruption of bacteria growth under the samples were examined.

2.5. Physical property evaluation

A moisture management tester (MMT) was used for quantitatively assessing liquid moisture transfer characteristics of the treated and untreated substrates in multi-directions, according to

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