Korean J. Chem. Eng., **29**(4), 507-512 (2012)
DOI: 10.1007/s11814-011-0194-2

Multifunctional wool fiber treated with ε-polylysine

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(*Received 24 April 2011 • accepted 31 July 2011*)

Abstract–A creative method for fabricating environmentally-benign multifunctional wool fibers was established and reported. Through coating the wool fibers with ε-polylysine, the surface morphology and biochemical properties of the fibers were altered, enhancing their antimicrobial, hygroscopic and finished properties. The process of ε-polylysine coating was dependent on the solution environment, which influenced the electrostatic interactions between ε-polylysine molecules and wool fibers. The results showed that a maximum ε-polylysine coating (23.60 mg/g) on the surface of wool fibers was reached when wool fibers were soaked at 50 °C for 2 h in the solution with 10% on weight of fabric (owf) ε-polylysine and pH 8.0. The coated wool fiber showed promising antimicrobial rates of 96.98% and 97.93% against *Escherichia coli* and *Micrococcus luteus*, respectively. The wool fiber coated with the ε-polylysine was more hydrophilic than the uncoated wool fabrics. The functional wool fibers after water scrubbing for two times still have good antibacterial efficiency against *Escherichia coli* and *Micrococcus luteus*, and antimicrobial rates were 96.77% and 97.33%, respectively. This study shows that wool fibers modified by the nontoxic ε-polylysine have a great potential to be used in constructing multifunctional textiles.

Key words: ε-Polylysine, Wool Fibers, Antibacterial Property, Hydrophilicity

INTRODUCTION

Wool fiber is regarded as one of the most precious raw materials in the textile industry. It has been used since historical times as a source for fabric and textiles, insulation and artistic expression [1,2]. But, under certain temperature and humidity, microorganisms could be generated on the wool textiles and result in damages, skin irritations, and infections for wool products. Thus, antibacterial wool fibers have been studied in recent years and have drawn a great attention in the field of fibers materials [3,4]. Current researches on antibacterial wool are mainly carried out through antibacterial dye, chemistry modification, antibacterial finish with nano-material Ag and chemical grafting technique [5-8]. However, antimicrobial dye has a narrow antibacterial spectrum, and the wool fibers change to yellow after crosslinkers (glutaraldehyde) are used. Most metal ion antibacterial agents are modified with Cu and Ag [9]. These heavy metals can be released to cause harm to the human body during the utilization of the modified wool fibers; moreover, wastewater produced from the chemical modification method has caused problems to the environment [10,11].

Hydrophobic surface, caused by fatty layer of the wool fibers, is another challenge in the use of wool fibers. The water absorption and sweat venting properties of wool fiber are destroyed by the hydrophobic surface and, therefore, result in poor wearing comfort of the wool textiles [12,13]. Wang et al. [14] combined corona discharge with a hydrogen peroxide treatment to improve the hydrophilic properties of wool fabrics. The method made the wool fabrics absolutely hydrophilic. However, scanning electron microscopy results showed that the tip of wool scales was etched after corona discharge and parts of the scales were peeled off after the hydrogen peroxide treatment; therefore the fabric became weaker and flexible. Chen et al. [15] coated wool fabrics with an ultrathin silica layer to improve the hydrophilicity of wool fabrics. Silica sols increased both the surface roughness and surface energy of the wool fabrics; however, these wool fabrics are suggested to have poor antibacterial property.

ε-Poly-l-lysine (ε-PL) is a homo-poly-amino acid characterized by peptide bond between carboxyl and ε-amino groups of *l*-lysine. ε-PL is water soluble, biodegradable, edible and nontoxic toward humans and environment. Thus, it and its derivatives have attracted much interest in the past few years for a broad range of industrial applications such as food, medicine, environment and electronics [16,17]. As a natural bio-antimicrobial agent, ε-PL has showed great advantages as a food preservative in Japan (Ministry of Health, Labor and Welfare List of Existing Food Additives) [18]. To our best knowledge, ε-PL has such advantages as broad antibacterial spectrum, high safety, good thermal stability and wide pH adaptability [19]. It inhibits the growth of both gram-positive and gram-negative bacteria even at a concentration of only 1-8 μg/ml [20]. Therefore, ε-PL seems to be the good choice in the fabrication of antibacterial wool fibers, which is of great importance for applications influencing our daily lives. Wang et al. [21] grafted ε-PL on wool fiber via the acyl transfer reaction catalyzed by microbial transglutaminase (mTGase). They developed a new strategy for antibacterial functionalization of proteinous materials.

In this paper, environmentally-benign antibacterial wool fibers were prepared by the molecular self-assembly method with the ε-PL. ε-PL was coated to original wool fibers to form an ultrathin layer on the surface of the wool fibers, in order to produce func-

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tional fibers that possess both antibacterial and hydrophilic activity.

MATERIALS AND METHODS

1. Materials

The wool fibers used in this work were obtained from a common shop in Nanjing, PR China. ε-PL was supplied by Nanjing Xuankai Biotech Co. Ltd. (Nanjing, China). *Escherichia coli* (ATCC11303) (*E. coli*) and *Micrococcus luteus* (CMCC (B)28001) (*M. luteus*) were provided by Nanjing University of Technology.

2. Preparation of Multifunctional Wool Fiber

The main experimental procedures are as follows: First, original wool fibers were washed in wool-silk detergent (2 g/L, 50 °C, 20 min), then dried in a vacuum drier at 60 °C to remove impurities on the surface. Second, the wool fibers were soaked into a ε-PL solution with a liquid-to-fabric ratio (L : R) of 30 : 1. Finally, the treated wool fibers were washed twice with distilled water and dried to obtain the functional wool fibers. The influence of several parameters, ε-PL concentration (2% to 12% owf), pH value (4 to 10), temperature (30 to 80 °C), and time (30 to 180 min) were investigated in this paper during the second step of preparation of the multifunctional wool fibers.

3. Measurements

3-1. Concentration Determination of ε-PL in Solution

The concentration of the ε-PL in solution was determined by Agilent 1200 HPLC (Agilent, USA) using a TSK-gel G3000PWXL column (718 mm×300 mm) [22]. Mobile phase: sodium sulfate solution, which concentration was 0.3 mol·L^{-1} and pH value was adjusted to 4.0 by acetic acid. The detective wavelength was at 210 nm, the column temperature was 30 °C with a flow rate of 0.5 ml/min and an injection volume of 20 μL. As shown in Fig. 1, the peak area is proportional to the concentration of ε-PL. The amount of ε-PL adsorbed on the surface of wool can be calculated in terms of changes in the concentrations of ε-PL in treatment bath.

3-2. Characterization of Wool Fibers

Scanning electron microscopy (SEM) analysis to the wool fibers was carried out with a QUANTA200 microscope (DEI, Holland), and samples were initially coated with gold. Fourier transform infrared (FTIR) spectra were used to characterize the wool fibers with a Spectrometer-Nexus 6700 (Nicolet, USA), at a 4,000-400 cm^{-1} scale with a resolution of 4 cm^{-1}. Samples were placed in a thin KBr disk under high pressure.

3-3. Antibacterial Performance Test

Antibacterial properties of treated wool fibers were measured by shake flask testing [23,24]. *E. coli* (gram negative bacterium) and *M. luteus* (gram positive bacterium) were selected as indicators of experimental bacterias. The ratio of bacteriostasis was calculated using the following equation:

$$X_S = \frac{A - B}{A} \times 100\% \quad (1)$$

Where X_s is antibacterial effect (%), A and B are mean numbers of the bacteria in 0.2 mL mixed solutions before and after shaking. The reported data in this work were the average value of three parallel runs.

To test washing fastness, the multifunctional wool fibers were washed in the water at 25 °C with a vigorous magnetic stirring for 5 min, when the weight ratio of wool fabric to water was controlled at 1 : 200. After washing with water, the wool fibers were dried in a vacuum drier at 60 °C. The multifunctional wool fibers were washed twice before the analysis of the antibacterial properties by using Eq. (1).

3-4. Hydrophilicity Test

The contact angle of a water droplet on surface of the wool fabrics was measured by a contact angle meter (CDCA2100F). The wetting time for a drop of distilled water to sink into the sample was recorded. Each sample was measured three times, and the average value was reported in this work.

RESULTS AND DISCUSSION

1. Possible Mechanism for ε-PL Layers on Wool Fibers

Fig. 2 shows the possible model of a ε-PL layer adsorbed on wool fibers. According to the model, coating a ε-PL layer onto wool fibers may be dependent on electrostatic interactions between the wool fibers and the ε-PL. The isoelectric points of the wool fibers and the ε-PL molecules were 4.2-4.8 and around 9.0, respectively [25]. A negative charge will be formed due to the formation of $^{-}$OOC-W-NH_2 ions, when the pH value of the solution is higher than the isoelectric point of the wool (4.2-4.8). A considerable number of amino groups in ε-PL molecules are protonated and P-NH_3^+ ions

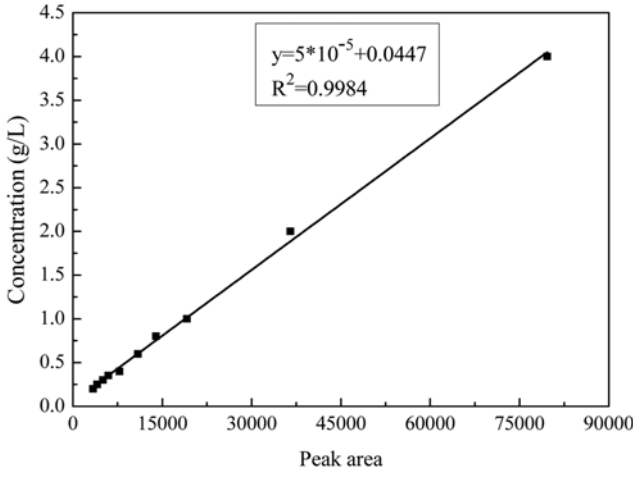

Fig. 1. Relations between concentration of ε-PL and peak area.

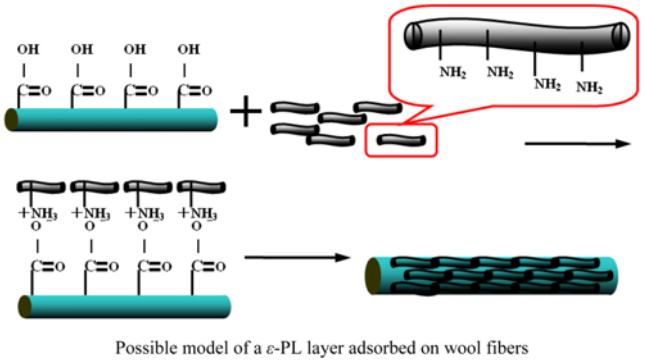

Fig. 2. Possible model of a ε-PL layer adsorbed on wool fibers.

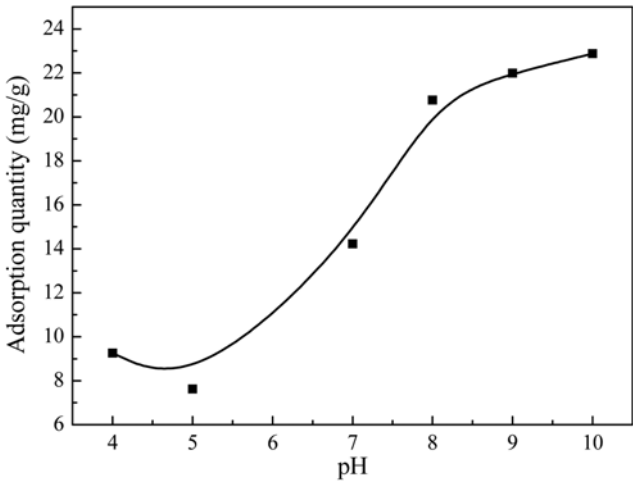

Fig. 3. Effect of pH on the amount of ε-PL adsorbed on the wool fibers (concentration of ε-PL was 8% owf, temperature was 50 °C, L : R was 30 : 1, time was 2 h).

formed when the pH is lower than the isoelectric point of the ε-PL (9.0), and hence the ε-PL molecules has a positive charge. Therefore, under the attraction of electrostatic forces, the ε-PL molecules will be adsorbed onto the surface of wool fibers and linked with electrovalent bond. The behavior of the ε-PL during the coating process was similar to dye molecules during the wet chemical processing. The antimicrobial activities of the ε-PL were observed in weak acidic or physiological pH conditions. Therefore, we suggest a ε-PL solution with pH between 5-8 will benefit the ε-PL coating on the wool surface.

2. Influence of Coating Conditions

2-1. Effect of pH

As shown in Fig. 3, the amount of ε-PL adsorbed on wool surface increased dramatically when the pH was increased from 5.0 to 8.0. This could be ascribed to the wool fibers and ε-PL molecules carrying negative charges and positive charges, respectively, at the pH between 5.0 and 8.0. Therefore, adsorption of the ε-PL on the wool fibers would occur with electrostatic forces. However, the amount of the ε-PL adsorbed on wool surface increased slowly, when the pH value was lower than 5.0 or higher than 8.0. It is suggested that the wool fibers and ε-PL molecules may have carried the same charges or lack charges when the pH value was lower than 5.0 or higher than 8.0; however, certain levels of adsorption of the ε-PL have still been obtained. It has to be pointed out that there might be other forces promoting ε-PL adsorption on the wool surface. For example, the $-NH_2$ of ε-PL combines with -OH among wool through hydrogen bonds and Vander Waals force.

2-2. Effect of ε-PL Concentration

Fig. 4 shows that the amount of ε-PL adsorbed on wool surface increased rapidly with a concentration of ε-PL lower than 8% owf and then increased at a lower rate at higher concentration of ε-PL (>8% owf). It is suggested that an equilibrium saturation point is reached when the concentration of ε-PL is higher than 8% owf. Therefore, the amount of the ε-PL adsorbed on the wool surface changed slightly at the concentration of ε-PL higher than 8% owf.

2-3. Effect of Temperature

The effect of temperature on the amount of ε-PL adsorbed on

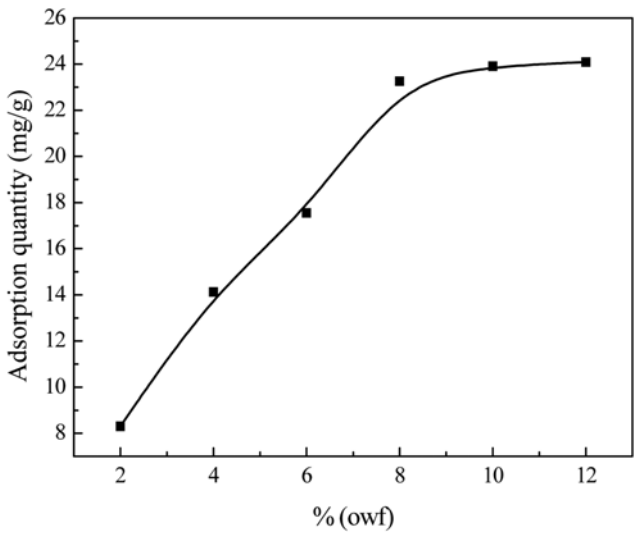

Fig. 4. Effect of ε-PL concentrations on amount of ε-PL adsorbed on wool fibers (pH value was 8.0, temperature was 50 °C, L : R was 30 : 1, time was 2 h).

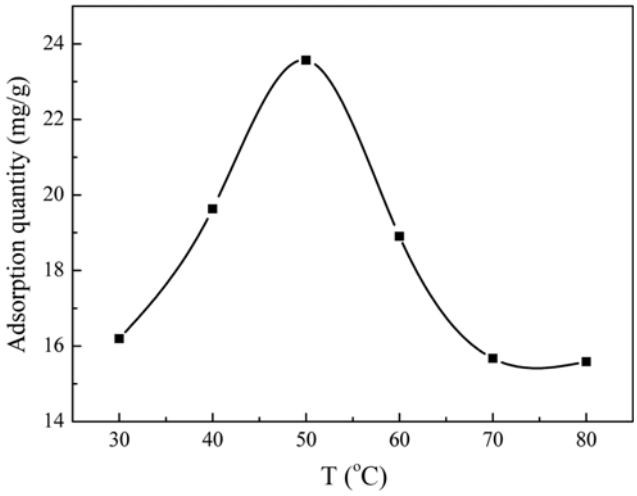

Fig. 5. Effect of temperature on amount of ε-PL adsorbed on wool fibers (pH value was 8.0, concentration of ε-PL was 8% owf, L : R was 30 : 1, coating time was 2 h).

the surface of wool is shown in Fig. 5. When the temperature was lower than 50 °C, the amount of ε-PL adsorbed on wool surface increased with the temperature. It is suggested that the increasing temperature will be beneficial to ε-PL diffuse to the wool fiber surface. But when the temperature was higher than 50 °C, the amount of ε-PL adsorbed on wool surface decreased with the temperature. The desorption rate of the ε-PL from the wool surface seemed to be dominant at a temperature higher than 50 °C. Therefore, 50 °C was the preferred operating temperature.

2-4. Effect of Coating Time

In Fig. 6, the amount of ε-PL adsorbed on the surface of wool first increased and then decreased with the coating time. It is suggested that the molecules of the ε-PL diffused to the wool fibers surface and combined with each other by electrostatic gravitation; therefore, the amount of adsorption increased at the initially coating

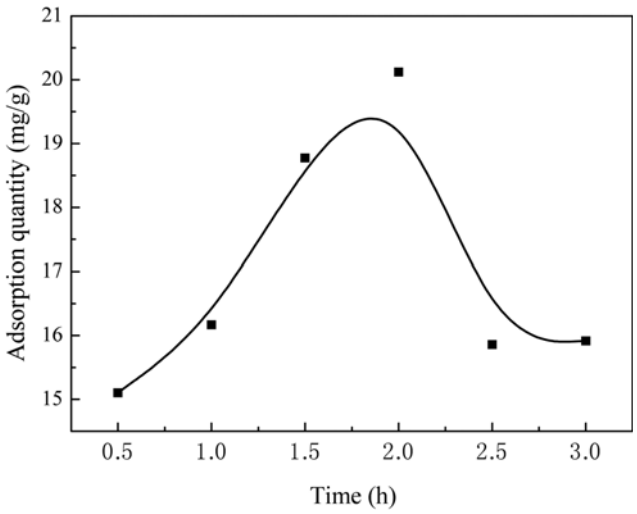

Fig. 6. Effect of coating time on amount of ε-PL adsorbed on wool fibers (pH value was 8.0, concentration of ε-PL was 8% owf, temperature was 50 °C, L : R was 30 : 1).

time. However, with the further increase of the coating time (after about 1.7 h), the amount of ε-PL molecules adsorbed on the wool surface decreased (Fig. 6). The ε-PL molecules adsorbed on the wool fibers surface may produce repulsion among themselves and result in desorption of the ε-PL molecules with the coating time longer than 1.7 h.

3. Characterization of Wool Fiber

3-1. SEM Analysis

Morphologic characteristics of the wool fibers before and after coating treatment have been shown in the SEM results (Fig. 7). Fig. 7(a) shows a piece of the native wool with well-defined scales layer covering on the shaft. Fig. 7(b) demonstrates the SEM result of the wool fibers coated with the ε-PL. The surface seems to be smooth without obvious scale structures. It indicates that the wool fibers have been effectively coated with a layer of ε-PL.

3-2. FTIR Analysis

The infrared spectra of the native and coating samples are shown in Fig. 8. All curves exhibit similar absorption bands at 3,430 cm^{-1} (N-H), 2,940 cm^{-1} (-CH_2), 1,640 cm^{-1} (Amide I), 1,510 cm^{-1} (Amide II) and 1,240 cm^{-1} (Amide III) [26,27]. Wool consists of 20 different kinds of amino acid residues, as a protein fiber. There are many -COOH, -NH_2, -OH chemical groups arranged in long strands of wool. As for ε-PL, there are similar structural characteristics in the infrared spectra [27]. For example, the peaks at 2,940 cm^{-1} are due to the -CH_2 stretching modes. It also can be found that no new functional groups and chemical bonds were produced in the ε-PL-wool.

4. Antibacterial Property

As shown in Fig. 9, the count of bacterial colonies in suspension with the functional wool was much less than that with original wool. The antibacterial efficiency against *E. coli* and *M. luteus* for the functional wool was 96.98% and 97.93%, respectively. It is indicated ε-PL molecules coating on the wool fibers could improve the antibacterial abilities dramatically compared to the uncoated wool fibers. This is because that the ε-PL have more amino groups and show aggregation state with high multivalent captions, which have the ability to destroy structure of microbial cell membranes, interrupt

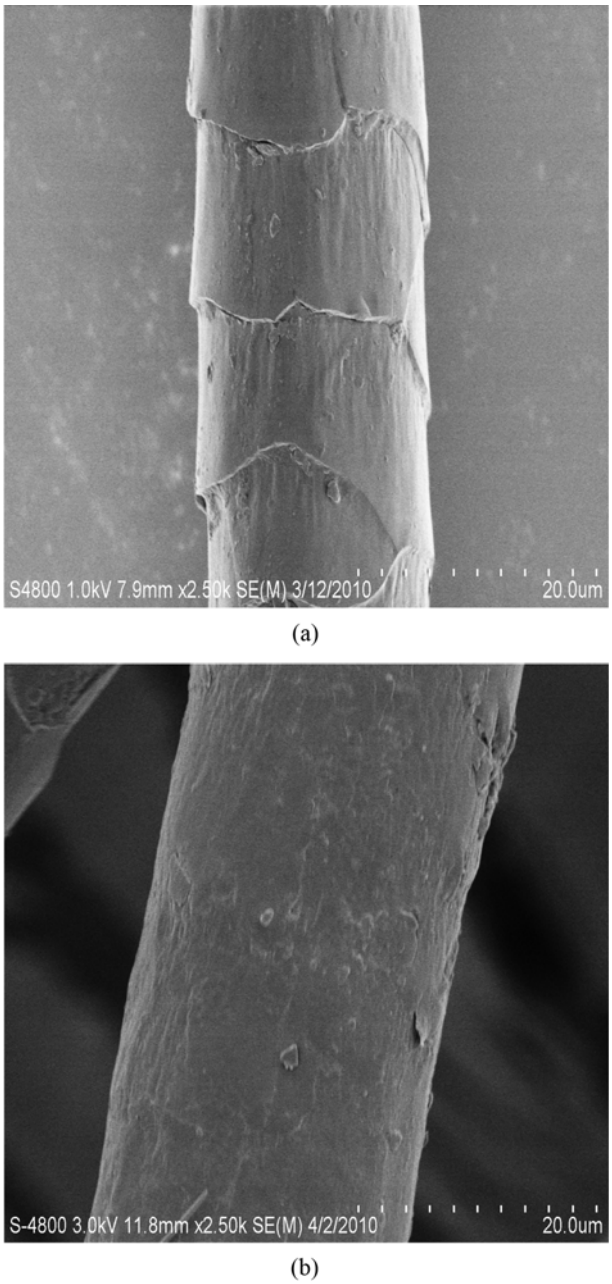

Fig. 7. The SEM images of wool fibers: (a) original, and (b) treated with ε-PL.

transmission of cell's material, energy and information. In addition, the multivalent captions could also combine with ribosomes of the cell, and affect the synthesis of biological macromolecules and result in the death of the cell finally [28].

Washing fastness is critical in the use of wool. In our daily life, machine-washable wool clothes are a growing trend that help people to do their part to reduce toxins that pollute the environment. Therefore, the durability of ε-PL -layer-coated wool fabrics with respect to water scrubbing was evaluated in this paper. The antibacterial efficiency against *E. coli* and *M. luteus* for functional wool fibers were still up to 96.77% and 97.33%, respectively, after water scrubbing for two times. The results indicated that the ε-PL coated on the wool fibers in the work has excellent physical and chemical

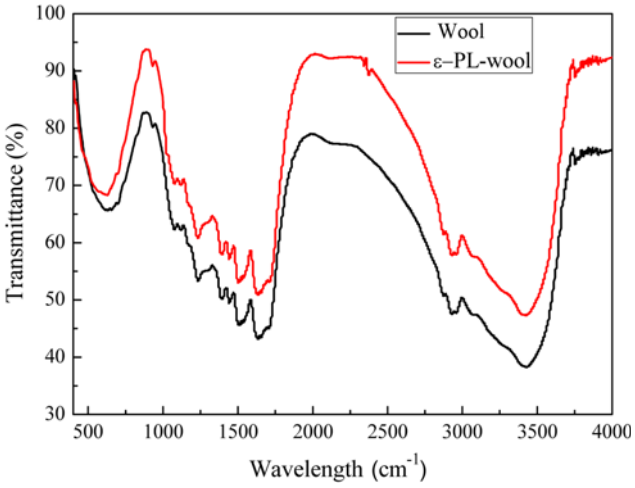

Fig. 8. FTIR spectrum of the different samples (400-4,000 cm^{-1}).

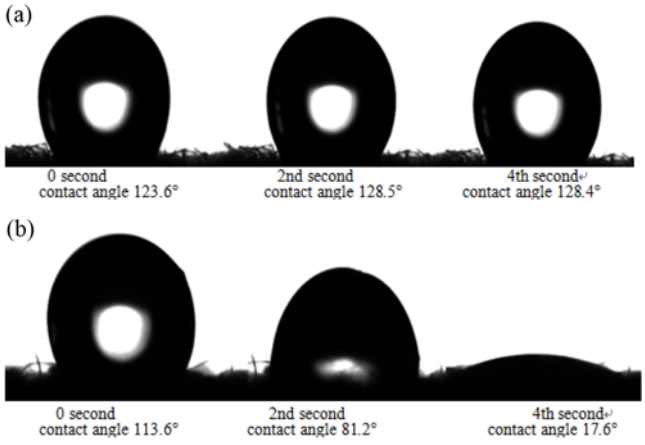

Fig. 10. Contact angle of a water droplet on wool fabrics: (a) original wool fabric and (b) ε-PL coated wool fabric.

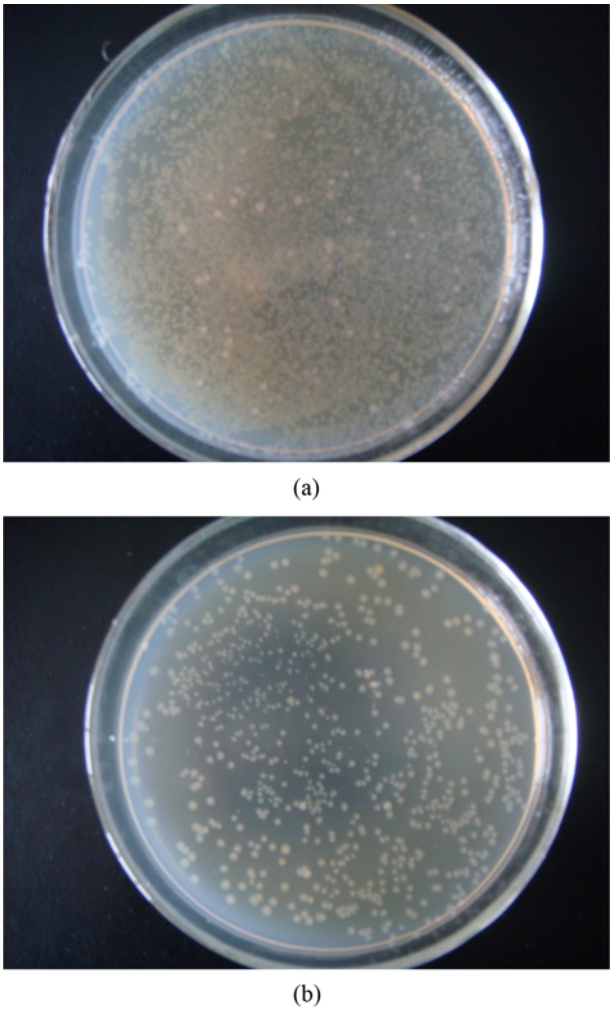

Fig. 9. (a) original wool in bacterial suspension for 18 h, (b) wool treated with ε-PL in bacterial suspension for 18 h.

stabilities. Through measuring the ε-PL concentration of washing liquid, the reduction of ε-PL on wool fibers was measured indirectly. After water scrubbing for two times, the remained content of ε-PL on wool fibers was 22.56 mg/g. Only about 4.43% of ε-PL on wool fibers was reduced, so the wool fibers still had good antibacterial properties.

5. Hydrophilicity of ε-PL Coated Wool Fabric

The hydrophilicity of the wool fabric was measured in terms of water contact angle and absorption rate of water. When liquid water was placed on the surface of the fabric, it was transferred to the fabric through capillary penetration [29]. Hydrophilicity of the fabric is known as an original force to drive the penetration. The contact angle of the original wool fabric was more than 120° during the test time because of the hydrophobic nature of the keratins (Fig. 10(a)). After ε-PL coating was applied, the water contact angle on the wool fabric decreased with time and became 17.6° at 4th second (Fig. 10(b)). A video clip was recorded to show the absorption of water droplets on the hydrophilic wool fabric. The video showed that the water absorption rate of the hydrophilic wool fabric is very fast.

The hydrophilicity improvement of wool fabric may be attributed to following reasons: First, the surface of the wool fibers has a fatty layer of 18-methyl eicosanoic acid covalently bound to the protein layer of the wool cuticle via a thioester linkage, which results in the hydrophobic property of the surface of wool [13]. After coating with a ε-PL layer on the surface of the wool fibers, the effect of the surface hydrophobicity of the nature fibers can be minimized. We need to take into consideration only the ε-PL layer wettability, which is hydrophilic because of the presence of large number of carboxyl groups and amino groups from the ε-PL molecules. Second, the surface roughness factor should also be considered during the evaluation of the surface wettability [30]. The roughness decrease of wool surface may also contribute to the improvement of wettability.

CONCLUSION

A simple method was adopted to achieve environmentally-benign antimicrobial and hydrophilic wool fibers by coating a ε-PL layer onto natural wool fibers.

In this paper, the concentration of the ε-PL in solution, the pH value and the temperature of the solution, the time for impregnation have been investigated for their influences on the amount of the ε-PL coated on the surface of the wool fibers. The results showed

that the maximum coating amount of the ε-PL (23.60 mg/g) on the surface of the wool fiber was obtained: when the pH value was 8.0, the concentration of ε-PL in solution was 8% owf, the temperature of the solution was 50 °C, and the time for impregnation was 120 min.

The antimicrobial rates of the wool fibers coated with ε-PL against *E. coli* and *M. luteus* were 96.98%, 97.93%, respectively. The ε-PL-wool fibers after being washed for two times retained good antibacterial efficiency against *E. coli* and *M. luteus*, and antibacterial rates were 96.77% and 97.33%, respectively. The wool fabrics coated with the ε-PL were more hydrophilic than the uncoated wool fabrics.

ACKNOWLEDGEMENTS

This work is supported by the National Natural Science Foundation of China (No. 20806038, 201006050), the Research Project of Natural Science for Universities Affiliated to Jiangsu Province (No. 10KJB530002), Specialized Research Fund for the Doctoral Program of Higher Education (No. 20103221120007).

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