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# Antibacterial efficacy of functionalized silk fabrics by radical copolymerization with quaternary ammonium salts

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**ABSTRACT:** Quaternary ammonium salts Quats-$C_8$, Quats-$C_{12}$, and Quats-$C_{18}$ with different alkyl chain lengths have been successfully synthesized, and used for modifying silk fabrics. The optimum reaction conditions of initiator concentration, curing temperature, curing time, and monomer concentration have been studied. The modified fabrics of silk-g-$C_8$, silk-g-$C_{12}$, and silk-g-$C_{18}$ were characterized by FTIR spectra. Antibacterial test showed that the modified silk fabrics possessed potent antibacterial activity against both Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli*. The carbon number in the alkyl chain of monomers Quats-$C_8$, Quats-$C_{12}$, and Quats-$C_{18}$ can affect the antibacterial efficacy. With longer alkyl chain, the antibacterial efficacy increased. The quaternary ammonium salts-modified silk fabrics have small change on the tensile strength and wrinkle recovery angle, and have shown potential practical application. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43450.

**KEYWORDS:** coatings; copolymers; fibres; grafting

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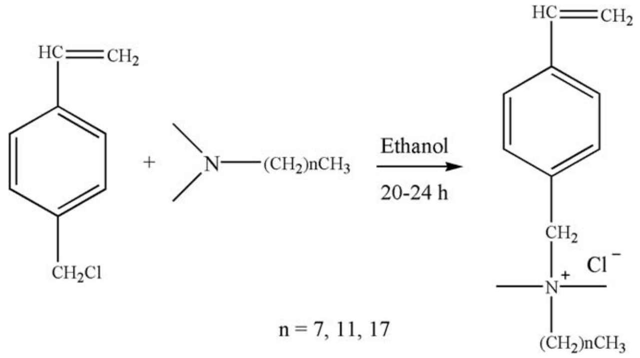
## INTRODUCTION

*Bombyx mori* silk is a natural material consisting of outside glue-like sericin and interior filament fibroin,[1,2] and has been widely used in textiles[3–5] and biomedical engineering.[6–8] Silk has been used in textiles for centuries, and has been regarded as “queen of textiles” because of its outstanding hydrophilicity, superior wear comfort, and elegant appearance. Silk also has remarkable mechanical properties, degradability, and biocompatibility. Although silk fabrics possess these favored properties, the protein component makes them easy to be contaminated by harmful microorganisms, resulting in deformation or even degradation of macromolecule chains.[9] Further applications of silk fabrics in industry are partly hindered by the bacterial adhesion. Therefore, it is considerably necessary to modify silk fabrics or silk-based materials with antibacterial property to meet the demand of consumers.

A lot of works targeting antibacterial functionalization of silk fabrics have been reported. Metal ions, such as $Ag^+$ and $Cu^{2+}$, are widely used as antibacterial agents for silk fabrics, and the influence of pH value of metal solution on the absorption of fabric surface is also investigated.[10] The in-situ synthesis approach assisted by UV light was developed to deposit silver nanoparticles onto the surface of silk fabrics with antibacterial activity, which could also postpone thermal degradation of silk fabrics.[11] $TiO_2$ and $TiO_2$@Ag nanoparticles were assembled onto the surface of silk fabrics through covalent linkages. The modified silk fabrics showed remarkable UV protection properties and potent antibacterial activity.[12] However, the disadvantages of nanoparticles such as uncontrollable release, easy aggregation and potential cytotoxicity could greatly affect the application of nanomaterial-modified silk fabrics.[13] Antimicrobial peptide was used to modify silk fabrics by carbodiimide chemistry method, and the modified fabrics were hydrophilic and easy for cell adhesion.[4] Tyrosinase was used to graft bovine lactoferrin onto silk fabrics, and the modified fabrics showed encouraging antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*. The enzymatic grafting method could also expand the washing durability of modified fabrics compared with using lactoferrin alone.[3]

Besides the aforementioned antibacterial agents, quaternary ammonium salts were also used for antibacterial modification of silk fabrics. Nanoparticles of N-[(2-hydroxy-3-trimethylammonium) propyl] chitosan chloride were coated onto silk




**Scheme 1.** Chemical structures of Quats-$C_8$ ($n = 7$), Quats-$C_{12}$ ($n = 11$), and Quats-$C_{18}$ ($n = 17$).

fabrics via a traditional dip-pad-dry-cure process. The treated fabrics demonstrated good antibacterial activity even exposed to 50 times of home laundering. However, the modification of silk fabrics caused a certain degree of breaking strength loss due to the usage of 1,2,3,4-butan etetracarbocylic acid (BTCA).[14,15]

In this study, three kinds of quaternary ammonium salts with different alkyl chain lengths were synthesized and grafted onto silk fabrics via radical copolymerization method without BTCA. The optimum conditions for this process were investigated. The modified fabrics were characterized with FTIR spectra. Antibacterial tests were conducted to reveal the relationship between antibacterial activities of the modified silk fabrics and the alkyl chain lengths of the quaternary ammonium salts. Tensile strengths and wrinkle recovery angles of the treated silk fabrics were also evaluated.

## EXPERIMENTAL

### Materials

Silk fabrics were purchased from Zhejiang Tongxiang Textiles Company, Zhejiang, China. N,N-dimethyl octylamine, N,N-dimethyl dodecylamine, N,N-dimethyl octadecylamine, and 4-vinylbenzyl chloride were provided by J&K Chemicals, Shanghai, China. Other chemicals were obtained from Sinopharm Chemical Reagent Company, Shanghai, China.

Fourier transform infrared spectra (FTIR) were recorded with a Nicolet Nexus 470 spectrometer (Nicolet Instrument Corporation). Surface morphology of treated fabric was characterized by a SU-1510 field-emission scanning electron microscope (SEM, Hitachi). Nuclear magnetic resonance (NMR) spectra obtained from the Avance III 400 MHz digital NMR spectrometer (Bruker AXS GmbH) were used to characterize the synthesized compounds. Tensile strength and winkle recovery angles of the treated samples were tested with Electronic Fabric Strength Tester (YG(B)026D-250, China) and fully automatic digital fabric crease-recovery tester (YG(B)5417, China), respectively.

### Synthesis of Dimethyl-Octyl-4-Vinylbenzyl Ammonium Chloride, Dimethyl-Dodecyl-4-Vinylbenzyl Ammonium Chloride, and Dimethyl-Octadecyl-4-Vinylbenzyl Ammonium Chloride

The 16.96 g of 4-Vinylbenzyl chloride (0.1 mol, 90%), 19.26 g of N,N-dimethyl octylamine (0.12 mol, 98%), and 150 mL of anhydrous ethanol were mixed in a 150-mL flask with the protection of $N_2$. The mixture was refluxed under 80 °C for 20–24 h. The solvent was removed by evaporation under high vacuum and the remaining product was light yellow. Diethyl ether was used to purify dimethyl-octyl-4-vinylbenzyl ammonium chloride (Quats-$C_8$) from the crude product dimethyl-dodecyl-4-vinylbenzyl ammonium chloride (Quats-$C_{12}$) and dimethyl-octadecyl-4-vinylbenzyl ammonium chloride (Quats-$C_{18}$) was synthesized using the same protocol. The reaction processes are shown in Scheme 1.

Quats-$C_8^1$H-NMR [400 MHz, (DMSO)-$d_6$]: 0.89 (3H), 1.20∼1.30 (10H), 1.74 (2H), 2.60∼2.80 (2H), 2.92∼3.00 (6H), 4.52 (2H), 5.30∼5.41 (1H), 5.90∼5.99 (1H), 6.75∼6.84 (1H), 7.49∼7.62 (4H) ppm.

Quats-$C_{12}^1$H-NMR [400 MHz, (DMSO)-$d_6$]: 0.86 (3H), 1.20∼1.47 (18H), 1.76 (2H), 2.95 (2H), 3.22∼3.30 (6H), 4.53 (2H), 5.30∼5.41 (1H), 5.93∼6.00 (1H), 6.75∼6.85 (1H), 7.49∼7.64 (4H) ppm.

Quats-$C_{18}^1$H-NMR [400 MHz, (DMSO)-$d_6$]: 0.85 (3H), 1.16∼1.38 (30H), 1.78 (2H), 2.97 (2H), 3.11∼3.25 (6H), 4.53 (2H), 5.31∼5.39 (1H), 5.92∼5.99 (1H), 6.75∼6.85 (1H), 7.50∼7.63 (4H) ppm.

### Grafting Quats-$C_8$, Quats-$C_{12}$, and Quats-$C_{18}$ onto Silk Fabric

Radical grafting copolymerization method was used to graft Quats-$C_8$, Quats-$C_{12}$, and Quats-$C_{18}$ onto silk fabrics. The modified silk fabrics were expressed as silk-g-$C_8$, silk-g-$C_{12}$, and silk-g-$C_{18}$, respectively. First, silk fabric was immersed into aqueous solution containing sodium persulfate as initiator at 60 °C for 5 min. Then the initiated silk fabric was rapidly soaked into solution containing a predetermined quantity of the synthesized antibacterial compounds. The fabrics were dipped and padded twice, dried at 100 °C for 5 min, followed by curing at higher temperature. The treated fabrics were washed vigorously with ethanol and distilled water. The percentage of weight add-on (AD) was calculated using the following equation:

$$Add-on(\%) = \frac{W_1 - W_0}{W_0} \times 100$$

Where $W_0$ was the initial weight of silk fabric (g) and $W_1$ was the weight of silk fabric after modification (g).

The influence of initiator concentration, curing temperature, curing time, and concentration of antibacterial agents was discussed. The effect of initiator concentration was evaluated with all the other three variables fixed (curing for 120 s at 150 °C with 100 g/L antibacterial agents). The appropriate initiator concentrations for each agent were used in the following discussion. Then the effect of curing temperature was evaluated (curing for 120 s with 100 g/L antibacterial agent), and followed by the evaluation of curing time with 100 g/L antibacterial agents. The influence of antibacterial agents' concentrations was discussed in the end to determine condition used in the following tests.

### Antibacterial Efficacy Test

Unmodified silk fabric—silk-g-$C_8$, silk-g-$C_{12}$, and silk-g-$C_{18}$—samples were challenged with gram-positive *S. aureus*

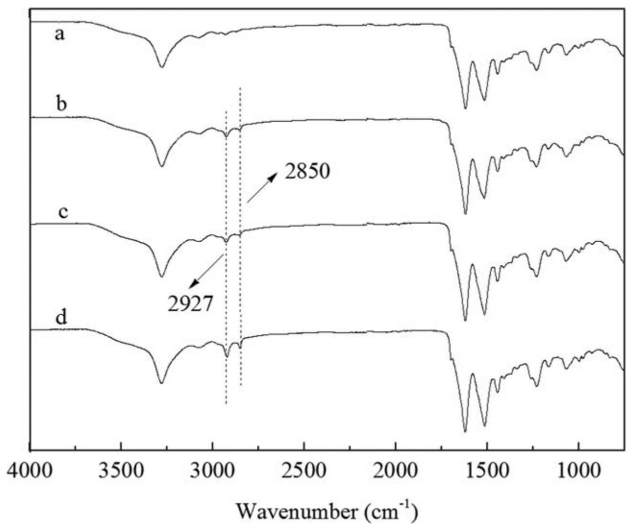



**Figure 1.** FTIR spectra of (a) unmodified silk, (b) silk-g-$C_8$, (c) silk-g-$C_{12}$, and (d) silk-g-$C_{18}$.

(ATCC6538P) and gram-negative *E. coli* O157:H7 (ATCC 11229). An aliquot of 25 $\mu$L bacterial suspension was added to the center of two 6.45 $cm^2$ (1 × 1 inch) tested samples. After 10, 30, and 60 min of contact, the bacteria were rinsed off from the tested samples and 100m*M* phosphate buffer, pH 7 was used to dilute the bacteria and each dilution was placed onto Trypticase soy agar plate duplicately. The plates were incubated at 37°C for 24 h, and the bacterial numbers were used to calculate the antibacterial activities of the tested samples. The antibacterial tests were repeated and assigned as Exp 1 and Exp 2.

### Tensile Strength Test

The tensile strength of unmodified silk fabric—silk-g-$C_8$, silk-g-$C_{12}$, and silk-g-$C_{18}$—samples was tested in Electronic Fabric Strength Tester (YG(B)026D-250, China). In detail, samples were prepared with size of 25 × 5 cm in both warp and weft directions. Before testing, all the samples were stored in conditioning room ($T = 25$°C, RH % = 65%) for 24 h. The sample was clamped on the testing machine, and tested automatically. And resulting data for mechanical strength were available after the sample was pulled apart. Samples were tested one by one at ambient temperature and each direction was tested in quintuplicate and the average was recorded as the result.

### Wrinkle Recovery Angle (WRA) Measurement

Wrinkle recovery angles of unmodified silk fabric—silk-g-$C_8$, silk-g-$C_{12}$, and silk-g-$C_{18}$—samples were measured by fully automatic digital fabric crease-recovery tester (YG(B)5417, China). Five samples in both warp and weft directions were prepared according to the size of template (4 × 4 cm in raised character). Before test, all the samples were stored in conditioning room ($T = 25$°C, RH % = 65%) for 24 h. After placing all the samples on the machine, the wrinkle recovery angles could be tested automatically. The measurement was carried out at ambient temperature in quintuplicate and the average was taken as the result. WRA of tested sample is the sum of wrinkle recovery angle of lengthwise yarns (abbreviated as $WRA_W$) and wrinkle recovery angle of widthwise yarns (abbreviated as $WRA_F$).

## RESULTS AND DISCUSSION

### Characterization of the Treated Silk Fabrics

FTIR spectra were analyzed and the existence of antibacterial agents on the surface of silk fabrics was determined (Figure 1). The spectrum of unmodified silk at higher than 3100 $cm^{-1}$ [Figure 1(a)] showed strong band absorption, which are attributed to O—H and N—H stretching vibrations. The various amide band absorptions in the range of 1650–700 $cm^{-1}$ were attributed to polypeptides and proteins in their conformational characterization of silk fibers.[16,17] After treated with Quats-$C_8$, Quats-$C_{12}$, and Quats-$C_{18}$, the vibrational bands appeared at 2927–2850 $cm^{-1}$ [Figure 1(b–d)]. The bands are the stretching vibration of C—H bond from monomers Quats-$C_8$, Quats-$C_{12}$, and Quats-$C_{18}$,[18] which are not observed in Figure 1(a). The new bands indicated that antibacterial agents Quats-$C_8$, Quats-$C_{12}$, and Quats-$C_{18}$ had been successfully grafted onto the surface of silk fabrics.

### Reaction Conditions Effect on Copolymerization

The copolymerization efficiency is evaluated by the weight gain of treated silk fabrics. The weight gains of Quats-$C_8$, Quats-$C_{12}$, and Quats-$C_{18}$ treated silk fabrics under different conditions were investigated and the results are shown in Figure 2. The weight gains of both Quats-$C_8$ and Quats-$C_{12}$ treated silk fabrics increased with the increase of initiator concentration and reached to the highest at 3% initiator concentration with weight gains of 4.6% and 6.2%, respectively. Then the weight gain decreased when the initiator concentration further increased due to the increase of homopolymerization.[19,20] The weight gain of Quatss-$C_{18}$-treated silk fabrics showed the same tendency as Quats-$C_8$ and Quats-$C_{12}$ treated samples, except the maximum weight gains of 7.8% at 5% initiator concentration. Therefore, the initiator concentrations used in this study were 3%, 3%, and 5% for Quats-$C_8$, Quats-$C_{12}$, and Quats-$C_{18}$, respectively. With the increases of curing temperature and curing time, all the weight gains of silk-g-$C_8$, silk-g-$C_{12}$, and silk-g-$C_{18}$ went up. To minimize the decomposition of macromolecular chain of silk, the condition of curing at 150°C for 120 s was used in the further modification process. Other factors such as monomer concentration were also studied. The concentrations of Quats-$C_8$, Quats-$C_{12}$, and Quats-$C_{18}$ were chosen at 85, 74, and 50 g/L, respectively, to treat silk fabrics for obtaining the same weight gain in the following tests.

### Antibacterial Test

Bacteria could be adsorbed onto the surface of the modified silk fabrics through an ionic interaction, and the alkyl chains in quaternary ammonium salts could penetrate the cell membrane, attach to cytoplasm, and cause leakage of intracellular components, resulting in inactivation of bacteria.[21–23] Silk-g-$C_8$, silk-g-$C_{12}$, and silk-g-$C_{18}$ samples were challenged with *S. aureus* and *E. coli* O157:H7, and the antibacterial efficacies are shown in Table I. Unmodified silk fabrics were used as control, and could only cause 0.58 log reduction of *S. aureus* and 0.42 log reduction of *E. coli* O157:H7 within 60 min in the Exp 1, mainly due to the adhesion of bacteria to the surface of fabrics. After treated with quaternary ammonium salts, silk-g-$C_8$, silk-g-$C_{12}$, and silk-g-$C_{18}$ could inactivate 99.10% (2.05 log reduction),

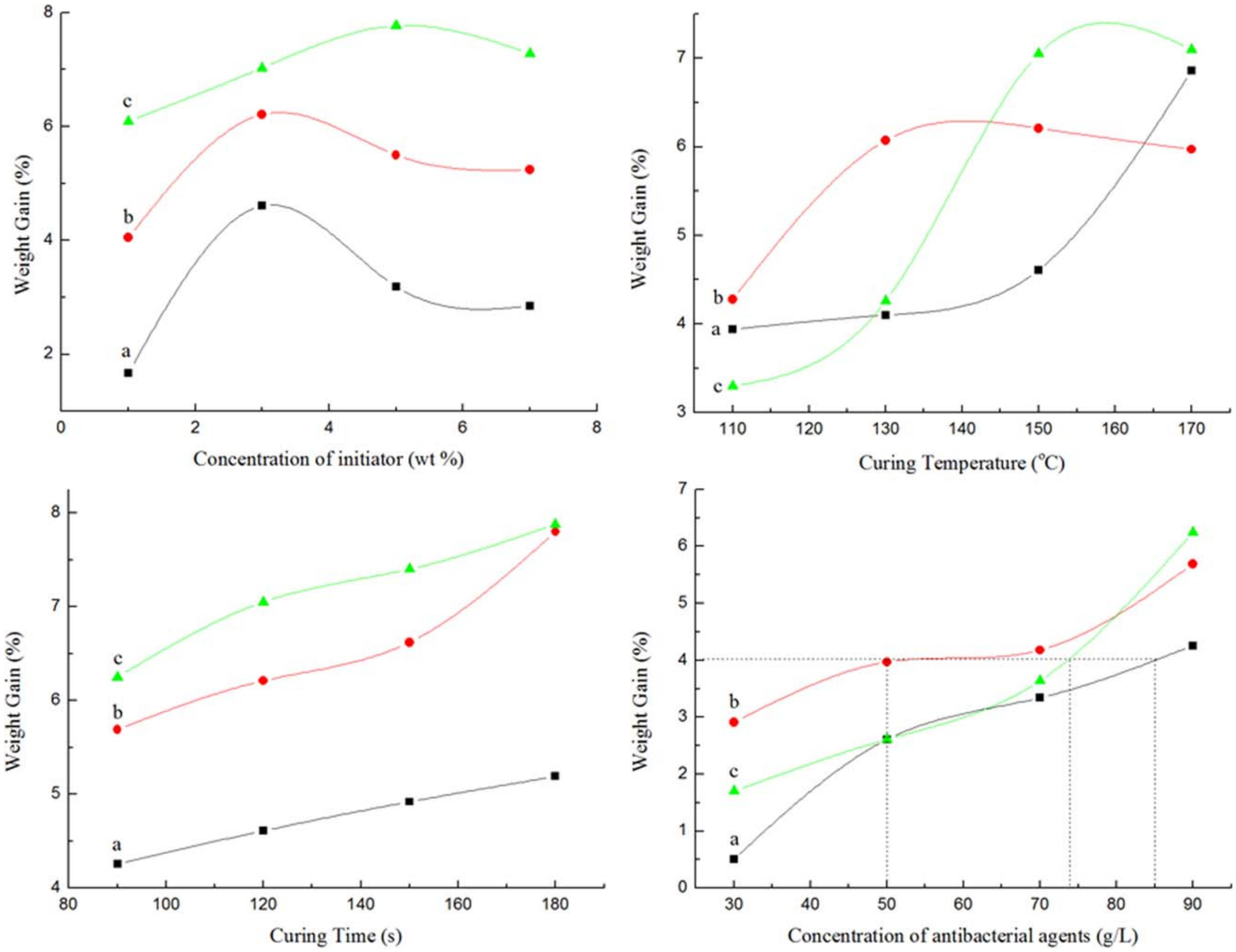



**Figure 2.** Weight gain of (a) silk-g-$C_8$, (b) silk-g-$C_{12}$, and (c) silk-g-$C_{18}$ versus different reaction conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

99.80% (2.70 log reduction), and 99.98% (3.70 log reduction) of *S. aureus* within 60 min, respectively. It can be seen clearly that with the increase of carbon number in the alkyl chain, antibacterial activity of the treated silk fabrics is generated, which is in accordance with other studies.[24] As for Gram-negative bacteria *E. coli*, 100% of these bacteria were killed within 60, 10, and 10 min for samples of silk-g-$C_8$, silk-g-$C_{12}$, and silk-g-$C_{18}$, respectively. In the Exp 2, samples of silk-g-$C_8$ could only inactivate 94.98% (1.30 logs reduction) and 93.45% (1,18 logs reduction) of *S. aureus* and *E. coli* O157:H7, respectively, within 60 min. Both silk-g-$C_{12}$ and silk-g-$C_{18}$ killed inoculated *S. aureus* completely within 10 min. *E. coli* O157:H7 were also inactivated completely by silk-g-$C_{12}$, and silk-g-$C_{18}$ within 60 and 30 min, respectively. The results in Exp 2 also showed that with the increase of alkyl length, antibacterial activities of quaternary ammonium salts-treated silk fabrics increased. The target site of cationic biocides is the cytoplasmic membrane of microorganism, and the main components of the cytoplasmic membrane are membrane proteins and phospholipids, which possess two long-chain fatty acid ends with alkyl chain length of 12–20. Thus, the quaternary ammonium salts with longer alkyl chain length can be self-assembly attached to

**Table I.** Antibacterial Efficacy Test

| Samples | Contact time (min) | Bacterial reduction (log) | | | |
|---|---|---|---|---|---|
| | | *S. aureus*[a] | | *E. coli* O157:H7[b] | |
| | | Exp 1 | Exp 2 | Exp 1 | Exp 2 |
| Silk | 60 | 0.58 | 0.19 | 0.42 | 0.37 |
| Silk-g-$C_8$ | 10 | 0.74 | 0.19 | 1.64 | 0.79 |
| | 30 | 2.00 | 0.24 | 1.70 | 1.00 |
| | 60 | 2.05 | 1.30 | 5.88 | 1.18 |
| Silk-g-$C_{12}$ | 10 | 2.30 | 6.27 | 5.88 | 0.98 |
| | 30 | 2.52 | 6.27 | 5.88 | 1.55 |
| | 60 | 2.70 | 6.27 | 5.88 | 6.12 |
| Silk-g-$C_{18}$ | 10 | 3.52 | 6.27 | 5.88 | 2.22 |
| | 30 | 3.70 | 6.27 | 5.88 | 6.12 |
| | 60 | 3.70 | 6.27 | 5.88 | 6.12 |

[a] The inoculum concentration of *S. aureus* in Exp 1 and Exp 2 were 1.62 $\times 10^6$ and 1.87 $\times 10^6$ CUF/sample, respectively.
[b] The inoculum concentration of *E. coli* O157:H7 in Exp 1 and Exp 2 were 7.52 $\times 10^5$ and 1.33 $\times 10^6$ CUF/sample, respectively.

**Table II.** Tensile Strength of Silk Fabrics Treated with Quaternary Ammonium Salts

| Samples | Warp direction (N) | Weft direction (N) |
|---|---|---|
| Silk | $1054 \pm 18$ | $486 \pm 10$ |
| Silk-g-$C_8$ | $919 \pm 47$ | $460 \pm 14$ |
| Silk-g-$C_{12}$ | $1021 \pm 12$ | $520 \pm 14$ |
| Silk-g-$C_{18}$ | $1013 \pm 26$ | $496 \pm 9$ |

the surface of microbes by strong hydrophobic affinity between the phospholipids and the alkyl chain of biocides, leading to a higher antibacterial activity.[25–27]

**Tensile Strength Test and Wrinkle Recovery Angle Test**

The results of tensile strength test of unmodified silk—silk-g-$C_8$, silk-g-$C_{12}$, and silk-g-$C_{18}$—are shown in Table II. Compared with the unmodified silk, the grafted silk fabrics showed a small degree loss of tensile strength, and more than 80% of original breaking strength in both warp and weft direction was maintained. The high curing temperature would promote the breaking of peptide bonds of protein. Considering the value-added antibacterial activity in fabrics, 20% of mechanical tensile strength loss is acceptable in practical application. The performance of wrinkle recovery angle of treated silk fabrics was investigated, and the results are shown in Figure 3. Compared with unmodified silk fabrics, the curing process had little effect on the wrinkle recovery angles of the grafted samples.

## CONCLUSIONS

Three kinds of quaternary ammonium salts—Quats-$C_8$, Quats-$C_{12}$, and Quats-$C_{18}$—have been successfully synthesized and grafted onto silk fabrics via radical grafting copolymerization process. The optimum initiator concentrations, curing temperature, curing time, and concentration of antibacterial agents were investigated. Antibacterial test showed that with increase of the number of carbons in alkyl chains, the antibacterial activity toward *S. aureus* and *E. coli* increased. The tensile strength and wrinkle recovery angles of treated samples were not significantly affected by the treating process, thus assured the practical application of quaternary ammonium salts Quats-$C_8$, Quats-$C_{12}$, and Quats-$C_{18}$-modified silk fabrics as apparel with antimicrobial properties. Also, Quats-$C_8$, Quats-$C_{12}$, and Quats-$C_{18}$ might be grafted onto other substrates by radical copolymerization method to obtain various antibacterial materials.

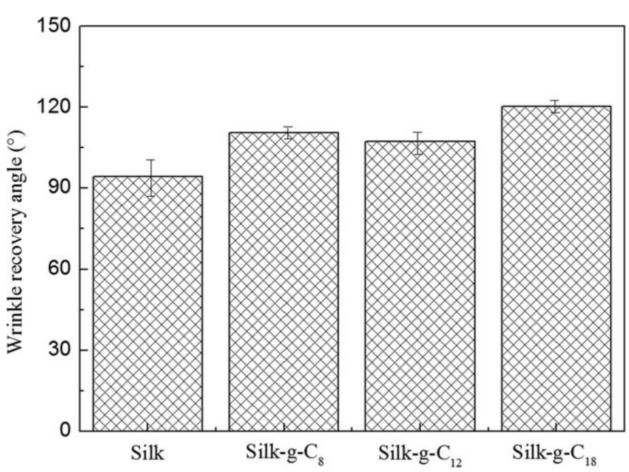



**Figure 3.** Wrinkle recovery angles of various quaternary ammonium salts-treated silk fabrics.

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