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Synthesis of pyridinium polysiloxane for antibacterial coating in supercritical carbon dioxide

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ABSTRACT: Antibacterial polysiloxane with pyridinium pendants was synthesized through hydrosilylation reaction of trimethylsiloxane terminated (45% methylhydrosiloxane)–dimethylsiloxane random copolymer and 4-vinylpyridine and subsequent N-alkylation of pyridine ring with 1-bromohexane. The pyridinium polysiloxane was coated on cotton and formed a 35 nm layer via a novel method of deposition in supercritical carbon dioxide ($scCO_2$) for biocidal application. The coated fabrics provided effective antibacterial activities against both *Staphylococcus aureus* and *Escherichia coli* compared with uncoated ones that did not exhibit noticeable biocidal activities. The pyridinium polysiloxane coating layer on cotton was stable toward storage in air and washing cycles. The $scCO_2$ deposition technique uses ecologically responsible CO_2 as solvent and is hypothesized to work on both reactive and nonreactive surfaces due to without the use of covalent tethering groups. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41723.

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INTRODUCTION

Cotton has long been recognized as a medium to support the growth of microorganisms such as bacteria and fungi due to its high hydrophilicity.[1] The growth of microorganisms on cotton inflicts a range of unfavorable effects including the generation of stains and unpleasant odor, reduced mechanical strength, and an increased likelihood of contamination. For these reasons, it is highly desirable to coat antimicrobial agents on cotton to prevent infections and protect public health.[2,3] N-halamines[4–11] and quaternary ammonium salts[12–17] are among the most widely used antibacterial agents since they kill bacteria and fungi efficiently.

Antimicrobial agents are generally low-molecular-weight compounds. The conventional approach to attach small antibacterial agents to surfaces is through physical interactions, such as hydrogen bonding, physisorption, and electrostatic attraction.[18] While certainly useful, this modification of materials is limited because of the short-term effectiveness due to the gradual release of the antimicrobial agents. Besides, the leached biocides pose a potential environmental risk. Covalently bonding antibacterial compounds to reactive groups on surfaces of substrates is then employed to avoid the leaching problem. Although chemical tethering confers durable biocidal function, the number of reactions involved to generate biocidal surfaces increases the difficulty in processing.[19] For instance, pretreatments are needed to form reactive sites on inert substrates for subsequent chemical conjugation with biocidal groups.

The use of polymeric antibacterial agents to modify polymers has steadily increased since they have advantages including enhanced antibacterial activity, reduced residual toxicity, increased selectivity, and prolonged durability.[20] Compared with small antibacterial agents, the functional polymers including antibacterial ones can be more easily immobilized onto substrates via different techniques such as covalent bonding, interpenetrating network, spin coating, and self-assembly.[21–29] Unlike covalent bonding, interpenetrating network, spin coating, and self-assembly do not require chemical bonds as tethering groups, yet still form long-lasting coatings due to the strong interactions between long chains. After ordered on the substrate, the biocidal groups segregate to the air–polymer surface and provide desirable interfacial properties, while parts of the antibacterial polymer impregnate

and entangle with chains of substrate to generate a stable coating layer. These physical techniques are thereby applicable to many substrates including inert ones.

$ScCO_2$ deposition as a means of surface modification has been successfully employed to generate new surface properties.[30,31] This method involves deposition of a CO_2-soluable functional polymer onto the surface of a CO_2-insoluable substrate in inert $scCO_2$ based on the following strategy. The functional polymer is designed to deliver functional groups onto substrate for new surface properties and is therefore also named as delivery polymer. Only a few polymers, including polysiloxanes and fluoropolymers, are noticeably soluble in $scCO_2$ under mild conditions and used as delivery polymers. Other polymers have very limited solubilities and can only swell even at high temperature and pressure. For example, although polyesters have some similar structure (C═O) to CO_2, they can only dissolve in CO_2 at over 1000 bar and 100°C.[32] Then, many polymers can serve as substrates and be modified in $scCO_2$. The dissolved delivery polymers impregnate into the swollen substrate surfaces during the $scCO_2$ deposition process. The substrates restore to original state after the release of CO_2 and thereby the impregnated delivery polymers are immobilized to form durable coating layers. Therefore, this modification is limited to the surfaces and does not alter the bulk properties of the substrates. Like other physical methods, this procedure does not rely on chemical bonding that limits the surface design. Besides, it has several unique advantages including the following: (1) it employs CO_2, which is relatively benign and has a readily accessible supercritical state, as a solvent; (2) it can easily achieve different coating results through adjustment of the solubility of the antibacterial polymer by varying operating temperature and pressure; (3) it does not need complex recovery steps since excess antibacterial polymer precipitates out after deposition process and is recycled. In previous studies, N-halamine and quaternary ammonium salt group were successfully delivered onto polymer substrates using silicones as delivery polymers and supercritical fluids as solvent.[19,31] In this article, an antibacterial polysiloxane with pyridinium pendants was synthesized for coating cellulose to offer durable biocidal activities by deposition in $scCO_2$. This study is necessary because the bactericidal function of the coating depends on not only the efficacy and the concentration of the antibacterial group, but also other factors including the architecture of the delivery polymer and the compatibility between different components of the substrate and the delivery polymer.[33] In addition, the state and surface tension of delivery polymer on substrate also have important effect on functionality of the coating layer.[34,35] For instance, it was reported that the bactericidal capacity was related to composition and organization of the surface layer and increased with increasing hydrophilicity.[36] The use of repeat Si—O—Si bonds as backbone to deliver pyridinium groups is because polysiloxanes are highly soluble in CO_2 and non-toxic to human beings.[37,38] Pyridinium salt of six carbon units in length is chosen as biocidal pendant due to its efficiency against bacteria and fungi by interaction with the constituents of the cell envelopes.[15] Antibacterial polysiloxane coating is reasonably stable since its backbone is constituted with siloxane bond that has a high bond energy. Cotton is used as substrate because cellulose materials are extensively used in everyday life and scientific research.[39,40] This modification procedure can be applied to materials of arbitrary chemistry and irregular shape since it has no such special requirements for substrates.

EXPERIMENTAL

Materials

Trimethylsiloxane terminated (45% methylhydrosiloxane)–dimethylsiloxane random copolymer (M_n: 3.1×10^3, $M_w/M_n = 2.5$) was purchased from KHS company. Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex was purchased from Shanghai SMMM, Ethanol, sodium thiosulfate, phosphate buffered saline (PBS), 1-bromohexane, and toluene were purchased from Haorong Chemical Reagent. 4-Vinylpyridine and isopropanol were purchased from J&K Scientific. Both *Escherichia coli* and *Staphylococcus aureus* were purchased from Guangzhou Industry Microbe Test Center.

Synthesis of Antibacterial Pyridinium Polysiloxane

Pyridinium polysiloxane was synthesized through hydrosilylation and subsequent N-alkylation of pyridine ring. Hydrosilylation reaction of trimethylsiloxane terminated (45% methylhydrosiloxane)–dimethylsiloxane random copolymer and 4-vinylpyridine was carried out using standard Schlenk technique. The two reactants were mixed in a round-bottom flask in the mole ratio of 1 : 1.5 (related to Si—H group and C═C group) and dissolved in degassed and dried toluene. Platinum-based catalyst was then added into the flask in such an amount to meet the ratio of 10^{-3} mol per 1 mol Si—H. The flask was sealed and thoroughly degassed with nitrogen to prevent the system from oxidation. The flask was placed in a thermostat bath that was kept at 110°C and subjected to reflux for 2 days under continuous stirring. Toluene and unreacted 4-vinylpyridine were removed using a rotary evaporator at reduced pressure after hydrosilylation to get an antibacterial precursor (the product of the first step of reaction in Figure 1). The conversion of the hydrosilylation was estimated to be 62% by weight. Unreacted Si—H bonds were sealed by isopropanol. The antibacterial precursor was then quaternaried with 1-bromohexane at 75°C overnight and then excess 1-bromohexane was removed using a rotary evaporator at reduced pressure to get the antibacterial pyridinium polysiloxane. The pyridinium polysiloxane is a viscous liquid with a viscosity of 904 mPa.s, much higher compared with 37.6 mPa.s of trimethylsiloxane terminated (45% methylhydrosiloxane)–dimethylsiloxane random copolymer measured using a NDJ-1 rotary viscometer. The overall synthesis procedure is schematically depicted in Figure 1.

Coating Procedure

Pyridinium polysiloxane and a magnetic stir were placed into a glass vial to avoid direct contact with cotton swatches. The vial and uncoated samples were placed inside a high pressure chamber with an internal volume of 100 mL and a design pressure of 30 MPa. CO_2 was used to flush the air out of the whole system for 1 min and then was pumped into the high pressure chamber to the 25 MPa using a syringe pump. The coating results depend on the pressure, temperature, and coating time.

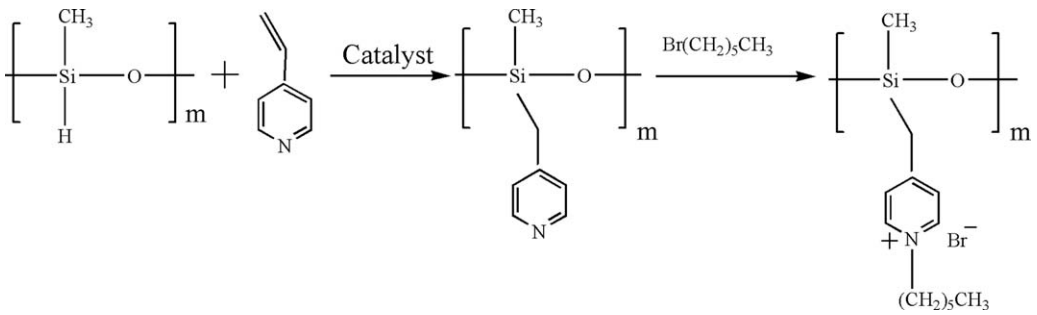

Figure 1. Schematic procedure for synthesis of pyridinium polysiloxane.

Polymers have higher solubilities under increased pressure of $scCO_2$. The pressure of 25 MPa was selected for safety reason because it is very close to the design pressure. The temperature of the high pressure chamber was maintained at 50°C during the coating process since polysiloxanes have maximum solubility at this temperature.[37] Coating time affects the thickness of coating layer since it takes time for the antibacterial polysiloxane to achieve equilibrium solubility in CO_2 and impenetrate into the fiber surface. The coating time was chosen to be three hours in this study because the coating results did not change measurably after such an incubation time. It is naturally expected that maximum amount of pyridinium polysiloxane can be coated on cotton with our equipment under these conditions to provide the best antibacterial activities.

Antibacterial Assay

All of the samples were immersed in water/ethanol (30/70 V/V) for five seconds and dried in a sterile hood before antibacterial testing. Our previous study has demonstrated that the mixed solution could kill microbes in the fabrics completely.[31] Gram-negative *E. coli* and gram-positive *S. aureus* were used to test the antibacterial capacity of the pyridinium polysiloxane coated samples according to a "sandwich test."[41] Both *E. coli* and *S. aureus* were cultivated in broth solutions for 24 h at 37°C. The bacteria containing broths were centrifuged and, after removal of the supernatants, the cells were washed with PBS, and then resuspended in PBS to densities of 10^7-10^8 CFU/mL. One hundred microliter of freshly prepared bacterial suspension was placed in the middle of two pieces of pyridinium polysiloxane coated samples (2.5 cm^2 per swatch). A sterilized beaker was put on the top of swatches to ensure sufficient contact. After various contact times, the swatches were placed into 10 mL of 0.05% sterilized sodium thiosulfate solution and vortexed for 2 min. The viable bacterial concentrations were determined using the serial dilution and spread plate technique. The vortexed solution was serially diluted and then 100 μL of each diluent was added onto agar plates (tryptic soy agar for *S. aureus* and LB agar for *E. coli*, respectively). Finally, colony forming units on the plates were counted after an incubation time of 24 h at 37°C. The same antibacterial tests were also performed for uncoated swatches as controls. The reported values were average values of three measurements in this study.

Washing Stability Test

The stability of the antibacterial function was investigated by washing cycles according to AATCC 61-1996 method (Test 2A procedure). 2.5×5.1 cm cotton swatches were subjected to repeated laundry washings inside canisters in which 50 stainless steel balls were added with 150 mL of 0.15% AATCC detergent water solution at 49°C. One washing cycle is equivalent to five machine washings. Samples were then rinsed with distilled water three times and dried at ambient temperature after washing. The dried samples were subsequently titrated to calculate the areal density of pyridinium group by measuring the bromine content using Volhard titration method.[42]

Instrumentation

X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Thermo Scientific Escalab 250Xi spectrometer. The working pressure of the spectrometer was maintained below 1×10^{-6} Pa and a low energy electron flood gun was used to neutralize surface charging. XPS survey spectra were obtained using an analyzer pass energy of 100 eV and a BE resolution of 1 eV, while high-resolution spectra were acquired with a pass energy of 50 eV and a BE resolution of 0.05 eV. Binding energies were referenced to the aliphatic C1s peak at 284.8 eV. Atomic concentrations were calculated by normalizing peak areas with the elemental sensitivity factor data provided in the XPS database.

FTIR data were collected by a Nicolet Magna IR-560 FTIR spectrophotometer using KBr pellets in the range from 400 cm^{-1} to 4000 cm^{-1} with 32 scans at a resolution of 4 cm^{-1}.

Cotton swatches and glass substrate were vacuum coated with gold using a KYKY SBC-12 evaporative coater. Morphology analysis of cotton swatches before and after coating was carried out on a KYKY-2800B scanning electron microscope equipped with a secondary electron detector at the accelerating voltage of 15 kV. The test chamber was maintained below 1×10^{-4} Pa and images were taken with a magnification between 200 times and 1500 times. Thickness of the coating layer on glass was measured using a FEI Nano SEM450 field emission scanning electron microscope equipped with a secondary electron detector. The image was taken using an accelerating voltage of 5KV and the test chamber was maintained below 1×10^{-4} Pa during the measurement.

RESULTS AND DISCUSSION

Synthesis of Biocidal Pyridinium Polysiloxane

The successful synthesis of the antibacterial pyridinium polysiloxane was confirmed with FTIR study as shown in Figure 2. In the spectrum of trimethylsiloxane terminated (45% methylhydrosiloxane)–dimethylsiloxane random copolymer [Figure 2(a)],

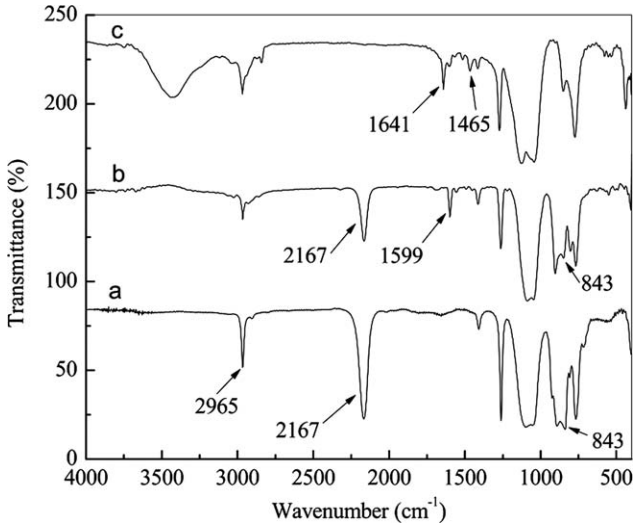

Figure 2. FT-IR spectra of trimethylsiloxane terminated (45% methylhydrosiloxane)–dimethylsiloxane random copolymer (a), antibacterial precursor (b), and pyridinium polysiloxane (c).

the peaks at around 2965 and 1407 cm^{-1} are associated with the C—H stretching and bending vibration of —CH_3, respectively. The peak at 1260 cm^{-1} is attributed to the deformations wagging of C—H in —Si—CH_3. The intense and broad band in the 1052–1101 cm^{-1} range is associated with the stretching vibration of Si—O bond. The peak at 767 cm^{-1} is attributed to stretching vibration of Si—C and in-plane deformations rocking of –CH_3. The peaks centered at 2167 and 843 cm^{-1} are attributed to the stretching and bending vibrations of Si—H bond, respectively. The intensities of these two peaks decreased significantly due to the hydrosilylation between the Si—H bonds of trimethylsiloxane terminated (45% methylhydrosiloxane)–dimethylsiloxane random copolymer and the C=C bonds of 4-vinylpyridine as shown in Figure 2(b). Besides, Figure 2(b) shows a new typical absorption band at 1599 cm^{-1} that arises from C=N stretching vibration of the pyridine ring. The following quaternization reaction resulted in an enhancement of the stretching and deformation vibrations of C—H at around 2965 and 1465 cm^{-1} caused by the introducing of the hexyl chain as shown in Figure 2(c). In addition, the specific absorption of pyridine stretches (C=N) was shifted to a higher frequency of 1641 cm^{-1} of the pyridinium form, indicating the success of the quaternization reaction. A small peak remains at 1599 cm^{-1} that is assigned to unquaternized pyridine rings. The broad band centered at 3300 cm^{-1} is assigned to the O—H stretching of adsorbed water since pyridinium groups are relatively hydrophilic. Therefore, the FTIR demonstrated that the antibacterial pyridinium polysiloxane was synthesized successfully.

$ScCO_2$ Deposition of Pyridinium Polysiloxane on Cotton

Synthesized pyridinium polysiloxane was then coated on cellulose by deposition in $scCO_2$. The success of supercritical deposition of pyridinium polysiloxane on cotton swatches can be ascertained from the XPS survey scans of the cellulose surfaces before and after the coating process as shown in Figure 3. The XPS survey spectrum of pyridinium polysiloxane coated cotton

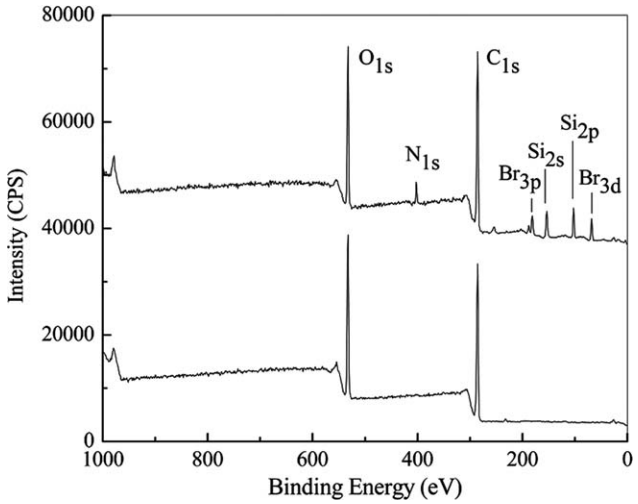

Figure 3. XPS survey scans of the surfaces of pristine cotton (bottom) and pyridinium polysiloxane coated cotton (top).

swatch exhibits new peaks that originate from the pyridinium polysiloxane as there are no such peaks in the pristine structure. The additional peaks are assigned to Si_{2s} at about 151 eV, Si_{2p} at about 102 eV, Br_{3p} at about 183 eV, Br_{3d} at around 68 eV, and N_{1s} at 402 eV, respectively. However, only peaks of C_{1s} at 284.8 eV and O_{1s} at 531.9 eV are present in the XPS spectrum of the surface of pristine cotton swatch. Furthermore, high-resolution spectrum of N_{1s} (Figure 4) shows a doublet centered at about 399 and 402 eV attributable to the imine moieties (—N=of pyridine rings and the N^+ groups of pyridinium ions, which confirms the derivatization of the imine groups by 1-bromohexane. This information indicates that the quaternization of N-pyridine rings with 1-hexylbromide is not complete, consistent with previous FTIR measurement. The degree of alkylation of the pyridine rings is estimated to be 71.3% based on the ratio of $[N^+]/[N]$ obtained from the XPS multiplex scan, in good agreement with the Br_{3d}/N_{1s} ratio of 73.4%.

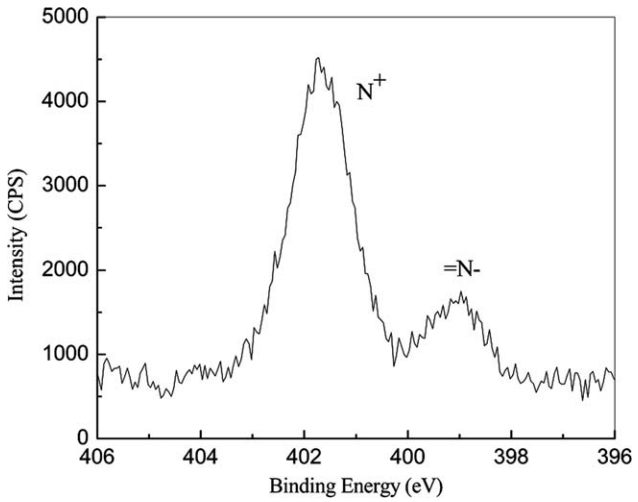

Figure 4. High-resolution N_{1s} XPS spectrum of surface of pyridinium polysiloxane coated cotton.

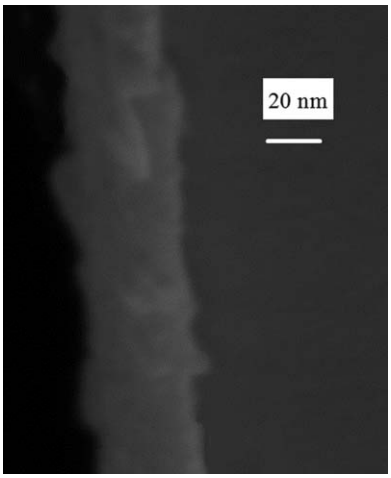

Figure 5. SEM image of pyridinium polysiloxane coated glass (magnification 5,00,000×).

Characterization of the Coating Layer

The thickness of the coating layer and the amount of pyridinium groups are important to the antibacterial efficiencies and can be estimated from the structure of pyridinium polysiloxane and the weight increase of cotton swatch before and after $scCO_2$ deposition.[31] The thickness of the pyridinium polysiloxane coating was estimated to be about 35 nm by using the following eq. (1):

$$h = {}^{d(W_1 - W_0)\rho_C}\Big/_{4W_0\rho_P} \quad (1)$$

where h is the thickness of the coating layer, d is the diameter of a cellulose fiber, W_1 and W_0 are weights of the fiber before and after supercritical coating process, respectively, and ρ_P (1.0 g/cm^3) and ρ_C (1.55 g/cm^3) are densities of pyridinium polysiloxane and cellulose, respectively.

The thickness of the coating layer was also characterized using FEI Nano SEM450 field emission SEM. In this study, a piece of glass was used as a model substrate and incubated with cotton swatch during the $scCO_2$ deposition process. After the coating, the cross-sectional of the glass was observed and its image was shown in Figure 5. The thickness of the pyridinium polysiloxane is about 40 nm, close to the value calculated from eq. (1). The slightly thicker coating on glass might be caused by that the pyridinium polysiloxane cannot impenetrate into the glass as it does to the cotton fibers.

The areal density of pyridinium group was calculated to be 4.62 $\times$ 10^{16}/cm^2 by using the following eq. (2):

$$N^+\% = {}^{W_P N_A}\Big/_{2AM_P} \quad (2)$$

where N_A is Avogadro's constant, A is the area of a sample, W_p is the weight of the pyridinium polysiloxane coated on the sample, and M_p (589 g/mol) is the molar weight of a segment of pyridinium polysiloxane that contains one pyridinium group.

The change of morphology of cotton yards before and after $scCO_2$ deposition was characterized by SEM. Low magnification of SEM images of pristine and modified yarn did not show obvious change on the surface morphology as shown in Figure 6(a,b) since the coating is thin and uniform. Under high magnification, clear morphological differences can be observed in the SEM images of the cotton yarns before and after coating with pyridinium polysiloxane as shown in Figure 6(c,d), respectively. The presence of the antibacterial polysiloxane coating increased the roughness of cotton fiber compared with the uncoated one. Since there is no a feasible way to find the same fiber for observation before and after the coating process, the two images in Figure 6(c,d) are different fibers and cannot be used to estimate the thickness of the coating because fibers have various diameters.

Antibacterial Efficacy of Pyridinium Polysiloxane Coated Surface

The extended application of modified substrate is determined by the functionality of the coating layer. The conferred biocidal efficacies of control samples (uncoated swatches) and antibacterial samples (pyridinium polysiloxane coated swatches) were measured by challenging with *S. aureus* and *E. coli*. It was observed that the antibacterial efficiency of pyridinium polysiloxane coated swatch was significantly enhanced and provided complete inactivation of *S. aureus* within 90 min of contact time. However, no noticeable decrease of bacteria was detected in the control experiment since the control sample showed only a 1.6 log reduction after 90 min of contact time, usually considered as the cause of the natural death and the adhesion of the bacteria to surfaces. The antibacterial activities of control and pyridinium polysiloxane coated samples against *E. coli* were similar to those against *S. aureus*. The pyridinium polysiloxane coated swatches provided to a total kill in 90 min, whereas

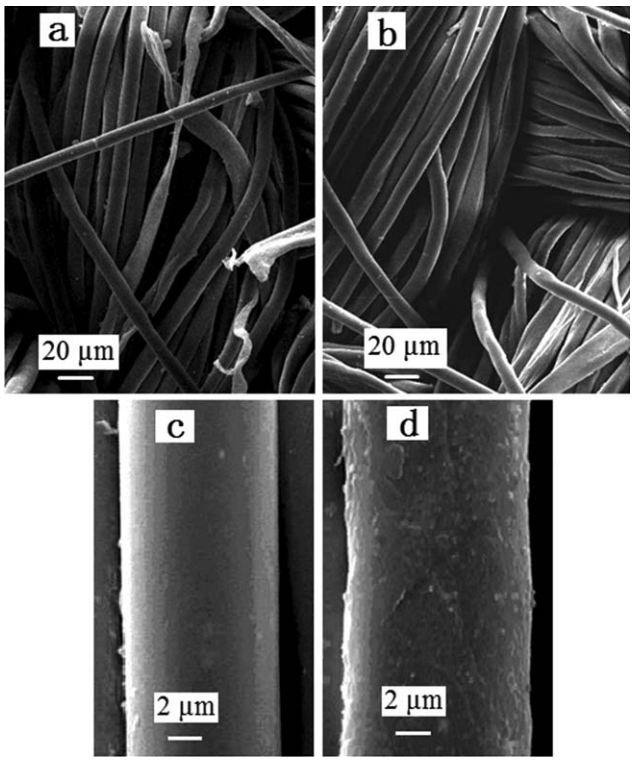

Figure 6. SEM images of pristine cotton swatch (a) (magnification 200×), pyridinium polysiloxane coated cotton swatch (b) (magnification 200×), pristine cotton fiber (c) (magnification 1500×), and pyridinium polysiloxane coated cotton fiber (d) (magnification 1500×).

Table I. Antibacterial Efficacies of the Pyridinium Polysiloxane Coated and Control Samples Against *S. aureus* and *E. coli*

Material	Contact time (min)	Log reduction of *E. coli*.	Log reduction of *S. aureus*
Control samples	30	0.75 ± 0.02	0.81 ± 0.03
	60	1.14 ± 0.03	1.02 ± 0.04
	90	1.52 ± 0.03	1.62 ± 0.04
Coated samples	30	4.71 ± 0.04	5.16 ± 0.05
	60	6.35 ± 0.02	6.84 ± 0.03
	90	7.40 ± 0.00	7.72 ± 0.00

S. aureus and *E. coli* at an inoculum population of 1.3×10^7 and 7.2×10^7 CFU, respectively.

control samples exhibited a limited degree of bacterial reduction. The antibacterial efficacies for both control and antibacterial coated samples are summarized in Table I.

Some images of the antibacterial test were shown in Figure 7 to illustrate the biocidal activities of the pyridinium polysiloxane coated cotton swathes. As described in the experimental section, the pristine cotton swatches and pyridinium polysiloxane coated cotton swatches were first contacted with *E. coli* and *S. aureus* and then vortexed. The vortexed solutions were serially diluted and 100 μL of each diluent was added onto agar plates to count formed colony forming units after incubation for 24 h at 37°C. Figure 7(a) represents the growth of colonies on the agar that was added 100 times diluted vortexed solution of pristine cotton swatches after 90 min contact time with *E. coli*. Many distinguishable *E. coli* colonies grew on the agar as seen, indicating

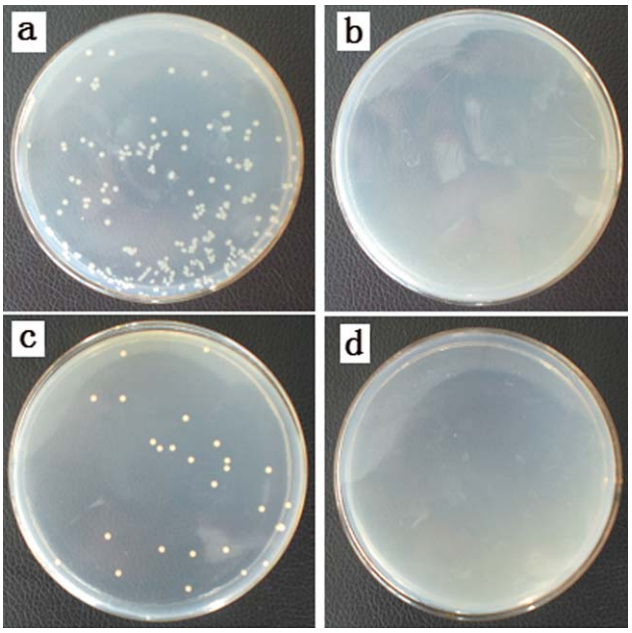

Figure 7. Photographs of growth of different bacteria on agar plates under descried conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

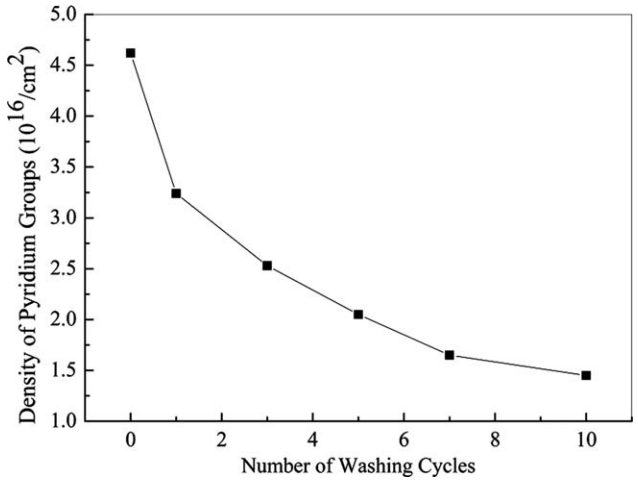

Figure 8. Remained pyridinium groups as a function of washing cycles.

that uncoated samples have little capability to inactivate the bacteria. In striking contrast, there was no visible colony formed on the agar that was added undiluted vortexed solution of pyridinium polysiloxane coated swatches after 90 min contact time with *E. coli* as shown in Figure 7(b). Similarly, *S. aureus* grew on the agar that was added 100 times diluted vortexed solution of pristine cotton swatches after 90 min contact time with *S. aureus* as shown in Figure 7(c). However, no colonies were formed on the agar that was added undiluted vortexed solution of pyridinium polysiloxane coated swatches after 90 min contact time with *S. aureus* as shown in Figure 7(d), suggesting the potent biocidal functions of the coated fabrics.

The antibacterial assay was also evaluated on the pyridinium polysiloxane coated samples by supercritical deposition after storage in air for 2 months. A similar biocidal effect was observed as for the freshly coated samples (data not shown for brevity). Hence, the antibacterial ability imparted by supercritical coating of pyridinium polysiloxane can be preserved for a relatively long period of time.

The stability of the pyridinium polysiloxane coating toward washing was also tested. The coating should be durable theoretically since the backbone of pyridinium polysiloxane is hydrophobic. Repeated washing cycles were performed to evaluate the hypothesis. After designed experiments, samples with pyridinium polysiloxane coating were rinsed with distilled water three times, allowed to dry at ambient temperature, and then measured the areal density of pyridinium group by titration to evaluate the stability of the coating. The loss of pyridinium groups increases with washing cycles as shown in Figure 8. However, pyridinium polysiloxane coatings via the $scCO_2$ deposition technique exhibited good stability since the coated samples still had more than 5×10^{15} pyridinium groups/cm^2 remaining after 50 machine washing, a concentration that would provide potent biocidal capability.[43]

CONCLUSIONS

The surface of cotton fibers was successfully coated with pyridinium polysiloxane using $scCO_2$ deposition method. CO_2-philic pyridinium polysiloxane was prepared for this purpose by

reactions of hydrosilylation and N-alkylation. The relatively benign $scCO_2$ can deliver the dissolved pyridinium polysiloxane to surfaces efficiently due to its zero surface tension. Antibacterial experiments showed that the coating provided powerful biocidal functions and was stable toward storage in air and washing. This procedure is hypothesized to work on materials of other chemistry and shape without the need for the covalent tethering groups.

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