Antimicrobial Polyester

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ABSTRACT: Two *N*-halamine siloxane precursors, 5,5-dimethyl-3-(3′-triethoxysilylpropyl)hydantoin and 3-(3′-triethoxysilylpropyl)-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]-decane-2,4-dione, have been synthesized and coated onto polyester fiber surfaces. The coated polyester was rendered biocidal after exposure to household bleach solution by converting the heterocyclic precursors to *N*-halamine moieties. The thermal properties of these coated polyester samples were determined with differential scanning calorimetry. The chlorinated polyester swatches were challenged with *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* O157 : H7 (ATCC 43895) with contact times ranging from 1 to 30 min. The biocidal testing showed that the chlorinated samples inactivated *S. aureus* and *E. coli* O157 : H7 within 5 and 30 min of contact, respectively. Standard washing tests indicated that the chlorinated coated fibers were very resistant to loss of the coating through hydrolyses. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2756–2761, 2008

Key words: biomaterials; biopolymers; functionalization of polymers; polyesters; polysiloxanes

INTRODUCTION

The introduction of antimicrobial activity into medical textiles has been extensively studied to control the growing problem of hospital-related infections. The desirable biocidal materials should be very effective at inactivating microorganisms, as well as not toxic to humans, and environmental friendly. Techniques such as coating, grafting, and blending have been employed to impart antimicrobial functions onto polymers and fabrics for protection against infectious disease pathogens.

Among the major biocidal materials such as quaternary ammonium salts,[1–3] phosphonium compounds,[4] and metal and metal salts,[5,6] the cyclic *N*-halamine compounds are the most promising candidates for use in manufacturing antimicrobial textiles due to their durable and regenerable properties upon exposure to washing cycles. The most common method to render the materials durable antibacterial activity is to produce covalent bonds between the precursor moieties and host polymers. Sun et al. have extensively applied the technology in making biocidal cellulose.[7–10] *N*-halamine compounds can be covalently bonded to nylon[7,11,12] by using similar methods. Another synthetic polymer, poly(ethylene terephthalate) (PET), can also be rendered biocidal by covalently incorporating *N*-halamine moieties.[7,13]

More recently in these laboratories, several reports addressed the synthesis and coating of a series of *N*-halamine siloxanes. These siloxanes included 3-(3′-triethoxysilylpropyl)-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione (siloxane **1**) (Fig. 1), (5,5-dimethyl-3-(3′-triethoxysilylpropyl)hydantoin (siloxane **2**) (Fig. 1), 4-[3′-triethoxysilylpropoxyl]-2,2,6,6-tetramethylpiperidine, and 3-triethoxysilylpropyl-2,2,5,5-tetramethylimidazolidin-4-one. Liang et al. have produced biocidal silica gel,[14,15] sand,[16,17] cellulose,[14,17–19] and paint[14,17] by covalently coating these *N*-halamine siloxanes onto the surfaces of the above materials. This study will demonstrate the creation of biocidal polyester by use of *N*-halamine siloxane coatings. Some ester linkages on the surfaces of polyester fibers were disassociated by treating with aqueous sodium hydroxide solution. The PET treated with NaOH was coated with 3-(3′-triethoxysilylpropyl)-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione (siloxane **1**) and (5,5-dimethyl-3-(3′-triethoxysilylpropyl)hydantoin (siloxane **2**) by the reaction of the resulting hydroxyl and carboxyl fragments with the siloxanes. After subsequent exposure to dilute household bleach, the PET fabrics coated with the *N*-halamine siloxanes will be shown to demonstrate excellent bicidal properties in inactivating *Staphylococcus*

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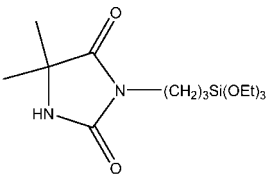
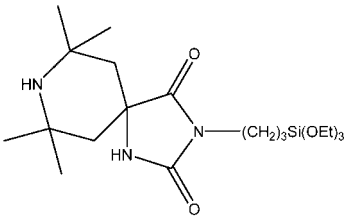


5,5-dimethyl-3-(3'-triethoxysilylpropyl)-hydantoin



3-(3'-triethoxysilylpropyl)-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione

Figure 1 Structures of siloxanes studied.

aureus and *Escherichia coli* O157 : H7 and to be stable under machine washing conditions.

EXPERIMENTAL

Materials

Fabric of 100% polyester was purchased from Testfabrics (West Pittston, PA). All chemicals used in this research were purchased from Fisher Scientific (Fair Lawn, NJ) or Aldrich Chemicals (Milwaukee, WI), and used without further purification.

Synthesis of 5,5-dimethyl-3-(3′-triethoxysilylpropyl)hydantoin and 3-(3′-triethoxysilylpropyl)-7,7,9,9-tetramethyl -1,3,8-triazaspiro[4.5]decane-2,4-dione

The potassium salts of the 5,5-dimethylhydantoin and 7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]-decane-2,4-dione were prepared by reacting 5,5-dimethylhydantoin or 7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]-decane-2,4-dione with equimolar quantities of KOH in ethanol and refluxing for 10 min.[14–16] The salts were isolated by removal of the solvent under vacuum. After drying for 2 days at 45°C, the salts described above were dissolved in DMF. Then, equimolar quantities of (3-chloropropyl)triethoxysilane were added to the above solutions, and the mixtures were stirred at 95–100°C for 16 h. The KCl produced was removed by filtration, and the DMF solvent was removed under vacuum. Hexane was used to extract the desired compounds from the residues.

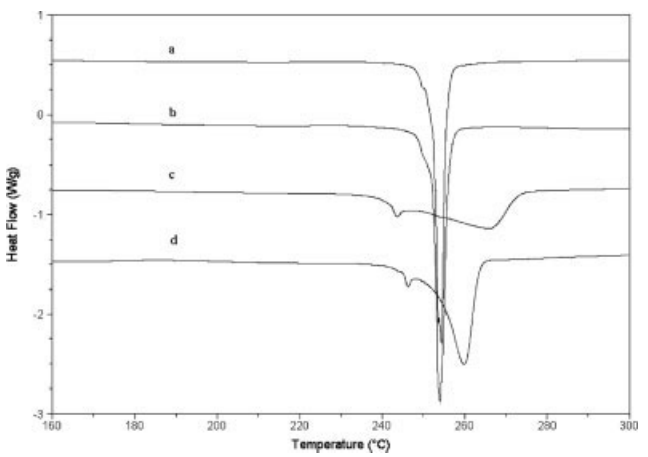


Figure 2 DSC traces of (a) PET, (b) PET treated with NaOH, (c) PET coated with siloxane **1**, and (d) Chlorinated PET coated with siloxane **1**.

Sodium hydroxide treatment of PET

The PET swatches were placed in 1*N* sodium hydroxide aqueous solution for 60 min at 95–98°C. The weight ratio of the swatch to solution was 1 : 20. The treated swatches were subsequently rinsed thoroughly with distilled water and air dried for further treatment and testing.

Coating of siloxanes onto PET

After treatment with NaOH, the polyester swatches were soaked in solutions containing 5% by weight of siloxane **1** in ethanol/water (3 : 1 w/w) or 5% by weight of siloxane **2** in ethanol/water (1 : 1 w/w) for 15 min. The swatches were dried at 100°C for 5 min, cured at 180°C for 10 min, and soaked in 0.5% detergent solution for 15 min before washing with water and drying in air.

Scanning electron microscopy

The morphologies of polyester fibers coated with siloxanes were determined by scanning electron microscopy (SEM), Jeol JSM-7000F. Samples were placed on the stub and coated with gold under argon purge before scanning.

Thermal analysis

Thermal analysis was conducted with differential scanning calorimetry (DSC) (DSC Q2000). 5–10 mg samples were scanned from 10 to 325°C at a heating rate of 10°C/min under nitrogen atmosphere.

TABLE I
Melting Point (T_m) and Heat of Fusion (ΔH_m)

Samples	T_m (°C)	ΔH_m (J/g)
PET	254.3	50.6
PET-NaOH	254.0	56.7
PET-siloxane **1**	266.3	53.8
PET-siloxane **1**-Cl	260.0	60.6

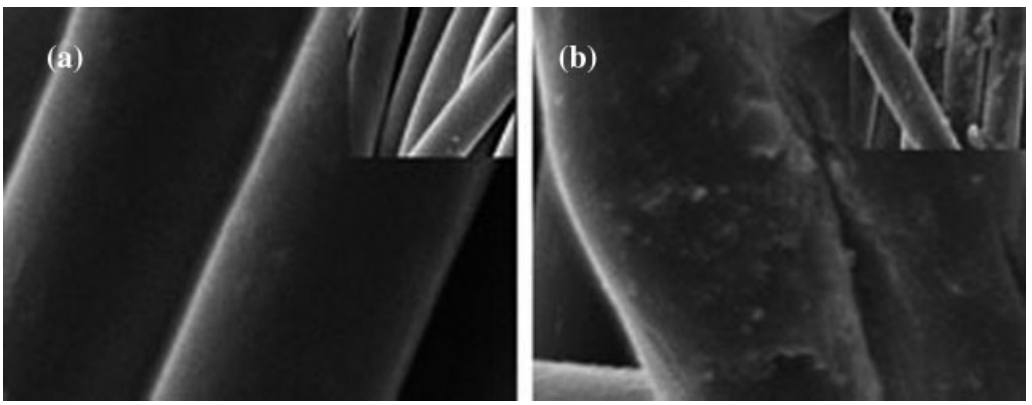


Figure 3 SEM images of (a) PET and (b) PET coated with siloxane **1** with magnification of 1000 and 5000.

Chlorination and analytical titration

The siloxane-coated PET fabric swatches were soaked in 10% solution of aqueous household bleach (NaOCl) (Clorox, Oakland, CA) solution buffered to pH 7 at room temperature for 1 h. The chlorinated PET samples were rinsed thoroughly with distilled water and dried at 45°C for 1 h to remove any remaining free chlorine. The loaded chlorine concentration on the samples was determined by the iodometric/thiosulfate titration method. The Cl^+ % on the polyester swatches was calculated from the following equation:

$$Cl^+(\%) = \frac{N \times V \times 35.45}{W \times 2} \times 100$$

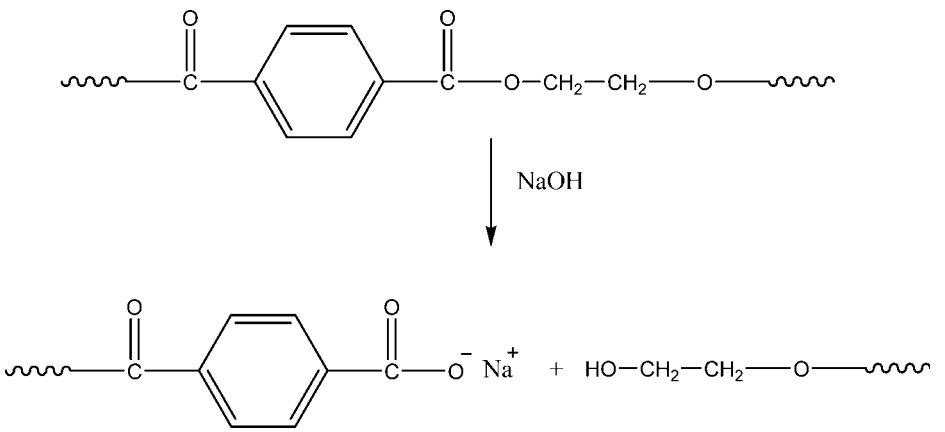
where Cl^+ (%) is the wt percent of oxidative chlorine on the samples, N and V are the normality (equiv/L) and volume (L) of the titrant sodium thiosulfate, respectively, and W is the weight of the PET swatch sample in grams.

Biocidal efficacy testing

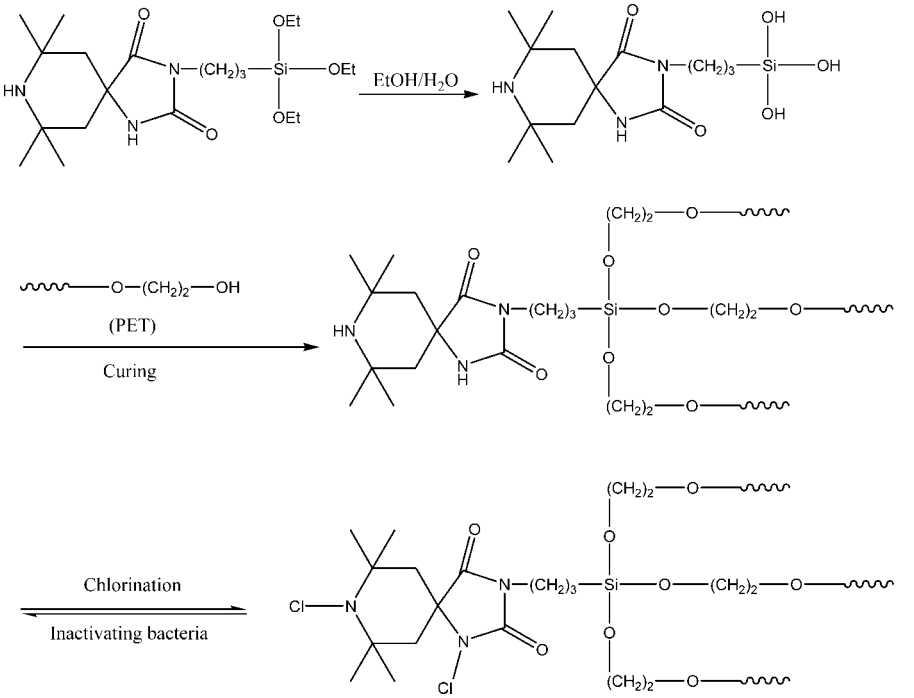
Control and chlorinated fabrics were challenged with *S. aureus* (ATCC 6538) and *E. coli* O157:H7 (ATCC 43895) using a ''sandwich test.'' Bacteria were suspended in pH 7, 100 μ*M* phosphate buffer, and 25 μL of the bacterial suspensions were added to the center of two pieces of 1 in. square polyester swatches that were held in place by sterile weights. The contact times for different samples were 1, 5, 10, and 30 min. Then, the samples were quenched with 5.0 mL of sterile 0.02*N* sodium thiosulfate solution to remove all oxidative chlorine and vortexed. Serial dilutions of the solutions of vortexed bacteria were made using pH 7, 100 μ*M* phosphate buffer, and they were plated on Trypticase soy agar. The plates were incubated at 37°C for 24 h, and viable bacterial colonies were recorded for biocidal efficacy analysis.

Tensile strength testing

The maximum loads of the PET coated with the siloxanes were determined by an Instron Model 1122 Textile Tester. The fabric swatches (1 in. × 3 in.) were tested for each sample with the results averaged. The testing was accomplished at 21°C and 65% relative humidity. The applied crosshead stress was 12 in./min.



Scheme 1 Hydrolysis of PET by NaOH.



Scheme 2 The production of antimicrobial polyester.

Standard washing testing

AATCC Test Method 61-1996 was used to evaluate the stabilities of chlorine and the coatings after repeated standard washing. Stainless steel canisters (1.5 × 2 in.) with 150 mL 0.15% AATCC detergent water solution and 50 stainless steel balls were fixed in a Launder-Ometer and rotated at 42 rpm and 49°C for 45 min. Each test sample was rinsed three times with distilled water and then dried in air at ambient temperature. Each cycle of washing using this method was equivalent to five machine washings.

RESULTS AND DISCUSSION

Characterization of polyester coated with *N*-halamine siloxanes

The thermal properties of the PET and the PET coated with siloxanes as measured by their DSC traces are shown in Figure 2. The melting point and the heat of fusion from the DSC traces are summarized in Table I. The strong sharp exothermic peaks of PET and NaOH treated PET are consistent with the processes of crystal melting. However, the DSC curves of the PET coated with siloxane **1** displayed a lower and broader melting range due to the surface coatings with the siloxane. The NaOH treatment of PET did not change the peak shape of the melting, or melting point. After siloxane coating and chlorination, the melting point of PET shifted to somewhat higher temperatures (244–246°C) and broadened due to the interaction with the siloxane. The broad peak at 260–266°C corresponds well to a broad one in the range 236–262°C, depending upon sample size, for neat **1**.

SEM images of the untreated and siloxane **1**-treated polyester fiber surfaces are shown in Figure 3. The SEM morphologies show that the PET coated with siloxane **1** had a layer of coating on the fiber compared with the uncoated sample. SEM morphologies also demonstrated the presence of coatings occurring only on the surface of the fibers, not in the interspace between the fibers in the yarns.

Biocidal test

The PET can be rendered biocidal by the forming of covalent bonds between the partially dissociated PET (Scheme 1) and the precursor *N*-halamine

TABLE II
Biocidal Test of Polyester Coated with Siloxane 1

Samples	Contact time (min)	Log bacterial reduction	
		S. aureus[a]	*E. coli* O157 : H7[b]
PET-siloxane **1**	1	0.31	0.10
	5	0.49	0.14
	10	0.54	0.23
	30	0.76	0.33
PET-siloxane **1**	1	0.15	0.10
0.32 wt % Cl^+	5	6.80	0.27
	10	6.80	1.17
	30	6.80	6.97

[a] Inoculum concentration was 6.33×10^6 CFU.
[b] Inoculum concentration was 9.33×10^6 CFU.

TABLE III
Biocidal Test of Polyester Coated with Siloxane 2

Samples	Contact time (min)	Log bacterial reduction	
		S. aureus[a]	*E. coli* O157 : H7[b]
PET-siloxane **2**	1	0.18	0.06
	5	0.19	0.14
	10	0.23	0.18
	30	0.29	0.21
PET-siloxane **2**	1	0.15	0.06
0.27 wt % Cl^+	5	6.80	0.26
	10	6.80	1.78
	30	6.80	6.97

[a] Inoculum concentration was 6.33×10^6 CFU.
[b] Inoculum concentration was 9.33×10^6 CFU.

siloxanes on the surface of the fibers (Scheme 2). The sodium hydroxide treatment mentioned in the experimental section dissociated a portion of the ester linkages of the PET and led to about a 10% weight loss of the PET. However, following the siloxane coating process, the add-on weight increased by 3%.

The biocidal test results of the PET fabrics coated with unchlorinated and chlorinated siloxanes against *S. aureus* and *E. coli* O157 : H7 are shown in Tables II and III. Clearly, all unchlorinated PET samples coated with siloxane only produced a small log reduction of the bacteria. The small reduction was caused by the adhesion of the bacteria to the PET swatches, rather than by inactivation. The inactivation rate of bacteria is always related to the contact time between the bacteria and the biocidal coating. The effect of contact time was also studied. The chlorinated swatches showed inactivation of *S. aureus* after a contact time of 1–5 min with a 6.80 log reduction, while longer contact time (10–30 min) was required to inactivate *E.coli* O157 : H7 with a 6.97 log reduction. Similar results were observed for the unchlorinated and chlorinated PET samples coated with siloxane **2**. Thus, both of the *N*-halamine siloxanes functioned well in producing antimicrobial PET.

Tensile strength of PET coated with *N*-halamine siloxanes

The results of tensile strength testing of the PET treated with sodium hydroxide and subsequently coated with siloxanes are shown in Table IV. The NaOH treatment of PET leads to about 18% strength loss compared with the control sample, because a portion of the PET ester linkages on the surface of fibers are hydrolyzed by the aqueous sodium hydroxide solution. Coating of hydrolyzed PET with siloxane **1** causes a small decrease in the fiber strength (1.5%), but subsequent chlorination does not weaken the strength of the fiber. Interestingly, the PET coated with siloxane **2** results in significant strength loss (25%), but again, chlorination of the PET coated with siloxane **2** does not affect the strength of the fibers. Thus, the process of coating PET with the *N*-halamine siloxanes to render it antimicrobial causes some loss of tensile strength, but a loss which should be acceptable given the value added by producing an antimicrobial fabric.

TABLE IV
Tensile Strength Testing of PET Samples

Samples	Load at peak (lbs)
PET	113 ± 7
PET-NaOH	93 ± 4
PET-siloxane **1**	91 ± 3
PET-siloxane **1**-Cl	90 ± 4
PET-siloxane **2**	85 ± 3
PET-siloxane **2**-Cl	85 ± 3

TABLE V
Machine Washing Testing of PET Samples Coated with Siloxane 1

Washing cycles[a]	Chlorination before washing (% Cl^+)[b]	Chlorination after washing (% Cl^+)[b]
0	0.37	
1	0.28	0.17
2	0.27	0.08
5	0.26	0.06
10	0.23	0.06

[a] A washing cycle is the equivalent of five machine washes.
[b] The samples were coated identically.

Standard washing tests

Table V shows the results of testing of PET fabric swatches coated with **1**, either prechlorinated or postchlorinated. It is evident that about 24% of the coating was hydrolyzed from the surface of the prechlorinated swatches after the equivalent of five machine washes, but little thereafter (only 38% after the equivalent of 50 machine washes). In contrast, those swatches not prechlorinated suffered more severe losses. Evidently, prechlorination renders the coated fibers more hydrophobic that protects them from hydrolyses loss. In practice, chlorination would be effected during every wash cycle leading to an extended antimicrobial lifetime.

CONCLUSIONS

N-halamine siloxanes have been successfully coated onto the surfaces of the PET fibers pretreated with aqueous sodium hydroxide. The coated PET fabrics were rendered antibacterial after chlorination exposure to the dilute NaOCl household bleach solution. The sodium hydroxide hydrolysis of the PET did not

substantially reduce the tensile strength of the fibers, because the treatment only dissociated a small percentage of ester bonds on the surface of the PET fibers. The chlorinated samples demonstrated significant biocidal efficacy against *S. aureus* with 6.8 log reduction within 5 min of contact and *E. coli* O157 : H7 with 6.97 log reduction within 30 min of contact. The coatings, when prechlorinated, were demonstrated to be durable to contact with aqueous solution, even under rigorous laundering conditions. This study represents a further use of *N*-halamine antimicrobial technology that is gaining momentum in several laboratories.[8–10,20–22]

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