Durable and Regenerable Antimicrobial Textile Materials Prepared by a Continuous Grafting Process

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ABSTRACT: A cyclic-amine monomer, 3-allyl-5,5-dimethylhydantoin (ADMH), was grafted onto various textile materials in a continuous finishing process to prepare durable and regenerable antibacterial textiles. Highly efficient radical grafting polymerizations occurred inside or on the surfaces of fibers with the assistance of different initiators. In the finishing process, particular factors such as types and concentrations of radical initiators, drying, and curing conditions were rather important in effecting the final grafts of ADMH on fabrics and were studied carefully. After exposure to chlorine, the grafted hydantoin structures in the samples could be transformed into N-halamines, which provided powerful, durable, and regenerable antibacterial activities. The influence of hydrophilic/hydrophobic properties of the fabrics on the antibacterial activities was discussed. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1592–1599, 2002; DOI 10.1002/app.10456

Key words: graft copolymers; modification; nylon; polyesters

INTRODUCTION

Textile materials are good media for growth of micro-organisms, particularly the drug-resistant bacteria, which have caused great concern to public health.[1–4] Although there is lack of direct evidence of infections caused by the contaminated textiles, better hygiene conditions in the hospital environment are always associated with lower contaminations of micro-organisms, thus less infections. Therefore, biocidal properties should be a necessary feature for medical-use textiles. Biocidal functions can be divided into sterilization, disinfection, and sanitization in an order of the strength. According to guidelines from the Centers for Disease Control and Prevention, medical use biocidal functions should be at least at the disinfection level, which can inactivate most infectious microorganisms.[5] In addition, the inactivation rate provided by the biocidal textiles is also critical. Among the currently investigated antimicrobial materials, only N-halamines have shown the capability of providing fast and total kill against a wide range of micro-organisms without causing resistance from micro-organisms.[6–9]

N-halamine structures have been incorporated into cellulose-containing and nylon fabrics by a conventional finishing method in the presence of formaldehyde.[10–13] Recently, a hydantoin-containing monomer, 3-allyl- 5,5-dimethylhydantoin (ADMH, as shown in Fig. 1) was prepared to incorporate the same hydantoin rings into textiles.[14–16] Due to the allylic structure, ADMH forms its own homopolymer only with difficulty, making it a good choice in grafting polymerization, where the formation of homopolymers, which could consume as much as 80% of the

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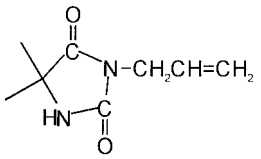

ADMH

Figure 1 Chemical structure of ADMH.

monomers added, should be minimized.[17,18] ADMH could be grafted onto several widely used natural and synthetic fabrics in the presence of a multifunctional monomer, triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATAT), in an exhaustion method.[16] The graft efficiency on the fabrics was quite low due to a competition of formation of copolymers in the solution.

The purpose of this study is to develop a continuous process that can effectively graft ADMH onto textile polymers. The continuous technique is preferred in chemical modifications of fabrics due to its high efficiency and productivity as well as low emission of waste chemicals. Furthermore, because almost no solution is involved in the curing process, the polymerization of the monomers may mainly take place in the amorphous regions and the surface areas of the fabrics, instead of in the solution.

EXPERIMENTAL

Materials

Fabrics of nylon-66 #306A, polyester #755H (PET), polypropylene #983 (PP), acrylic (Orlon #864), polyester/cotton blend #7431(PET/Cotton), and pure cotton print cloth # 400 were purchased from TestFabrics Inc. ADMH was synthesized in this laboratory according to a method reported previously.[14] Benzoyl peroxide (BPO, Acros), 2,2′-Azobisisobutyronitrile (AIBN, Acros), and potassium persulfate (PPS, Acros) were recrystallized from systems of chloroform/methanol, EtOH and distilled water, respectively. Ammonium cerium (IV) nitrate (ACN, Acros), 2′,2′-Azobis(2-methylpropionamidine) dihydrochloride (AMPAD, Aldrich), triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATAT,Aldrich), and a polyethylene softener (Sequa Chemicals, Inc.) were used without further purification. Other chemicals were purchased from either Aldrich or Fisher Scientific and used as received.

Instruments

FTIR spectra were taken on a Nicolet Magana IR-560 spectrometer using KBr pellets. The samples were made thin enough to ensure that the Beer-Lambert law was fulfilled.

Grafting Polymerization

Because both water-soluble and water-insoluble initiators were selected for the reaction, two separate ways were employed in the preparation of finishing baths. In the case of using water-insoluble initiators (BPO and AIBN), TATAT, the fabric softener, and the selected initiators were first mixed together, to which a certain amount of ADMH aqueous solution was slowly added with stirring. When water-soluble initiators (ACS, PPS, and AMPAD) were used, all of the chemicals (ADMH, TATAT, the softener and the initiator) were mixed in distilled water. Fabrics were dipped in finishing baths and padded at a required expression. This "dip-pad" process was repeated twice. Padded fabrics were dried under two conditions: (1) at 50°C for 5 min in an oven (method 1), or (2) air dried for 2 h (method 2). In some cases, the padded samples were directly cured without drying (method 3). The samples were cured in an oven at an elevated temperature for a certain period of time, and then washed with a large amount of distilled water, dried at 60°C for 24 h, and stored in a conditioning room (21°C, 65% RH) for over 72 h to reach constant weights. Percentage graft was calculated from the relation:

$$\text{Graft } \% = (W_2 - W_1)/W_1 \times 100 \qquad (1)$$

where W_1 and W_2 were the weights of the original and the grafted fabric, respectively.

Chlorination

Conversion of hydantoin structures in the grafted samples into N-halamines was conducted under two conditions: (1) synthetic fabrics and PET/Cotton blend samples were immersed in 10% (vol/vol) of a commercial regular chlorine bleach (the prepared solution contained about 3000 ppm of free chlorine), padded (80% expression), dried in an oven at 75°C for 10 min, and then washed and air dried; and (2) pure cotton samples were immersed in the above bleach solution at room temperature for 30 min with stirring (bath liquor ratio was 1:50), and then washed and air dried.

Table I Influence of Initiators on Grafting Yields

Fabrics	Grafting Yield (%)				
	BPO	AIBN	AMPAD	ACN	PPS
Nylon	4.8	2.6	1.1	0.3	UD[a]
PET	5.3	3.8	0.7	UD	UD
Acrylic	3.9	3.3	2.4	0.6	0.5
PP	5.4	2.9	1.6	UD	UD
Cotton	3.3	3.1	2.2	1.9	1.3
PET/Cotton	4.9	3.3	2.5	1.1	UD

[a]No weight increases of the fabrics were detected. Grafting conditions: padding bath contained: ADMH, 4 wt %; TATAT, 1.5 wt %; the softener, 1.5 wt %; the initiators, 0.2 wt %. The fabrics were dipped and padded twice at a 100% expression, dried at 50°C for 5 min, cured at 130°C for 5 min (for PP, the fabric was cured at 105°C for 5 min), washed, and dried.

Antibacterial Assessment

The antibacterial properties of the grafted samples were examined according to a modified Test Method 100 of American Association of Textile Chemist and Colorists (AATCC) against a Gram-negative bacterium *Escherichia coli*. The fabrics were cut into four small pieces (ca.4 cm^2), and two samples of the fabrics were put together in a sterilized container, and 10 μL of an aqueous suspension containing 10^5–10^6 colony forming units (CFU)/mL of *E. coli* were placed onto the surfaces of the fabrics. The fabrics were then covered by another two portions of the identical fabrics. To ensure sufficient contact, a sterilized 50-mL beaker was placed onto the top of the fabrics. After variable contact times, the inoculated samples were placed into 10 mL of 0.03% sodium thiosulfate aqueous solution to neutralize any active chlorine. The mixture was then vigorously shaken for 5 min. An aliquot of the solution was removed from the mixture and then serially diluted, and 100 μL of each dilution were plated onto a nutrient agar plate. The same procedure was also applied to the unhalogenated samples as controls. Viable bacterial colonies on the agar plates were counted after incubation at 37°C for 24 h. Bacterial reduction is reported according to the following equation. Durability of the biocidal properties was tested with machine washing following the AATCC Test Method 124. AATCC standard reference detergent 124 was used in all of the machine-washing tests.

$$\text{Reduction rate in numbers of bacteria (\%)} = (A - B)/A \times 100 \quad (2)$$

where A is the number of bacteria counted from untreated fabrics, and B is the number of bacteria counted from treated fabrics.

RESULTS AND DISCUSSION

In continuous textile finishing processes, fabrics will go through several steps continuously to ensure a complete incorporation of the intended chemicals. For example, they will be dipped into a solution of chemicals in a certain concentration, padded through a pressure padder to control the amount of chemicals deposited, dried under 100°C to remove any water, and finally cured at an elevated temperature to complete chemical reactions inside the polymers. The convenient setup of the chemical finishing system provides an access of incorporating allylic hydantoin monomers onto fabrics. The ADMH, radical initiator, and auxiliary chemicals can be loaded onto fabrics in dip and nip steps, while initiation of radical and grafting reactions can be accomplished in curing steps after the chemicals diffuse into the fibers in the drying process.

Influence of Initiators

Radical initiators were employed in the grafting polymerization, and typical examples are shown in Table I. These initiators can be grouped into two categories—water-insoluble (BPO and AIBN) and water-soluble (ACS, PPS, and AMPAD). In initialization of grafting reactions on both hydrophilic and hydrophobic fabrics, water-insoluble initiators performed much better than the water-soluble ones, which can be seen in terms of increased percentage grafts. Water-insoluble initiators are strongly hydrophobic and thus have high affinity to textile materials in aqueous emulsions due to the more hydrophobic characteristics of the fibers than that of water. In the drying process, these initiators could migrate or diffuse into the inner areas of the fibers. In addition,

additional monomers and auxiliaries could be adsorbed by the fibers, and therefore, could diffuse into the fibers for the same reason. Thus, under an elevated temperature at curing, the initiators could generate the grafting polymerization inside the fibers efficiently, resulting in high percentage grafts. Conversely, the water-soluble initiators were less efficient in generating grafting polymerization inside fibers due to their strong hydrophilic characteristics.

The effect of varying the BPO concentrations on percentage graft is presented in Figure 2. It can be seen clearly that the percentage grafts of the monomers increase initially, and then gradually reach to relatively constant values at 0.1–0.2 wt % of BPO. As the concentration of BPO increases, a large number of textile polymer macroradicals can be produced, which will initiate the grafting polymerization, therefore increasing the grafting yield. At even higher BPO concentration, the grafting yields increased slightly, but the properties of the fabrics were severely deteriorated, which could be caused by the increased cross-linking of the polymers.

It should be mentioned that the optimal BPO concentrations for the grafting reactions in the present continuous process are several times lower than those in the exhaustion method, as reported previously.[15] Furthermore, the grafting yields of monomers correspond to about 60–93% of the theoretical add-on of the chemicals, which are also much higher than those obtained in the exhaustion process (below 50%). In the continuous finishing process, the polymerization might occur dominantly inside and on surfaces of polymers rather than in solution because the treatment setup ensures the proper incorporation and initiation of the monomers on polymers. In the exhaustion process, self-polymerizations of monomers in the finishing solution are unavoidable under elevated temperatures, which significantly reduce grafting yield on the fabrics.

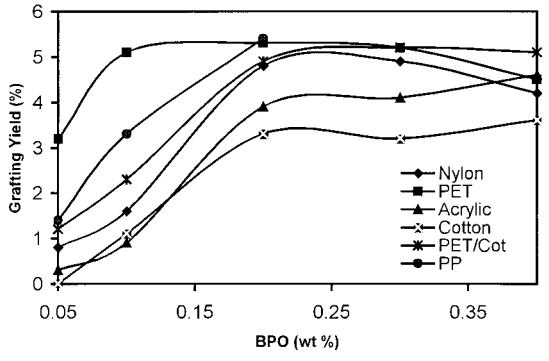

Figure 2 Influence of BPO concentration (wt %) on graft%. Grafting conditions: padding bath contained: ADMH, 4 wt %; TATAT, 1.5 wt %; the softener, 1.5 wt %; and different amount of BPO. The fabrics were dipped and padded twice at a 100% expression, dried at 50°C for 5 min, cured at 130°C for 5 min (for PP, the fabric was cured at 105°C for 5 min), washed, and dried.

Table II Influence of Drying Method on Grafting Yields

	Grafting Yield (%)		
Fabrics	Method 1	Method 2	Method 3
Nylon	4.8	5.1	2.1
PET	5.3	4.6	1.9
Acrylic	3.9	3.7	2.5
PP	5.4	4.9	1.8
Cotton	3.3	3.7	0.8
PET/Cotton	4.9	5.0	2.7

Grafting conditions: padding bath contained: ADMH, 4 wt %; TATAT, 1.5 wt %; the softener, 1.5 wt %; BPO, 0.2 wt %. The fabrics were dipped and padded twice at a 100% expression, dried at: Method 1, 50°C for 5 min, Method 2, air dried for 2 h, and Method 3, without drying. The fabrics were then cured at 130°C for 5 min (for PP, the fabric was cured at 105°C for 5 min), washed, and dried.

Influence of Drying Condition

Table II shows the influence of the drying conditions on the grafting reactions of different monomers. As described earlier, the functional chemicals are physically loaded on the surfaces of fibers after the dipping and nipping steps, and should be placed inside the polymers to promote a more efficient grafting polymerization. However, the monomers and initiators should migrate from surface areas to inside amorphous regions by diffusion, which may require some time or additional heating without the initiation of the polymerization. As expected, both method 1 and method 2 resulted in very similar percentage grafts, two to four times higher than that of method 3. In the curing process, grafting polymerization should take place on the surfaces and in the amorphous regions of the fibers due to the proper delivery of the chemicals and removal of water, while self-polymerizations of monomers, mainly occurring in the solution, are restricted. The results in Table II confirm the importance of

diffusion of chemicals in the grafting polymerization.

Influence of Curing Temperature and Time

The effect of the curing temperature on the grafting polymerization was investigated over a range of 60–140°C, which were selected based on decomposition temperatures and rates of the initiators and glass transition temperatures of the polymers. The results are shown in Figure 3. The percentage grafts were mostly lower than 1 wt % when the curing occurred under 80°C, and then increased as the curing temperatures were raised. As discussed previously,[16] higher temperature accelerated the dissociation of BPO as well as the initiation and propagation rates, resulting in higher grafting yields. More importantly, with the curing temperatures raised above the glass transition temperatures of the synthetic fibers, the amorphous areas in the polymeric fibers become more open, and the diffusion rates of the monomers and initiators in the amorphous regions can increase significantly, resulting in better grafting yields. However, for the polypropylene fabric, because of its low melting point, when the curing temperature is higher than 120°C, the fabric properties can be damaged.

The influence of curing time on the grafting polymerizations was explored under a curing temperature of 130°C, and the results are plotted in Figure 4. Increasing curing time improved grafting yields initially, but the impact became weaker as the time exceeded 5 min. Prolonged heating under elevated temperature (130°C) will promote polymer decomposition and other adverse reactions, which might be competitive factors to the grafting polymerization. A reaction time of 5 min is proper to obtain optimal grafting results in the continuous process. Compared with the exhaustion method, the optimal reaction time was reduced from 50–60 min to about 5 min in this continuous process.[15,16] This feature again demonstrates that the present continuous process has many merits in grafting modifications of fabric materials.

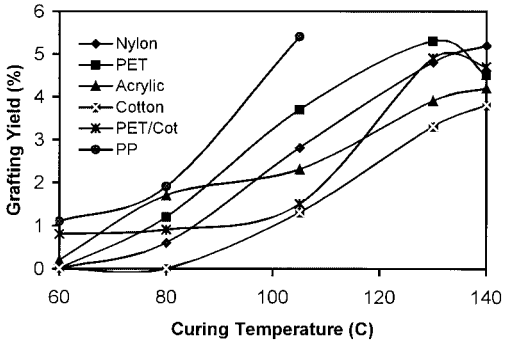

Figure 3 Influence of curing temperature (°C) on graft%. Grafting conditions: padding bath contained: ADMH, 4 wt %; TATAT, 1.5 wt %; the softener, 1.5 wt %; and BPO, 0.2 wt %. The fabrics were dipped-padded twice at a 100% expression, dried at 50°C for 5 min, and cured at different temperatures for 5 min.

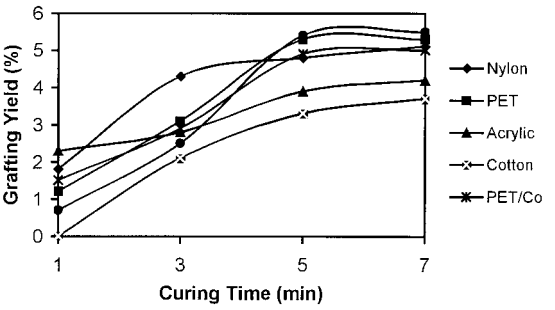

Figure 4 Influence of curing time (minutes) on graft%. Grafting conditions: padding bath contained: ADMH, 4 wt %; TATAT, 1.5 wt %; the softener, 1.5 wt %; and BPO, 0.2 wt %. The fabrics were dipped and padded twice at a 100% expression, dried at 50°C for 5 min, and cured at 130°C (for PP, the fabric was cured at 105°C) for different times.

FTIR Study

The products of the grafting polymerization were characterized by FTIR spectroscopy. As an example, Figure 5 shows the FTIR spectra of nylon (A), ADMH/TATAT grafted nylon (B), and their difference spectrum (spectrum C, subtracting spectrum A from B) in the region of 1470–1990 cm^{-1}. Due to the strong absorption band of nylon centered at 1645 cm^{-1}, little difference could be detected between the grafted and ungrafted samples. However, after subtracting spectrum A from B, three new bands at 1764, 1712, and 1685 cm^{-1} could be observed. The 1764 cm^{-1} band could be attributed to the amide structure of ADMH,[14,19] and the 1712 and 1685 cm^{-1} bands are most likely due to the overlapping of the carbonyl bands of the imide groups of ADMH and TATAT. Similar results could also be observed in other ADMH/TATAT grafted fabrics.

Antibacterial Properties

After exposure to sodium hypochlorite solutions, the hydantoin structures on the grafted fabrics

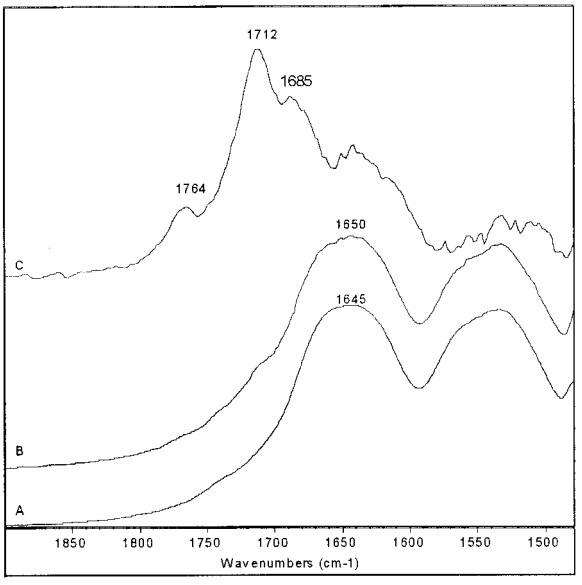

Figure 5 FTIR spectra of (A) nylon, (B) ADMH/TATAT grafted nylon, and (C) their difference spectrum (subtracting spectrum A from B) in the region of 1470–1990 cm^{-1}.

could be transformed into N-halamines, which provide powerful, durable, and regenerable antibacterial activities.[10–13,15,16] Similarly, in the present study, all of the ADMH grafted fabrics showed powerful antibacterial activities against *E. coli* after chlorination, with results presented in Table III. Significant differences were found between the synthetic fabrics and cotton. The synthetic fabrics (PET, PP, Acrylic) provided total kill of 10^5–10^6 CFU/mL of *E. coli* after a contact time of at least 20 min. However, the cotton sample demonstrated a total kill (99.999% reduction of *E. coli*) after only a contact time of 5 min, although its percentage graft of ADMH was the lowest of all the modified fabrics (see Table III). The most striking structural difference between the cotton and the rest of the fabrics is the absolute hydrophilicity of cellulose, which might be the key factor for the difference in antibacterial functions. When the inoculum of bacterial suspension was placed on the sample surface, the liquid could easily diffuse into its inner parts, and thus both of the inner and surface N-halamines could contribute to the killing power of the samples in the antibacterial test. The hydrophobic feature of the synthetic fabrics prevents good contact between the aqueous suspension of bacteria and the surface of the fiber polymers. While only the surface available active chlorine on the materials can directly contact bacteria and provide the antibacterial activities, the active chlorine inside of the materials cannot make contact with the bacteria and will require time to migrate to the surface areas from inside after the outside chlorine is consumed.[9] It would thus take the hydrophobic materials a longer contact time to provide sufficient kill due to such a migration of chlorine. Also, nylon and PET/Cotton showed similar antibacterial activities to cotton, probably due to the more hydrophilic properties of these fabrics compared to the real hydrophobic synthetic fabrics (PP, PET, Acrylic).

To further investigate the effect of hydrophilicity on antibacterial functions, Figure 6 shows the antibacterial activities of a chlorinated nylon sample before and after a water-repellent treatment. The water repellent agent was a commercially available fluorine–carbon emulsion (3M), which is widely used in chemical treatments for reducing hydrophilicity of polymer surfaces. The sample was wiped with the emulsion and air dried. As expected, although the chlorinated ny-

Table III Percentage Reduction of *E. coli* after Different Contact Time (*E. coli* concentration: 10^5–10^6 CFU/mL)

		Percentage Reduction of *E. coli* at Different Contact Times (%)			
Fabric	Graft%	5 min	10 min	20 min	30 min
Nylon	4.8	99.9	99.999	99.999	99.999
PET	5.3	UD[a]	99	99.9	99.999
PP	3.9	UD	90	99.9	99.999
Acrylic	5.4	90	99.9	99.999	99.999
Cotton	3.3	99.999	99.999	99.999	99.999
PET/Cotton	4.9	99.99	99.999	99.999	99.999

[a]No reduction of *E. coli* was detected.

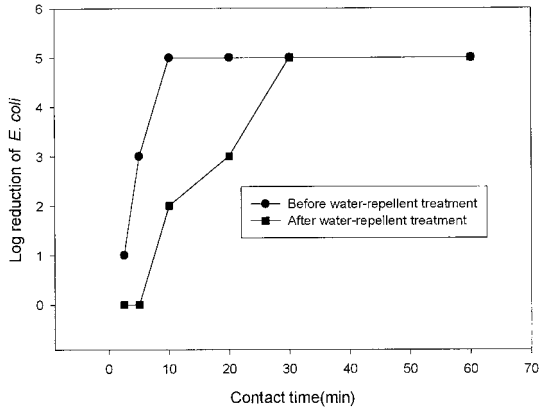

Figure 6 Antibacterial activities of a grafted and chlorinated nylon sample before and after water-repellent treatment (graft% of the nylon sample was 4.4 wt %. In the antibacterial test, the concentration of *E. coli* was 10^5–10^6 CFU/mL).

lon sample can provide a 99.999% reduction of *E. coli* after a 10-min contact time, the water repellent-treated sample demonstrated no kill at 5 min contact time, and only 99% reduction after 10 min, and a total kill after 30 min of contact time. Besides, as mentioned in the Experimental section, to ensure sufficient contact between the inoculum and the fabric surface, a sterilized 50-mL beaker was placed onto the top of the fabrics in the antibacterial tests. Separate studies showed that without this beaker, the same chlorinated nylon provided a 99.999% reduction after 60 min of contact, and for the same water-repellent sample, a contact time of 6.5 h was needed for a 99.999% reduction. Theses results further support contact kill function provided by N-halamines. However, in many cases, because of the hydrophobic properties and/or rigid conformations of the tested samples, the surface contact between the bacteria and the fibers may not be sufficient, and consequently, a false result might be obtained. Special care should be taken in the design of antibacterial test method, especially for these hydrophobic materials.

The hydrophobic characteristic of the synthetic fabrics is not necessarily a disadvantage because it could ensure excellent washing durability of the antibacterial activities to the grafted samples. For the synthetic fabrics, after 15 washes, the contact time necessary for a total kill of *E. coli* was unchanged; even after 50 washes, some of the samples could still provide 90% reduction of *E. coli* at a contact time of 30 min. As for the cotton samples, after 15 washes, the antibacterial activity was almost totally lost (see Table IV for details). Even though the antibacterial functions are lost due to application and laundering, the samples could again provide total kill at a contact time of 30 min after rebleaching (Table IV). After 10 of these "bleach → wash 20 times → rebleach" cycles, the antibacterial properties of the samples were essentially unchanged, indicating that the antibacterial properties were regenerable.

CONCLUSIONS

A continuous finishing process was developed to graft ADMH onto several popular textile materials including nylon, polyester, acrylic, polypropylene, and natural fabrics. The new technique is a much more efficient finishing process than the previously used exhaustion process in terms of possessing lower initiator concentrations, higher

Table IV Percentage Reduction of *E. coli* after Washing

	Percentage Reduction of *E. coli* (%)					
Wash Time	Nylon	PET	PP	Acrylic	Cotton	PET/Cotton
0	99.999	99.999	99.999	99.999	99.999	99.999
5	99.999	99.999	99.999	99.999	99.9	99.999
15	99.999	99.999	99.999	99.999	90	99.999
30	99.9	99.9	99	90	UD[a]	99.9
50	UD	90	90	90	UD	UD
50[b]	99.999	99.999	99.999	99.999	99.999	99.999

[a]No reduction of *E. coli* was detected.
[b]These samples were rebleached after 50 times of washing. Contact time = 30 min (*E. coli* concentration: 10^5–10^6 CFU/mL, all the samples were tested with machine washing following AATCC Test Method 124. AATCC standard reference detergent 124 was used in all the machine-washing tests.

graft efficiencies, and shorter reaction times. After exposure to diluted chlorine solutions, the hydantoin structures in the grafted samples could be easily transformed into N-halamines, which provide powerful, durable and regenerable antibacterial activities against *E. coli*. It was also found that the hydrophobic properties of polymers could affect antibacterial results due to poor contact between the bacterial suspension and the fibers.

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