Durable and Regenerable Antimicrobial Textiles: Improving Efficacy and Durability of Biocidal Functions

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ABSTRACT: 2,2,5,5-Tetramethylimidazolidinone (TMIO)–modified cotton-containing fabrics could provide excellent durable antimicrobial properties, but the biocidal speeds were low because of its amine halamine structures. To prepare biocidal fabrics that can inactivate microorganisms rapidly and survive repeated laundering and long duration of storage, 3-methylol-2,2,5,5-tetramethylimidazolidinone and dimethylol-5,5-dimethylhydantoin were combined in different ratios in chemical modifications of cellulose fabrics. The mixtures of TMIO and hydantoin rings on the grafted cellulose provided a hybrid of imide, amide, and amine halamine structures in different ratios after chlorination, and led to varied efficacy and durability of biocidal properties on the finished fabrics. The effect of the combined halamine structures on biocidal efficacy and durability of the fabrics were discussed in this article. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2588–2593, 2004

Key words: graft copolymers; functionalization of polymers; modification; antimicrobial properties; fabrics

INTRODUCTION

N-Halamine compounds have shown excellent biocidal functions against a wide range of microorganisms including bacteria, viruses, fungi, and yeasts.[1–4] These *N*-halamines have proved to be nontoxic and environmentally friendly and, more important, they provide durable and rechargeable antibacterial properties.[5] The antibacterial functions of *N*-halamine compounds are attributed to the oxidative properties of halamine bonds (N—Cl) in contact with germs.[6] In recent years, 5,5-dimethylhydantoin rings were incorporated into cotton-containing fabrics by using dimethylol-5,5-dimethylhydantoin (DMDMH) in a wet-finishing process, which provides powerful and regenerable biocidal functions on textile materials.[5–7] However, the washing durability of biocidal functions on the DMDMH-treated fabrics was relatively low, and thus the functions should be recharged by chlorine bleaching after each laundering. More recently, a new amine compound, 3-methylol-2,2,5,5-tetramethylimidazolidinone (MTMIO), was synthesized and imparted onto cellulose, and the incorporated 2,2,5,5-tetramethylimidazolidinone (TMIO) rings on cellulose could be converted to more stable amine halamines.[8] The amine halamines from TMIO rings provided improved washing durability of antimicrobial functions, although at a slower bactericidal speed because of the stronger bond strength of amine halamines.[8]

The stability of halamine bonds depends on the different halamine structures (**Scheme 1**), in an order of imide < amide < amine halamines,[8–11] which is in a reverse order of their biocidal activities. An imide halamine bond is the most reactive among the three halamine bonds, and is the easiest one to dissociate chlorine in aqueous solutions, whereas an amine halamine bond is the most stable structure and is thus more difficult to dissociate chlorine.[10,11] As a result, both power and durability of biocidal functions are determined by the conflicting stabilities of halamine structures. The difference in the killing power and stability on the treated fabrics is ascribed to the rich active imide and amide halamine structures existing on the DMDMH-treated fabrics and the very stable amine halamines in the incorporated TMIO rings. An ideal antibacterial fabric, particularly those used for bioprotective purposes, should be both powerful in inactivation of microorganisms and stable to survive repeated laundering and prolonged storage. In exploration of achieving such a goal, both DMDMH and MTMIO were mixed in chemical finishing of fabrics, in such a way that imide, amide, and amine halamines could all be brought to the materials. This article reports the impacts of different precursor compositions in treatments of cellulose on the power and durability of the biocidal functions.

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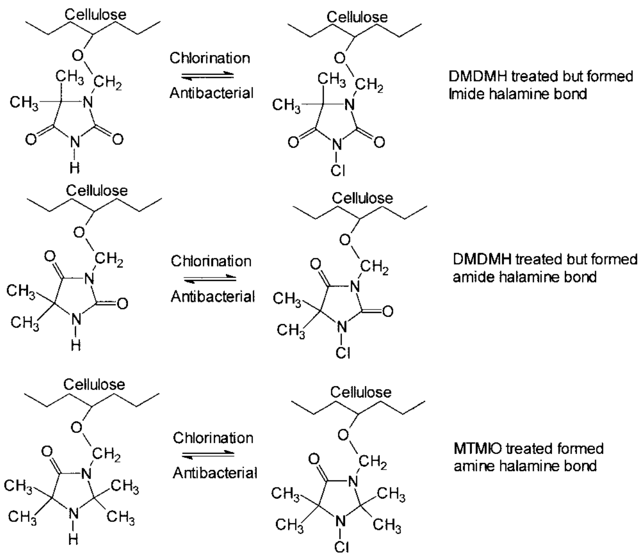


Scheme 1

EXPERIMENTAL

Materials

1,3-Dimethylol-5,5-dimethylhydantoin (DMDMH) was generously provided by Troy Corp. (Florham Park, NJ). 3-Methylol-2,2,5,5-tetramethylimidazolidinone (MTMIO) was synthesized in this lab according to a method reported previously.[8] All other chemicals were purchased from Fisher Scientific (Pittsburgh, PA) and used as received. Fabrics used in the research were cotton print cloth #400, #423, and polyester/cotton blend fabric (65/35) #7409 purchased from Testfabrics Inc. (West Pittston, PA).

Chemical finishing

Fabric wet treatment was conducted in both lab and pilot scales by using a conventional "pad-dry-cure" finishing method. The lab-scale finishing of fabrics was carried out by using a lab padder with a wet pick-up rate of 100%. The fabric samples were dried at 80°C for 5 min and cured at 160°C for 5 min.[8] The pilot scale treatment was carried out on a continuous production padder (Cotton Incorporated, Cary, NC) with a wet pick-up of 70%. Then the fabrics were dried at 80°C and cured at 160–170°C with a speed of 10 m/min on a tenter frame. The finished fabrics were washed and dried according to AATCC test method 124. The add-on rates of grafted precursors in lab finishing were calculated according to eq. (1), in which the weights of the fabric were measured after the samples were conditioned (21°C, 65% relative humidity) for 24 h.

$$\text{Add-on } \% = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

where W_0 and W_1 are the weights of the fabric samples before and after grafting.

The grafted fabrics were activated and recharged by immersing the samples in a diluted chlorine solution containing 150 ppm of active chlorine for 10 min in a liquid/solid ratio of 50 to 1. The chlorinated fabrics were then rinsed in water and dried.

Testing methods

Laundry durability and regenerability of the biocidal functions were examined by using an extended home laundry method according to AATCC test method 124. AATCC standard reference detergent 1993 WOB was used, and the fabrics were laundered in different cycles in a washing machine and then tumble-dried. The antibacterial efficacy of the fabrics was quantitatively evaluated against Gram-negative *Escherichia coli* (*E. coli*) according to AATCC test method 100.[6] The testing results are expressed as the log reduction against the bacterium after incubation compared to the control sample inoculated. Although the Gram-negative bacterium *E. coli* was studied in this work, prior studies have shown that *N*-halamine polymers are very effective against Gram-positive bacteria such as *Staphylococcus aureus* as well.[6,7]

The chlorine content of the fabric samples was determined by using a back iodometric titration, modified from AATCC testing method 92-1999, as previously described.[8] The nitrogen contents of the fabric samples were measured by using a modified Kjeldahl method according to ASTM standard test method E 258-67 (1987). A 2.000-g sample of shredded fabric sample, weighed to 0.0001 g, was placed in a Kjeldahl digestion flask, along with 0.7 g of HgO, 15 g of K_2SO_4 and 25 mL of H_2SO_4 (98%). The mixture was gently heated until frothing ceased and the solution was kept boiling for about 2 h. After the mixture was cooled to room temperature, to the digestion mixture 250 mL of distilled water, 25 mL of Na_2S solution (40 g/L), zinc granules, and 90 mL of NaOH solution (450 g/L) were added. By keeping the mixture boiling, the distillate was collected in a receiving flask containing 50 mL of 0.01*N* H_2SO_4 and 5 drops of methyl purple as an indicator until the total of 200 mL solution was collected. The distillate solution was titrated with 0.01*N* of NaOH. The nitrogen content of the fabric sample was calculated by the following equation:

$$\text{Nitrogen } \% = \{[(A - B)N \times 0.01401]/C\} \times 100 \quad (2)$$

where A is the standard NaOH solution required for titration of the blank (mL), B is the standard NaOH solution required for titration of the sample (mL), N is the normality of the NaOH solution, C is the sample used (g), and the value 0.01401 is the milliequivalent weight of nitrogen.

RESULTS AND DISCUSSIONS

Improved antimicrobial potency

Cotton fabrics containing both imide and amide halamine structures exhibited rapid and powerful biocidal functions,[6] whereas the samples possessing amine halamine structures demonstrated relatively slower biocidal functions than those of the DMDMH-treated ones.[8] As a comparison, cotton fabrics treated by using 4 wt % DMDMH could completely inactivate more than 10^6 clone forming units (CFU) of bacteria in a contact time of 2 min, whereas the 4 wt % MTMIO-treated fabrics needed more than 30 min contact time to achieve the same level of biocidal efficacy. In addition, DMDMH is bireactive with cellulose, which increases the overall yields of the grafting reaction and resulted a much higher add-on rate on the fabrics than MTMIO. Because both DMDMH and MTMIO are grafted to cellulose following the same reaction, a formation of acetals between the methylol groups and hydroxyl groups on cellulose, they are compatible in one finishing bath. By mixing DMDMH with MTMIO in different ratios we were able to control the amounts of imide, amide, and amine structures on the fabrics. Table I shows both add-on rates and biocidal properties of fabrics treated at an overall concentration of 4% of different chemicals. With more DMDMH in the mixed system, the treated fabric demonstrated higher add-on rates of the agents. Similarly, the potency of the antibacterial properties was improved significantly in the mixed systems as the content of hydantoin was increased. As an example of improved biocidal potency, the contact times to execute a complete inactivation of *E. coli* (over 10^6 CFU) by two chlorinated fabrics treated with mixtures of MTMIO/DMDMH (M/D) in w/w ratios of 1/2 and 1/3 were shortened to 15 min (Table I). The greater the amount of DMDMH in the finishing system, the quicker the biocidal functions on the fabrics. The improved power of biocidal action from the combined systems is attributed to the content of active imide and amide halamine bonds.

TABLE I
Inactivation of *E. coli* at Different Mixing Ratios[a]

Formulation	Add-on (%)	Log reduction of *E. coli* at different contact time		
		5 min	15 min	30 min
MTMIO	1.85	ND	3	6
M:D = 1:2	3.05	2	6	6
M:D = 1:3	3.32	2	6	6
DMDMH	3.15	6	6	6

[a] Pure cotton fabric 423 treated in 4% of solution with a wet pick-up 70%. The *E. coli* concentration of 10^6 CFU/mL; 6 log reduction means a complete kill; ND, not detectable.

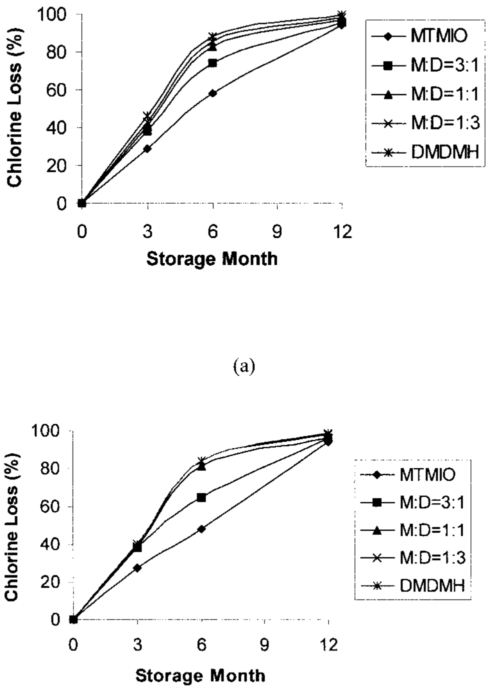
TABLE II
Log Reduction of *E. coli* on the Finished Fabrics before and after Several Washings[a]

Wash cycle	MTMIO	M:D = 1:2	M:D = 1:3	DMDMH
0	6	6	6	6
1	6	5	5	3
3	5	5	5	2

[a] Pure cotton fabric 423 treated in 4% of solution with a wet pick-up 70%. The *E. coli* concentration of 10^6 CFU/mL; 6 log reduction means a complete kill; ND, not detectable. Washing was conducted following AATCC standard test method 124-1999.

Improved durability and stability

Having proved that the mixing biocide systems could provide improved antibacterial efficacy against microorganisms, further tests were arranged to examine the washing durability of the antibacterial functions. Table II shows the biocidal properties of the fabrics treated with the MTMIO, DMDMH, and their mixtures after several repeated machine washings. After three cycles of washing, the sample containing only amine halamine (MTMIO-treated) exhibited the best durability, whereas the DMDMH-treated fabrics lost some of the biocidal power resulting from the loss of the active imide halamine bonds. Quite interestingly, however, the fabrics treated with mixed formulations of 25 or 33 wt % of MTMIO exhibited improved stability against washing, and the antimicrobial properties (in term of log reductions) after washings were very close to the result of the pure MTMIO-treated fabric. It appeared that a small addition of MTMIO could significantly improve washing durability of the fabrics. The improvements in both of biocidal power and washing durability suggest that imide and amine halamine structures may have some direct interactions in the treated cellulose, possibly chlorine transfer among imide, amide, and amine halamines. In fact, chlorine transfers among imide, amide, and amine halamines occur in a system in which all three exist (**Scheme 1**). Every halamine bond should follow an equilibrium reaction, shown in eq. (3). The dissociated chlorine from the halamine bonds should meet the equilibria of all three different halamine bonds because they are in one system, thus providing the source for chlorine transfers. The mixture of TMIO and hydantoin rings brings all three halamine structures, imide, amide, and amine, together in one system. Imide bonds can provide rapid killing power, whereas stable amine halamine could serve as the reserve of active halamines. During laundering, labile imide halamine could be removed by water, but could be recharged within the system by the stable amine halamines because they are not removed by washing.



(a)

(b)

Figure 1 Chlorine loss of(a) treated cotton (#423) and (b) polyester/cotton (#7409) during storage.

$$>N{-}Cl \;\underset{+Cl^{+}}{\overset{-Cl^{+}}{\rightleftharpoons}}\; >N{-}H \qquad (3)$$

In addition to the improved washing durability, the mixed systems could also increase storage time of the halamine materials attributed to the existence of amine halamine. Figure 1 shows storage stability tests of pure cotton and polyester/cotton blends treated with five different formulations of hydantoin and imidozalidinone rings. Although after 12 months of storage the fabrics lost almost all of the active chlorine, the losses on the fabric samples containing amine halamine structures were slower than those of the DMDMH-treated sample; and the greater the amine content, the slower the losses of chlorine.

Active chlorine content after repeated washings

The laundry durability of the biocidal functions can be examined by quantitatively measuring contents of active chlorine on the chlorinated fabrics with respect to the biocidal sites on the fabrics. Figure 2 reveals a plot of chlorine loss on five fabric samples after repeated laundering. Similar to Figure 1, the pure MTMIO-treated fabric showed least chlorine loss during the entire round of laundry tests, whereas the pure DMDMH-treated fabric exhibited the highest chlorine loss. The amount of active chlorine on the samples

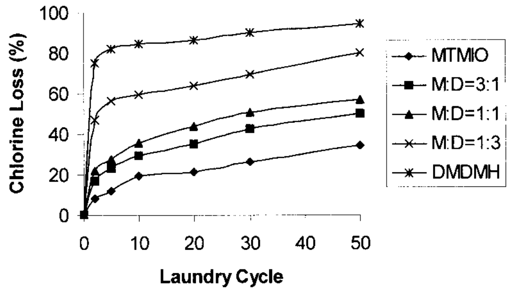


Figure 2 Chlorine loss of cotton fabric samples after repeated washings.

treated with M/D ratios of 3/1, 1/1, and 1/3, respectively, demonstrated a reasonable trend of increase in durability as the amine halamine content increased in the system. At the ratios of M/D = 1/1 and 3/1, the maximum losses of the chlorine were lower than or around 50% after 50 repeated washings, indicating the outstanding washing durability of these sample fabrics. Obviously, the stable amine halamine contributed predominantly to the improvements.

The active chlorine in halamine structures can be completely removed by repeated laundering, but can be mostly recharged in repeated chlorine bleaching. Table III shows active chlorine contents on the fabrics of the initial activation, after 50 launderings, and after recharging. The results further demonstrate that the stability of imide and amine halamine structures under laundering conditions is perfectly consistent with the antibacterial results shown in Table II. However, after 50 washings the recharged amounts of active chlorine on the fabrics were lower than that of the initially activated one. The difference between the "initially activated" and "recharged after 50 launderings" conditions is expressed as an unrechargeable chlorine loss on fabrics, and becomes wider as the hydantoin content increases on the treated fabrics. The

TABLE III
Chlorine Content (ppm) and Chlorine Loss (%) on Cotton Fabric after 50 Cycles of Washing and Recharging

Formulation	No laundry Cl (ppm)	50 cycles		After recharging	
		Cl (ppm)	Cl loss (%)	Cl (ppm)	Cl loss (%)
MTMIO	565	370	34.5	548	3.0
M:D = 3:1	764	381	50.1	737	3.5
M:D = 1:1	785	338	57.0	746	5.0
M:D = 1:3	902	180	80.0	847	6.1
DMDMH	863	50	94.2	807	6.5

[a] Pure cotton fabric 423 treated in 4% of solution with a wet pick-up 70%. Washing was conducted following AATCC standard test method 124-1999. Activation and recharging were both conducted in a washer with chlorine bleach solution containing 150 ppm of active chlorine.

TABLE IV
Nitrogen Content (ppm) and Nitrogen Loss (%) on Cotton Fabrics after 10 and 50 Cycles of Washing[a]

Formulation	No laundry N (ppm)	10 cycles N (ppm)	10 cycles N loss (%)	50 cycles N (ppm)	50 cycles N loss (%)
MTMIO	1550	1520	1.93	1450	6.45
M:D = 3:1	2157	2090	3.11	1961	9.09
M:D = 1:1	2592	2446	5.63	2215	14.54
M:D = 1:3	2839	2614	7.93	2305	18.81
DMDMH	2724	2471	9.29	2170	20.34

[a] Same as in Table III.

unrechargeable chlorine loss might be caused exclusively by losses of the grafted heterocyclic rings, such as hydantoin and imidozalidinone rings. It should be pointed that the active chlorine content on the treated fabrics is much lower than the available rings grafted on the cellulose, which is discussed in the following section. Therefore, the measured active chlorine amount on the fabrics represents only the halamines formed under the same chlorination condition.

Nitrogen content after repeated launderings

The loss of the grafted heterocyclic rings on cotton fabrics can be quantitatively measured by using nitrogen elemental analysis. Table IV shows the nitrogen contents on the five different fabrics before and after 10 and 50 times of washing. Nitrogen contents on the fabrics increased with the increase of DMDMH in the mixture, and reached maximum at M/D = 1/3, which is consistent with increased add-ons of the agents (Table I). Such a trend was maintained even after 50 laundering cycles. However, after 10 and 50 repeated laundering cycles, the nitrogen contents were lost gradually to certain levels. The loss of the nitrogen intensified as the washing cycles and the hydantoin content were increased in the treatment. Laundering in water may damage the linkages between the heterocyclic rings with cellulose, which are a hemiacetal bond on imide or amide nitrogen in the rings. Imide nitrogen may have a weaker connection with cellulose than that of the amide nitrogen because the resonance structures of the imide nitrogen stabilize its hydrolyzed structure, thus making the imide halamine bond more vulnerable to water. The pure MTMIO (imidozalidinone)-treated fabrics showed only about 6.45% nitrogen loss after 50 washings, but the pure DMDMH (hydantoin)-treated fabrics lost over 20% of the original nitrogen, a significant hydrolysis of the incorporated hydantoin rings. In addition, the MTMIO-treated cellulose has only the amide type of connections, and the DMDMH-treated fabrics should have both amide and imide connections with cellulose. However, high nitrogen loss on the DMDMH-treated fabrics reveals that they may contain more imide type connections between the hydantoin and cellulose.

Chlorination rate of grafted rings

The nitrogen content on cellulose can be used to estimate grafted hydantoin and imidozalidinone rings, if the crosslinking effect caused by DMDMH is omitted. The molecular weight of grafted tetramethylimidozalidinone (TMIO) is 155, which is higher than that of the grafted dimethylhydantoin (DMH) (MW = 141) but very close to that of crosslinked DMH (MW = 154). Now, we use a molecular weight of 150 to estimate the grafted mixture of TMIO and DMH. Thus, the number of micromoles (μmol) of grafted rings per gram of cotton fabrics can be calculated based on the nitrogen contents (listed in Table V). Similarly, the measured chlorine amount can be converted to moles of active chlorine per gram of cotton fabrics, which are listed in Table V as well. Comparing the numbers of micromoles of the grafted rings and active chlorine, it can be concluded that the chlorination rates on the fabrics were quite low (<30%). Such a low chlorination rate may be attributed to crosslinking caused by DMDMH at a small scale, but is largely the result of the chlorination efficacy under the employed bleaching conditions (low concentration of chlorine bleach solution). The imide connection between DMDMH and cellulose is usually vulnerable to repeated launderings, thus

TABLE V
Chlorination Degrees in Activation and Regeneration on Cotton Fabrics[a]

	Chlorinating degree (%)				
	MTMIO	M:D = 3:1	M:D = 1:1	M:D = 1:3	DMDMH
Grafted ring (μmol) (initial)	55.36	77.04	92.57	101.39	97.29
Grafted ring (μmol) (after 50 washing cycles)	51.79	70.03	79.11	82.32	77.5
Cl (μmol) (initial)	15.94	21.55	22.14	25.44	24.34
Cl (μmol) (after 50 washing cycles and recharge)	15.46	20.79	21.04	23.89	22.76
Chlorination rate, %	27.93	27.97	23.92	25.09	25.02
Chlorination rate, % (after 50 washings)	29.85	29.69	26.60	29.02	29.37

[a] Activation and recharging were both conducted in a washer with a chlorine bleach solution containing 150 ppm of active chlorine. Chlorination degree was calculated by chlorine content divided by nitrogen content of the same fabric sample.

resulting in more breakage of crosslinking between imide bonds and cellulose. Therefore more N—H sites become available for chlorination and thus there are higher chlorination rates of the fabrics after repeated washings.

CONCLUSIONS

Mixing DMDMH and MTMIO in textile finishing systems could bring a combination of imide, amide, and amine halamine structures on cellulose. Such combinations are able to improve both the power and the stability of biocidal functions of the treated fabrics. The repeated laundering tests revealed that even a small amount of added amine halamines could substantially reduce the loss of active chlorine and increase the power of the biocidal functions on the fabrics. The chlorination rates of the imide, amide, and amine sites on cellulose were quite low under the current bleaching conditions. The loss of nitrogen contents on the fabrics was mostly attributed to breakage of the imide connections between hydantoin rings and cellulose. After 50 washings, the maximum loss of the nitrogen (or loss of the grafted rings) on the purely DMDMH-treated fabrics was around 20%, but had less impact of the active chlorine content because of the low chlorination degree.

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