Biocidal Halamine Chemistry for Woven and Nonwoven Textiles

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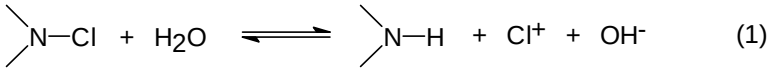
ABSTRACT

Halamine structures are proven to be ideal biocidal groups on biologically protective clothing materials and have been chemically incorporated to polymers and textiles to provide powerful biocidal functions using chemical modification processes. Textile chemical finishing is suitable for woven textiles and can be applied to nonwoven fabrics as well. However, a novel chemical modification process is under development in this lab to chemically bind halamine precursor into manufactured fibers during extrusion process. This presentation will address halamine biocidal effects and their textile applications.

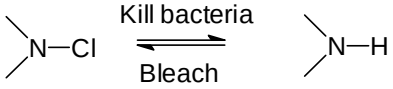
INTRODUCATION

Antimicrobial textiles can be defined as biocidal and biostatic materials based on their functions. Biostatic functions can inhibit growth of microorganisms on textiles and prevent the materials from biodegradation, or so called preservative functions; biocidal materials are able to kill microorganisms and eliminate growth of microorganisms, and can therefore protect wearers of the textiles from biological attacks, in addition to preserving the materials. Biocidal materials are often termed antibacterial materials. For protective purposes, biocidal functions that can provide rapid and efficient inactivation of a broad spectrum of microorganisms are required. The biostatic or simple antimicrobial functions are insufficient in protection in these applications, particularly in areas such as medical-use textiles or protective clothing for occupational uses.

In recent years N-halamine structures were incorporated to textiles and polymeric materials for providing biocidal functions [1-6]. N-halamine chemistry can be expressed in equations 1 and 2. When N-halamine structures are exposed to water, the reaction shown in equation 1 may occur. The equilibrium in equation 1 may shift toward either reactants or products depending on the N-halamine structures[7-8].



(1)

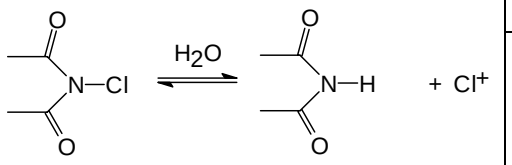
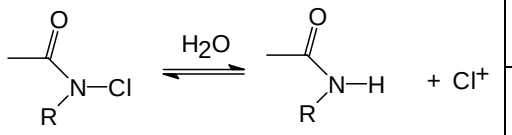
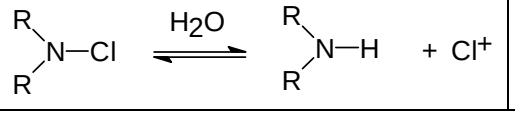


(2)

N-halamine structures can kill microorganisms directly also without the release of free chlorine, as in equation 2. In fact, N-halamine structures may only release very limited amounts of free chlorine because the dissociation constants of equation 1 are in the scale of $10^{-4\text{-}12}$ for imide, amide and amine halamines (Table 1)[4]. Since N-halamine structures are biocidal, and more importantly quite stable in ambient environments, incorporation of the N-halamine into

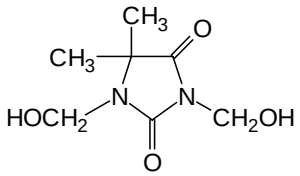
polymeric and textile materials will bring biocidal functions to them. Moreover, since equation 2 is a reversible reaction, the biocidal functions on the materials are rechargeable with a chlorinating agent, such as chlorine bleach. This rechargeable function is most suitable for reusable medical textiles and clothing. In this paper we will review the latest progresses in the application of N-halamine chemistry to textiles and polymers.

Table 1. Stability of N-halamine structures [4]. (Journal of Applied Polymer Science © 2003)

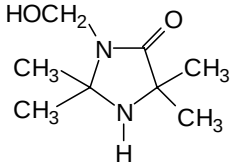
Dissociation Reaction	Dissociation Constant for Examples
Imide Structure 	1.6×10^{-2}-8.5×10^{-4} Trichlorocyanuric acid
	2.54×10^{-4} 1,3-dichloro-5,5-dimethylhydantoin
Amide Structure 	2.6×10^{-8} 1,3-dichloro-2,2,5,5-tetramethyl-4-imidazolidinone
	2.3×10^{-9} 3-chloro-4,4-dimethyl-2-oxazolidinone
Amine Structure 	$<10^{-12}$

Incorporation of N-halamine to fabrics

Both amide and imide N-halamines have been incorporated into cellulose-containing fabrics by a conventional finishing method with 1,3-dimethylol-5,5-dimethylhydantoin (DMDMH)[2-4]. The DMDMH-treated fabrics exhibited rapid biocidal functions, but the washing durability of the functions requires improvement, due to the dominating imide N-halamine functionality, which is the most reactive, but least stable on the fabrics. However, DMDMH fabrics can be employed in personal protection against various biological agents such as bacteria, viruses, fungi, yeasts, and spores. Examples of the treated fabrics demonstrated a complete elimination of pathogens in a contact time as short as two minutes. The biocidal functions could be recharged repeatedly for at least 50 machine washes.



1,3,-dimethylol-5,5-dimethylhydantoin (DMDMH)



3-methylol-2,2,5,5-tetramethylimidazolidin-4-one (MTMIO)

Figure 1 Structures of DMDMH and MTMIO

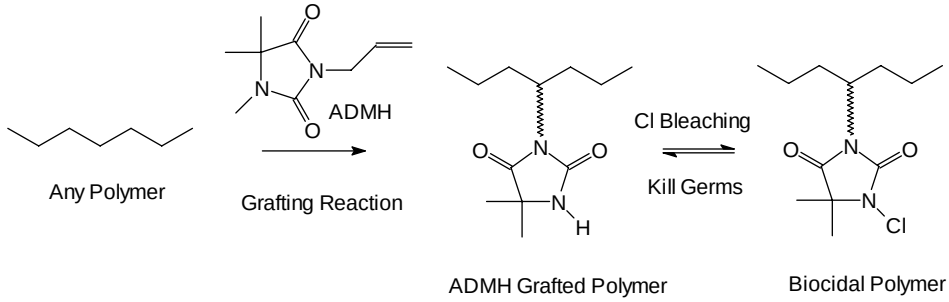
In order to increase washing durability of the N-halamine-treated textiles, the more stable amine N-halamine has been grafted to cellulose in a similar approach by using 3-methylol-2,2,5,5-tetramethylimidazolidin-4-one (MTMIO). The resulting fabrics contained the more stable, and less reactive, amine N-halamine structure, thus providing slow, but durable, biocidal functions.

Table 2 Chlorine loss and antimicrobial effects of MTMIO- and DMDMH-modified cotton samples

Chemical	Washing cycles	Against *E. coli*			Against *S. aureus*		
		Cl ppm	Cl loss %	Log reduction	Cl ppm	Cl loss %	Log reduction
MTMIO	0	565	-	6	654	-	6
	2	507	10.2	5	616	6.1	6
	5	498	11.9	4	601	8.4	4
DMDMH	0	863	-	6	934	-	6
	2	218	74.7	1.5	380	59.3	3
	5	157	81	0.9	274	70.7	2

Pure cotton fabric 493#; total finishing bath concentration: 4 %. Wet pick-up: 70 %. Concentrations of bacteria: *E. coli* 5 x10^6 CFU/mL and *S. aureus* 7 x10^6 CFU/mL. A six log reduction is equivalent to 99.9999% inactivation. Contact time: 60 min.. Machine-washing according to AATCC standard test method 124-1999; tests 1 and 2. The MTMIO-treated fabric was bleached separately from the DMDMH-treated fabric with the same concentration of active chlorine (150 ppm) used in each case. [4] (Journal of Applied Polymer Science © 2003)

Recently, a hydantoin-containing monomer, 3-allyl-5,5-dimethylhydantoin (ADMH, as shown in Scheme 1) was prepared to incorporate only amide N-halamine structures into synthetic fibers. Due to the amide structure, the thus-produced fabrics could demonstrate both powerful and durable biocidal functions. Synthetic fabrics such nylon-66, polyester (PET), polypropylene (PP), acrylics, and aramide fibers, as well as pure cotton fabrics, were used in the chemical modification. The ADMH can be incorporated in surfaces of fibers by a controlled radical grafting reaction which can ensure short chain grafts instead of long chain self-polymerization of the monomers(Scheme 1)[9-10].



Scheme 1. Structure of ADMH and its grafting reactions on synthetic polymers.

Biocidal properties of the modified fibers could be demonstrated after a chlorination reaction by exposing the grafted fibers to a diluted chlorine solution, with which the grafted hydantoin rings were converted to N-halamine structures. The polymeric N-halamines could provide powerful and rapid antibacterial activities against *E. coli* and *S. aureus*. Most of the fibers could

completely inactivate a large number of bacteria (1 x 10^6 CFU) in a 10-30 minute contact time. In addition, the antibacterial activities of these polymeric N-halamines could be easily recovered after usage by simply exposing to chlorine solution again.

Table 3. Log reduction of *E. Coli* after washing [9] (Journal of Applied Polymer Science © 2002)

Washing times	Log reduction of *E. Coli* (%)					
	Nylon	PET	PP	Acrylic	Cotton	PET/ cotton
0	5	5	5	5	5	5
5	5	5	5	5	3	5
15	5	5	5	5	1	5
30	3	3	2	1	UD*	3
50	UD	1	1	1	UD	UD
50**	5	5	5	5	5	5

*: no reduction of E. *coli* was detected. **: these samples were re-bleached after 50 times of washing. Contact time = 30 min (*E. coli* concentration: 10^5~ 10^6 CFU/mL; all of the samples were tested with machine washing following AATCC Test Method 124. AATCC standard reference detergent 124 was used in all of the machine-washing tests.

Incorporation of Halamine structures to synthetic fibers

Currently used chemical and biological protective clothing is mostly made of nonwoven fabrics [13-14]. The nonwoven fabrics could resist liquid and aerosol microorganisms and toxic chemicals penetrating through the fabrics due to the dense fiber entanglements and hydrophobic structures. These nonwoven fabrics are widely employed in most personal protective gear such as disposable protective clothing, filters and respirators with different performance against different toxicants and biological agents. Novel technologies have been developed to incorporate self-decontamination functions to many woven fabric materials, but failed to treat nonwoven fabrics. In addition, most nonwoven fabrics are made of polyolefins, which are the polymers that are hardly modified in regular textile chemical finishing processes. The only possible approach is to introduce the functions the nonwovens during fiber formation processes, where thermoplastic polymers are molten and extruded through spinnerets to form fine fibers.

In order to incorporate the self-decontaminating functions to the currently used biological and chemical protective clothing, we propose to develop an innovative manufacturing process that can combine fiber spinning process and chemical modification into one step, an integrated functional spinning of synthetic fibers. Functional vinyl monomers such as 3-allyl-5,5-dimethylhydantoin (ADMH), shown in Scheme1, can react with polymers in the fiber spinning process if polymeric radicals can be initiated. Radical reaction is an effective chemical route that can make polyolefins reactive to other agents, and is thus can be employed in the fiber formation, where high temperature and sufficient reaction time are provided. To illustrate this novel process, a meltblown fiber spinning process is shown in Figure 2. The functional agents are added into and mixed with the polymers in extruders and co-spun into chemically modified fibers.

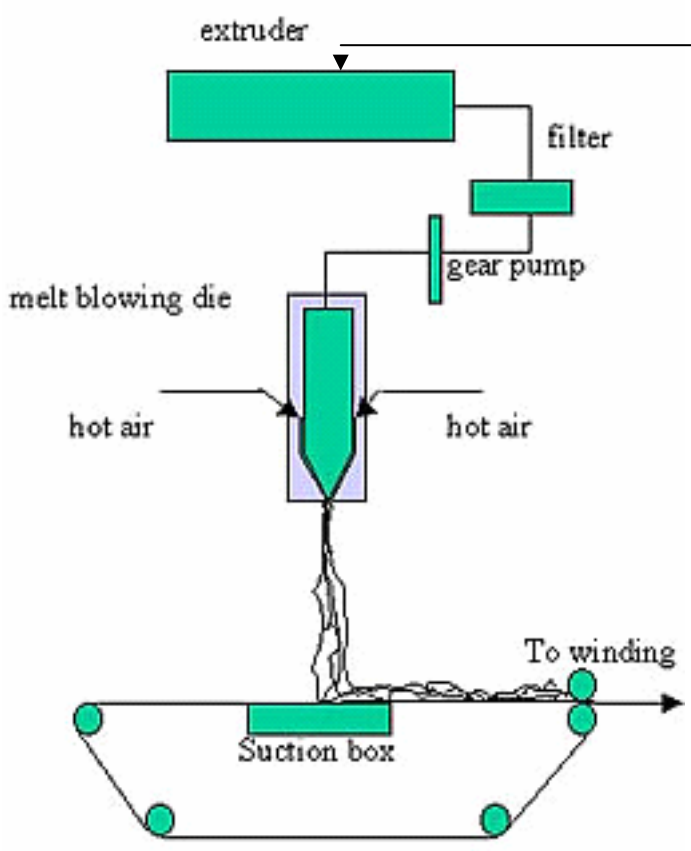


Figure 2. Manufacturing fibers by using meltblown process and possible addition of functional agents

FUTURE DIRECTIONS

Integrated manufacturing of functional fibers is feasible based on the preliminary study. In this presentation, results of functional polypropylene fibers will be discussed. We will continue to explore reactive extrusion process and incorporate different functional monomers to polypropylene fibers. We will also explore different polymers that have high melting and processing temperatures.

ACKNOWLEDGEMENTS

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