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〈Research Paper〉

Improved Antimicrobial Efficacy of *m*-Aramid

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Abstract— Poly(*m*-phenyleneisophthalamide), *m*-aramid has no adjacent α-hydrogen of a nitrogen-halogen bond causes dehydrohalogenation. This fact proposes that *m*-aramid is one of good antimicrobial precursors. To enhance the surface area of *m*-aramid, electrospinning was employed. Scanning electron microscopy(SEM) was conducted to inspect the morphology change of *m*-aramid. The surface area of regular and electrospun *m*-aramid was calculated. Swatch test was applied to measure antimicrobial activity of the samples. The results showed that within 10 min contact time the electrospun *m*-aramid inactivated *Escherichia coli* KCTC 1039 (Gram-negative bacteria) with 8 log reductions.

Keywords: *N-halamine, antimicrobial, biocidal, electrospinning, m-aramid*

1. Introduction

N-Halamines are materials which contain nitrogen-halogen covalent bonding in their structure. Due to strong inactivation properties of oxidative halogen (especially chlorine) against wide spectrum of bacteria, *N*-halamines have been applied in several area including water disinfection and textiles[1-5]. However, *N*-halamine moieties containing adjacent α-hydrogen of a nitrogen-halogen bond are less stable in antimicrobial activity. This may be due to the fact that adjacent α-hydrogen of a nitrogen-halogen bond causes dehydrohalogenation. Thus, *N*-halamine compounds containing nitrogen without adjacent α-hydrogen are preferred as *N*-halamine precursors[4,6].

Poly(*m*-phenyleneisophthalamide), *m*-aramid namely Nomex in industrial area are known as high-performance aromatic polyamide in variety of applications in daily life. Since there is no adjacent α-hydrogen of a nitrogen-halogen bond in the structure, it is highly difficult for the elimination of halogen to occur after chlorination[1,7,8]. This fact suggests that *m*-aramid can have a stable antimicrobial activity and is one of good *N*-halamine precursors.

Although *m*-aramid has advantages as an *N*-halamine precursor, regular *m*-aramid fiber contains limited oxidative chlorine to apply in medical or industrial area. It is assumed that high crystallinity and glass transition temperature as dyeing difficulty cause limitation of rendering biocidal[1,6,9,10]. Hence, only the surface of *m*-aramid might be halogenated instead of penetration through the fiber.

In this study, *m*-aramid was employed to prepare nano-sized fiber which might be chlorinated with relatively enhanced chlorine content. The nano-sized fiber was manufactured through electro-spinning using an organic solvent, *N,N*- dimethylacetamide (DMAc).

The change of morphology and surface area were characterized by Scanning Electron Microscope (SEM).

Oxidative chlorine contents of *m*-aramid regular fiber and nano-sized fiber were also discussed.

This study might support to widen applications of *m*-aramid toward medical/antimicrobial or industrial area.

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2. Experimental

2.1 Materials

N,N-Dimethylacetamide (DMAc) and calcium chloride (catalyst) were purchased from either Aldrich Chemical Co. or Fisher Scientific Co.

They were used as supplied without further purification. The *m*-aramid was a Dupont fiber product.

2.2 Preparation of *m*-aramid nano fiber

A weight of 15 g of *m*-aramid fiber was soaked in 100 mL of DMAc (DMAc/*m*-aramid, 100/15, w/w) with a weight of 10 g of calcium chloride ($CaCl_2$) as a catalyst to dissolve *m*-aramid in the solvent. Then the mixture was stirred at 120℃ for 4 h until the solution was homogeneous.

A voltage controller (NNC-30K-2mA Portable Type, NanoNC. Co., Ltd., Korea) was employed to electrospin the fibers.

The experimental conditions were fixed at 20 kV, 20 cm and 4 mL/h, for voltage, distance between the tip and collector (Al material), and spinning speed, respectively. The electro-spinning diagram was depicted in Fig. 1.

2.3 Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) investigation was conducted with a Hitachi S-570 at 15 kV accelerating voltage.

Samples were coated with gold under argon purge before examination.

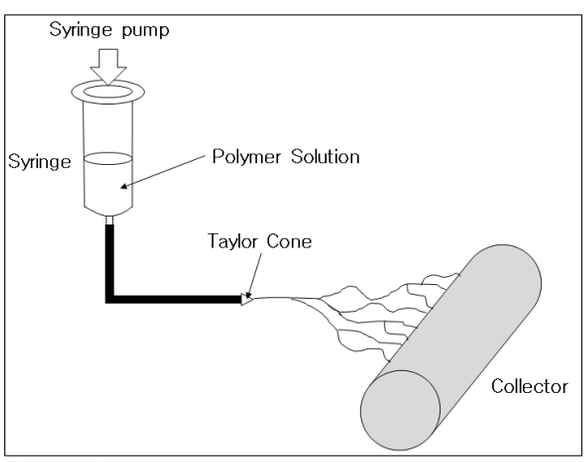


Fig. 1. The diagram of electrospinning.

2.4 Chlorination

A commercial 4.5% sodium hypochlorite solution was diluted to 3300 ppm of the commercial strength with distilled water. The diluted solution was applied to chlorinate the *m*-aramid fibers and the chlorination treatment was adjusted to pH 7 with acetic acid. The *m*-aramid fibers were soaked in the solution at ambient temperature for 60 min and rinsed with a large excess of distilled water. Then, the samples were dried at 45℃ for 2 h to remove any unbounded chlorine.

2.5 Oxidative chlorine content (Titration)

A volume of 100 mL-distilled water was prepared with 1 mL of acetic acid followed by adding 0.1 g of KI. After treated *m*-aramid fibers were soaked in the solution over 12 h, sodium thiosulfate solution was added to titrate the amount of starch which stands for the amount of oxidative chlorine.

An iodometric/thiosulfate titration procedure was employed to analyze the oxidative chlorine content. The $[Cl^+]$% in the sample was calculated with the following equation:

$$[Cl^+]\% = (V \times N \times 35.45)/(W \times 2 \times 100)$$

Where $[Cl^+]$% is the wt% of oxidative chlorine on the sample, V is equal to the volume of the titrant (sodium thiosulfate solution (mL)), N is equal to the normality of the titrant, and W is the weight of the sample (g).The constants, 35.45, are molecular weight of Cl and 2 is the change in oxidation state of Cl during titration.

2.6 Antimicrobial test

The control and chlorinated fibers were challenged with *Escherichia coli* KCTC 1039 using a modified AATCC Test Method 100-1999.

Bacterial suspensions (50 μL) made with pH 7 phosphate buffer were added to one square inch swatches. A second swatch was sandwiched over the first to ensure contact between the suspension and the fiber. After contact times of 10 and 30 min, the samples were quenched with 5.0 mL of sterile 0.02 N sodium thiosulfate solutions.

The quenched samples were diluted using pH 7 phosphate buffer and plated on Typticase soy agar.

The plates were incubated at 37℃ for 18 h, and the number of bacteria was counted to determine the presence or absence of viable bacteria.

3. Results and discussion

3.1 Characterization of *m*-aramid fibers

Aramid fibers have been applied in diverse areas as high performance materials. Although *m*-aramid does not show any decomposition after chlorination with diluted bleach, *p*-aramid(Kevlar®) was decomposed seriously. Akin et al proved the degradation of *p*-aramid under sodium hypochlorite solution[11]. It implies that *m*-aramid can be rendered biocidal as a good *N*-halamine precursor. (See Fig. 2) In terms of antimicrobial activity, *m*-aramid regular fiber possessed relatively lower oxidative chlorine content under exposure to bleach solution[1,7].

It is due to the fact that chlorination occurred only onto the surface of *m*-aramid fibers. Thus, in order to increase antimicrobial efficacy, enhanced surface area of *m*-aramid is suggested. Since electrospinning is a suitable method to produce enhanced surface area of polymeric materials, this technique was employed. The morphologies of regular and electrospun *m*-aramid fibers were shown in Fig. 3. The results indicated that reduced diameter of *m*-aramid fibers was produced under electrospinning. Average diameter of regular fiber and electrospun fiber were 12 ㎛ and 0.6 ㎛, respectively. The calculated surface area based on SEM trace and measured oxidative chlorine content were shown in Table 1.

The surface area was calculated with the following equation:

$$\text{Denier} = (\pi D^2)/4 \times 900000\text{cm} \times \rho$$

Where π is number π, D is Diameter of fiber (cm) and ρ is density of fiber (g/cm^3)

$$\text{Surface area } (m^2/g) = (\pi D) \times \text{length (m) of 1 g of fiber}$$

Where π is number π, D is Diameter of fiber (m)

As shown in Table 1, regular *m*-aramid had 0.02[Cl^+]%, whereas electrospun *m*-aramid contained 5.3[Cl^+]% . The oxidative chlorine content of *m*-aramid after elecrospinning was increased dramatically. In fact, surface area of regular fiber and elecrospun fiber were 40.37×10^{-2} m^2/g and 847.80×10^{-2} m^2/g, respectively.

It implies that enhanced surfaced area of *m*-aramid provided improved oxidative chlorine content. When all *N*-H bonds in *m*-aramid were substituted by N-Cl bonds, the theoretical value of oxidative chlorine on *m*-aramid is 29.7[Cl^+]%. Hence, the electrospun *m*-aramid might have chlorinated around 17.8% of total N-H bonds.

Table 1. Surface area and oxidative chlorine content of regular *m*-aramid fiber and electrospun *m*-aramid fiber

m-Aramid fiber type	Diameter of the fiber(㎛)	Denier (g/9000m)	[Cl^+]%	Surface area(m^2/g)
Regular	12	0.84	0.02	40.37×10^{-2}
Electrospun	0.6	0.002	5.3	847.80×10^{-2}

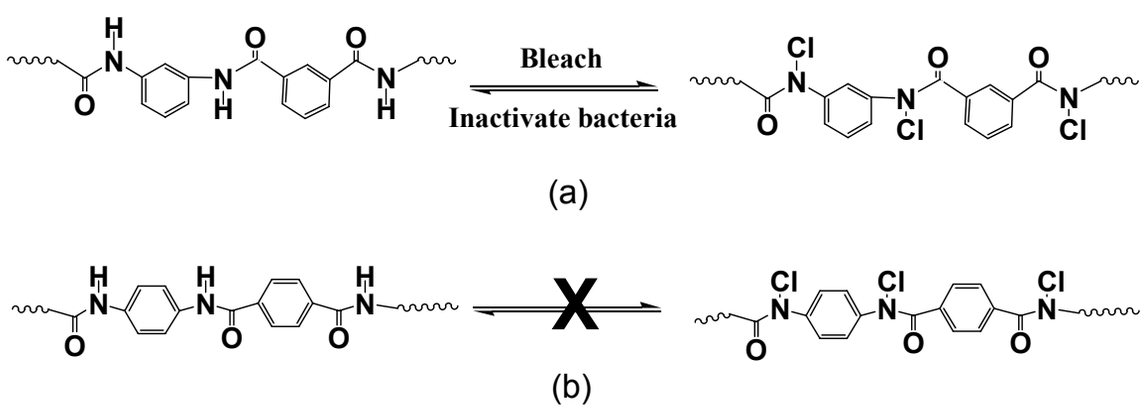
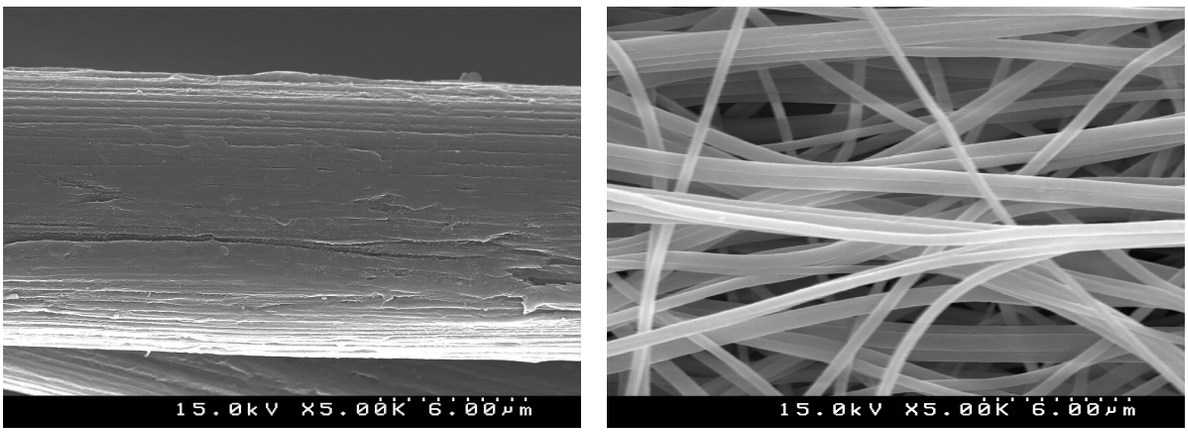


Fig. 2. The scheme of disinfection of (a) *m*-aramid and (b) *p*-aramid.



(a) (b)

Fig. 3. SEM images of (a) regular *m*-aramid fiber and (b) electrospun *m*-aramid fiber.

Table 2. Antimicrobial efficacy against *E. coli* KCTC 1039

Samples (*m*-Aramid fibers)		Contact time (min)	*Escherichia coli* KCTC 1039[a]		
			Bacterial No. (cfu/mL)	Total bacteria(cfu/sample)	Log reduction
Unchlorinated	Regular	10	6.7×10^5	1.0×10^6	2.7
		30	4.2×10^5	7.3×10^5	2.8
	Electrospun	10	8.4×10^5	1.0×10^6	2.7
		30	1.8×10^5	4.2×10^6	2.1
Chlorinated	Regular	10	2.1×10^6	2.4×10^6	2.3
		30	6.7×10^5	9.6×10^5	2.7
	Electrospun	10	0	0	8.7
		30	0	0	8.7

[a] Total bacteria: 5.7×10^8 cfu/sample.

3.2 Antimicrobial efficacy

Antimicrobial activity of *N*-halamine is increasing with enhanced chlorine content of the structure. It is reported that 0.1% of [Cl^+] is the appropriate amount of oxidative chlorine to inactivate bacteria since the mentioned amount have sufficient antimicrobial properties[12].

Antimicrobial efficacy of regular *m*-aramid fiber and electrospun *m*-aramid fiber was demonstrated in Table 2. The results indicated that electrospun *m*-aramid which was chlorinated, inactivated the *Escherichia coli* KCTC 1039 within 10 min contact time with 8 log reductions.

Chlorinated regular *m*-aramid fiber could not inactivate the bacteria even at 30 min contact time. It demonstrated that 0.02% of oxidative chlorine was not enough amount against Gram-negative bacteria within 30 min.

Therefore, for improved inactivation against Gram-negative bacteria, the surface area of regular fiber should be increased and electrospinning would be a suitable method for enhanced antimicrobial activity of *m*-aramid. In addition, only Gram-negative bacteria were employed to conduct antimicrobial efficacy in this study. Hence, Gram-positive bacteria is needed to ensure biocidal properties against wide spectrum of bacteria of *m*-aramid for further research.

4. Conclusions

The nano-sized *m*-aramid fiber was produced by electrospinning. The electrospun fiber showed 0.6 ㎛ diameter whereas regular fiber had 12 ㎛ diameter. The enhanced surface area of electrospun fiber was proved by SEM images and increased oxidative chlorine content. The surface area of regular and electrospun fiber

were 40.37 x 10^{-2} and 847.80 x 10^{-2} m^2/g, respectively. The oxidative chlorine content of regular was 0.02% and electrospun *m*-aramid was 5.3%. The antimicrobial efficacy test showed that electrospun *m*-aramid fiber inactivated *Escherichia coli* KCTC 1039 (Gram-negative bacteria) within 10 min contact time with 8 log reductions.

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