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ANTIBACTERIAL ACTIVITY OF SULFONATED STYRENE-GRAFTED POLYPROPYLENE FABRIC AND ITS METALLIC SALT

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Key Words: Antibacterial Effect, Biocide, Metallic Complex, Radiation Graft, Styrene-Grafted Polypropylene Fabric, Sulfonation

ABSTRACT

Antibacterial activities of sulfonated styrene-grafted polypropylene fabric and its metallic complexes against *Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa* were evaluated by a viable cell counting method. After styrene was grafted to polypropylene fabric, a sulfonation reaction was carried out. Various metals were introduced to the sulfonated styrene-grafted polypropylene fabric to evaluate their antibacterial activities. Ag complex of sulfonated styrene-grafted polypropylene

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fabric (3.95 mM SO_3H/g) had a strong biocidal effect to kill all bacteria within 30 minutes. From the antibacterial activity of the metallic salts of sulfonated-grafted PP fabric, it was found that Ag complexed fabric had strong biocidal effects for all bac-teria and the other metal complexed fabrics had different antibacterial activity depending on each bacterium.

INTRODUCTION

Various kinds of plastics are rendered sterile by subjecting them to a suitable sterilization process using either dry/wet heat, ethylene oxide or ionizing radiation. However, these polymers can be contaminated or infected again by microorganisms such as bacteria when they are exposed to the atmosphere, or used for catheters, sutures in human body. One of the techniques to solve this problem is to develop polymer materials which have binomial activity themselves.

Biocides are usually added to the polymers themselves, they may be added during processing, such as during mastication of rubber, during mixing and fusion of polymer compounds [1, 2]. Another method is to endow biocidal function to the surface of polymer [3]. The surface of existing polymers can be modified in order to give them the required biocidal effect. Various chemical and physical methods have been known for the modification of polymer. The grafting method needs free radicals or peroxides to modify the surface of polymers. The production of these initiation species are possible by UV [4, 5], plasma [6, 7], radiation [8-10] and chemicals. Radiation-induced grafting is one of the most effective methods because of the rapid and uniform creation of active radical sites on the existing polymer matrix. The methods of achieving a grafting reaction using radiation include simultaneous irradiation of the backbone polymer in the presence of the monomer, and preirradiation. In this study, a simultaneous radiation grafting method was used to give biocidal function to polypropylene fabrics which are suitable for air filters. After styrene was grafted to polypropylene fabric, a sulfonation reaction was carried out. Various metals were introduced to the sulfonated styrene-grafted polypropylene fabric to evaluate their antibacterial activities.

Antibacterial activities of modified fabrics were examined by a viable cell counting method against *Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa*.

EXPERIMENTAL

Material

Commercial polypropylene fabric of 140 g/m^2 (Chonbang Industries Co. Ltd.) was used as a substrate for grafting reaction. Styrene was supplied from Merck-Schuchardt. Other chemicals were reagent grade.

Grafting Procedure

The grafting experiments were performed in pyrex test tubes, methanol as diluent being added first, followed by sulfuric acid (2×10^{-1} M), then monomer. Polypropylene fabric (0.2 g) was immersed in a pyrex tube containing 30 mL monomer solution. The V_o-rays from Co-60 source were introduced in a total dose of 40 kGy at an exposure rate of 5.9 kGy/hr. After the grafting reaction, the grafted fabrics were removed from the monomer solution in a glass ampoule and washed with benzene to remove the remaining homopolymer. The degree of grafting was determined as the following:

$$\text{Degree of grafting (\%)} = \frac{Wg - Wo}{Wo} \times 100$$

Where, Wg and Wo are the weights of the grafted and the starting polypropylene fabric, respectively.

Sulfonation

The styrene-grafted fabric with 96.7% grafting yield was sulfonated with a mixture of $ClSO_3H/H_2SO_4$, and a mixture of $ClSO_3H/ClCH_2CH_2Cl$ at different temperatures. After sulfonation reaction, sulfonated fabric was immersed into sulfuric acid, followed by 50% sulfuric acid, and then 20% sulfuric acid, and distilled water lastly to minimize the damage of the fabric during the washing process. The content of sulfonation was evaluated by titration method.

Metallic Complex of Sulfonated Styrene-Grafted Polypropylene Fabric

Sulfonated styrene-grafted polypropylene fabric (3.95 mM SO_3H/g) was immersed into 2×10^{-2} M metallic solution containing $AgNO_2$, $FeSO_4{\cdot}7H_2O$,

$(CH_3COO)_2Zn{\cdot}2H_2O$, $(CH_3COO)_2Ni{\cdot}4H_2O$, $CuSO_4{\cdot}5H_2O$, $CoCl_2{\cdot}6H_2O$ for 3 hours at room temperature. After sulfonated styrene-grafted polypropylene fabrics were placed in various metallic solutions, the concentrations of the adsorbed metals by fabrics were determined by calculating the concentrations of residual metallic solutions using ICP spectrometer.

Antibacterial Assessment

Bactericidal activity was evaluated by examining the kill rate by the viable cell counting technique against *E. coli*, *S. aureus*, and *P. aeruginosa*. One loopful of the bacteria was inoculated in 100 mL of nutrient broth (peptone 5.0 g/L, beef extract 3.0 g/L, pH 6.8) at 36˚C for 24 hours, and 1 mL from former bacteria solution was cultured again at 36˚C for 20 hours in a test-tube shaker at 100 rpm. At this stage, the culture of *E. coli* involves ca. 10^9 cells/mL, that of *S. aureus* involves 10^8 cells/mL, and that of *P. aeruginosa* involves 10^8 cells/mL. Sulfonated styrene-grafted fabric and its metallic complex were cut into the weight of 0.145 g. These cut fabrics were put in contact with 5 mL solution having 10^9 cells/mL for *E. coli*, 10^8 cells/mL for *S. aureus* and *P. aeruginosa* to assess their bactericidal activities. At a specified time, 1 mL of the same culture was added to 9 mL distilled water, several decimal dilutions were repeated. From this dilution solution, the surviving bacteria were counted by the spread plate method. After inoculation, the plates were kept at 36˚C, and the colonies were counted after 12 hours.

RESULTS AND DISCUSSION

Radiation conditions can be readily chosen to graft aromatic type monomers such as styrene especially when dissolved in a solvent like methanol, with little competing homopolymer formation. It was found that the grafting yield of styrene was 96.7% when a styrene concentration of 60% was used for grafting styrene to polypropylene fabric in the presence of 2×10^{-1}M sulfuric acid, 40 kGy irradiaton dose was applied to the grafting reaction [11].

The styrene-grafted fabric with 96.7% grafting yield was sulfonated with a mixture of $ClSO_3H/H_2SO_4$. Sulfonation reaction almost did not take place with 20 v% $ClSO_3H$ concentration in H_2SO_4 at temperature of 0˚C. However, elevating the reaction temperature from 0˚C to 20˚C led to a small sulfonation reaction. The content of sulfonation in 30 v% $ClSO_3H$ concentration in H_2SO_4 was higher than that of 20 v% $ClSO_3H$ in H_2SO_4 (Figure 1). The sulfonation reaction depended linearly on the reaction temperature and the concentration of $ClSO_3H$, but the reaction condition, which brought a high degree of sulfonation, tended to cause a color change in the fabric.

The styrene-grafted polypropylene fabric with 96.7% grafting yield was sulfonated with a mixture ranging from 5 v% to 20 v% $ClSO_3H$ concentration in $ClCH_2CH_2Cl$. Figure 2 shows the degree of sulfonation in these reaction conditions. In 20 v% $ClSO_3H$ concentration, the maximum peak of sulfonation appeared within 5 minutes, and then the degree of sulfonation decreased with increasing reaction time. The phenomenon is assumed to be attributable to the brittleness of fabric after sulfonation. On the other hand, in 5 v% $ClSO_3H$ concentration, the sulfonation reaction increased with increasing reaction time up to 30 minutes. It was found that the sulfonation reaction was carried out smoothly with 5 v% $ClSO_3H$ concentration in $ClCH_2CH_2Cl$. 3.95 mM SO_3H/g of sulfonic acid was obtained when 96.7% styrene-grafted polypropylene fabric was sulfonated with 5 v% $ClSO_3H$ concentration in $ClCH_2CH_2Cl$ for 30 minutes.

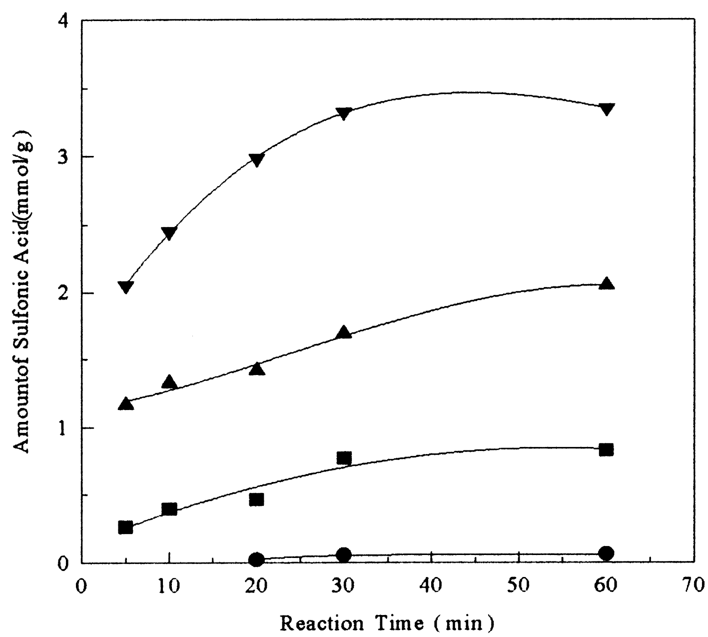

Figure 1. Extent of the sulfonation of St-g-PP in $ClSO_3H/H_2SO_4$ solution. Grafting yield 97.6%, 20% $ClSO_3H/H_2SO_4$ at (●) 0˚C, (■) 20˚C, and 30% $ClSO_3H/H_2SO_4$ at (▲) 0˚C, (▼) 20°C.

TABLE 1. The Content of Metals Introduced in Sulfonated Styrene-Grafted Polypropylene Fabric (3.95 mM SO_3H /g)

Metal	Ag	Fe	Cu	Zn	Ni	Co
Content (mmol M/g)	0.61	1.56	1.69	1.50	1.87	0.42

Sulfonated styrene-grafted polypropylene fabric (3.95 mM SO_3H/g) was reacted with 2 x 10^{-2} M of metallic solution containing $AgNO_2$, $FeSO_4{\cdot}7H_2O$, $(CH_3COO)_2Zn{\cdot}2H_2O$, $(CH_3COO)_2Ni{\cdot}4H_2O$, $CuSO_4{\cdot}5H_2O$, $CoCl_2{\cdot}6H_2O$ for 3 hours at room temperature. The contents of metals introduced in the sulfonated styrene-grafted polypropylene fabric (3.95 mM SO_3H /g) are given in Table 1.

Figure 3 shows logarithmic plots of the viable cell number of *E. coli* after contacting with styrene-grafted polypropylene fabric and the metal complexes of sulfonated styrene-grafted polypropylene fabric (3.95 mM SO_3H/g).

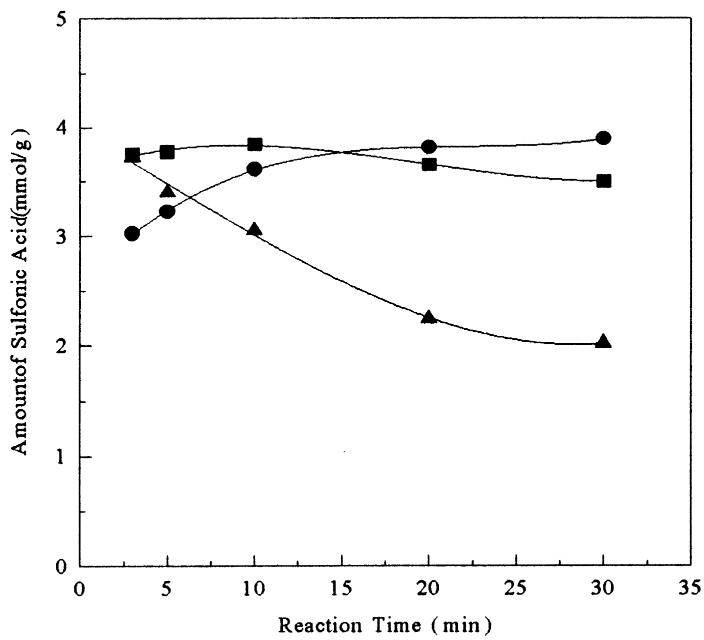

Figure 2. Effect of $ClSO_3H$ concentration on the sulfonation of St-g-PP in $ClSO_3H/ClCH_2CH_2Cl$ solution at room temperature. Grafting yield 97.6%, (●) 5%, (■) 10%, (▲) 20%.

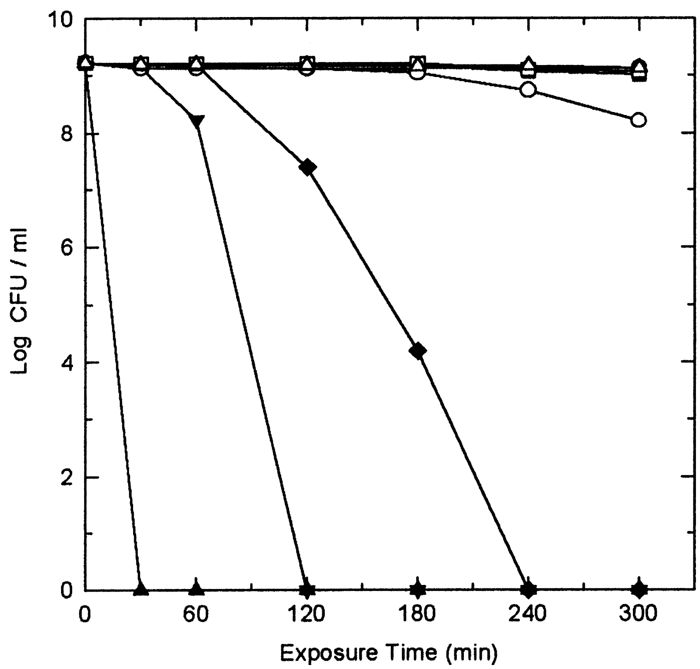

Figure 3. Changes of the viable cell number of *E. coli* with exposure time for the metal complexes of sulfonated St-g-PP (3.95 mmol H^+/g). (●) blank, (■) St-g-PP, (▲) Ag^+, (▼) Fe^{2+}, (◆) Cu^{2+}, (❍) Zn^{2+}, (❑) Ni^{2+}, (Δ) Co^{2+}.

About 10^9 cells/mL of bacteria had contact with 0.145 g of the treated fabric. Its Ag complexed fabric had strong biocidal effect in killing all bacteria within 30 minutes, its Fe and Cu complexed fabrics were capable of killing *E. coli* within 120 and 240 minutes, respectively. In the other hand, styrene-grafted polypropylene, Co and Ni complexed fabrics did not have any bactericidal effect, with Zn complexed fabric having a little biocidal effect.

S. aureus was applied to the same samples as in Figure 3, and the logarithmic plots of the viable cell number of the bacteria were shown in Figure 4.

Ag and Fe complexes of sulfonated styrene-grafted polypropylene fabrics (3.95 mM SO_3H/g) had an intensive biocidal effect in killing all bacteria within 30 minutes, Cu and Ni complexed fabrics were capable of killing *S. Aureus* within 180 minutes. Zn and Co complexed fabrics also had a bactericidal effect against *S. aureus*, showing a different pattern from *E. coli*. On

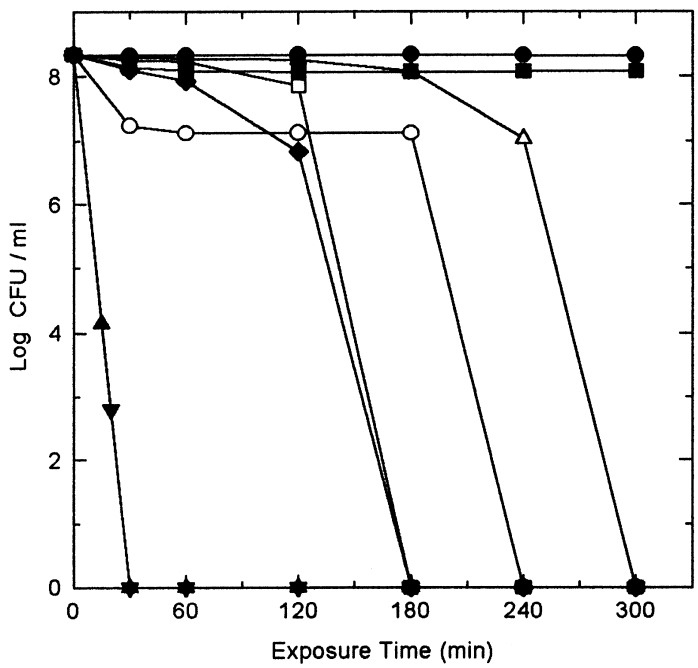

Figure 4. Changes of the viable cell number of *S. aureus* with the exposure time for the metal complexes of sulfonated St-g-PP (3.95 mmol H^+/g). (●) blank, (■) St-g-PP, (▲) Ag^+, (▼) Fe^{2+}, (◆) Cu^{2+}, (❍) Zn^{2+}, (❑) Ni^{2+}, (Δ) Co^{2+}.

the other hand, styrene-grafted polypropylene did not have any bactericidal effects at all.

P. aeruginosa was applied to the same sample as in Figure 3, and the results were shown in Figure 5 as the logarithmic plots of the viable cell number of the bacteria. Ag and Fe complexed fabrics had strong biocidal effects in killing all bacteria within 30 minutes. And Cu complexed fabric was intensive in killing *P. aeruginosa* within 60 minutes. Zn and Ni complexed fabrics were capable of killing *P. aeruginosa* within 240 and 300 minutes, respectively. On the other hand, Co complexed fabric and styrene-grafted polypropylene fabric did not have bactericidal effect at all.

From the antibacterial activity of metallic salts of sulfonated-grafted PP fabric, it was found that the Ag complexed fabric had strong biocidal effects for all bacteria and the other metal complexed fabrics had different antibacterial activity depending on each bacterium. On the other hand, styrene-grafted polypropylene fabric did not have any bactericidal effect at all.

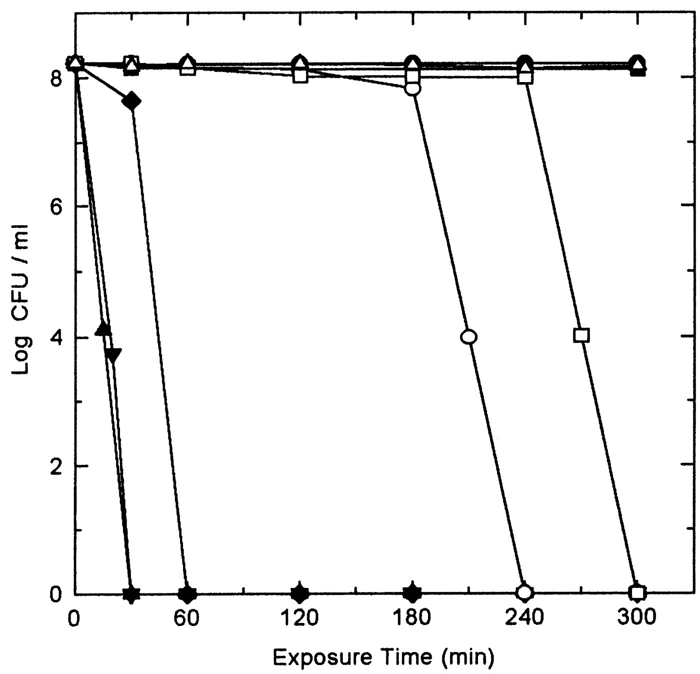

Figure 5. Changes of the viable cell number of *P. aeruginosa* with the exposure time for the metal complexes of sulfonated St-g-PP (3.95 mmol H^+/g). (●) blank, (■) St-g-PP, (▲) Ag^+, (▼) Fe^{2+}, (◆) Cu^{2+}, (○) Zn^{2+}, (□) Ni^{2+}, (Δ) Co^{2+}.

CONCLUSION

Antibacterial activities of sulfonated styrene-grafted polypropylene fabric and its metallic complexes against *Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa* were evaluated by a viable cell counting method. From the antibacterial activity of the metallic salts of sulfonated-grafted PP fabric, it was found that Ag complexed fabric had strong biocidal effects for all bacteria, and the other metal complexed fabrics had different antibacterial activity depending on each bacterium.

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