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항균성과 난연성을 함유하고 있는 인계고분자 코팅용액의 합성

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Synthesis of Phosphoric Polymer Coating Solution with Antimicrobial Activity and Flame Retardant Efficiency

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초록: 아크릴계 이중인산과 과황산암모늄을 개시제로 사용하여 고분자 코팅용액의 기반인 poly(acryloyl diphosphoric acid) (poly(ADP))를 70 ℃의 수용액에서 라디칼 중합반응으로 제조하였다. 제조된 고분자 코팅용액인 poly(ADP)는 salmonella typhimurium, pseudomonas aeruginosa, escherichia coli, 그리고 staphylococcus aureus에 대한 항균성을 보였으며, 또한, Asperigillus niger와 조류인플루엔자 바이러스인 H1N1 바이러스에 대해서도 좋은 항진균성을 보여주었다. 더욱이 면섬유에 제조된 코팅용액 poly(ADP)를 코팅시켰을 경우에 우수한 난연성을 보여주었다.

Abstract: A polymeric coating solution based on poly(acryloyl diphosphoric acid) (poly(ADP)) was prepared via a radical polymerization of acryloyl diphosphoric acid using ammonium persulfate (APS) as an initiator in water at 70 ℃. The prepared polymeric coating solution exhibited significant antibacterial activity against salmonella typhimurium, pseudomonas aeruginosa, escherichia coli, and staphylococcus aureus. It also exhibited good antifungal activity against Asperigillus niger and good antiviral activity against the influenza (H1N1) virus. Additionally, it exhibited good flame retardant efficiency after applying it as a coating to a cotton fabric.

Keywords: polymeric coating solution, antibacterial activity, antifungal activity, antivirus activity, flame retardant efficiency.

Introduction

Recently, antimicrobial polymers have been used in various fields, such as interior materials,[1,2] seal materials,[3] construction materials,[4,5] consumer products,[6-8] and products for food.[9-13] Antimicrobial polymers, generally known as polymeric biocides, are polymers with antimicrobial activity or the ability to prevent the growth of microorganisms, such as bacteria, fungi, or viruses.[14] They can be classified as follows: (1) polymers that contain antimicrobial agents and (2) polymers that are antimicrobial by themselves, such as chitosan derivatives or enzymes. In the case of polymers containing antimicrobial agents, molded products, such as sheets, fibers, films, hollow fibers, panels, fabrics, etc., are commercially available. However, they are very expensive and polymer molding is difficult due to the presence of antimicrobial agents. Also, these systems exhibit low antimicrobial activity since the antimicrobial agents exist mostly inside the polymer matrix rather than on the surface even though a high concentration of antimicrobial agents is used in the polymer molding process. On the other hand, researchers have developed a method to apply the polymer matrix (e.g., chitosan, chitosan derivatives, or enzymes) itself to a variety of surfaces, such as fabrics, plastics, metals, etc., by coating from a solution. However, antimicrobial polymers are insoluble in common solvents and not easy to apply to surfaces by coating since they have low viscosity, adhesion, and solubility in common solvents; they are even non-transparent. Therefore, the solubility of these polymers needs to be improved in order to prepare solutions in a solvent(s) that

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can be coated onto surfaces to create active coatings.

The use of flame retardant polymer materials has been increasingly required in many fields dealing with construction, electrical/electronic components, and transportation to reduce combustibility and suppress smoke or toxic fume production.[15] These polymer materials have been typically developed using halogen-containing flame retardant formulations. Particularly, halogenated compounds act mostly in the vapor phase by a radical mechanism that interrupts the exothermic processes and suppresses combustion. Polymers with halogen-containing flame retardants provide excellent flame retardants at low preparation costs and are still in use.[16,17] However, the use of halogenated flame retardants has given rise to some concerns. In particular, much attention has been focused on the corrosiveness and toxicity of smoke and emission products, such as dioxins or hydrogen chloride, generated during the combustion of these materials.[18] In recent years, there has been much speculation that legislation will arise restricting the use of these compounds as flame retardants. In contrast to the potentially hazardous halogenated flame retardants, phosphorus-containing flame retardants are non-toxic, environment-friendly, highly efficient flame retardants.[16] In order to impart flame retardancy to polymer materials, there are two main types of flame retardants used for polymers, additive and reactive.[16] The additive flame retardants are incorporated into the polymer by physical means prior to, during, or after polymerization. Additive flame retardants are not chemically bonded to the polymer. They may therefore, be released from the polymer and discharged to the environment. Also, a variety of problems may arise, such as poor compatibility and a reduction in polymer mechanical properties. On the other hand, reactive flame retardants are added during the polymerization process and become an integral part of the polymer. The result is a modified polymer with flame retardant properties and a different molecular structure compared to the original polymer molecule.

In this study, we synthesized a polymeric coating solution with poly(ADP) via radical polymerization of acryloyl diphosphoric acid (ADP) using ammonium persulfate (APS) in water at 70 ℃. The prepared polymeric coating solution was evaluated for its antimicrobial activity against bacteria, fungi, and viruses. In order to evaluate the flame retardant properties of the polymer coating solution, we applied the coating to a cotton fabric by a dip coating method. We then evaluated the flame retardant efficiency of the poly(ADP) coating.

Experimental

Reagents. Diphosphoric acid, acryloyl chloride, triethylamine (TEA), and ammonium persulfate (APS) were obtained from Sigma Aldrich (Korea). Other chemicals were of reagent grade.

Synthesis of the Poly(ADP) Coating Solution by Radical Polymerization. In order to prepare the polymeric coating solution, first, ADP was synthesized according to Figure 1. Diphosphoric acid (0.562 mol) was dried under reduced pressure for 12 hrs, and then dissolved in tetrahydrofuran (THF, 210 mL). TEA (80 mL) was added to the diphosphoric solution and the reaction mixture was stirred for 20 min. Acryloyl chloride (0.468 mol) in THF (40 mL) was added drop by drop to the reaction mixture over 3 hrs while the temperature was maintained at 0 ℃. The reaction mixture was then stirred for another 3 hrs at room temperature. The ADP monomer was obtained after evaporation of the solvent. The chemical structure of the ADP monomer was confirmed by ^{1}H NMR (DMSO-d_6), FTIR, and MS spectroscopy.

^{1}H NMR(DMSO-d_6, TMS): 3.0-3.2(t, 1H,=CH-), 1.1~1.3 ppm(d, 2H, CH_2=); FTIR(KBr): 1730 cm^{-1}(>C=O), 1000 cm^{-1}(P=O), 3500 cm^{-1}(-OH); MS m/z 232.

Second, the poly(ADP) coating solution was prepared by radical polymerization of the ADP monomer (13.0 g) with APS (3.25 g) used as an initiator in deionized water (90 mL) while stirring with a mechanical steering machine (8 rpm) at 70 ℃ for 24 hrs.

Evaluation of the Antimicrobial Activity of the Poly(ADP) Coating Solution. The antimicrobial activity of the prepared poly(ADP) coating solution was investigated against four types of bacteria and a fungus. The antimicrobial activity

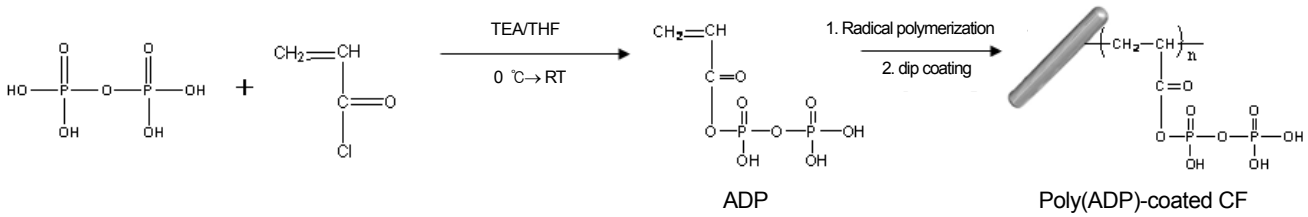


Figure 1. Schematic preparation procedure of the poly(ADP)-coated cotton fabric(CF) by dip coating method.

of the coating solution was also compared to that of a $AgNO_3$ solution. The Escherichia coli was streaked out on a Luria-bertani (LB) plate and incubated at 37 ℃ while being shaken for 24 hrs. 3.0 mL of a single colony obtained from the cultured LB plate was used to inoculate 5 mL of LB broth, which was then incubated with shaking at 37 ℃ for 24 hrs. 100 μL of the LB broth was patched onto a Petri dish, and then a paper disc was placed onto an LB plate film. The desired concentration of poly(ADP) coating solution was added onto the paper disc to measure the antibacterial activity after incubating at room temperature for 24 hrs. Same procedure was used for other bacteria.

The antifungal activity measurements of various concentrations of the poly(ADP) coating solution against Asperigillys niger were performed as follows: first, Asperigillys niger was cultured in a Potato dextrose agar (PDA) plate at room temperature for 7 days. 20 mL of the cultured fungus was then added into a phosphate buffered saline (PBS) solution to obtain spores using a spreader. Lastly, 100 μL of the obtained solution was patched onto a Petri dish, and then a paper disc was placed onto the PDA plate film. The desired concentration of the poly(ADP) coating solution was added onto the paper disc and the antifungal activity was measured after incubating it at room temperature for 24 hrs.

Antiviral activity of the poly(ADP) coating solution against the influenza (H1N1) virus was performed according to the references.[19,20] All procedures were performed at Institute of Influenza Research center, Chungnam National University.

Evaluation of the Flame Retardant Efficiency of the Poly(ADP)-coated Cotton Fabric. The prepared poly(ADP) was coated onto a cotton fabric to determine the flame retardant properties by a dip coating method. In this study, the coating yield was calculated with the following equation:

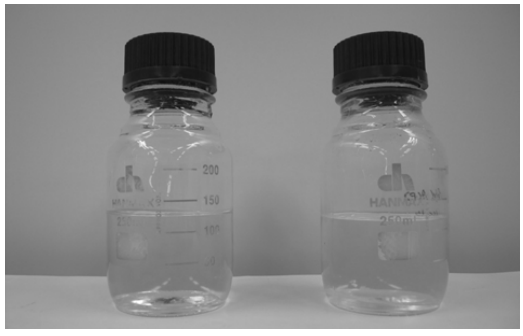
$$\text{Coating yield}(\%) = [(W_g - W_o)/W_o] \times 100 \quad (1)$$

Where W_g and W_o denote the weights of the coated and uncoated cotton fabric, respectively. The poly(ADP)-coated cotton fabric was ignited using a butane lighter for the combustibility test.

Instrumentation. ^{1}H NMR data were collected on a Varion spectrometer (400 MHz, Voyager DE-STR, USA) using a DMSO-d_6 solvent. Tetramethylsilane (TMS) was used as an internal standard. IR spectra were recorded on a Perkin-Elmer Spectrum 1000 system (Perkin-Elmer life and analytical sciences, USA). The mass spectra were recorded on a Maldi-TOF Mass Spectrometer (Voyager DE-STR, Applied Biosystems, Inc. USA). The morphology of the coated sample was obtained using a Field-emission scanning electron microscope (FE-SEM) (FEI, Sirion, Netherlands). The XPS spectra of the sample were recorded using X-ray photoelectron spectroscopy(XPS)(MultiLab. ESCA 2000, ThermoVG Scientific, England).

Results and Discussion

Antimicrobial Activity of the Poly(ADP) Coating Solution. The light yellow color in the solution disappeared as ADP polymerization occurred, as shown in Figure 2. Table 1 and Figure 3 show the antibacterial activity and antifungal activity of the poly(ADP) coating solution and the comparative compounds, the diphosphoric acid solution and the $AgNO_3$ solution. Phosphoric acid has been routinely used in dental practices as a conditioner and to remove smear layers and open dentin tubules. The antimicrobial activity of this acid may be related to an increased external hydrogen-ion concen-



(a) (b)

Figure 2. Photograph of the ADP solution (a); poly(ADP) coating solution (b).

Table 1. Antibacterial and Antifungal Activity of Diphosphoric Acid, Poly(ADP) Solution and $AgNO_3$ Solution

Sample	0.1 M Diphosphoric acid			0.1 M Poly(ADP) solution			0.1 M $AgNO_3$ solution		
	50 μL	10 μL	5 μL	50 μL	10 μL	5 μL	50 μL	10 μL	5 μL
Salmonella typhimurium	0.2 cm	0 cm	0 cm	0.4 cm	0 cm	0 cm	0.2 cm	0 cm	0 cm
Pseudomonas aeruginosa	0.4 cm	0 cm	0 cm	1.6 cm	0.4 cm	0 cm	0.8 cm	0.4 cm	0.1 cm
Escherichia coli	0.2 cm	0 cm	0 cm	1.2 cm	0 cm	0 cm	0.8 cm	0.4 cm	0.2 cm
Staphylococcus aureus	0.6 cm	0 cm	0 cm	2.6 cm	1.2 cm	0.6 cm	1.2 cm	0.8 cm	0.4 cm
Asperigillus niger	0.2 cm	0 cm	0 cm	0.4 cm	0 cm	0 cm	1.2 cm	0.2 cm	0 cm

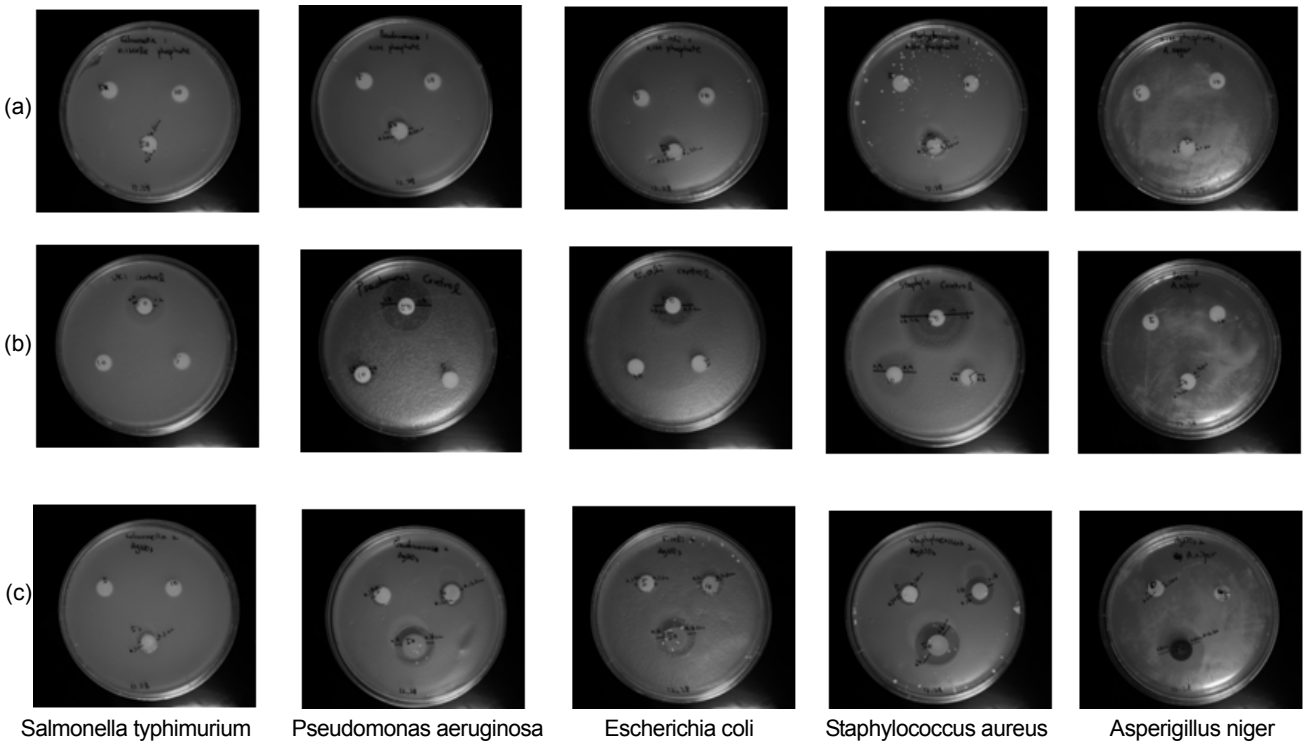


Figure 3. Antibacterial and antifungal activity of the diphosphoric acid solution (a); poly(ADP) solution (b); $AgNO_3$ solution (c).

tration, which inhibits the metabolism and hence the growth of many microorganisms.[21] Arias-Moliz *et al.*[22] reported on the bactericidal activity of phosphoric acid, citric acid, and EDTA solutions against Enterococcus faecalis. However, phosphoric acid cannot be coated onto polymer molded products due to the resulting lower adhesion properties. The $AgNO_3$ solution was also used as a counterpart since the antimicrobial effects of silver ions or salts are well known.[23-25] As shown in Table 1, 50 μL of 0.1 M $AgNO_3$ solution had pronounced antibacterial activity against Salmonella typhimurium, Seudomonas aeruginosa, Escherichia coli, and Staphylococcus aureus. However, when 5 μL of 0.1 M $AgNO_3$ solution were used, there was no antibacterial activity against Salmonella typhimurium. 50 μL of 0.1 M $AgNO_3$ solution exhibited antifungal activity against Asperigillus niger. Poly(ADP) had more pronounced antibacterial activity against all microorganisms tested compared to those of the diphosphoric acid and $AgNO_3$ solutions. Although, the $AgNO_3$ solution exhibited the highest antifungal activity and a somewhat better antimicrobial effect at low concentrations (10 and 5 μL), silver ions are unstable in the presence of light or other radiation. Here, the concentration of poly(ADP) was determined from the ADP monomer.

Figure 4 shows the antiviral activity of the prepared poly(ADP) coating solution: (a) control, (b) diphosphoric acid solution, and (c) poly(ADP) solution. We used influenza virus

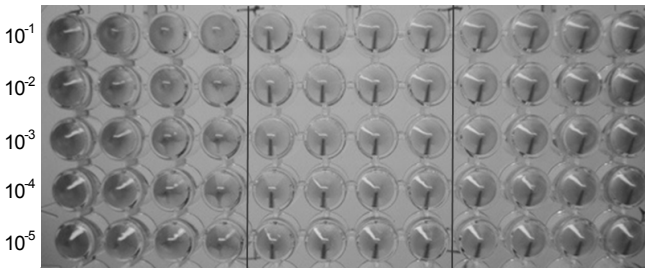


Figure 4. Antiviral activity for influenza (HIN1) virus of the control (a); diphosphoric acid solution (b); poly(ADP) solution (c).

[A/California/04/09(H1N1)] to determine the antiviral activity against the influenza H1N1 virus according to the reference.[19,26] The aggregation of blood cells in allantoic fluid appeared in the presence of diphosphoric acid (b) and the poly(ADP) solution (c). As a result, diphosphoric acid and poly(ADP) solution exhibited potent antiviral activity against the influenza H1N1 virus.

Flame Retardant Efficiency of Poly(ADP)-coated Cotton Fabric. Figure 5 shows the SEM image of base cotton fabric (a), and poly(ADP)-coated CF with coating yields of 10% (b), 15% (c), and 25% (d). The SEM images confirm that the poly(ADP) polymer was successfully coated on the surface of the commercial cotton fabric.

Figure 6 exhibits the XPS survey scan spectra of the

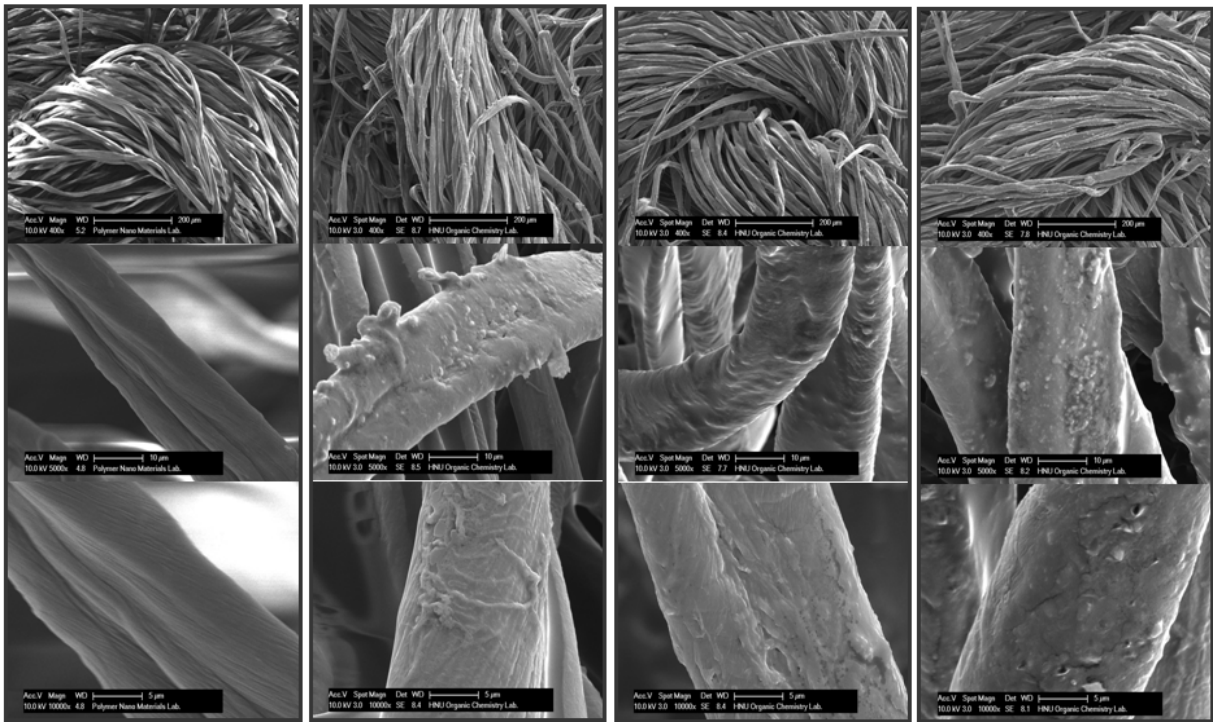


Figure 5. SEM images of base cotton fabric (a); poly(ADP)−coated CF with coating yields of 10% (b); 15% (c); 25% (d).

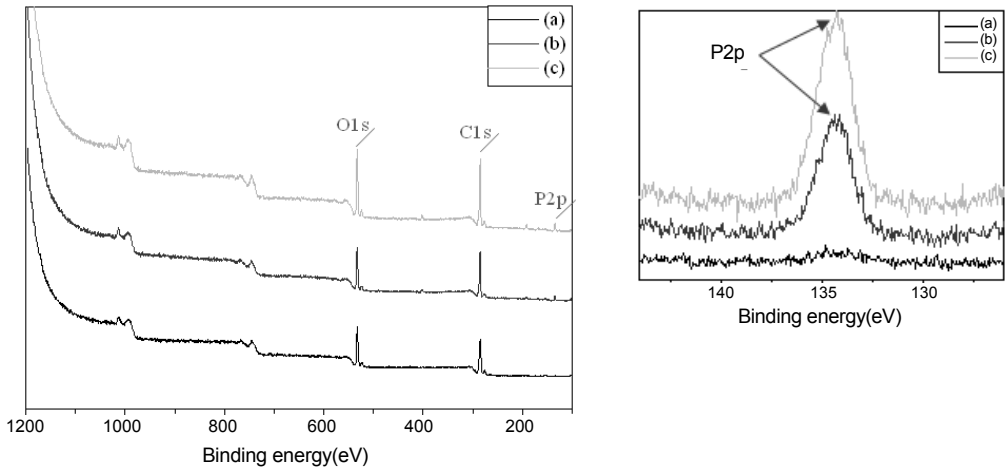


Figure 6. XPS survey spectra of the base cotton fabric (a); poly(ADP)−coated CF with coating yields of 10% (b); with coating yields of 25%(c).

base cotton fabric (a), and poly(ADP)−coated CF with coating yields of 10% (b) and 25% (c). The P2p peak of the poly(ADP)−coated cotton fabric appears at about 135 eV due to the side chain of the diphosphoric acid. From this result, we confirm the successful coating of the poly(ADP) on the surface of the cotton fabric.

Figure 7 presents the effects of the flame retardant treatment on the cotton fabric. (a) base cotton fabric, (b) and poly(AP)−coated cotton fabric with coating yields of 10%, (c) 15%, and (d) 25%. The top and bottom photographs show the cotton fabric of before combustion and after combustion, respectively. Figure 7(a) shows the remaining ashes after the non−coated cotton fabric was completely burned whereas the poly(ADP)−coated cotton fabrics that were partially burned are shown in Figure 7(b, c), and (d). Hwang *et al.*,[26] reported on phosphorus flame retardants and found that a PO・radical forms first during the combustion of phosphorus flame retardants. Then, the generated phosphorus oxygen

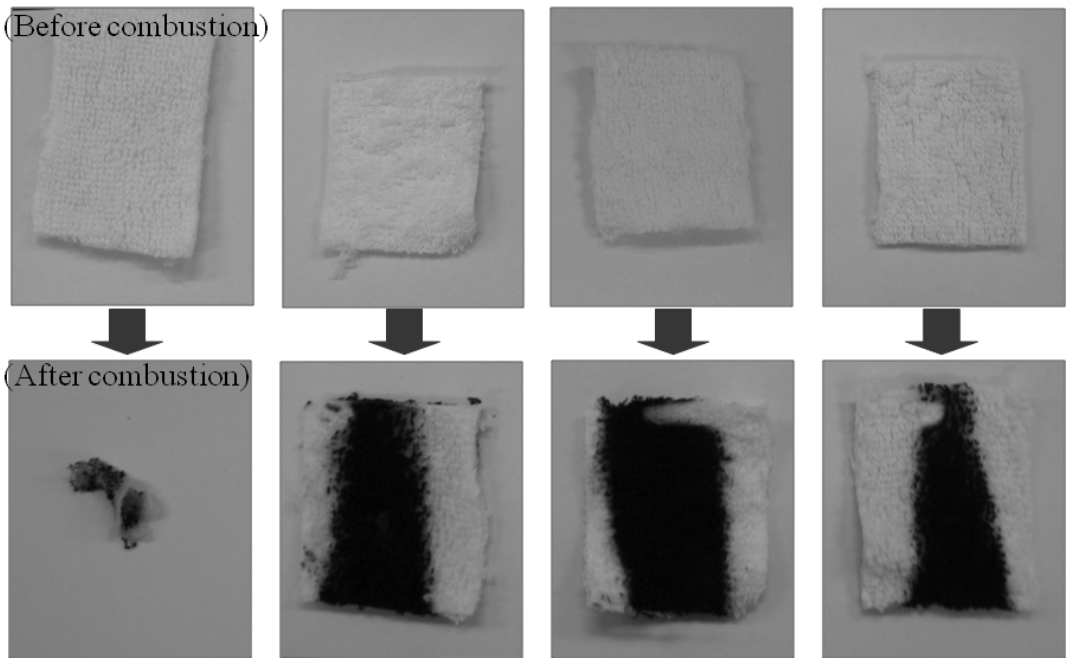


Figure 7. Effects of flame retardant for cotton fabric: (a) base cotton fabric; (b) poly(ADP)-coated cotton fabric with coating yields of 10%; (c) with coating yields of 15%; (d) coating yields of 25%.

radical rapidly reacts with oxygen in air. This is the reason the poly(ADP)-coated cotton fabrics were totally unburned after combustion since the carbons of cotton fabric were protected from the reaction with oxygen by the poly(ADP) coating. These results suggest that the prepared poly(ADP) coating solution has the potential to be used as a flame retardant agent.

Conclusions

In this study, we synthesized a polymeric coating solution based on poly(ADP) via radical polymerization of acryloyl diphosphoric acid using ammonium persulfate (APS) as an initiator in water at 70 ℃. The antimicrobial activity and the flame retardant efficiency of the prepared the polymer coating solution were investigated. The following conclusions are based on the results:

(1) The poly(ADP) coating solution had pronounced anti-bacterial activity against Salmonella typhimurium, Pseudo-monas aeruginosa, Escherichia coli, and Staphylococcus aureus.

(2) The poly(ADP) coating solution exhibited significant antifungal activity against Asperigillus niger.

(3) The poly(ADP) coating solution exhibited some antivirus activity against the influenza (H1N1) virus.

(4) Additionally, the poly(ADP) coating solution exhibited good flame retardant efficiency after applying it as a coating to a cotton fabric.

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