

Fabrication of Deodorizing Fabric by Grafting of Metal Phthalocyanine Derivative onto Nonwoven Polypropylene Fabric

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ABSTRACT: Fabrication of deodorizing fabric was tried by grafting metal phthalocyanine derivative, a catalytic deodorant, onto polypropylene (PP) nonwoven fabric. Fe(III)-4,4',4'',4'''-tetra carboxamide phthalocyanine (Fe-TCMP) was synthesized. The Fe-TCMP showed high-deodorizing performance when tested for the elimination of 2-mercaptoethanol, an index material for bad-smelling compounds. The Fe-TCMP was converted to Fe(III)-4,4',4'',4'''-tetracarboxylic acid phthalocyanine (Fe-TCAP) by hydrolysis to have carboxyl groups. It was chemically grafted on the surface of PP nonwoven fabric, which was surface modified to have amine groups with diaminocyclohexane (DACH) plasma. Such fabricated deodorizing fabric showed high-deodorizing performance for 2-mercaptoethanol. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 839–846, 2001

Key words: deodorizing fabric; metal phthalocyanine derivative; grafting; low-temperature plasma process

INTRODUCTION

As the demand for a comfortable life grows, a large amount of attention is directed to the development of efficient deodorizing methods to eliminate bad-smelling compounds. Currently, sensory deodorization using aromatic, masking, or neutralizing compounds and physical deodorization are the most widely used methods. However, these methods cannot provide an ultimate solution for the elimination of bad-smelling compounds. Sensory deodorization only changes per-

ception of the smell by using different smelling compounds. Physical deodorization eliminates smelling compounds through physical adsorption. Therefore, deodorizing capacity is rather limited and also adsorbed smelling compounds can be desorbed depending on the conditions.

The methods by which smelling compounds can be converted into odorless substances are chemical and biological deodorizations. Various materials are available as a deodorant in those methods.¹ Among them, metal phthalocyanine derivatives are given special attention.^{2–7} They act similar to an oxidizing enzyme with oxidative catalytic function. Therefore, they can continuously convert smelling compounds into odorless substances through cyclic oxidation and reduction reactions without being consumed. They are

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known to be efficient, especially for the oxidation of mercaptan or hydrogen sulfide, which is not only bad-smelling but also hazardous to human health.

One drawback of the metal phthalocyanine derivatives as a deodorant is that they are not convenient to use in field applications because they are generally found in the form of solution or powder. If they are fixed to a material that is convenient to use in field applications, however, the drawback can be overcome. For such a material, fiber may be the best candidate because it not only is easy to handle, but also can supply a large contact area with smelling compounds.

Some technologies have already been developed for the fabrication of deodorizing fiber, including deodorant-mixed-in spinning, spraying, immersion, padding, coating, laminating, and printing.¹ However, those technologies are applicable to a limited number of fibers such as cellulose, acrylic, rayon, and polyester. Also, durability of the fixed deodorant is still a problem.

In this study, chemical grafting of metal phthalocyanine derivative onto polypropylene (PP) nonwoven fabric was investigated to fabricate a durable deodorizing fabric. As a metal phthalocyanine derivative, Fe(III)-4,4',4'',4'''-tetra carboxamide phthalocyanine (Fe-TCMP) was synthesized. The Fe-TCMP was converted to Fe(III)-4,4',4'',4'''-tetracarboxylic acid phthalocyanine (Fe-TCAP) by hydrolysis to have carboxyl groups. It was chemically grafted on the surface of PP nonwoven fabric, which was surface modified to have amine groups with diaminocyclohexane (DACH) plasma.⁸ Deodorizing performance of the derivative and the fabricated deodorizing fabric was tested for the elimination of 2-mercaptoethanol as an index material for bad-smelling compounds.

EXPERIMENTAL

Synthesis of Fe-TCMP and Conversion to TCAP

Fe-TCMP was synthesized by reacting trimellitic anhydride (Aldrich) and urea (Aldrich) with FeCl₃ (Aldrich) in nitrobenzene (Aldrich) in the presence of ammonium molybdate (Aldrich) for 3 h at 170°C.⁹ Unreacted residues are removed by using methanol (Aldrich). Then, it was converted to TCAP by hydrolyzing it in 50% KOH (Aldrich) solution for 24 h at 100°C.¹⁰

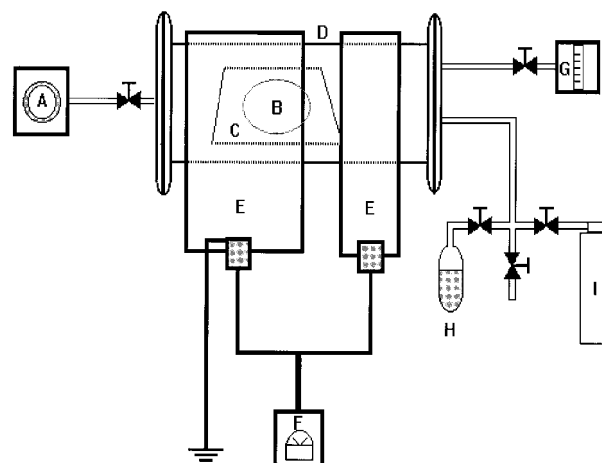


Figure 1 Schematic diagram of the plasma reactor: i.d., 14.2 cm; length, 28 cm. (A) Vacuum pump; (B) sample; (C) sample holder; (D) reaction chamber; (E) electrodes; (F) R.F. power supply; (G) pressure gauge; (H) liquid monomer reservoir; (I) gas reservoir.

Modification of PP Nonwoven Fabric

Modification of PP nonwoven fabric was carried out in an RF tubular plasma reactor (inner diameter of 14.2 cm and length of 28 cm) shown in Figure 1. PP nonwoven fabric (0.15-cm thick) was cut into small pieces (3 × 3 cm) and located at the center of a reaction chamber after cleaning with 1 : 1 water : ethanol solution in an ultrasonic cleaner for 15 min. As a monomer for plasma polymerization, DACH, which has two amino groups per molecule, was used.

Grafting of Fe-TCAP onto PP Nonwoven Fabric

Before the grafting, 0.05 g of TCAP and 0.04 g of water-soluble carbodiimide (WSC, 1-ethyl-3-dimethylaminopropyl carbodiimide, Sigma) were dissolved together in 20 mL of 0.075*N* sodium citrate (Duksan, Seoul, Korea) for 30 min to activate carboxyl groups in TCAP.¹¹ Then, PP nonwoven fabric was immersed in the solution for the carboxyl groups in Fe-TCAP to react with amine groups on the surface of PP nonwoven fabric. The reaction scheme is shown in Figure 2. For pH adjustment of the solution, 1*N* HCl (Aldrich) was used.

Analysis and Measurement

Chemical structures of the synthesized Fe-TCMP, Fe-TCAP, and plasma-treated PP surface were analyzed with an FTIR spectrophotometer (Jasco

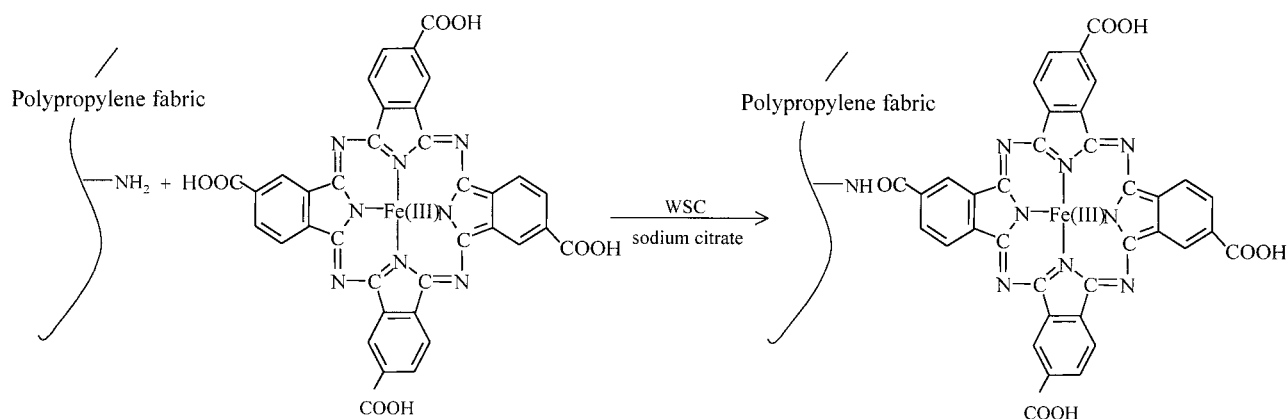


Figure 2 Reaction scheme for grafting of Fe-TCAP onto DACH plasma-modified PP nonwoven fabric.

430). Complex formation of Fe(III) ions with phthalocyanine derivative was confirmed by measuring the content of Fe(III) ions in the Fe-TCMP with an atomic absorption spectrophotometer (Perkin–Elmer 5100PC) and by testing its catalytic function for the decomposition of H_2O_2 (Aldrich).¹ After mixing a small amount of Fe-TCMP with 3% H_2O_2 in 1 : 4 $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ (Aldrich) solution, the solution was titrated with 0.1N KMnO_4 (Aldrich). The amount of remaining H_2O_2 was calculated by the following equation¹²:

$$\text{H}_2\text{O}_2 \text{ (mg)} = \text{volume of 0.1N KMnO}_4 \text{ (ml)} \\ \times 1.017 \text{ mg/ml}$$

Deodorizing performance of the Fe-TCMP or deodorizing fabric was evaluated on the basis of the oxidation yield of 2-mercaptoethanol. After putting a small amount of Fe-TCMP or deodorizing fabric into 0.1% 2-mercaptoethanol hexane/dioxane (60/40 v/v) solution, a concentration of the 0.1% 2-mercaptoethanol was measured by HPLC analysis (LC-10A, Shimadzu). Oxidation yield was calculated by the following equation:

$$\text{Oxidation yield (\%)} = (A - B)/A \times 100$$

where A refers to the initial concentration of 2-mercaptoethanol and B refers to the concentration of 2-mercaptoethanol after the reaction.

RESULTS AND DISCUSSION

Characterization of Fe-TCMP and Its Deodorizing Performance

Figure 3 shows the FTIR spectra of the trimellitic anhydride, Fe-TCMP, and Fe-TCAP. Although

$\text{C}=\text{O}$ peak appears at 1780 cm^{-1} in trimellitic anhydride spectrum, it appears at 1660 cm^{-1} in the Fe-TCMP spectrum and at 1700 cm^{-1} in the Fe-TCAP spectrum, indicating that $\text{C}=\text{O}$ of anhydride was converted to that of carboxamide and carboxylic acid. Also, a double peak that represents the NH_2 peak of carboxamide is shown at 3335 and 3187 cm^{-1} in the Fe-TCMP spectrum and a peak that represents hydrogen-bonded OH peak of carboxylic acid is shown at 3340 cm^{-1} in the Fe-TCAP spectrum. From this, it was confirmed that synthesis of Fe-TCMP and its conversion to Fe-TCAP were successfully carried out. The content of Fe^{3+} ions in Fe-TCMP was measured to be approximately 50% by atomic absorption (AA) analysis.

The Fe-TCMP could decompose H_2O_2 at a high rate, indicating that it has catalytic function.¹

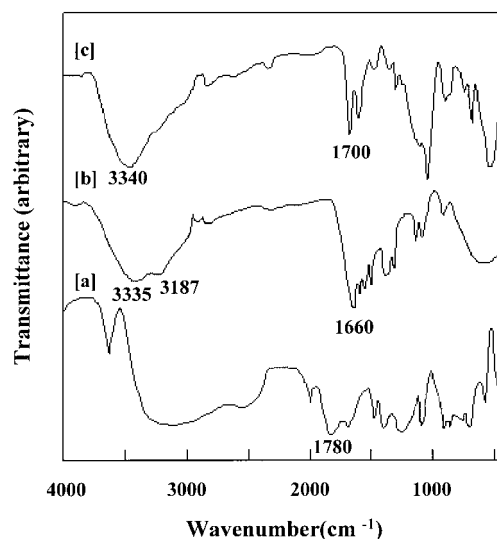


Figure 3 FTIR spectra of (a) trimellitic anhydride; (b) Fe-TCMP; and (c) Fe-TCAP.

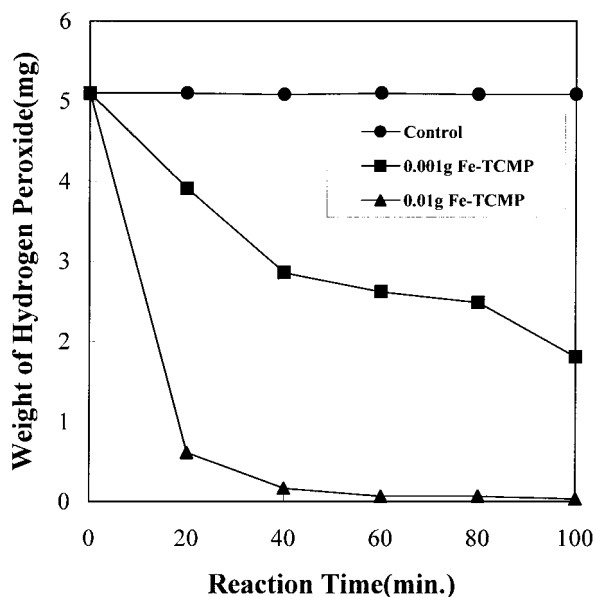


Figure 4 Amount of hydrogen peroxide in the presence of Fe-TCMP as a function of reaction time.

Figure 4 shows how the amount of H_2O_2 changes with time after addition of the Fe-TCMP. The amount of H_2O_2 decreases rapidly with time at a much higher rate for a larger amount of TCMP (0.01 g) than a smaller amount of Fe-TCMP (0.001 g). All the H_2O_2 was decomposed in 60 min when Fe-TCMP was added to H_2O_2 at a ratio of 1 : 5.

Deodorizing performance of the Fe-TCMP was evaluated on the basis of the oxidation yield of 2-mercaptoethanol. According to the reaction mechanism proposed by Shirai,¹³ 2-mercaptoethanol would be eliminated through the following oxidation reaction:

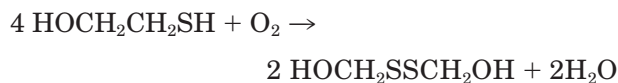


Figure 5 shows HPLC chromatograms of 2-mercaptoethanol before and after the reaction. After the reaction, the peak of 2-mercaptoethanol at retention time of 4.9 min almost disappeared and two new peaks appeared at the retention times of 3.8 and 8.1 min. In the calculation of oxidation yield, area of the peak at retention time of 4.9 min was used.

The Fe-TCMP showed high-deodorizing performance. Figures 6 and 7 show oxidation yields of 2-mercaptoethanol as a function of reaction time for various Fe-TCMP concentrations at 20°C and

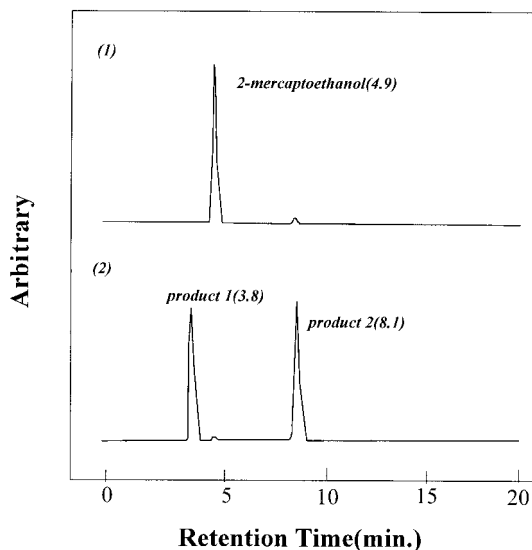


Figure 5 HPLC chromatograms of 2-mercaptoethanol (1) before and (2) after the oxidation reaction by Fe-TCMP.

as a function of Fe-TCMP concentration for three different reaction temperatures after a 60-min reaction. As shown in the figures, oxidation yields sharply increased in the beginning and saturated as the reaction time and concentration increased. At concentrations > 2% and reaction temperatures > 40°C, all the 2-mercaptoethanol was eliminated by Fe-TCMP.

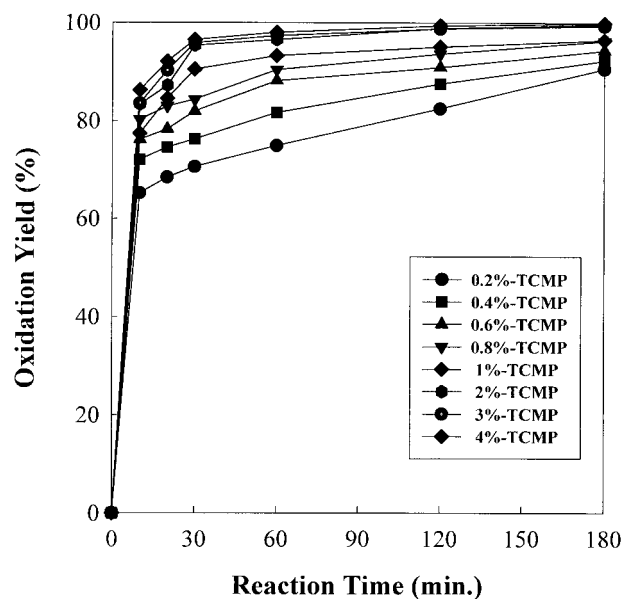


Figure 6 Oxidation yields of 2-mercaptoethanol by Fe-TCMP as a function of reaction time for various Fe-TCMP concentrations (reaction temperature: 20°C).

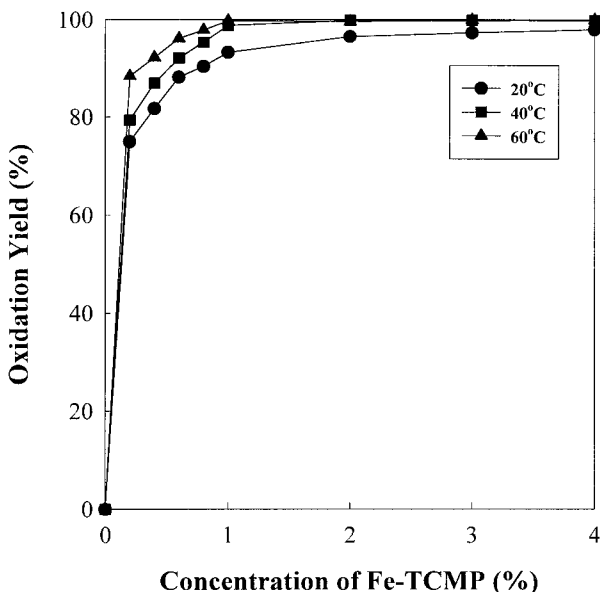


Figure 7 Oxidation yields of 2-mercaptoethanol by Fe-TCMP as a function of Fe-TCMP concentrations at 4, 20, and 40°C (reaction time: 60 min).

Fabrication of Deodorizing Fabric and Its Deodorizing Performance

When PP nonwoven fabric was exposed to DACH plasma, an ultrathin film with amine groups was deposited on solid surfaces. Thickness and chemical structure of the film depended on the plasma condition. Figure 8 shows deposition rates of the film as a function of discharge power. It increases sharply with discharge power at low-power levels but becomes saturated at high-power levels. To find the optimum discharge power for the deposited film to have the highest concentration of amine groups, water contact angles of the films were measured after being deposited on PP film at various discharge powers. Because the NH_2 group is hydrophilic whereas PP film is hydrophobic, water contact angle decreases as concentration of NH_2 groups in the deposited film increases. The water contact angles are shown in Figure 9 as a function of treatment time for various discharge powers. As shown in the figure, lower discharge power resulted in the lower water contact angle. According to this data, 10 W may be the optimum discharge power. When water contact angles were measured again after washing the films with water, however, the films deposited at 20 W showed the lowest water contact angles, as shown in Figure 10. This may be due to the existence of washable materials such as free polymers and oli-

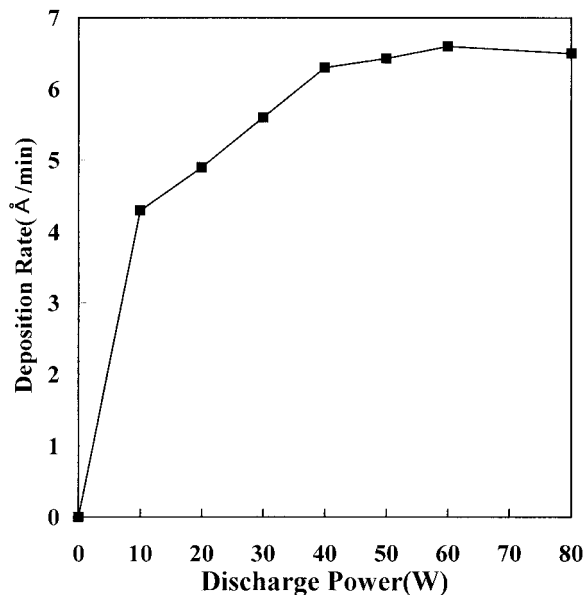


Figure 8 Deposition rates of a film in DACH plasma as a function of discharge power (flow rate: 0.723 SCCM).

gomers, which are not grafted to the PP film. There is more possibility for such materials to be formed at lower discharge power. FTIR/ATR (attenuated total reflection) spectra of a film deposited at 20 W for 20 min are shown in Figure 11. NH_2 peak is observed at 1636 cm^{-1} . Note that the area of the peak gets smaller after washing.

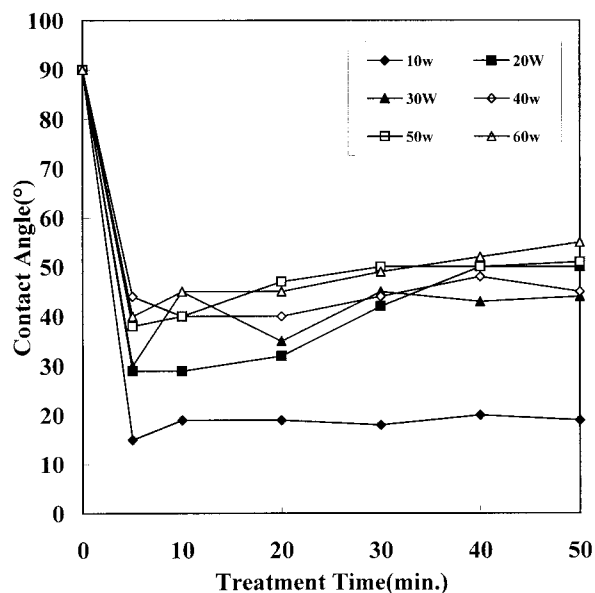


Figure 9 Water contact angles of DACH plasma-treated PP films as a function of treatment time for various discharge powers (flow rate: 0.723 SCCM).

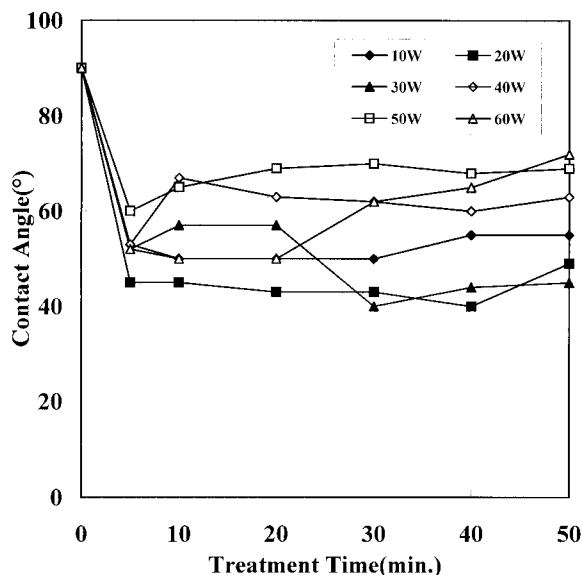


Figure 10 Water contact angles of DACH plasma-treated PP films after washing with water as a function of treatment time for various discharge powers (flow rate: 0.723 SCCM).

Deodorizing fiber was fabricated by chemically grafting Fe-TCAP onto PP nonwoven fabric treated with DACH plasma at 20 W for 20 min. The grafting reaction was carried out for 5, 20, and 20 h at various pHs^{6,7,8} and reaction temperatures (4, 20, 40°C). The optimum condition for the grafting reaction was determined on the basis

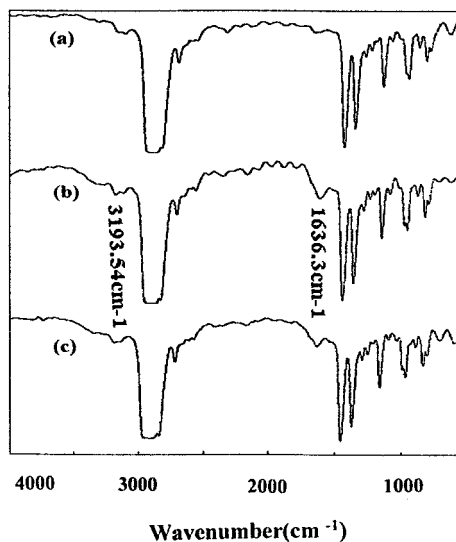


Figure 11 FTIR spectra of (a) untreated, (b) DACH plasma-treated (discharge power: 20 W; reaction time: 20 min), and (c) DACH plasma-treated PP films after washing with water.

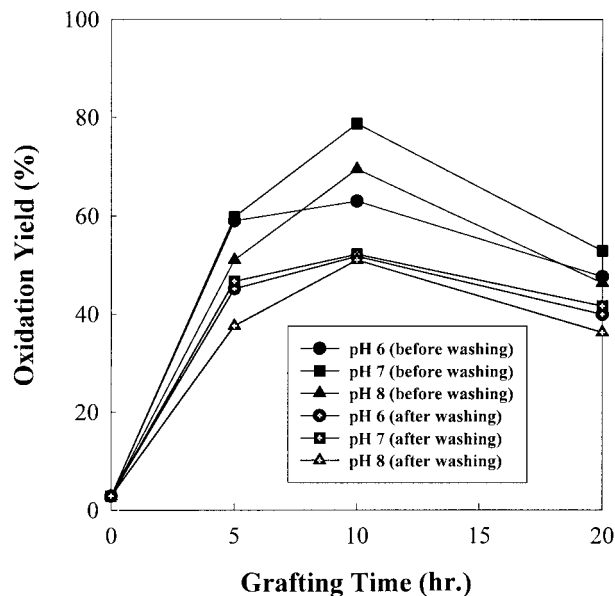


Figure 12 Oxidation yields of 2-mercaptoethanol by deodorizing fabrics grafted at various solution pHs as a function of grafting time (grafting temperature: 4°C; reaction time: 120 min).

of the oxidation yield of 2-mercaptoethanol at 20°C. A deodorizing fabric with a size of $3 \times 3 \times 0.15$ cm (washed and unwashed) was immersed in 5 mL 0.1% 2-mercaptoethanol for 2 h.

Oxidation yields of 2-mercaptoethanol by deodorizing fabric grafted at 4, 10, and 40°C are shown in Figures 12, 13, and 14 as a function of grafting time for various pHs. The oxidation yield increases as the grafting time increases until 10 h and decreases again if the grafting time further increases. The optimum pH of the solution and grafting temperature was 7 and 20°C, respectively. Lower oxidation yields were obtained when deodorizing fabrics were washed with water before use, which indicates that some portion of the Fe-TCAP was just physically adsorbed. Nevertheless, the deodorizing fabric grafted for 10 h at 20°C and pH 7 showed reasonably good deodorizing performance even after the washing.

Grafting state of Fe-TCAP was investigated by grafting Fe-TCAP onto PP film for easy analysis by FTIR/ATR. The FTIR/ATR spectra of the film grafted for 5, 10, and 20 h at 20°C are shown in Figure 15. C=O peak and NH peak of amide groups are shown at 1696 and 1585 cm^{-1} , indicating that Fe-TCAP was chemically grafted by condensation reaction between carboxyl groups in Fe-TCAP and amine groups on the surface of the film. Note that there is a close relationship between peak intensity of the amide groups and the oxidation yields.

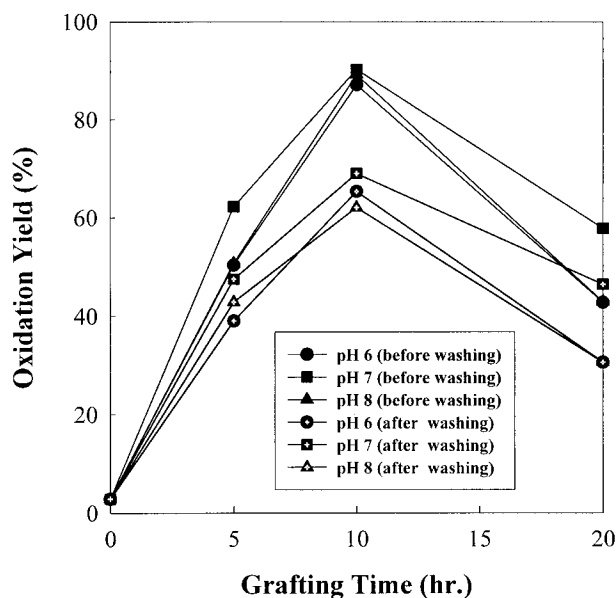


Figure 13 Oxidation yields of 2-mercaptoethanol by deodorizing fabrics grafted at various solution pHs as a function of grafting time (grafting temperature: 20°C; reaction time: 120 min).

Finally, catalytic functions of Fe-TCMP and deodorizing fabric were checked by repeating the oxidation reaction of fresh 2-mercaptoethanol five times with the same Fe-TCMP and deodorizing fab-

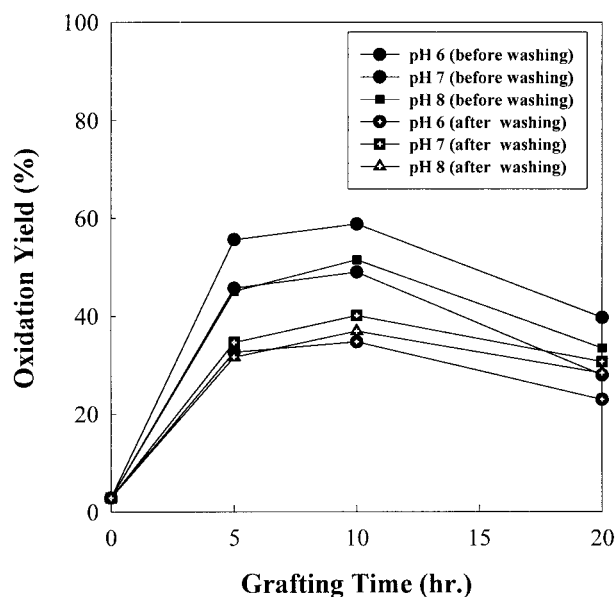


Figure 14 Oxidation yields of 2-mercaptoethanol by deodorizing fabrics grafted at various solution pHs as a function of grafting time (grafting temperature: 40°C; reaction time: 120 min).

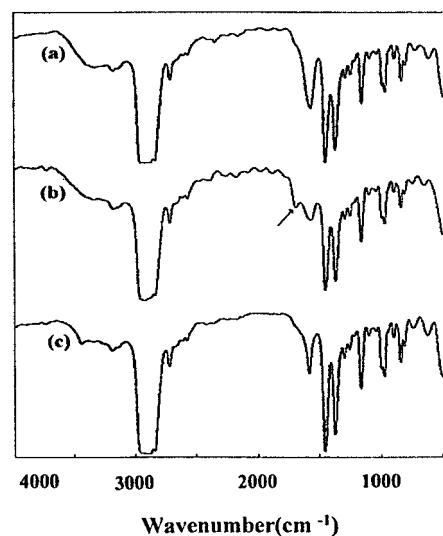


Figure 15 FTIR/ATR spectra of Fe-TCAP grafted PP films at pH 7 and 20°C for (a) 5; (b) 10; (c) 20 h.

ric. The results are shown in Table I. As shown in the table, there was no steady decrease in the oxidation yield, although there was some deviations between runs. Therefore, it is clear that Fe-TCMP (or TCAP), by itself or in the grafted state, acts as a catalyst for the oxidation of 2-mercaptoethanol.

CONCLUSION

From this study, the following can be concluded:

1. Fe-TCMP, a metal phthalocyanine derivative, has high potential for continuous deodorization of bad-smelling compounds such as 2-mer-

Table I Oxidation Yields of 2-Mercaptoethanol by Fe-TCMP and Deodorizing Fabric in Five Repeated Runs

No. of Runs	Oxidation Yield (%)		
	Fe-TCMP ^a	Deodorant Fabric (before washing) ^b	Deodorant Fabric (after washing) ^b
1	90.3	92.2	69.1
2	87.2	88.2	72.3
3	90.0	93.4	75.5
4	95.5	86.7	65.3
5	91.3	92.4	67.2

^a Concentration: 1.0%; reaction time: 60 min; reaction temperature: 20°C.

^b Grafting conditions: 20°C, pH 7, 10 h; reaction time: 120 min; reaction temperature: 20°C.

captoethanol by cyclic oxidation/reduction with catalytic function.

2. Durable deodorizing fabric, which would be practical in field applications, can be fabricated by chemically grafting the metal phthalocyanine derivative onto substrates such as PP nonwoven fabric.

3. Fe-TCMP can be chemically grafted onto PP nonwoven fabric by converting the Fe-TCMP to Fe-TCAP and modifying the PP nonwoven fabric with DACH plasma.

4. The grafting reaction, which proceeds by condensation reaction between carboxyl groups in Fe-TCAP and amine groups on the modified surface of PP nonwoven fabric, depends on temperature, solution pH, and reaction time. The optimum condition for the reaction is 20°C, pH 7, and 10 h.

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