Electrically Conductive Textiles by *in situ* Polymerization of Aniline

KYUNG WHA OH,[1] KYUNG HWA HONG,[1] SEONG HUN KIM[2]

[1] Department of Home Economics Education, Chung-Ang University, Seoul 156-756, Korea

[2] Division of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

ABSTRACT: Two methods of obtaining electrically conductive fabrics by *in situ* polymerization of aniline were compared. Conductive fabrics were prepared by immersing the nylon 6 fabrics in 100% aniline or *an* aqueous hydrochloride solution of aniline followed by initiating successive polymerization in a separate bath (DPSB) or in a mixed bath (DPMB) of oxidant and dopant solution with aniline. In each case, the polymerization conditions were optimized to obtain the maximum quality of polyaniline (PAn) on the fabrics. The higher conductivity of composite fabrics, whose value reached up to 0.6×10^{-1} s/cm, was obtained by the DPMB process. Moreover, this method induced the least decrease in the degree of crystallinity as compared to the DPSB process. The serviceability of the PAn–nylon 6 composite fabrics was also evaluated. No significant changes in the conductivity were observed after abrading the composite fabrics over 50 cycles and multiple acid and alkali treatment. The stability of conductivity was slightly decreased by less than 1 order after exposure to light for 100 h, but it was significantly decreased after washing with detergent. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2094–2101, 1999

Key words: conductive fabric; polyaniline; *in situ* polymerization; nylon 6; serviceability

INTRODUCTION

Electrically conductive fabrics are mainly used for industrial materials like filters, deelectrifying and electro-magnetic interference shield materials, and special purpose clothing, which is dust and germ free. Demand for them has increased strongly in recent years. The reason is that electrostatic and electromagnetic interference have proliferated and become commonplace due to human lifestyle changes and the increasing sophistication of industrial technology.[1]

Among the manufacturing processes used to produce conductive materials, there have been great expectations of π-electron conjugate polymers, such as polythiophene, polyaniline,[2,3] and polypyrrole.[4,5] Within the class of conducting polymers, polyaniline (PAn) has attracted extensive attention as a conducting material, since the monomer is inexpensive, the polymer can be easily prepared by the oxidation polymerization with high yield, and products are stable under ambient conditions.[2,6,7] Various attempts to apply polyaniline to polymeric materials such as film[1,2,5,6] and fabric,[3,4,7–9] have been made, but application technology still has not been adequately perfected.[7] Conductive polymer composites could be produced either by inclusion of polyaniline or by *in situ* oxidative polymerization of aniline mono-

mer. Owing to their low thermal stability and insolubility, the former method is hardly acceptable for producing conductive composite fabrics. Therefore, most studies have been focused on *in situ* polymerization to produce conductive fabric since this method does not require the destruction of the substrate and provides reasonably good conductivity. Aniline monomer can be polymerized on the fabrics from the aqueous solution,[3,7,10] or the vapor phase,[11] using appropriate oxidizing agents. Their conductivity depends on a deposition of conductive polymer on the surface or in the interstices of the fabric.[3,9] Thus, research on developing polymerization techniques that allows the production of an even and satisfactory deposition of polyaniline on fabrics should be continuously made to improve the quality of conductive fabrics.

The objective of this study is to develop the highly conductive clothing materials with improved performance and durability. Two methods of obtaining conductive fabrics by *in situ* polymerization of aniline were compared in terms of physical properties as well as their conductivity. In each case, polymerization conditions were optimized to obtain the maximum conductivity. In addition, the stability of the fabric conductivity was evaluated after exposing the prepared fabrics to light, abrasion, chemicals, and multiple washing.

EXPERIMENTAL

Materials

Scoured nylon 6 plain weave fabrics (70 × 70 d, 43 × 30/cm) obtained from KATRI (Korea) were washed with distilled water. Aniline (Shiny Pure Chemicals Co., Ltd.) was distilled under vacuum prior to use. Ammonium peroxydisulfate (Junsei Chemical Co., Ltd.) and hydrochloric acid (Duksan Pure Chemical Co., Ltd.) of the special reagent grade were used.

Fabric Treatment

Two laboratory procedures were used to produce electrically conductive fabrics as shown in Figure 1. Freshly distilled aniline and ammonium peroxydisulfate were separately dissolved in 0.35N HCl solution for diffusion and polymerization, respectively. In the DPSB process, the commonly used method,[7,10] the nylon 6 fabrics were im-
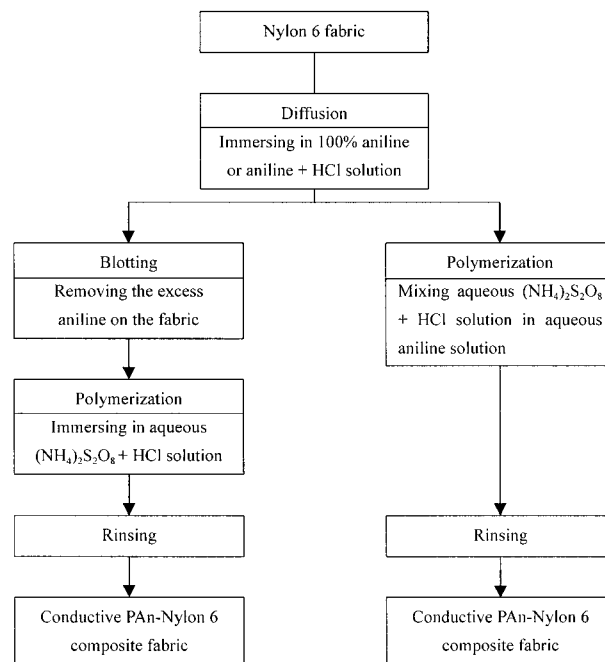
Figure 1 Schematic diagram of PAn–nylon 6 composite fabric preparation process.

mersed in 100% pure aniline or an aqueous hydrochloride solution of aniline at 40°C for a specified diffusion time and drawn out. After the excess solution on the fabric surface was blotted with filter paper, polymerization was then initiated by immersing it into the mixture of oxidant and dopant solution prepared in a separate bath. In the DPMB process, fabrics were immersed in an aqueous hydrochloride solution of aniline at 40°C for a specified time. Successive polymerization was then initiated by mixing the prepared oxidant and dopant solution in the diffusion bath in such a manner that the mixed solution contained various molar ratios of aniline/oxidant. Polymerization was carried out at 5°C for a specified time and fabrics were then vacuum dried.[12]

Evaluation

Sorption property of aniline was measured by the weighing method on the basis of the weight changes of the fabric before and after treatment. The conductivity of the composite fabric was measured by four straight lines and equidistant points, taking the thickness as that of the fabric.[13] Differential scanning calorimetry studies were performed on Du Pont DSC 2100V 4.1C system under nitrogen atmosphere with programmed heating of 10°C/min. X-ray diffraction

patterns were registered using a Rigaku RAD-C employing Cu-Kα radiation.

In addition, the serviceability of the conductive fabrics as a clothing material was also evaluated in terms of the conductivity stability against light (AATCC 164-1988), abrasion (AATCC 8-1988), washing (AATCC 16-1986), and multiple acid-alkali treatments.

RESULTS AND DISCUSSION

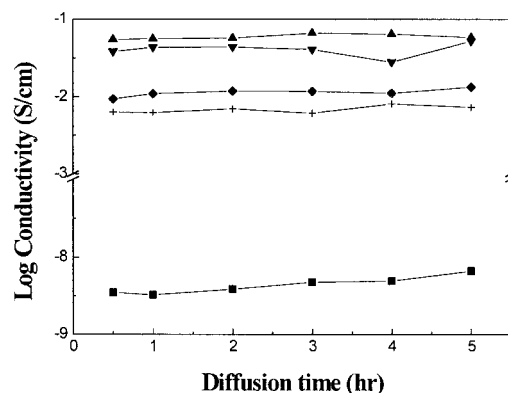### Effect of Polymerization Process

Diffusion

Effects of diffusion conditions on the variations of the fabric conductivity and percent add-on of polyaniline on nylon 6 fabrics were determined as a function of monomer concentration and diffusion time with both DPSB and DPMB processes.

With the DPSB process, the diffusion controlled system was found only when the fabric was immersed in 100% aniline. In this case, the fabric conductivity and polyaniline content on the fabric increased as the diffusion time increased, as shown in Figures 2(a) and 3(a). Similar results were observed in Im and Byun's studies,[10] in which nylon 6 film was used as substrate. However, the fabric conductivity and polyaniline content on the fabric did not change with diffusion time when diluted monomer solutions of low concentration were applied. It seemed that dissolved aniline in 0.35N HCl solution was hardly diffused into the nylon fiber.

With the DPMB process, on the other hand, the conductivity of the fabric treated with 100% aniline was the lowest. It is probably due to the phase separation of 100% aniline and aqueous oxidant solution, and gelation of concentrated aniline initiated by contacting with oxidant at the aniline/oxidant solution interface in the mixed bath. The phase-separated aniline of high viscosity could not be effectively deposited on the fabric even though 100% aniline was applied. With a diluted monomer solution, however, the fabric conductivity and polyaniline content on the treated fabric increased with increasing monomer concentration, as shown in Figures 2(b) and 3(b). This can be explained by the adsoption of polyaniline at the liquid/solid interface.[9] Aniline is soluble in HCl solution to some extent. This solubility drastically decreases for the oligomer, which causes precipitation of polymerizing species. Therefore when the polymerization is conducted
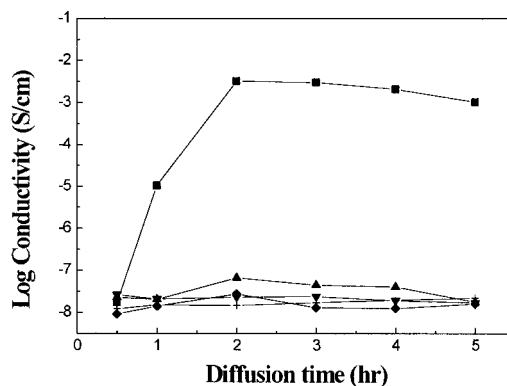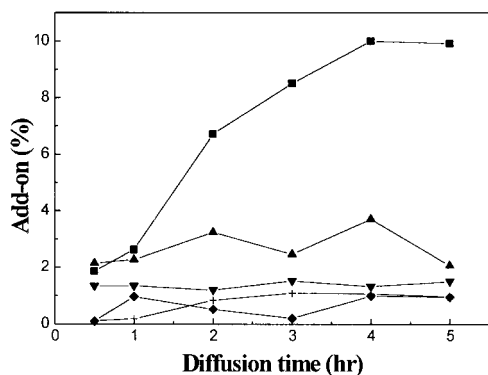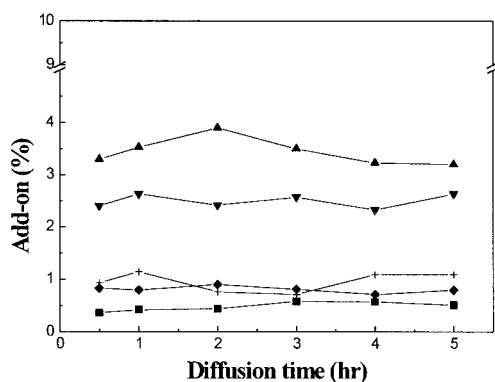

(a)

(b)

Figure 2   Effect of diffusion time on the conductivity of PAn–nylon 6 composite fabrics prepared by (a) the DPSB process and (b) the DPMB process. Diffusion temperature: 40°C; polymerization temperature/time: 5°C/1 h; oxidant concentration: (a) 0.25M, (b) molar ratio of aniline:oxidant = 1 : 1 (+, 0.1M aniline; ◆, 0.2M aniline; ▼, 0.33M aniline; ▲, 0.5M aniline; ■, 100% aniline).

in the presence of a high surface area structure such as fabrics, the entire polymerization occurs on the fabric surface. And thicker coating can be generally obtained with higher concentration, which results in higher conductivity.[9]

Overall, the fabric conductivity increased with an increase in the amount of polyaniline on the fabric in both processes. But higher fabric conductivity was obtained with a relatively small amount of polyaniline deposit with DPMB process as compared to DPSB process. This indicates that it was more difficult to form linear polyaniline of high molecular weight inside of the fiber, due to

(a)

(b)

Figure 3 Effect of diffusion time on the % add-on of PAn on nylon 6 fabrics prepared by (a) the DPSB process and (b) the DPMB process. Diffusion temperature: 40°C; polymerization temperature/time: 5°C/1h; oxidant concentration: (a) $0.25M$, (b) molar ratio of aniline:oxidant = 1 : 1 (+, $0.1M$ aniline; ♦, $0.2M$ aniline; ▼, $0.33M$ aniline; ▲, $0.5M$ aniline; ■, 100% aniline).
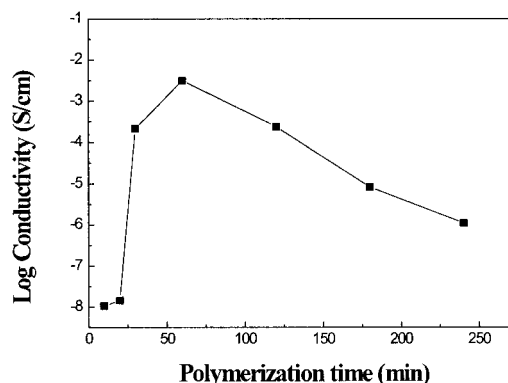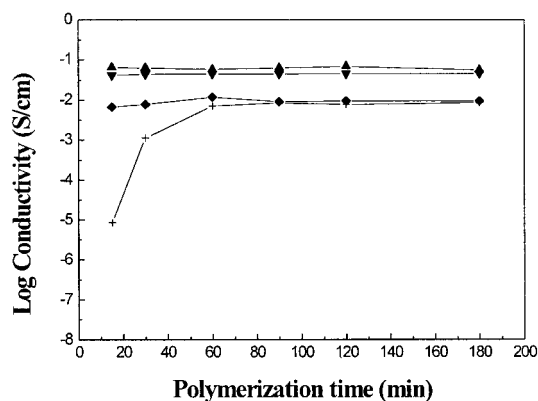
Polymerization

Effects of polymerization time and oxidant concentration on the fabric conductivity in two different polymerization processes were investigated and compared. Optimum diffusion temperature, time, and polymerization temperature were selected from the previous study.[12] For the DPSB process, nylon 6 fabrics were immersed in 100% pure aniline at 40°C for 3 h. For the DPMB process, fabrics were immersed in aqueous hydrochloride solution of aniline of various concentra-

tions (0.1–0.5M) at 40°C for 1 h. Then polymerization was carried out following the procedures described in Experimental.

As shown in Figure 4(a), the conductivity of PAn–nylon 6 composite fabrics increased with polymerization time and reached a maximum value at 60 min, then tended to decrease as the polymerization time increased with DPSB process. This is presumably due to the fact that de-doping and chemical oxidative decomposition of polyaniline tends to occur when the fabric is immersed in the oxidant solution for a prolonged time after
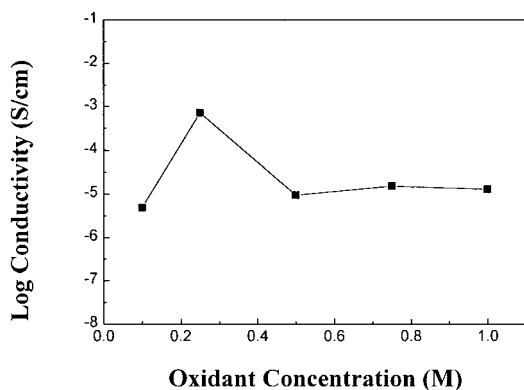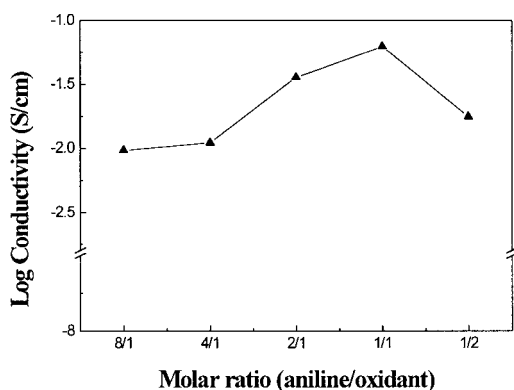

(a)

(b)

Figure 4 Effect of polymerization time on the conductivity of PAn–nylon 6 composite fabrics prepared by (a) the DPSB process and (b) the DPMB process. Diffusion temperature/time (a) 40°C/3 h and (b) 40°C/1 h; polymerization temperature: 5°C; oxidant concentration: (a) $0.25M$, (b) molar ratio of aniline:oxidant = 1 : 1 (+, $0.1M$ aniline; ♦, $0.2M$ aniline; ▼, $0.33M$ aniline; ▲, $0.5M$ aniline; ■, 100% aniline).

the structural hindrance of nylon matrix with DPSB process.

(a)

(b)

Figure 5 Effect of oxidant concentration on the conductivity of PAn–nylon 6 composite fabrics prepared by (a)100% aniline with the DPSB process and (b) the 0.5M aniline with the DPMB process. Diffusion temperature/time: (a) 40°C/3 h and (b) 40°C/1 h; polymerization temperature/time: (a) 5°C/1 h and (b)5°C/30 min.

polymerization is completed. On the other hand, no significant effect of polymerization time on the fabric conductivity without further depression was observed, except 0.1M with DPMB process as

shown in Figure 4(b). It seems that rapid polymerization occurred at the liquid/solid interface as soon as the oxidant solution was added to diffusion bath containing monomer solution, and unreacted monomers or polymers remaining in the bath also prevented chemical oxidative decomposition of polyaniline absorbed on the fiber surface.

In Figure 5(a), the conductivity of the PAn–nylon 6 composite fabric increased with $(NH_4)_2S_2O_8$ concentration and reached a maximum value at 0.25M, then tended to decrease with the DPSB process. Above 0.25M $(NH_4)_2S_2O_8$ concentrations, it seems that a polyaniline layer that retarded the diffusion of the oxidant solution was formed on the surface of nylon 6 fabric, since the polyaniline was polymerizing too rapidly.[10] For the DPMB process, the maximum fabric conductivity was achieved by immersing the fabric in 0.5M aqueous solution and mixing the prepared oxidant solution to the diffusion bath in which the mixed solution contained 1 : 1 molar ratio of aniline:oxidant. Fabric conductivity tended to decrease similar to that with DPSB process as shown in Figure 5(b).

Thermal and X-Ray Diffraction Analyses of PAn–Nylon 6 Composite Fabrics

Thermal properties of the PAn–nylon 6 composite fabric prepared by both the DPSB and DPMB processes along with control nylon 6 fabric were analyzed and compared in Table I. The heat of fusion and degree of crystallinity of PAn–nylon 6 fabric prepared by DPSB process were slightly reduced as compared to that of control nylon 6. The melting point of the composite fabric also tended to shift to a slightly lower temperature. But no significant changes in thermal properties were found with the composite fabric prepared by DPMB process. Overall results indicate that the crystal structures of nylon in the PAn–nylon 6 composite fabrics are not greatly affected by the presence of polyaniline in either the DPSB or DPMB processes. The X-ray diffraction pattern of the control nylon 6 fabric contained maxima at 2θ

Table I   Variation of Heat of Fusion, Melting Temperature, and Degree of Crystallinity of the PAn–Nylon 6 Composite Fabrics

Sample	Heat of Fusion ΔH_f (J/g)	Melting Temperature T_m (°C)	Crystallinity X_c (%)
Pristine nylon 6	67.8	213.6	26.7
DPSB	61.2	211.2	24.1
DPMB	67.6	214.3	26.6
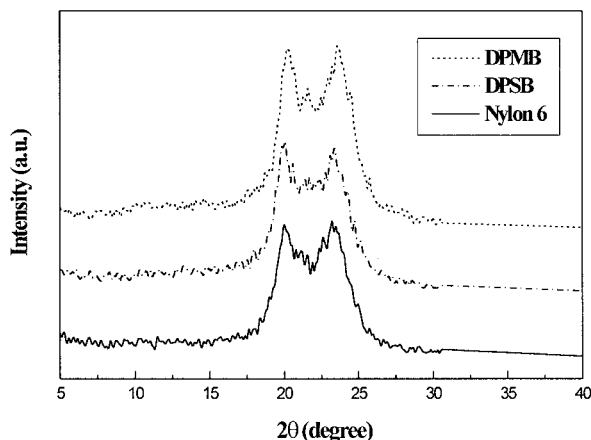
Figure 6 X-ray diffraction patterns of control nylon 6 fabric and PAn–nylon 6 composite fabrics prepared by the DPSB and DPMB processes. DPSB conditions: diffusion (40°C/3 h), polymerization (5°C/1 h), 100% aniline, 0.25M (NH$_4$)$_2$S$_2$O$_8$, 0.35N HCl: DPMB conditions: diffusion (40°C/1 h), polymerization (5°C/30 min), 0.5M aniline, 0.5M (NH$_4$)$_2$S$_2$O$_8$, 0.35N HCl.

values of 20.0° and 23.2°, which were reasonably close to the values assigned by previous researchers for the α_1 and α_2 peaks, respectively.[13] Peak maxima of PAn–nylon 6 composite fabrics located at 2θ = 20.1 and 23.4 (DPSB) and 20.3 and 23.6 (DPMB). The α_2 values were slightly shifted to higher values. It was supposed that ordered hydrogen bondings are formed between polyaniline and nylon 6.[14] Maximum of α_2 in the DPSB diffraction pattern was slightly decreased due to a slight decrement of percent crystallinity confirmed by DSC measurement as shown in Table I. (See Fig. 6.)

The effect of polymerization method on fiber morphology was further confirmed by observing the cross sectional view of fiber, as shown in Figure 7. Deeper penetration of polyaniline within the fiber was observed with PAn–nylon 6 composite fabric prepared by DPSB process, while a thin and continuous polyaniline layer on the fiber surface was found with that prepared by DPMB process.

The Stability of the Fabric Conductivity

The stability of the conductivity of PAn–nylon 6 composite fabric formed by two different polymerization processes against light, abrasion, washing and chemical treatments were investigated. Overall, we have found that the stability of the conductive polymers formed by two processes was similar.

PAn–nylon 6 composite fabrics were exposed to a Carbon-Arc lamp for 100 h by employing Fade-O-meter, and the variation of the fabric conductivity with light exposure time was measured as shown in Figure 8. The fabric conductivity decreased gradually as exposure time increased. Total reduction was less than 1 order after exposure to light for 100 h. The conductivity decay was presumably due to the dissociation of dopant by light and an elevated temperature in Fade-O-meter chamber.[16] Previous studies[2,16,17] have shown that thermal stability of polyaniline depended on the dopant used. We assume that proper selection of stable anionic dopants can improve the light fastness; thus we are now continuously studying on various dopants.

No significant changes in the conductivity were observed after abrading the composite fabrics
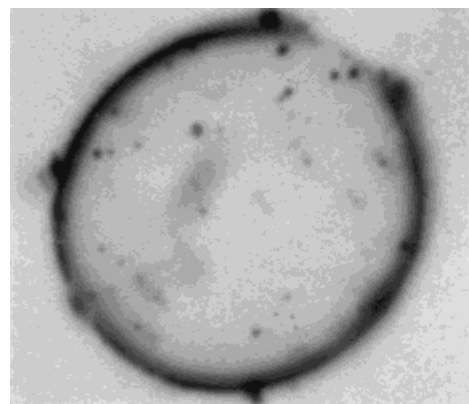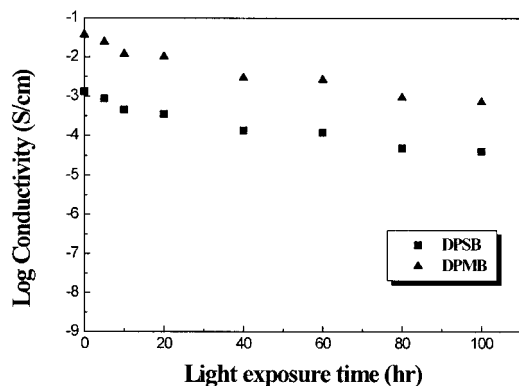

(a)
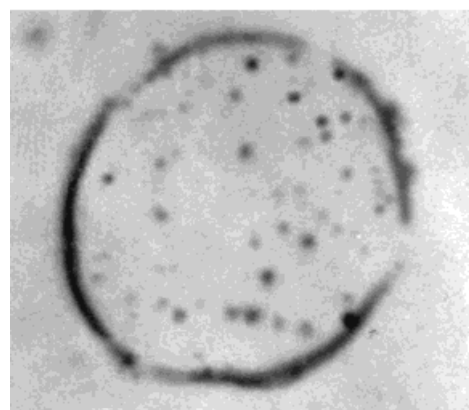
(b)

Figure 7 Cross section of nylon 6 fiber treated with PAn in (a) the DPSB process and (b) the DPMB process.
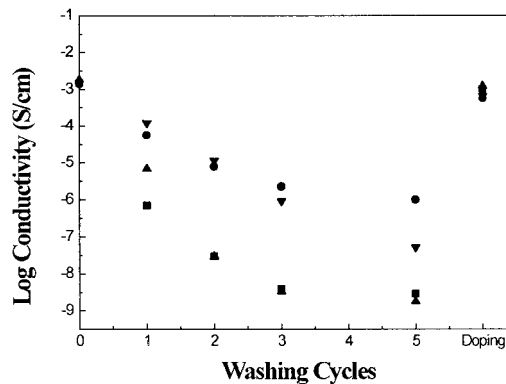
Figure 8 Variation of the conductivity of PAn–nylon 6 composite fabrics with light exposure time.

over 50 cycles as shown in Figure 9. It indicated that good adhesion of PAn layer on the nylon 6 substrate was formed.

Figure 10 shows typical results obtained under normal home laundry conditions with different types of water and detergents. Faster degrees of fabric conductivity degradation were observed when alkali detergent or tap water was used for washing medium rather than neutral detergent or distilled water. With alkali detergent and tap water, the fabric conductivity decreased significantly after first washing, and no fabric conductivity remained after washing three times. This shows results similar to that of Gregory et al.[8] Even though fast de-doping occurred with multiple washings, we proved that the fabric conductivity could be recovered to the value before washing by re-doping with $0.35N$ HCl for 3 h as shown in Figure 10. Therefore, we assumed that the degradation of conductivity by washing is mainly
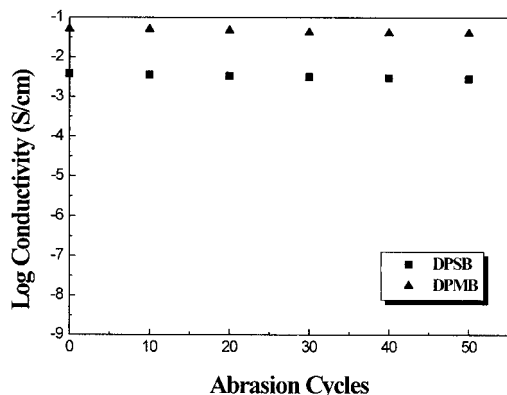
Figure 9 Variation of the conductivity of PAn–nylon 6 composite fabrics with abrasion cycles.


(a)
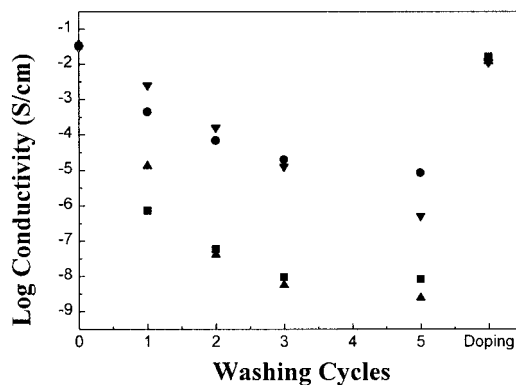
(b)

Figure 10 Variation of the conductivity of PAn–nylon 6 composite fabrics with washing cycles; (a) DPSB process and (b) DPMB process (■, alkali detergent; ●, neutral detergent; ▲, tap water; ▼, distilled water).

due to anion de-doping rather than removal of the polyaniline deposit on the fabric.

PAn–nylon 6 fabric was repeatedly immersed in $0.1M$ NH$_4$OH for 1 h and $0.35M$ HCl for 3 h to evaluate the stability of the fabric conductivity. These de-doping and re-doping treatments shift polyanilne to Emeraldine base form and to Emeraldine salt form in turns. As shown in Figure 11, we found that the conductivity stability of PAn–nylon 6 composite fabrics prepared in this study was quite stable against repeated acid-alkali treatments.

CONCLUSIONS

Highly conductive PAn–nylon 6 composite fabrics could be prepared by both the DPMB and DPSB
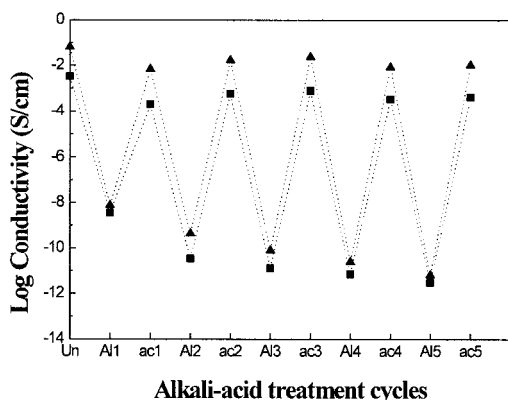
Figure 11 Variation of the conductivity of PAn–nylon 6 composite fabrics with alkali (Al) and acid (ac) treatments (■, DPSB; ▲, DPMB).

processes under the optimum polymerization conditions. For the DPSB process, the maximum conductivity was obtained by immersing the fabric in 100% aniline at 40°C for 3 h and polymerizing in 0.25M ammonium peroxydisulfate solution at 5°C for 1 h. For the DPMB process, the maximum conductivity was achieved by immersing the fabric in 0.5M aqueous solution of aniline hydrochloride at 40°C for 1 h. Polymerization was then followed by mixing the prepared oxidant solution into the diffusion bath in which the mixed solution contained 1:1:0.7 molar ratio of aniline : oxidant : HCl at 5°C for 30 min.

The higher conductivity of composite fabric, the value of which reached up to 0.6×10^{-1} s/cm was obtained by the DPMB process. And the least decrease in the degree of crystallinity was found in the composite fabric prepared by the DPMB process. However, the crystalline structures of PAn–nylon 6 composite fabrics prepared by both DPSB and DPMB were not significantly altered by inclusion of PAn.

No significant changes in the fabric conductivity were observed after abrading the composite fabrics over 50 cycles and multiple acid and alkali treatments. The stability of conductivity was slightly decreased by less than 1 order after exposure to light for 100 h. Even though the fabric conductivity was significantly decreased after washing, we found that the fabric conductivity could be recovered by acid re-doping with proper dopant.

REFERENCES

1. Chopra, K. L.; Major, S.; Pandya, D. K. Thin Solid Films 1983, 102, 1.
2. Wei, Y.; Hsueh, K. F. J Polym Sci Part A Polym Chem 1989, 27, 4351.
3. Gregory, R. V.; Kimbrell, W. C.; Kuhn, H. H. Synth Metals 1989, 28, C823.
4. Heisey, C. L.; Wightman, J. P.; Pittman, E. H.; Kuhn, H. H. Text Res J 1993, 63, 247.
5. Byun, S. W.; Im, S. S. Synth Metals 1993, 55, 3501.
6. Abraham, D.; Bharathi, A.; Subramanyam, S. V. Polymer 1996, 37, 5295.
7. Forveille, J. L.; Olmedo, L. Synth Metals 1994, 65, 5.
8. Gregory, R. V.; Kimbrell, W. C.; Kuhn, H. H. J Coated Fabrics 1991, 20, 167.
9. Kuhn, H. H. Text Chem Color 1997, 29, 17.
10. Byun, S. W.; Im, S. S. J Appl Poly Sci 1994, 51, 1221.
11. Park, Y. H.; Choi, S. H.; Miyata, S. J Appl Poly Sci 1992, 45, 843.
12. Oh, K. W.; Hong, K. H.; Kim, E. A. J Korean Soc Clothing Textiles 1999, 23, 326.
13. Muellerleile, J. T.; Freeman, J. J. J Appl Polym Sci 1994, 54, 135.
14. Murthy, N. S.; Curran, S. A.; Aharoni, S. M.; Minor, H. Macromolecules 1991, 24, 11. 15. Sze, S. M. VLSI Tech 1988, 300.
16. Byun, S. W.; Im, S. S. J Appl Poly Sci 1995, 56, 425.
17. Kulkatmi, V. G.; Campbell, L. D.; Mathew, W. R. Synth Metals 1989, 30, 321.