Effect of Dopant Mixture on the Conductivity and Thermal Stability of Polyaniline/Nomex Conductive Fabric

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ABSTRACT: Electrically conductive polyaniline (PANI)/[poly(m-phenylene isophthalamide)] Nomex composite fabric was prepared by *in situ* polymerization of aniline doped by a mixture of hydrochloride (HCl) and various sulfonic acids such as benzene-sulfonic acid (BSA), sulfosalicylic acid (SSA), and dodecylbenesulfonic acid (DBSA); their effect on conductivity and physical properties were then investigated. PANI/Nomex composite fabrics doped by a mixture of protonic acids exhibited higher conductivity than those doped by other single dopants such as camphorsulfonic acid (CSA), p-toluenesulfonic acid (TSA), BSA, SSA, and HCl. The conductivity of PANI/Nomex fabrics especially doped by a mixture of HCl and DBSA was evenly maintained up to 100°C without depression of mechanical properties of Nomex. Their conductivity was also maintained under extension of the composite fabric. In addition, electrical conductivity of PANI/Nomex fabrics was highly increased by ultrasonic treatment, which facilitated better diffusion and adsorption of aniline by cavitation and vibration. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2245–2254, 2002

Key words: conductive fabric; dopant mixture; Nomex; polyaniline; ultrasonic treatment

INTRODUCTION

The intrinsic conducting polymer (ICP) has gained importance with the discovery of doped polyacetylene (PA) in 1977. Its high conductivity approached the level of metals interested in many fields, such as electromagnetic compatibility, energy storage, and superconductorion.[1,2] However, the great instability of PA has drawn us to study other ICPs, such as polyaniline, polypyrrole, and polythiophene. Among the conducting polymers, polyaniline (PANI) was widely studied in the last decades because of its environmental stability, low cost of raw materials, and easy synthesis.[3–10] Also, the large range of conductivity versus doping level allowed the application of PANI to specific applications in light-emitting diodes, batteries, electromagnetic shielding, antistatic coating, gas sensors, and activators.

However, the industrial development of polyaniline is considerably hampered by infusibility, insolubility, and low mechanical strength. One of the ways to avoid these pitfalls is to prepare conductive composite fabrics by depositing the conductive polymer on a substrate. To this point,
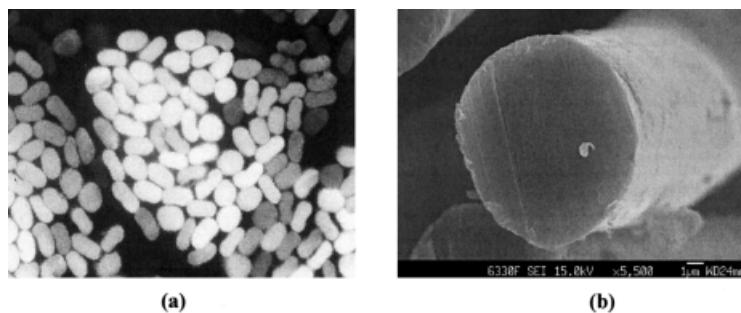
Figure 1   Cross-sectional views of PANI/Nomex composite fabrics. (a) Fabric, ×200; (b) single fiber, ×5500.

interest is growing in preparing an electrically conductive composite fabric using high modulus and strength fiber, such as aramid fiber, carbon fiber, polyarylate fiber, or ultrahigh molecular-weight polyethylene fiber.[11,12]

To prepare the conductive composite fabrics, many scientists have focused on *in situ* oxidative polymerization because this method does not require the destruction of the substrate and provides reasonably good conductivity.[13–16] Furthermore, *in situ* polymerization is expected to be one of the most convenient methods, because it is a relatively simple and easy method to control the conductivity by maintaining the high strength of the substrate fabric.[11,17,18]

The conductivity of composite fabrics depends on a deposition of conductive polymer on the surface or in the interstices of the fabric.[19–21] Research should be continuously concentrated on improving the quality of conductive fabrics on the basis of even and satisfactory deposition of conductive polymer on the fabrics.

Electrically conductive fabrics coated with polyaniline can be used for electro-magnetic wave interference shielding materials, antistatic agents, dust and germ-free clothes, and camouflage nets.[22,23] However, the application range of conductive fabric is notably limited, because the conductive fabrics have much lower conductivity and thermal stability than metals. To diversify the utilization of conductive fabrics, enhancement of conductivity and thermal stability is definitely needed.[22–24]

Conductivity and the thermal stability of the conductive fabric strongly depend on a substrate of fabric and dopant of polyaniline.[22–25] Therefore, choice of textile and dopant might be very important factors. In a recent study[26] of polyaniline doped with various protonic acids, it was found that hydrochloric acid (HCl) and sulfonic

acid were the best dopants in terms of conductivity and thermal stability. In addition, many researchers also reported that the dopant mixtures induced high conductivity and processability.[27,28]

In this article, PANI/poly(*m*-phenylene isophthalamide) (Nomex) fabric was prepared by *in situ* polymerization of aniline monomer on the highly thermostable Nomex. To improve the conductivity and the thermal stability of the PANI/Nomex composite fabric, we doped polyaniline composite fabrics with dopant mixtures such as HCl/sulfosalicyclic acid (SSA), HCl/benzenesulfonic acid (BSA), and HCl/*n*-dodecylbenzenesulfonic acid (DBSA) and then investigated conducting stability of the composite fabric at elevated temperatures. Also, with the use of ultrasonic treatment at the aniline diffusion step, diffusion and adsorption of aniline into fabric increased.

EXPERIMENTAL

Materials

Aniline (Shinyo Pure Chemical) was distilled under vacuum before use. Nomex fabrics manufactured by DuPont U.S.A. (60 × 60 in., plain weave), cordially supplied by DuPont Korea Co.,

Table I   Conductivity of PANI/Nomex Fabrics Doped with Various Dopants

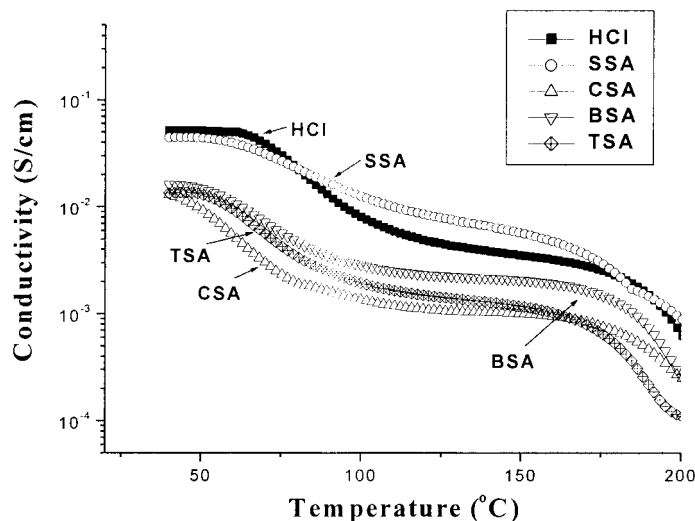| Dopant Used	M_W	Conductivity
Hydrochloric acid (HCl)	36.5	5.1×10^{-2} S/cm
Camphorsulfonic acid (CSA)	232.0	1.2×10^{-2} S/cm
Sulfosalicylic acid (SSA)	218.1	4.4×10^{-2} S/cm
Benzenesulfonic acid (BSA)	158.1	1.6×10^{-2} S/cm
p-Toluenesulfonic acid (TSA)	190.2	1.3×10^{-2} S/cm

Figure 2 Electrical conductivity change of PANI/Nomex fabrics with heating rate of 10°C/min.

were washed with distilled water and dried prior to use. Ammonium peroxydisulfate (APS; Junsei Chemical), HCl (Duksan Pure Chemical), BSA (Lancaster Synthesis), SSA (Kanto Chemical), *p*-toluenesulfonic acid (TSA; Yakuri Pure Chemicals), camphorsulfonic acid (CSA; Aldrich Chemical), and DBSA (Kanto Chemical) of special reagent grade were used without further purification.

Fabric Treatment

PANI/Nomex composite fabrics were doped by using either single dopant or mixed dopants. In the single-dopant process, freshly distilled aniline was dissolved in 0.5 mol/L acid solutions of HCl, SSA, CSA, BSA, and TSA for diffusion. Nomex fabrics were immersed in an aqueous dopant solution of aniline at 40°C for 1 h. Successive polymerization was then initiated by mixing the prepared oxidant (APS) and dopant solution in the diffusion bath. In the mixed solution, the molar ratio of aniline, dopant, and oxidant was 1 : 1 : 1, respectively. In the mixed dopants process, fabrics were immersed in an aqueous HCl solution of aniline at 40°C for 1 h. Polymerization was initiated by mixing the solution of APS and various
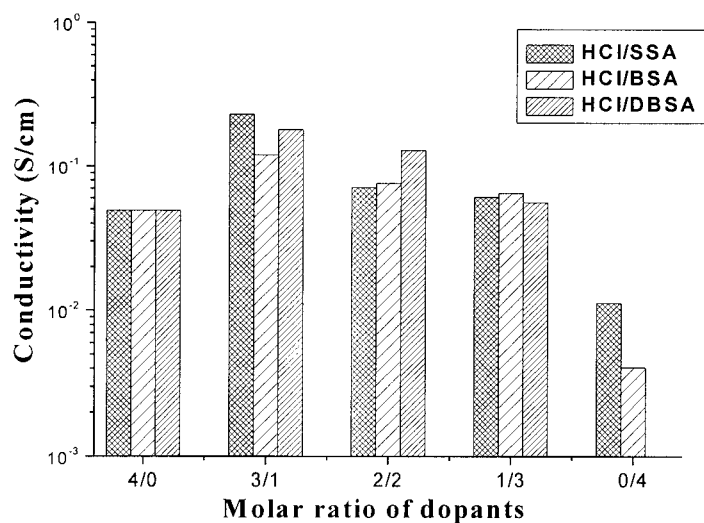

Figure 3 Effect of dopant molar ratio on the conductivity of PANI/Nomex fabrics.
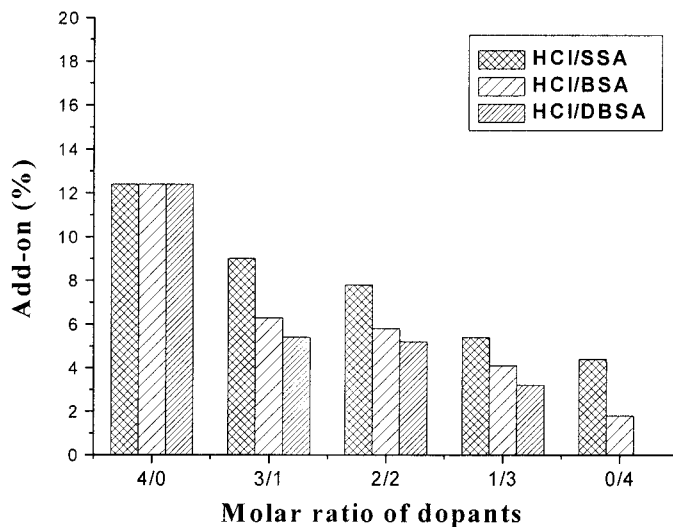
Figure 4   Effect of dopant molar ratio on add-on (%) of PANI/Nomex fabrics.

sulfonic acid dopants such as SSA, BSA, or DBSA. The molar ratio of mixed HCl and sulfonic acid in the bath was varied from 0.25 to 1. Polymerization was carried out at 5°C for 1 h. Composite fabrics were then dried after rinsing. During the aniline diffusion step, ultrasonic treatment was performed in a Bransonic 3510R-DTH ultrasonic cleaner at 42 KHz.

Characterization

The amount of polyaniline adsorbed into the fabric was measured by add-on (%) on the basis of the weight changes of the fabrics before and after polymerization. Thermal stability and conductivity of PANI/Nomex fabric were measured with a multimeter (Keithley 2000) on a Mettler hot stage FP82HT. A JOEL JSM-6340F field emission scanning electron microscope (FE SEM) was used for high-magnification observation. The FTIR studies were taken by attenuated total reflectance (ATR) method on a Nicolet Magna IR. Thermal gravitation analysis (TGA) studies were performed on DuPont TA Instruments SDI 2960 un-

Table II   FTIR Peaks of PANI/Nomex Composite Fabric

Dopant Used	C=C (cm^{-1})	C—N (cm^{-1})
HCl	1612	1311
HCl/SSA	1610	1307
HCl/BSA	1596	1307
HCl/DBSA	1594	1299

der argon atmosphere with a programmed heating rate of 20°C/min. Mechanical property studies were performed on Instron 4465 by raveled strip method (ASTM D 1682).

RESULTS AND DISCUSSION

Conductivity and Stability of PANI/Nomex by Single Dopant

Electrically conductive fabrics can be prepared by *in situ* polymerization with aniline monomer, oxidant, and dopant. When the polymerization of aniline is performed in the presence of fabrics with high surface area, the entire polymerization occurs on the surface of the fabric.[14,16,19–22] From our previous work,[20,21] it was found that immersing the fabric in an aqueous acid solution of aniline and initiating polymerization by mixing the prepared oxidant and dopant solution with dilute aniline solution could easily produce highly conductive fabric. When a small amount of oxidant and dopant solution was slowly dropped into the solution at the polymerization step, the slightly limpid white tone of the reaction solution changed to green, and finally, acquired a dark-green coloration. Also, the tone of fabrics slowly changed to about the same tint as polymerization solution.

PANI/Nomex fabrics were prepared by various single dopants such as HCl, BSA, SSA, CSA, or TSA, which were well known as effective dopants for polyaniline. The cross-sectional view of PANI/
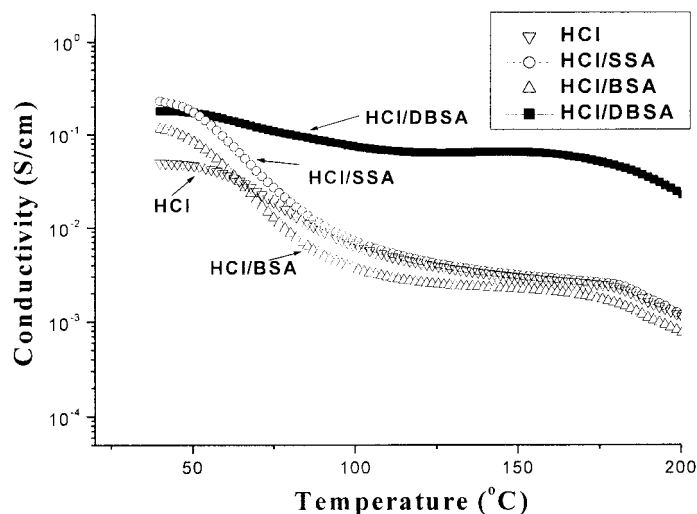
Figure 5 Electrical conductivity change of PANI/Nomex fabrics with heating (10°C/min, molar ratio of dopants 3/1).

Nomex is shown in Figure 1. It was observed that polyaniline spread on the surface of fibers in PANI/Nomex fabric [Fig. 1(a)]. After pulling out the single fiber from PANI/Nomex fabric, we observed a cross section of this single fiber by FE SEM. It was covered with a thin and coherent layer of polyaniline as shown in Figure 1(b). The image of cross section was very similar to the conducting fabric coated with polypyrrole.[14]

The conductivity of PANI/Nomex fabrics doped with these dopants is shown in Table I. The conductivity of all PANI/Nomex fabrics appeared to

be $\sim 10^{-2}$ S/cm at room temperature, HCl > SSA > BSA > TSA > CSA in decreasing order. It is known that the electrical conductivity was influenced by the size and shape of the counter ion due to the intervention of counter ion-separated hopping path of the interchain.[29] Therefore, if large molecular dopants were used, then the conductivity of polyaniline decreased. However, SSA dopant, a comparatively larger dopant, induced higher conductivity of the PANI/Nomex than BSA and TSA. It was suspected that SSA increased adhesion ability between fabric and
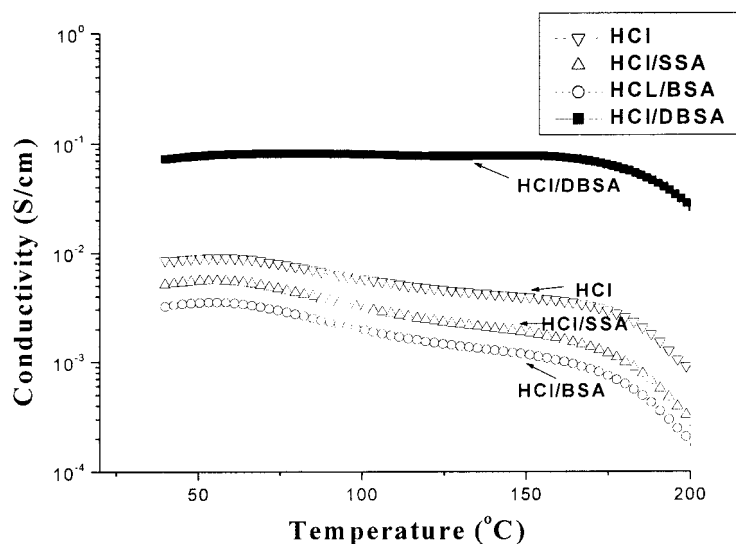

Figure 6 Electrical conductivity change of PANI/Nomex fabrics with heating after 5 min holding at 100°C (10°C/min, molar ratio of dopants 3/1).
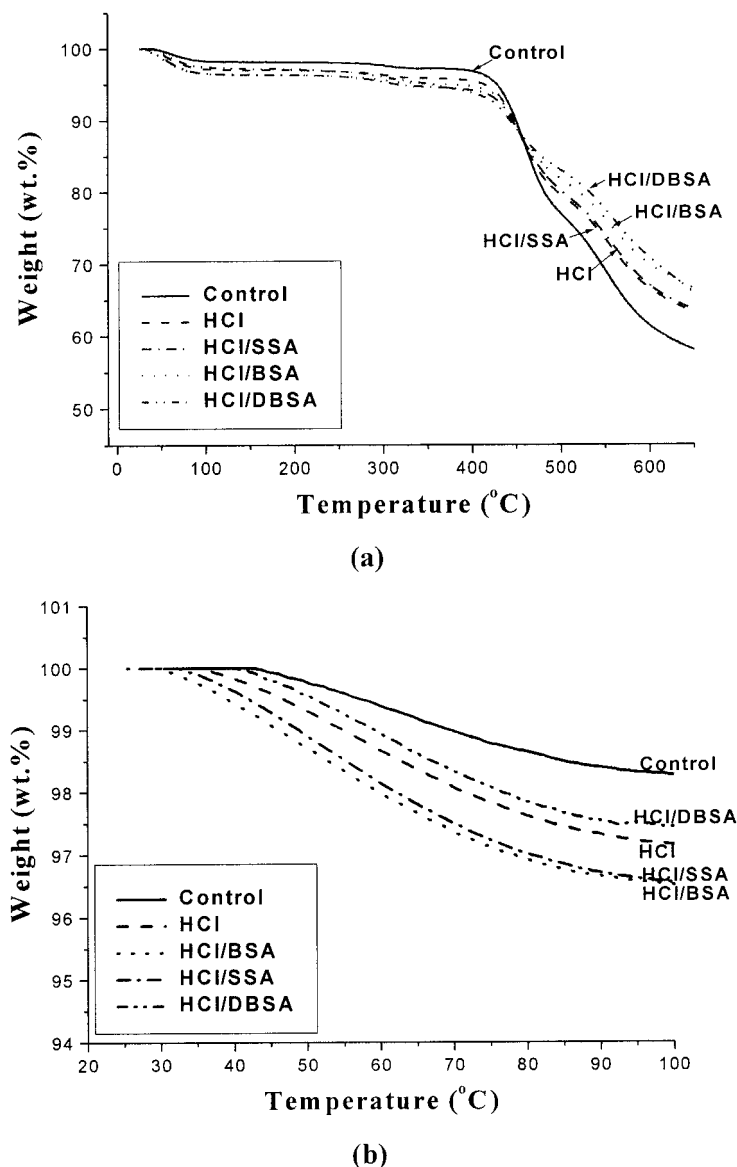
Figure 7 The TGA curves of PANI/Nomex fabrics doped with dopant mixture under air. (a) Full scale; (b) enlarged 20–100°C.

polyaniline by polar groups such as OH and COOH. Actually, the PANI/Nomex fabric doped with SSA showed the higher add-on than BSA or TSA (Fig. 4).

Changes in electric conductivity of PANI/Nomex composite fabric during heating is shown in Figure 2. The conductivity of PANI/Nomex fabrics decreased rapidly to nearly 10^{-3} S/cm with an increase in temperature to 100°C and their conductivity decreased at over 200°C, which was caused by a degradation of dopants and overoxidation of polyaniline.[30] As doped with HCl, decay of conductivity was greater than other dopants at

100°C, because the sulfonic-doped polyaniline had excellent stability.[10,31]

Improved Conductivity and Stability of PANI/Nomex by Dopant Mixture

To improve the conductivity and stability of PANI/Nomex fabric, we prepared PANI/Nomex fabrics doped with dopant mixtures and compared them with single dopants in terms of the conductivity and the stability. As a dopant mixture, HCl was mixed with the organic sulfonic acids with high-molecular
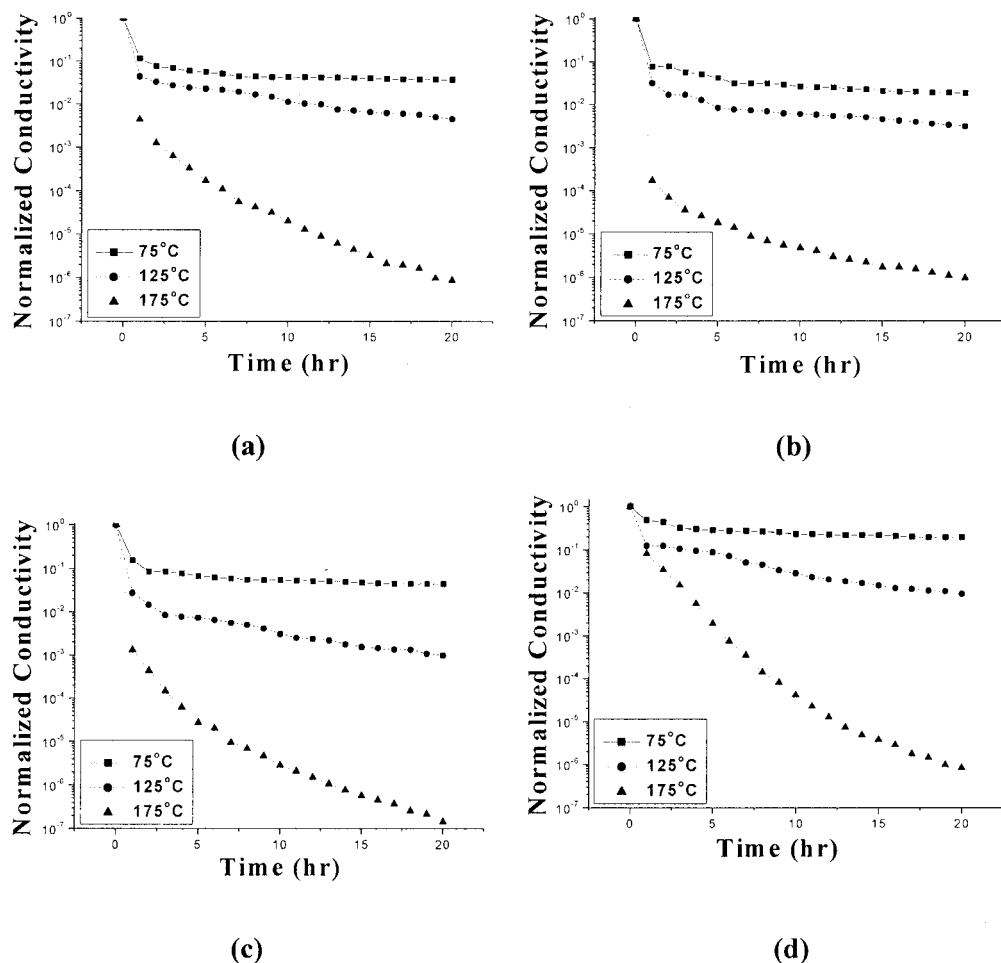
Figure 8 Electrical conductivity change versus time of thermal aging on the PANI/ Nomex fabrics at 75, 125, and 175°C. Molar ratio of dopants 3/1, (a) HCl; (b) HCl/SSA; (c) HCl/BSA; (d) HCl/DBSA.

weight such as SSA, BSA, and DBSA, because the dopants were stable up to 150°C (Fig. 2).

The effect of the molar ratio of dopants on the conductivity and add-on of PANI/Nomex fabrics doped with dopant mixture is shown in Figures 3 and 4. Add-on of polyaniline on Nomex fabric increased as the concentration of HCl in polymerization bath increased, because polyaniline doped with HCl had smaller size and higher yield on the fabric than that doped with other sulfonic acids. However, we found a synergetic effect on conductivity with mixed dopant. The conductivity of PANI/Nomex fabric was improved by using the dopant mixture as compared with single HCl dopant. In the mixed dopant system, the conductivity of PANI/Nomex fabric was improved as the molar ratio of HCl increased. It was attributed to the ideal conjugation length produced by mixing various dopants. Recently, Yin and Ruckenstein[32]

reported that polyaniline doped with dopant mixture exhibited higher conductivity than polyalanine doped with HCl dopant. The article presented the finding that the polyaniline doped with dopant mixture had the optimum conjugation length; thereby, polaron and bipolaron in the polyaniline were more delocalized.

Table II lists the main FTIR absorption peaks of the PANI/Nomex composite fabrics. The absorption peak of the C=C stretching appeared at 1612 cm^{-1} for the fabric doped with HCl and 1594 cm^{-1} for the fabric doped with HCl/DBSA, and the peak of the $C_{aromatic}$—N stretching vibration appeared at 1311 cm^{-1} for the fabric doped with HCl and 1299 cm^{-1} for the fabric doped with HCl/DBSA. The absorption peak of PANI/Nomex shifted to high wave numbers compared with peak of polyaniline powder (the C=C peak of polyaniline doped with HCl appeared at 1581

Table III   Mechanical Properties of PANI/Nomex Composite Fabrics

Dopant Used	Tensile Modulus (MPa)	Tensile Strength (MPa)	Strain (mm/mm)	Toughness (MPa)
Control	370	55	0.42	19
HCl	338	54	0.41	17
CSA	345	54	0.40	17
HCl/DBSA	346	54	0.41	17

cm^{-1}), because the aromatic ring of Nomex and polyaniline overlapped. However, the peaks of PANI/Nomex doped with dopant mixtures were regarded as peaks by quinoid ring of polyaniline, because the peak of aromatic ring in the Nomex was not transformed by aniline polymerization.

From the above results, it was confirmed that the fabric doped by HCl/DBSA was more protonated than the others. Moreover, it was suspected that long alkyl chains of DBSA hindered hydrogen bonding between Nomex and polyaniline, which helped keep the conductivity of polyaniline itself.

The thermal stability of PANI/Nomex fabric prepared by dopant mixture is shown in Figures 5 and 6. After heat drying under air (Fig. 6) for 5 min, the conductivity of all PANI/Nomex fabrics diminished significantly except for PANI/Nomex doped with HCl/DBSA in the temperature range between 50 and 150°C. The thermal stability of PANI/Nomex fabric doped with hydrophilic dopant might be influenced by moisture. It was confirmed by the fact that PANI/Nomex fabric doped with hydrophilic dopant (HCl, HCl/SSA, HCl/BSA) contained a larger amount of moisture in the composite as analyzed by TGA (Fig. 7). Therefore, the conductivity of PANI/Nomex doped with HCl/DBSA was steadily maintained to 150°C because of the hydrophobic nature of DBSA (Figs. 5 and 6).

Figure 8 represents the conducting stability versus time of thermal aging on the PANI/Nomex doped with dopant mixtures. The conductivity of PANI/Nomex fabrics was slightly decreased at 75 and 125°C. However, their conductivity rapidly decreased from initial time of measurement at 175°C. Among the PANI/Nomex fabrics doped with dopant mixture, PANI/Nomex fabric doped with HCl/DBSA showed the highest conductivity to 5 h. Thus, based on the combined results of Figs. 5, 6, and 8, the HCl/DBSA dopant mixture provided the high thermal conducting stability of polyaniline.

Mechanical Properties of PANI/Nomex Composite Fabrics

Table III lists the mechanical properties of the PANI/Nomex composite fabric and control Nomex fabric. Mechanical properties of the PANI/Nomex fabric had changed slightly in terms of tensile modulus, strength, and strain as compared with control Nomex.

It was suspected that oxidant agent and acidic dopants rarely penetrated into the inside of Nomex fiber in polymerization bath because Nomex fabric consisted of delicate structure (microfibrillar structure from liquid crystal wet spinning). Consequently, the high-performance conducting fabric can be obtained without a large deterioration in mechanical properties. This indicates that the *in situ* polymerization method is one of the ways for obtaining high modulus and strength conducting fabrics.

Figure 9 represents the change of electrical conductivity versus the applied strain of the conducting PANI/Nomex fabric. The breaking strain of PANI/Nomex did not nearly exceed 15%. The
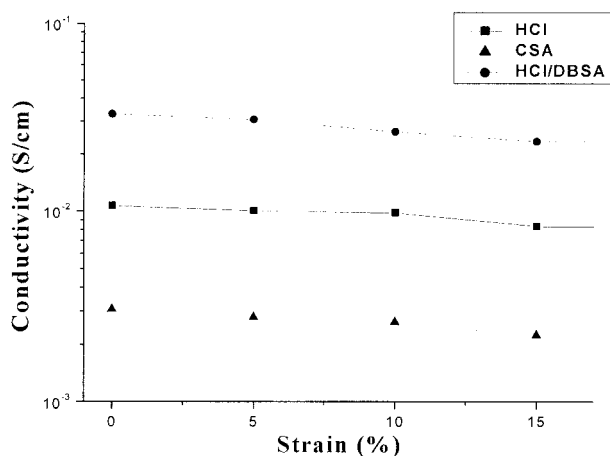

Figure 9   Electrical conductivity change versus strain of PANI/Nomex fabrics. Crosshead speed 10 mm/min.
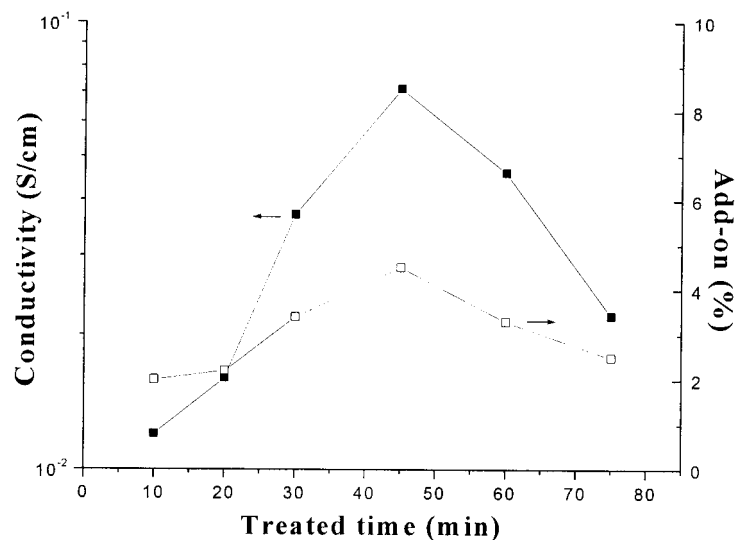
Figure 10 Electrical conductivity and add-on changes of PANI/Nomex fabrics with ultrasonic treatment, 40°C, 42 KHz.

conductivity of composite fabrics decreased slightly with increasing strain to breaking point. The slight reduction of conductivity occurred by a small separation of PANI layer on the fabric. On the removal of the applied strain, the conductivity of PANI/Nomex was not recovered.

Ultrasonic Treatment of PANI/Nomex Composite Fabrics

Because aniline monomers formed conductive polymers by the adsorption step at the interface of the fabric, diffusion of aniline into fabric was very important to improve conductivity on the *in situ* polymerization method. From this point of view, ultrasonic treatment was expected to be an effective method for diffusion of aniline.

Figure 10 showed the effect of ultrasonic treatment on the conductivity of PANI/Nomex. The conductivity of PANI/Nomex fabric was improved with increasing ultrasonic treatment time up to 45 min. Hereby, we confirmed that ultrasonic treatment provided better diffusion and adsorption of aniline by cavitation and vibration. However, excessive ultrasonic treatment over 45 min decreased the conductivity of PANI/Nomex.

CONCLUSIONS

In polymerization, the nature of dopant has a significant influence on the conductivity and ther-

mal stability of the PANI/Nomex fabric. Dopant mixtures introduced higher conductivity to the PANI/Nomex composite than a single dopant such as HCl, CSA, TSA, BSA, and SSA, because they could provide effective conjugation length and a high protonated level. In addition, the conductivity of PANI/Nomex fabric doped with hydrophilic dopant was significantly affected by moisture content under an atmosphere < 100°C. Therefore, PANI/Nomex doped with a mixture of HCl and hydrophobic dopant, DBSA, could improve electric conductivity and thermal stabilities. This indicates the possibility for the application of conducting PANI/Nomex composite fabric doped with hydrophobic dopant mixture under severe conditions.

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