

Synthesis of Highly Conducting Nylon-6 Composites and Their Electrical Properties

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SYNOPSIS

Highly conducting nylon-6 composites are synthesized by exposing nylon-6 films or fabrics impregnated with an oxidizing agent, cupric chloride, simultaneously to aniline and hydrochloric acid vapors. The conductivity of composite films reaches up to 10^{-2} S/cm and can be controlled by varying the experimental conditions for the composite synthesis. The effects of the concentration of cupric chloride, exposure time to aniline and hydrochloric acid vapors, and concentration of hydrochloric acid to the polyaniline content and the conductivity of nylon-6/polyaniline composites are analyzed by means of statistical *F* test. The morphology change of composite films resulting from the synthesis conditions, conductivity in relation to the morphology, and stability of conductivity to ambient air exposure have been investigated.

INTRODUCTION

Polyaniline (PAN) has attracted considerable interest as a conducting polymer. It has been reported as existing in various forms such as "aniline black," "emeraldine," "nigraniline," etc., synthesized by the oxidative chemical^{1,2} or electrochemical^{3,4} polymerization of aniline in aqueous acid solutions. PAN films are studied extensively for a variety of applications, including rechargeable batteries,³ electrode materials,⁵ and electrochromic display devices,⁶ but PAN is mechanically weak and electrically unstable in the atmospheric conditions. It is, therefore, of great interest to prepare composites of PAN so that mechanical properties and electrical stabilities are improved. Although one group,⁷ recently, has reported the preparation of polyblend fibers of PAN and poly-(*p*-phenylene terephthalamide) (PPTA) by codissolving PAN and PPTA in concentrated H₂SO₄ and blending them, the preparation of PAN composite by the conventional methods is largely limited because PAN degrades before melting and

only limited solubility in organic solvents like *N*-methylpyrrolidone and tetrahydrofuran had been reported.⁸ Accordingly, several workers^{9,10} have made PAN composite films with polyurethane⁹ or polystyrene sulfonic acid¹⁰ by electrochemical polymerization of aniline. The electrochemical approach of preparing conductive polymer composites has the advantage that the electrical properties of the composite can be changed simply by varying the electrolysis conditions, but it has the disadvantages that the area of the prepared composite films depends on that of electrodes and the appropriate matrix polymer-electrolyte solution system should be available for the penetration of ionic species (monomer and electrolyte) into the matrix polymer. Meanwhile, relatively little attention has been paid to the chemical polymerization of aniline in the vapor phase.

Thus, in this work, we have studied the new preparation technique of conducting nylon-6/PAN composites by simultaneous chemical oxidation of aniline vapor and protonation of PAN with a hydrochloric acid vapor. The effects of protonation and the morphologies on the conductivity for composite material are investigated.

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EXPERIMENTAL

Materials

The matrix polymer, nylon-6, with the relative viscosity of 2.60 at the concentration of 0.01 g/mL 96% sulphuric acid is obtained from Kolon as a form of chip. The nylon-6 chip has been washed several times with ethanol in the Soxhlet apparatus and dried before film preparation. White commercial nylon-6 fabric (thickness, 105 μm ; warp density, 114 ends/in; weft density, 76 ends/in; plain weave) has been washed several times with ethanol and distilled water in the Soxhlet apparatus and dried prior to use.

Aniline (Kokusai), cupric chloride (Junsei), formic acid (Yakuri), and hydrochloric acid (Junsei) of the special reagent grade have been used without further purification.

Preparation of Nylon-6/PAn Composites

The nylon-6 chip is dissolved in formic acid. The oxidizing agent, cupric chloride, dissolved in formic acid is added to the nylon-6 solution using a syringe. After thorough mixing with a magnetic stirrer, the nylon-6 solution containing cupric chloride is casted in the form of film. Formic acid contained in the film is evaporated under vacuum at room temperature for 48 h. The thickness of films is 20–30 μm . Nylon-6 films containing cupric chloride are suspended over aniline and HCl aqueous solution in a reactor and kept in a static vacuum of 160 torr at room temperature. The vapors of aniline and HCl diffuse into the matrix polymer film and the simultaneous oxidative polymerization of aniline and the protonation of PAn occur. Aniline salt has been, also, formed and deposited at the bottom of reactor. The composite fabrics are prepared by soaking nylon-6 fabrics in ethanol solution of cupric chloride followed by exposing to aniline and hydrochloric acid vapors as in the case of films. The content of PAn in the composite films or fabrics has been determined gravimetrically by weighing the samples prior and subsequent to exposure to the aniline vapor or aniline and HCl vapors.

Characterization of Composite Films

The IR spectra are obtained using a Digilab Division biorad FTS-20/80 spectrophotometer. The X-ray diffraction scans are taken using a Rigaku DMax IIIA wide-angle diffractometer with Ni-filtered

CuK α radiation. The electron micrographs are obtained using a Jeol JSM-35 CF scanning electron microscope.

Measurement of Electrical Properties

An electrical conductivity and a maximum electrostatic potential, V_{max} , and the time for the electrostatic potential to drop to 50% of its maximum value (the half-life time), $t_{1/2}$, are measured by using a four-probe technique and an Electrostatic Tester-7 (Kanebo), respectively. The details of experiments on measuring electrical properties have been described in our previous papers.^{11–13}

Measurement of the Temperature Dependence of Conductivity

The effect of temperature on conductivity was studied by attaching the film to a four-probe apparatus in a container immersed in a constant-temperature bath.

RESULTS AND DISCUSSION

As the polymerization of aniline and the protonation of PAn at and within the surfaces of nylon-6 films

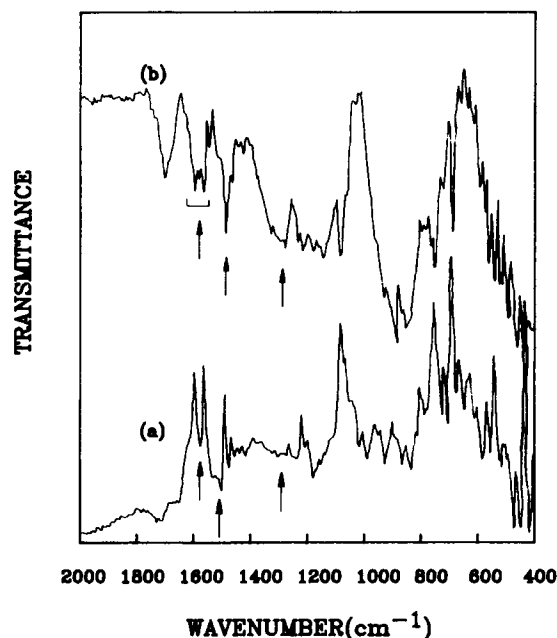
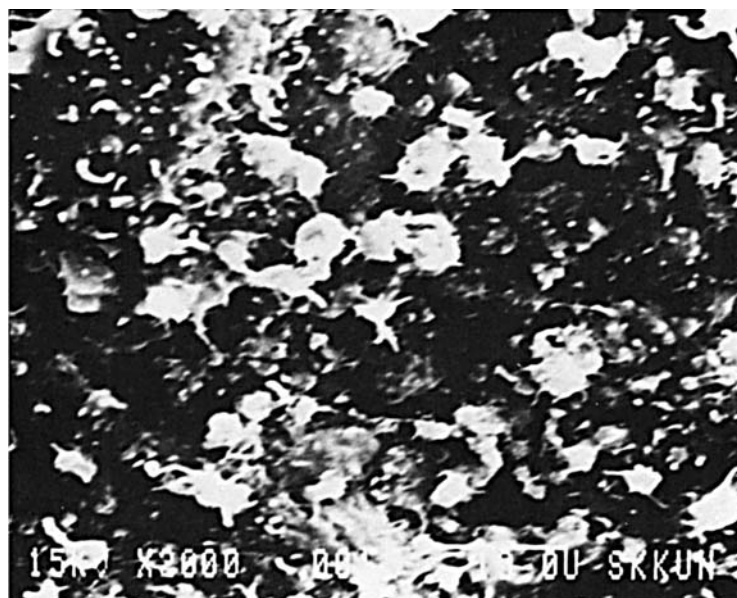


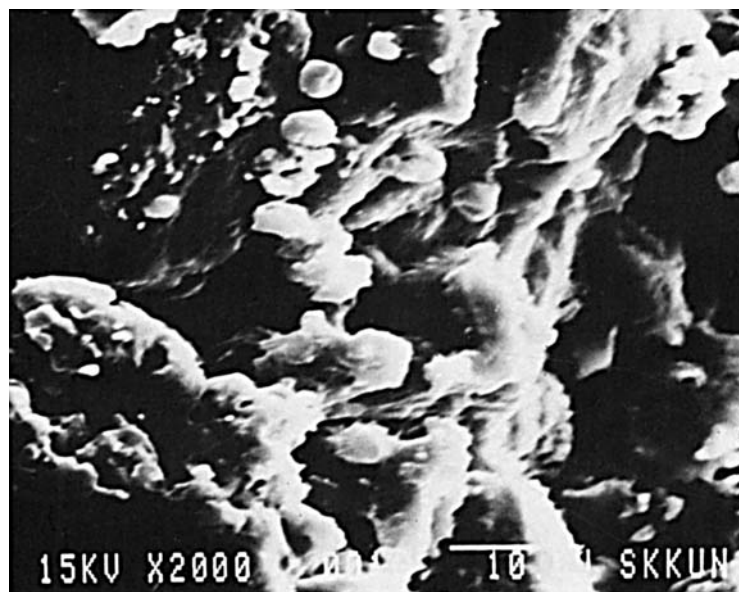
Figure 1 IR spectra of nylon-6/PAn composite films synthesized with (a) 23 wt % CuCl_2 and 3 h of exposure time to aniline vapor and (b) 23 wt % CuCl_2 and 3 h of exposure time to aniline and 0.5N HCl vapors.

proceed, they have turned gradually dark green. PAN has good adhering properties. To confirm spectrally the formation of PAN and the protonation of PAN in the matrix polymer films, the IR spectra are obtained both on the samples prepared by exposing nylon-6 films containing cupric chloride to aniline

vapor [Fig. 1(a)] and to aniline and hydrochloric acid vapors [Fig. 1(b)]. The IR spectra of composites indicate that the materials definitely contain PAN moieties, which are characterized by the peaks at near 1600 cm^{-1} ($\text{C}=\text{C}$ stretching in quinoid ring) and 1500 cm^{-1} ($\text{C}=\text{C}$ stretching in benzenoid ring).



(a)



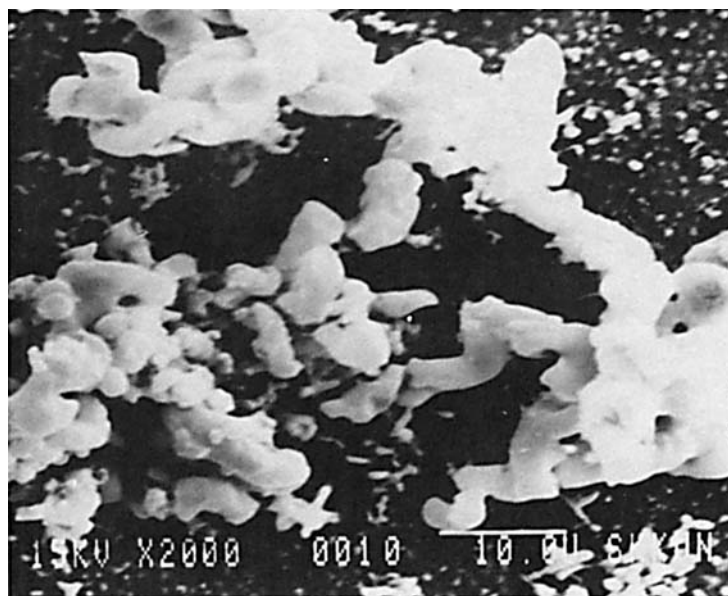
(b)

Figure 2 Scanning electron micrographs for the surface of nylon-6/PAN composite films synthesized with 23 wt % CuCl_2 and (a) 3 h and (b) 6 h of exposure time to aniline vapor.

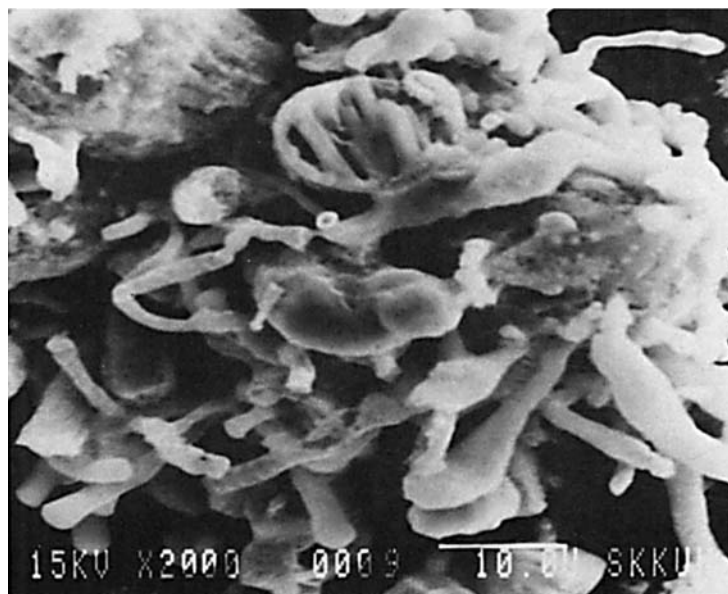
The absorption band observed at 1290 cm^{-1} in Figure 1 (b) is a halogen-sensitive band¹⁴ that confirms the salt formation between chlorine anions and protonated nitrogen atoms next to the quinoid rings. This IR absorption at 1290 cm^{-1} is consistent with the

higher conductivity of the protonated composite films than that of the unprotonated samples.

Examination of X-ray data clearly has indicated that the insertion of cupric chloride and the formation of PAn in nylon-6 induced disorder in nylon-



(a)



(b)

Figure 3 Scanning electron micrographs for the surface of nylon-6/PAn composite films synthesized with 23 wt % CuCl_2 and (a) 3 h and (b) 6 h of exposure time to aniline and 0.5N HCl vapors.

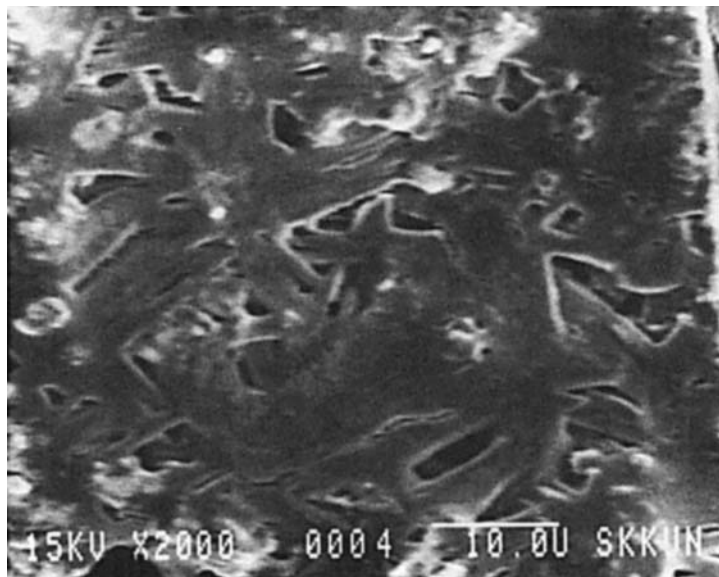


Figure 4 Scanning electron micrograph for the fracture surface of the sample used in Fig. 3(b).

6; however, PAn in the composite retained the crystallinity by showing sharp peaks at $2\theta = 7.8$ and 16.4° in the X-ray diffraction pattern.

To investigate the growth of the conducting polymer in the matrix polymer and the morphological features of the composites, especially in relation to their electrical properties, some electron micro-

graphs of nylon-6/PAn composite (Fig. 2) and protonated nylon-6/PAn composite films (Fig. 3) have been taken. From a comparison of Figures 2 and 3, it is evident that the continuous PAn fibrils are formed as a result of the simultaneous polymeriza-

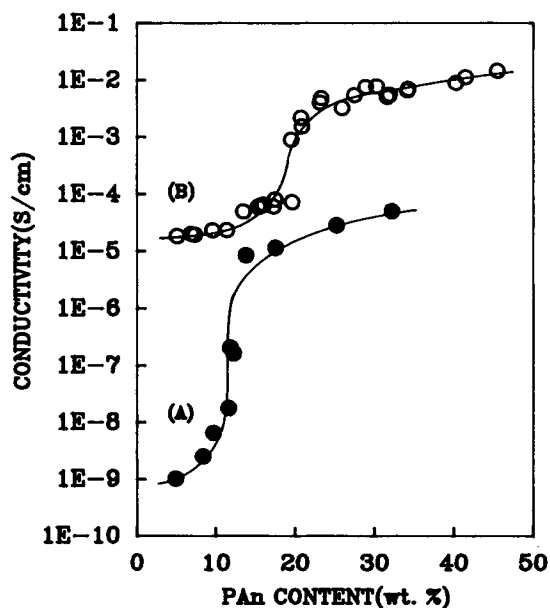


Figure 5 Conductivity v. PAn content for (a) unprotonated and (b) protonated nylon-6/PAn composite films.

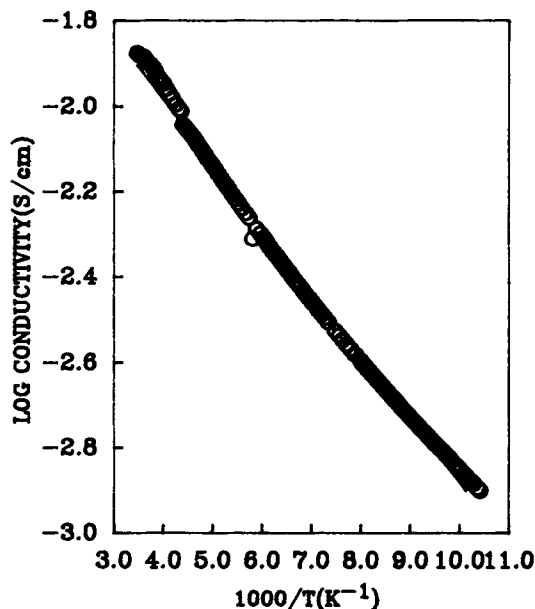


Figure 6 Log conductivity v. reciprocal temperature for nylon-6/PAn composite film synthesized with 33 wt % CuCl_2 and 6 h of exposure time to aniline and 0.5N HCl vapors.

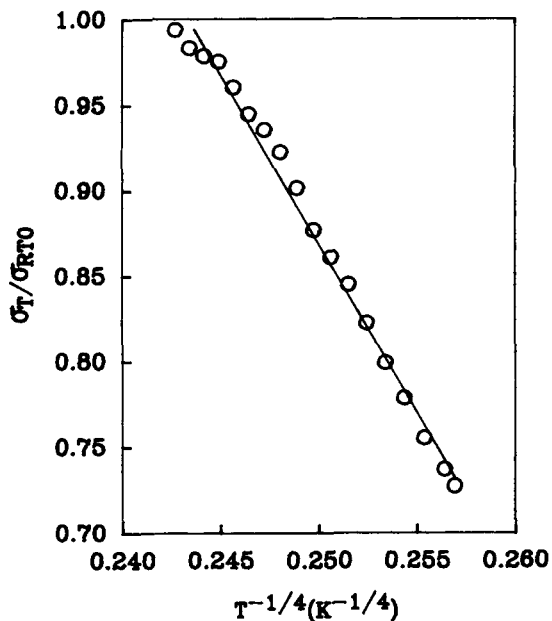


Figure 7 σ_T/σ_{RT} v. $T^{-1/4}$ for the sample used in Fig. 6.

tion of aniline and protonation of PAN in the composite, while the discontinuous PAN domains are formed as a result of the polymerization of aniline only in the composite. Figures 2 and 3 indicate that

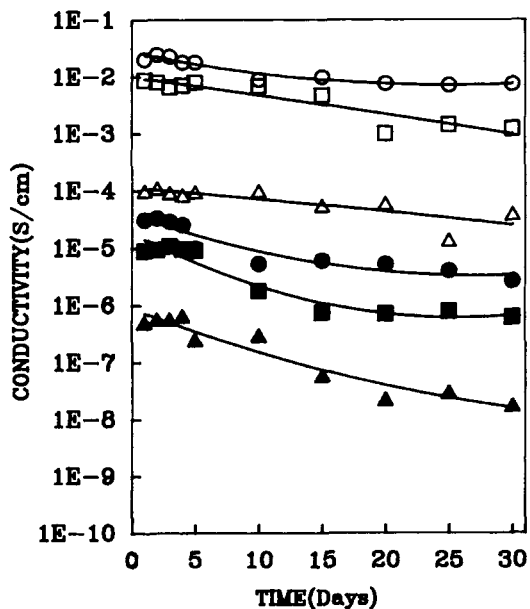


Figure 8 Conductivity v. exposure time to ambient air for nylon-6/PAN composite films synthesized with (○) 50, (□) 33, and (△) 23 wt % CuCl_2 and 0.5N HCl and (●) 50, (■) 33, and (▲) 23 wt % CuCl_2 without HCl (exposure time to aniline vapor or aniline and HCl vapors, 6 h).

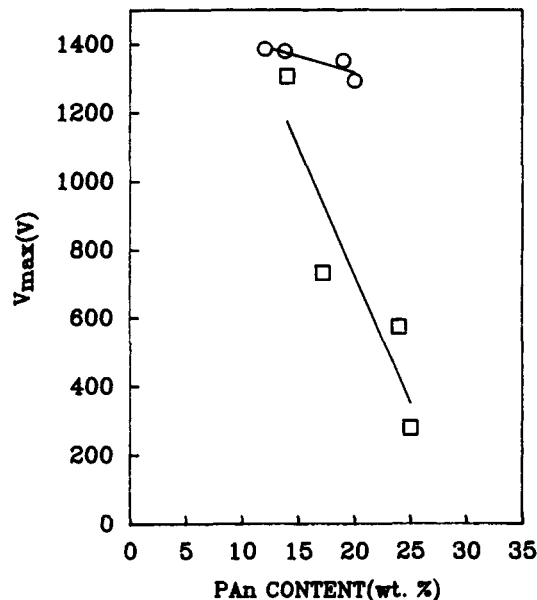


Figure 9 Maximum electrostatic potential v. PAN content for (○) unprotonated and (□) protonated nylon-6/PAN composite fabrics (exposure time to aniline vapor or aniline and HCl vapors, 4 h).

the discontinuous PAN domains or the continuous PAN fibrils grow to be more continuous as the exposure time to aniline vapor or to aniline and HCl vapors is longer. Figure 4 shows a scanning electron micrograph for the fracture surface of the sample used in Figure 3 (b). This figure indicates that the

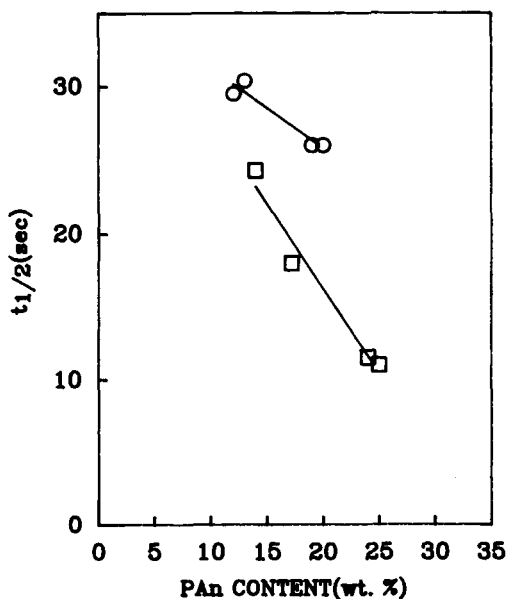


Figure 10 Half-life time v. PAN content for the samples used in Fig. 9.

continuous PAn fibrils are also formed within the surfaces of the composite.

The electrical behavior of mixtures of two components, each having a very different conductivity, is predicted by the "effective medium" model of Landauer¹⁵; the conductivity of the mixture undergoes a transition at critical concentration of con-

ducting component, called the percolation threshold. The conductivities of unprotonated nylon-6/PAn and protonated nylon-6/PAn composites are plotted as a function of the PAn content of the films in Figure 5. The unprotonated nylon-6/PAn composite (curve A) exhibits a threshold at around 12 wt % PAn content, but the protonated composite (curve

Table I PAn Content and Conductivity of Nylon-6/PAn Composites Synthesized under Various Conditions

Concentration of HCl (N)	Exposure Time (h)	Concentration of CuCl ₂ (wt %)	PAn Content (wt %)	Conductivity (S/cm)
0	2	23	4.90	1.02×10^{-9}
0	2	33	9.69	6.52×10^{-9}
0	2	50	11.62	1.79×10^{-8}
0	4	23	8.39	2.52×10^{-9}
0	4	33	11.82	2.08×10^{-7}
0	4	50	17.53	1.15×10^{-5}
0	6	23	12.22	1.64×10^{-7}
0	6	33	13.79	8.47×10^{-6}
0	6	50	25.21	2.85×10^{-5}
0.1	2	23	11.38	2.35×10^{-5}
0.1	2	33	17.45	8.03×10^{-5}
0.1	2	50	24.07	2.15×10^{-4}
0.1	4	23	13.45	4.99×10^{-5}
0.1	4	33	19.48	8.93×10^{-4}
0.1	4	50	25.90	3.21×10^{-3}
0.1	6	23	17.25	6.05×10^{-5}
0.1	6	33	20.84	1.53×10^{-3}
0.1	6	50	31.90	5.53×10^{-3}
0.5	2	23	15.31	5.99×10^{-5}
0.5	2	33	20.72	2.18×10^{-3}
0.5	2	50	31.58	5.08×10^{-3}
0.5	4	23	16.02	6.53×10^{-5}
0.5	4	33	23.27	4.83×10^{-3}
0.5	4	50	34.23	6.97×10^{-3}
0.5	6	23	21.21	7.85×10^{-5}
0.5	6	33	28.88	7.55×10^{-3}
0.5	6	50	41.49	1.12×10^{-2}
1.0	2	23	15.64	6.25×10^{-5}
1.0	2	33	23.12	4.02×10^{-3}
1.0	2	50	34.15	6.53×10^{-3}
1.0	4	23	19.60	7.21×10^{-5}
1.0	4	33	27.47	5.43×10^{-3}
1.0	4	50	40.26	8.91×10^{-3}
1.0	6	23	21.73	1.05×10^{-4}
1.0	6	33	30.26	7.72×10^{-3}
1.0	6	50	45.49	1.45×10^{-2}

B) at around 21 wt % PAn content. We are not quite certain why the protonation of the composite shifts the threshold to a higher content of PAn, but it is easily postulated that the differences of the dimensionality, arrangement, degree of dispersion, and other morphological details of PAn between two species of composite result in the threshold at different content of PAn. The conductivity differences between protonated and unprotonated composites are about four orders of magnitude below a threshold of curve A and about two orders of magnitude above a threshold of curve B, respectively. It is presumed that the conductivity difference between protonated and unprotonated composites results from the effects of protonation and morphology difference.

To analyze the effects of the experimental conditions on the PAn content and the conductivity of nylon-6/PAn composites, the experimental data are tabulated in Table I and the analysis of variance (ANOVA) performed on the PAn content and the conductivity from the data of Table I is shown in Tables II and III, respectively. From the results of F in Table II, the effects of the concentrations of HCl and CuCl_2 , interaction of them, exposure time, interaction of CuCl_2 concentration, and exposure time are significant at the 1% level to the PAn content, but the effect of interaction of HCl concentration and exposure time is not significant at the 1% level but significant at the 10% level. The effect of experimental factors to the PAn content lies in the order of CuCl_2 concentration, HCl concentration, exposure time, interaction of the concentrations of HCl and CuCl_2 , interaction of CuCl_2 concentration and exposure time, and interaction of HCl concentration and exposure time. From Table III, the effects of the concentrations of HCl and CuCl_2 , exposure time and interaction of HCl concentration, and exposure time to the conductivity are significant at the 1% level, but those of the interactions of the HCl and CuCl_2 concentrations and CuCl_2 concentration and exposure time to the conductivity are

significant at the 25% level. The effect of experimental factors on conductivity lies in the order of HCl concentration, CuCl_2 concentration, exposure time and interaction of HCl concentration, and exposure time. The results of F in Tables II and III strongly support that the effect of CuCl_2 concentration is most significant to the PAn content, whereas that of HCl concentration is most significant to the conductivity. The correlation coefficient between the PAn content and the conductivity is calculated to be 0.8968, which is significant at the 0.1% level.

Figure 6 shows the temperature dependence of the conductivity of protonated nylon-6/PAn composite film. The conductivity increases with increasing temperature over a range of 95–286 K. The activation energy from the slope of the straight line in Figure 6 was found to be 0.15 eV, which is higher than the value of 0.07 eV reported for PAn-tetracyanoethylene complex.¹⁶ An apparent linear fit is obtained when σ_T/σ_{RT} (σ_T and σ_{RT} are the conductivity at temperature T and room temperature, respectively) is plotted against $T^{-1/4}$ as shown in Figure 7. This behavior of the 1/4 power temperature dependence is interpreted in terms of Mott's model¹⁷ of variable range-hopping conduction.

The stability of protonated and unprotonated nylon-6/PAn composites upon exposure to air under ambient conditions is represented in Figure 8. The conductivities decrease less than one order of magnitude on exposure to ambient air for 30 d; the protonated composite samples especially retain very good stability. This is probably a result of the ability of nylon-6 to protect the composite materials from oxygen in air. It is noted that the protonated composite synthesized with 50 wt % CuCl_2 achieved a final ambient conductivity of 10^{-2} S/cm. The good stability of this composite material may be sufficient for applications that do not depend too strongly on a constant conductivity, such as antistatic devices and shielding equipments for electromagnetic interference. For the estimation of the electrostatic

Table II ANOVA Performed on PAn Content of Nylon-6/PAn Composites

Source of Variance	Sum of Square	df	Mean Square	F	Significance of F
HCl	1321.29	3	440.43	460.82	0.000
Exposure time	345.47	2	172.73	180.73	0.000
CuCl_2	1477.24	2	738.62	772.81	0.000
HCl \times exposure time	14.78	6	2.46	2.58	0.077
HCl \times CuCl_2	117.70	6	19.62	20.53	0.000
CuCl_2 \times exposure time	31.14	4	7.79	8.15	0.002
Error	11.47	12	0.96		
Total	3319.09	35	94.83		

Table III ANOVA Performed on the Log Conductivity of Nylon-6/PAn Composites

Source of Variance	Sum of Square	df	Mean Square	F	Significance of F
HCl	98.84	3	32.95	361.54	0.000
Exposure time	7.67	2	3.83	42.06	0.000
CuCl ₂	26.79	2	13.40	147.00	0.000
HCl × exposure time	6.59	6	1.10	12.06	0.000
HCl × CuCl ₂	1.03	6	0.17	1.89	0.164
CuCl ₂ × exposure time	0.87	4	0.22	2.38	0.110
Error	1.09	12	0.09		
Total	142.88	35	4.08		

propensities for unprotonated nylon-6/PAn and protonated nylon-6/PAn composite fabrics, V_{\max} and $t_{1/2}$ against the content of PAn have been plotted, as shown in Figures 9 and 10. V_{\max} and $t_{1/2}$ of the original nylon-6 fabric are 3700 V and 72 s, respectively. But, V_{\max} and $t_{1/2}$ drop rapidly as PAn is composited; in particular, the protonated nylon-6/PAn composite fabric with 25 wt % PAn has 280 V of V_{\max} and 11 s $t_{1/2}$. These results indicate that the protonation is very effective to endow nylon-6/PAn composite materials with the antistatic functions. According to the basis¹⁸ that V_{\max} lower than 2000 V is required for materials suited for avoiding electrostatic charges, this composite material is expected to be used for antistatic applications.

CONCLUSION

Highly conducting nylon-6 composite films or fabrics can be synthesized by exposing nylon-6 samples containing cupric chloride simultaneously to aniline and hydrochloric acid vapors.

The continuous PAn fibrils have been found in the protonated composite films. The conductivity of the protonated composite films reaches as high as 10^{-2} S/cm. The results of the maximum electrostatic potential and the half-life time have represented a good antistatic function of the protonated composite fabrics. It is presumed that the high conductivity of the protonated composites are due to the effects of the protonation of PAn and the morphology with the continuous PAn fibrils in the composites.

The stability of conductivity to ambient air exposure is very good; the conductivity decreases less than one order of magnitude on 1 month's exposure.

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