Preparation and Electrostatic Properties of Antistatic Acrylics

YUN HEUM PARK,* YONG KWEON KIM,† and SUNG WOO NAM

Department of Textile Engineering, College of Engineering, Sung Kyun Kwan University, Su Won 440-746, Korea

SYNOPSIS

Very good antistatic acrylic films or fabrics can be prepared by exposing the acrylic samples containing oxidizing agent to aniline vapor. The conductivity, the maximum static charge, and the half-life time are used for estimation of electrostatic properties. The effects of the content of polyaniline and the temperature and time of exposure to aniline vapor on the electrostatic properties have been investigated. The stability of conductivity to ambient air exposure and the temperature dependence of conductivity for antistatic acrylic films have also been investigated.

INTRODUCTION

The generation of static electricity on fibers leads to a variety of problems, both during manufacturing and during consumer use. For instance, soil pick-up due to static electricity is an annoying problem for the consumer, as is the clinging of garments to each other and to the body. Static electricity, generated on fabrics, can interfere with the operation of computers and other sensitive electronic instruments and can set off discharges of sufficient magnitude to ignite flammable vapors and dusts. Specific antistatic requirements also must be met by textiles to be used in operating rooms where flammable anesthetic gases are present. Schiff et al.[1] have pointed out other potential hazards, such as injury due to electric discharge to a conductor leading into the heart or major blood vessels of a patient, injury due to involuntary movement of surgical personnel receiving a static shock during a critical moment of surgery, and equipment failure due to discharge through sensitive components of electronic equipment.

The control of these static problems can be achieved by aftertreatment of textiles by antistatic

agents, by dispersing conductive carbon particles into synthetic fibers,[2-4] by depositing a metallic coating such as copper sulfide,[5] silver, copper, cobalt, gold, or nickel[6,7] onto the fiber surface, or by manufacturing the fibers from a metal such as stainless steel or aluminum.

In this article we present a study of the method used in obtaining antistatic acrylic films and fabrics by the formation of electrically conducting polyaniline within and at the surfaces of insulating acrylic materials.

The effects of the compositions of polyaniline and oxidizing agent and the polymerization conditions for aniline on the conductivity or the static charge, and the stability of the conductivity are investigated, as well as the characterization of antistatic acrylic materials.

EXPERIMENTAL

Materials and Chemicals

Commercial white acrylic fabric (thickness, 230 μm; warp density, 79 ends/in; weft density, 77 picks/in, plain weave), which is a copolymer (PAN) of acrylonitrile 92% and a minor constituent 8%, was washed several times with ethanol and distilled water in the Soxhlet apparatus and then was dried. All chemicals used in this work, such as aniline (Ko-

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kusan Chem.), ferric chloride (Sigma Chem.), cupric chloride (Junsei Chem.), and DMF (Junsei Chem.) were special reagent grade and were used without further purification.

Preparation of Antistatic PAN Films and Fabrics

For the preparation of antistatic PAN films, the washed and dried PAN fabric was dissolved in DMF (2% W/V) and a required amount of oxidizing agent (ferric chloride or cupric chloride) was added to the acrylic solution. The content of the oxidizing agent was based on the weight of PAN samples unless otherwise noted. After stirring this solution for 24 h with a magnetic stirrer, a few drops of the solution was poured on a glass plate and dried at room temperature for 24 h in vacuum. The films thus cast (thickness, $10 \sim 20$ μm) were exposed to aniline vapor in the reactor in a static vacuum of 60 torr at, unless otherwise noted, 25°C. The reactor has been shown in detail in previous articles.[8,9] For the preparation of antistatic PAN fabrics the washed and dried PAN fabric was soaked in methanol solution of the oxidizing agent for a required time and then dried in vacuum. This fabric was exposed to aniline vapor as in the case of the film.

Measurement of Electrostatic Properties

An electrical conductivity or a maximum electrostatic potential, Vmax, and the time for the electrostatic potential to drop to 50% of its maximum value (the half-life time), $t\frac{1}{2}$, was used as an indicator of electrostatic properties of sample films or fabrics. The measurement of electrical conductivity was made by the four probe technique as in our previous works.[8,9] A major advantage of using the electrical conductivity as the electrostatic property was that it was specific to the sample itself and was generally more reproducible than Vmax and $t\frac{1}{2}$. This was because the charge generation by rubbing, although more realistic, was dependent on many variables, such as the choice of the rubbing surface, speed, pressure, etc.

For the measurement of Vmax and $t\frac{1}{2}$, sample fabrics (7 cm × 7 cm) were charged by rubbing with a cotton fabric under the conditions of 20°C and 40% relative humidity using a Electrostatic Tester-7 (Kanebo, Japan). The fabrics were then allowed to discharge to the atmosphere. The rubbing speed of the Electrostatic Tester was 120 rpm and the rubbing pressure was 1.0 kg/m². The electrical conductivity was measured using the four-probe technique.

RESULTS AND DISCUSSION

During exposure of PAN samples containing an oxidizing agent to aniline vapor they turned gradually dark, due to the formation of electrically conducting polyaniline (PNE) at and within the surfaces of insulating PAN samples. In order to confirm spectrally the formation of PNE in PAN samples, IR spectra were obtained and are represented in Figures 1 and 2. The new bands at 3200 $\sim$ 3300 cm^{-1}, 1550 $\sim$ 1600 cm^{-1}, and 800 $\sim$ 900 cm^{-1}, marked by arrows in Figures 1 (C) and 2 (C), are attributed to the N–H stretching vibrations, N–H bending vibrations (overlapped with the stretching vibrations of aromatic C=C double bonds), and C–H out-of-plane bending vibrations. These results from the IR spectroscopy imply that PNE has been formed in PAN samples.

For the investigation of electrostatic properties of the antistatic PAN samples, the conductivities, as a function of the exposure time to aniline vapor, are measured for PAN films containing given contents of oxidizing agents. The conductivities are shown in Figure 3. The conductivities of PAN and PAN films containing 30 $\sim$ 100 wt % of ferric chloride or cupric chloride are $10^{-14} \sim 10^{-13}$ S/cm and
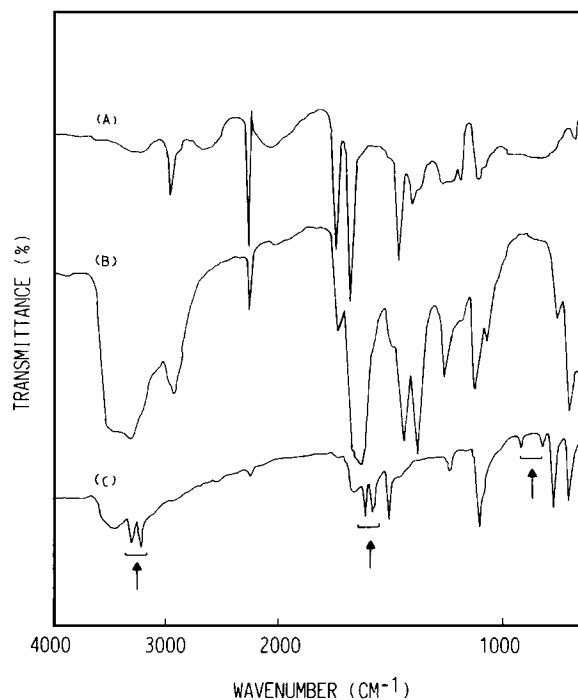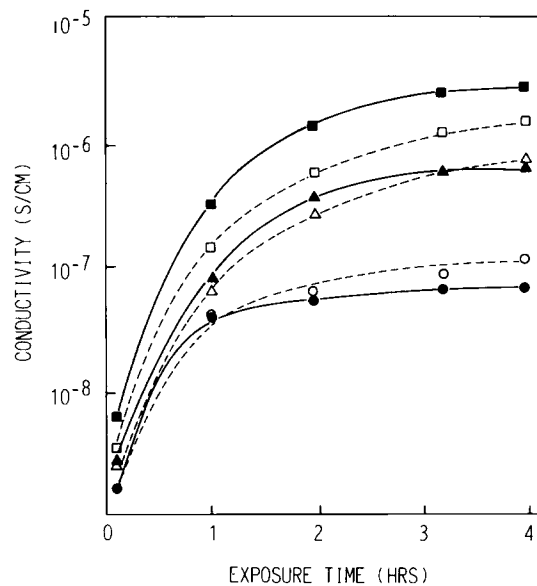

Figure 1 (A) IR spectra of PAN, (B) PAN containing 100 wt % of $CuCl_2$, and (C) antistatic PAN film prepared by exposing B to aniline vapor for 4 h.
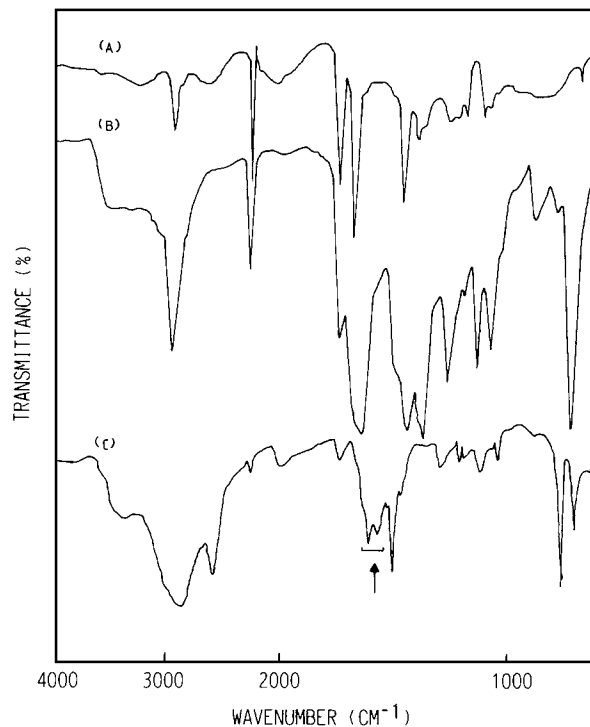
Figure 2 (A) IR spectra of PAN, (B) PAN containing 100 wt % of $FeCl_3$, and (C) antistatic PAN film prepared by exposing B to aniline vapor for 4 h.
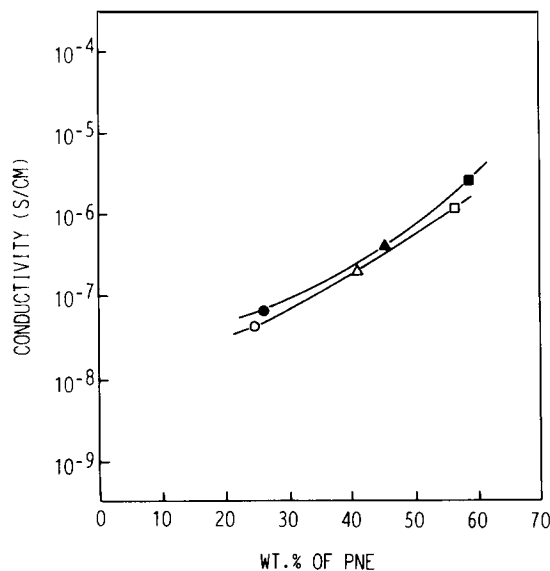

Figure 3 Conductivity vs. exposure time to aniline vapor for PAN films containing given contents of oxidizing agent; (○) 30, (△) 50, and (□) 100 wt % of $FeCl_3$; (●) 30, (▲) 50, and (■) 100 wt % of $CuCl_2$.

$10^{-11} \sim 10^{-10}$ S/cm, respectively. As shown in Figure 3, upon exposure to aniline vapor for 2 h the conductivities reach as high as $10^{-7} \sim 10^{-6}$ S/cm, depending upon the content of the oxidizing agent used. Generally, conductivities higher than 10^{-8} S/cm are required for materials which are suited for avoiding electrostatic charges. Such conductivity values can be reached easily with these antistatic PAN samples. It was also found that the effects of both ferric chloride and cupric chloride on the oxidative polymerization of aniline were almost the same; thus the conductivity values of the antistatic PAN samples prepared with corresponding content of each oxidizing agent were almost the same.

It can be inferred from Figure 3 that the higher the content of the oxidizing agent, the more PNE is formed in PAN samples and thus the higher the conductivity. In order to confirm this inference, the PAN films containing 30, 50, and 100 wt % of an oxidizing agent, respectively, are exposed to aniline vapor for a constant time of 4 h. The weight percent of formed PNE in PAN samples has been determined gravimetrically by weighing the PAN samples prior and subsequent to exposure to the aniline vapor and the conductivity is plotted as a function of PNE

content (Fig. 4). Aniline is oxidized to PNE in PAN samples by the oxidizing agent. The location of the oxidizing agent can be a site for the formation of conducting PNE. Therefore, the amount of PNE

Figure 4 Conductivity vs. wt % of PNE for antistatic PAN films prepared with PAN films containing (○) 30, (△) 50, and (□) 100 wt % of $FeCl_3$ and (●) 30, (▲) 50, and (■) 100 wt % of $CuCl_2$ (exposure time to aniline vapor, 4 h). Weight % on the weight of antistatic PAN films.
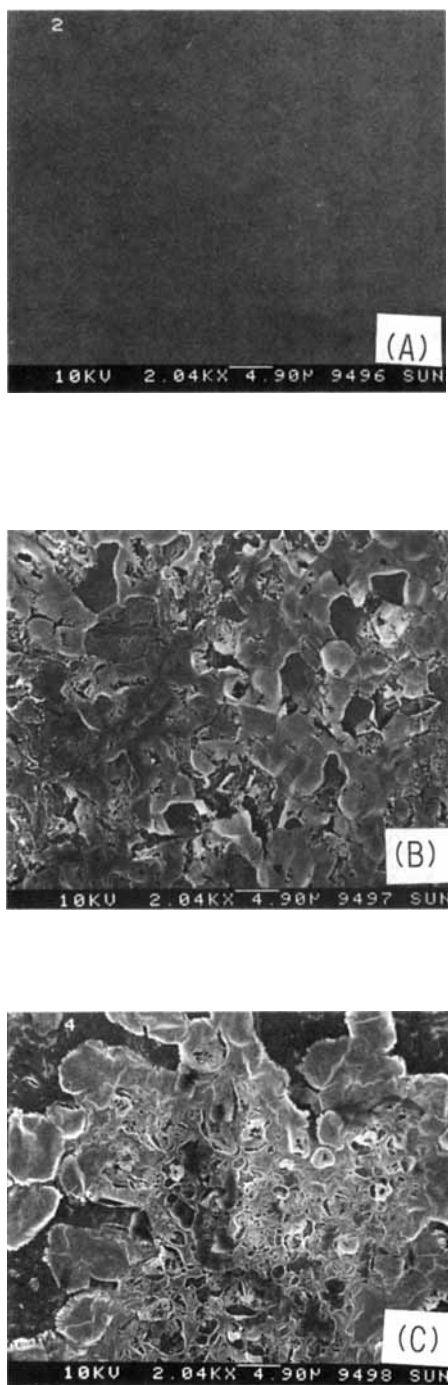
Figure 5 (A) Scanning electron micrographs of PAN film containing 50 wt % of FeCl₃, (B) antistatic PAN films prepared under the conditions of 30 wt % of FeCl₃ and exposure time 4 h, and (C) 50 wt % of FeCl₃ and exposure time, 4 h.

formed in PAN samples increases with the content of oxidizing agent. Greater numbers of conducting paths are formed by the higher amount of PNE and

result in higher conductivity. However, about 40% of the ultimate tensile strength and about 35% of the ultimate tensile elongation have been decreased by about 25% add-on of PNE in pure PAN sample. Figure 5 supports our explanation fairly well; as shown in Figure 5(A), PAN film containing only ferric chloride does not have any specific morphological features, while the antistatic PAN sample prepared with PAN film containing 50 wt % of ferric chloride (Fig. 5(C)) consists of more continuous PNE phases than that prepared with PAN film containing 30 wt % of ferric chloride. It is generally felt that, for maximum antistatic efficiency, the conductive polymer must be present as a continuous phase, preferably on the surface rather than in the bulk of the polymer, because it is often presumed that conduction occurs along the surface of the material.

For the estimation of electrostatic properties, Vmax and $t\frac{1}{2}$ have been measured and given in Table I. Rubbing or contact between two surfaces enables electrons to flow continuously in both directions across the interface. If the materials are electrically conductive, the electrons equalize themselves by backflow instantly when the bodies are separated. However, if the materials are insulators, the charge resulting from the change in electron distribution between two surfaces on their separation may survive for a measurable length of time. Vmax and $t\frac{1}{2}$ of the original PAN fabric are 13,680 V and 23.8 sec, respectively. But antistatic PAN fabrics have Vmax and $t\frac{1}{2}$, which are two orders and one order of magnitude smaller, respectively, than those of original PAN fabric. It is generally agreed that most static-electrical problems arising from the use of textile materials are reduced to manageable levels if Vmax is reduced to below 2000 V.[10] On this basis it can be said that our antistatic PAN samples possess high antistatic propensity.

Table I   Maximum Static Charges and Half-Life Times of Antistatic PAN Fabrics[a] Containing Various Wt Fractions of Polyaniline

| Wt %[b] of PNE	Vmax (V)	$t_{1/2}$ (sec)
0	13,680	23.8
22.5	55	3.4
25.1	48	3.0
27.4	40	2.8

[a] Samples are prepared by exposing PAN fabrics containing 2.3, 5.3, and 9.9 wt % of FeCl₃ to aniline vapor for 2 h, respectively.
[b] Wt % on the weight of antistatic PAN fabrics.
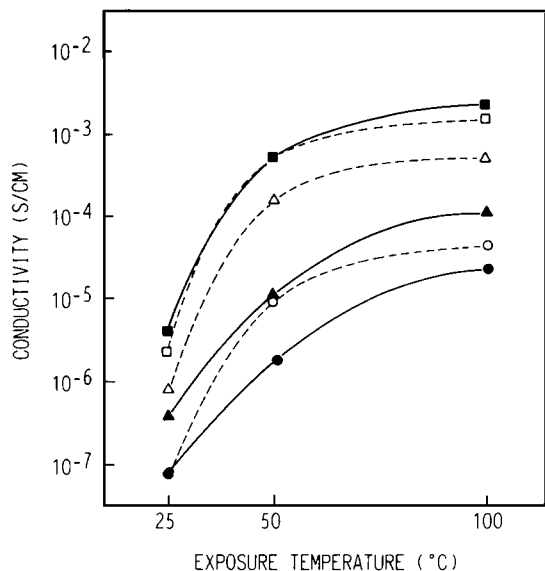
Figure 6 Conductivity vs. exposure temperature to aniline vapor for PAN films containing given contents of oxidizing agent; (O) 30, (△) 50, and (□) 100 wt % of $FeCl_3$; (●) 30, (▲) 50, and (■) 100 wt % of $CuCl_2$ (exposure time 4 h).

PAN molecules have strong intermolecular forces along the PAN chains due to the polar cyano groups. These forces tend to restrict the molecular motions in PAN samples and thus sorption and permeation of aniline vapor are restricted. However, at higher temperatures the structural segments can acquire sufficient thermal vibrations by which sorption and permeation of aniline vapor will increase. Based on this assumption, the conductivities of antistatic PAN films are measured as a function of the exposure temperature to aniline vapor; the results are represented in Figure 6. The conductivity increases with an increase of the exposure temperature to aniline vapor. The increases of sorption and permeation of aniline vapor into PAN samples by the increase of temperature will confer more chances of the oxidative polymerization of aniline by the role of oxidizing agent dispersed within and at the surfaces of PAN samples and thus will result in an increase in conductivity. For the antistatic PAN films prepared under the conditions used in Figure 6, scanning electron micrographs were taken, which are represented in Figures 7 and 8. The samples prepared at an exposure temperature of 25°C show significantly different morphologies, depending upon the type of oxidizing agent. However, as the exposure temperature increases to 50 and 100°C, the morphologies of each sample pair prepared at the same exposure temperature are closer to each other. Both
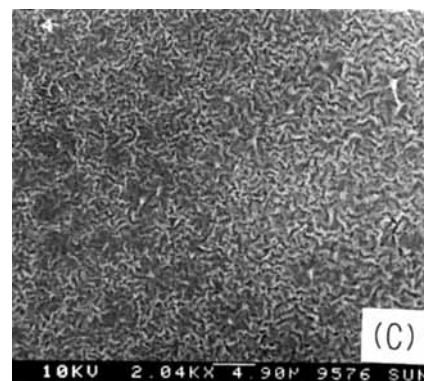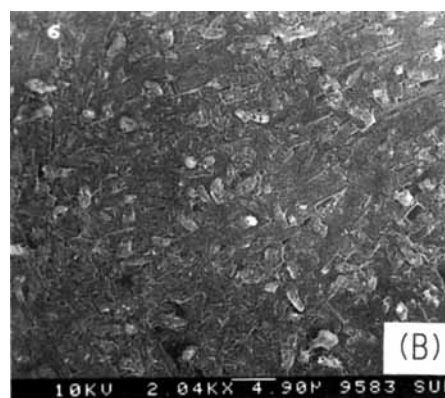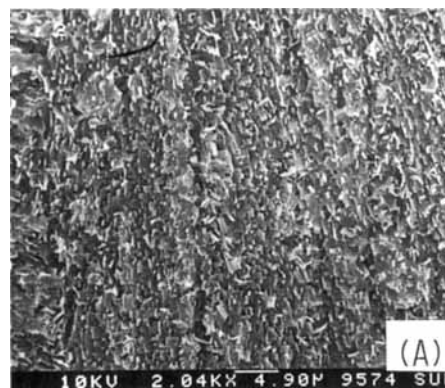
Figure 7 Scanning electron micrographs of antistatic PAN films prepared with PAN films containing 30 wt % of $CuCl_2$ at exposure temperature to aniline vapor (A) 25, (B) 50, and (C) 100°C.
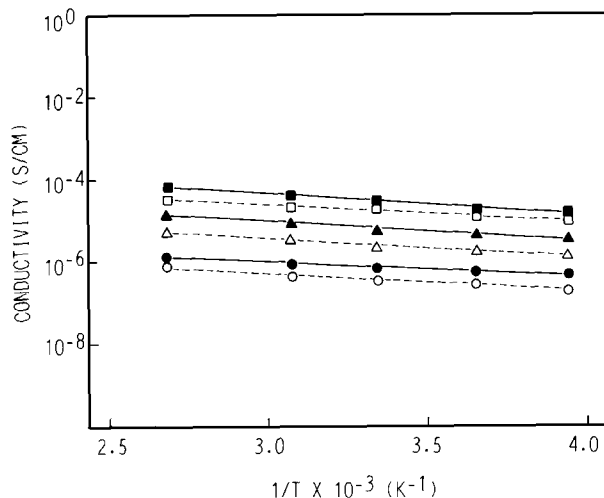
samples prepared at 100°C show uniform morphologies. It is postulated that these uniform morphologies also contribute to the higher conductivities by
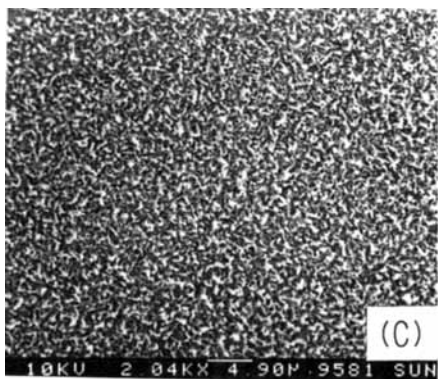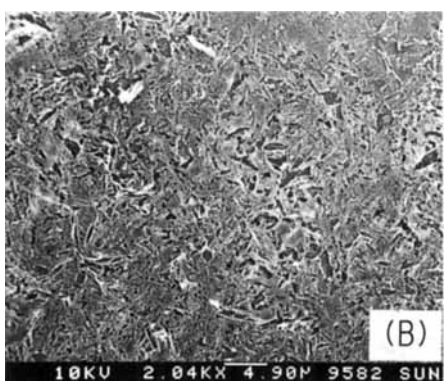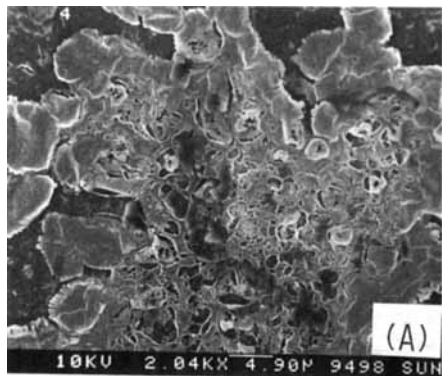
Figure 8 Scanning electron micrographs of antistatic PAN films prepared with PAN films containing 50 wt % of FeCl₃ at exposure temperature to aniline vapor (A) 25, (B) 50, and (C) 100°C.

Figure 9 Conductivity vs. reciprocal temperature for antistatic PAN films prepared under the conditions used in Figure 4.

antistatic PAN film and placing it in a container immersed in a constant temperature bath. Figure 9 shows that the conductivity change of antistatic PAN samples is insignificant in a temperature range of 253 ~ 375 K. The slight increase of conductivity with temperature may be attributed to an increase in the number of available charge carriers due to the input of thermal energy, even if the increase of
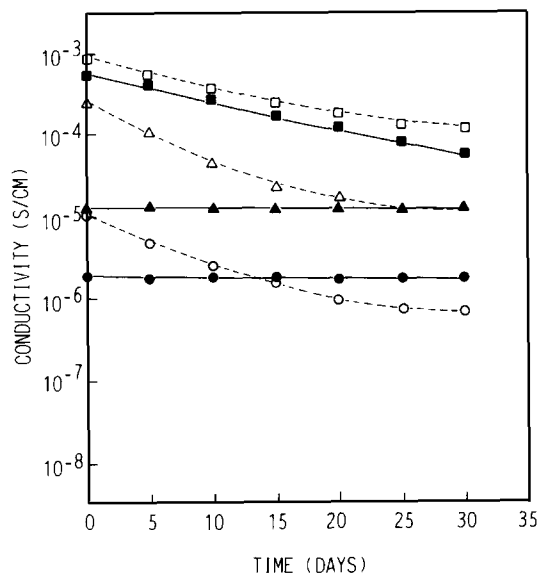
reducing the gaps between the conductive phases or by interconnecting the conductive phases.

The effect of temperature on conductivity has been investigated by sticking a four-probe into the

Figure 10 Conductivity vs. time upon ambient air exposure for antistatic PAN films prepared under the conditions used in Figure 4, except the exposure temperature to aniline vapor, 50°C.

conductivity is less than 1 order of magnitude regardless of the kind and the content of the oxidizing agent contained in antistatic PAN samples.

The stability of antistatic PAN films upon exposure to ambient air is investigated and the results are shown in Figure 10. The stability is good; the conductivity decreases less than 1 order of magnitude on exposure to ambient air for 30 days. This is especially true for the antistatic PAN samples prepared with PAN films containing 30 and 50 wt % of $CuCl_2$, which maintain a constant conductivity for one month. Thus, our antistatic PAN samples may be sufficient for antistatic applications.

The X-ray diffraction scans for antistatic PAN films were taken using a Rigaku DMax IIIA wide angle diffractometer with Ni-filtered CuK_α radiation. The scans showed the absence of any reflections.

CONCLUSION

The oxidative polymerization of aniline vapor within and at the surfaces of PAN films or fabrics creates the possibility of preparing antistatic PAN materials. The higher the content of PNE in antistatic PAN samples, the better the antistatic properties. The content of PNE can be controlled by varying the exposure time to aniline vapor under a given content of oxidizing agent, or vice versa. The morphologies consisting of uniform and continuous PNE phases in antistatic PAN samples represent higher conductivities. The exposure temperature to aniline vapor and the content of oxidizing agent have some influence on the morphologies. The stability of conductivity to ambient air exposure is good; the conductivity decreases less than 1 order of magnitude after one month's exposure.

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