

Preparation of Transparent Conducting Acrylic Composite and Its Electrical Properties

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Synopsis

Polyacrylonitrile (PAN)/polythiophene (PTP) composite films were prepared by polymerizing thiophene vapor in PAN films impregnated with sulfuric acid or aluminum chloride as an initiator. After polymerization of thiophene for 1 h, the electrical conductivities of composites reach in the range of 10^{-7} – 10^{-3} S/cm depending on the initiator and its concentration. The stability of conductivity to ambient air exposure is excellent. The transparency of composite films has been estimated by transmittance at the maximum absorption wavelength of 593 nm. The transmittance of composite film prepared with 10% of sulfuric acid on the weight of PAN reaches above 90%. The transparency has been maintained for the period of experiment, i.e., 1 month under ambient air exposure. Sulfuric acid is more effective than aluminum chloride for the preparation of transparent conducting PAN/PTP composite films.

INTRODUCTION

Electrically conducting organic polymers have excited considerable interest since many applications can be envisioned for electroactive materials, but technical applications of the conducting polymers,^{1–3} such as polyacetylene, polypyrrole, polythiophene, etc., have been hampered by at least one undesirable characteristic such as environmental instability, unprocessability, and poor physical properties. In order to circumvent these problems the synthesis of copolymers^{4–7} and composites^{8–16} is traditionally applied. The alternative method for overcoming the unprocessability includes derivatization of the intractable conducting polymers, such as the synthesis of alkyl derivatives of polythiophenes.^{17–21}

Although composites could be prepared by simply dispersing conducting polymer particle in a polymer matrix, the composite formation of polythiophene with nonconducting polymer is very difficult because of the unprocessability of polythiophene.

In this work we have attempted to synthesize composites by polymerizing thiophene vapor in initiator-impregnated polyacrylonitrile copolymer films. The composite films prepared by this method may possess intimate mixing at the molecular level. Galvin et al.¹¹ prepared a composite of polyacetylene and polyethylene film by using this technique. Our composite films possessed excellent transparency as the PAN film did. Thus it may be widely applied as fiber and plastic materials because it can be dyed or pigmented to any desired color.

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EXPERIMENTAL

Materials

Polyacrylonitrile copolymer (PAN), which constitutes 87.9 wt % of acrylonitrile and 12.1 wt % of vinylchloride, was obtained as a form of tow. Thiophene (Sigma Chem. Co.), sulfuric acid (95%, Junsei Chem. Co.), aluminum chloride (Hayashi Pure Chem. Co.), and DMF (Junsei Chem. Co.) were used directly without purification.

Preparation of PAN/Polythiophene (PTP) Composite Films

Two grams of PAN was dissolved in 14 mL of DMF in a flask. PAN was washed several times with ethanol and distilled water in the Soxhlet apparatus and dried before dissolving in DMF. The initiator (sulfuric acid or aluminum chloride dissolved in DMF) was added to PAN solution by means of a syringe. The added concentration of the initiator was represented as weight percent on the weight of PAN. After thorough mixing, the initiator-impregnated PAN solution was cast in the form of film. The film was dried for 6 h under vacuum.

Initiator-impregnated PAN films were suspended over thiophene and kept in a static vacuum of 160 torr at room temperature as shown in Figure 1. Thiophene vapor was diffused into the film and was polymerized at the initiator sites. The composite films were transparent and the thickness of the films was around 10 μm .

Measurement of Electrical Conductivity

Conductivity measurements were made by the four-point probe technique. A row of pointed electrodes, equispaced 5 mm apart, were rested on the flat

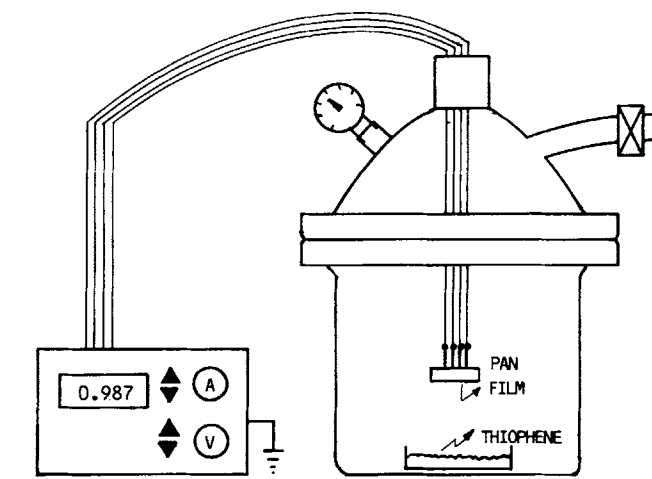


Fig. 1. Apparatus for the preparation of PAN/PTP composite films.

surface of the specimen. Care was taken in controlling the electrode pressure. Current I was passed through the outer probes and voltage V measured between the inner probes. The measured resistance (V/I) was converted to conductivity σ using the formula

$$\sigma = I \ln 2 / V \pi d$$

where d is the probe spacing.

Visible Absorption Spectra

For the estimation of the transparency of composite films, the transmittance was measured with a Shimadzu UV-240 spectrophotometer at the maximum absorption wavelength of 593 nm.

RESULTS AND DISCUSSION

The characterization of PAN/PTP composites has been carried out by IR, X-ray, and electron microscopic studies.

Figures 2a and 2b show the IR spectra of PAN and PAN/PTP composites synthesized by varying the concentrations of sulfuric acid and aluminum chloride, respectively, as an initiator. The characteristic absorption peaks at 2250, 600, and 720 cm^{-1} correspond to the $\text{C}\equiv\text{N}$ and $\text{C}-\text{Cl}$ stretching vibration and $\text{C}-\text{H}$ out-of plane deformation, respectively. In comparison with the absorption peaks of PAN and PAN/PTP composites at 720 cm^{-1} , it is indicated that thiophene has been polymerized in the PAN film.

Figure 3 shows the scanning electron micrograph of PAN/PTP composite film. In the electron micrograph, brighter regions are the areas where PTP has been formed while darker regions are PAN phase. PTP phase appears to be discontinuous in the continuous PAN matrix, but there are a lot of small microdomains in the PAN matrix that make the composite film electroconductive.

Figures 4a and 4b show the conductivity as a function of the polymerization time of thiophene at a given concentration of the initiators. The conductivities reach to the saturation values within one hour of polymerization time, except in the cases of concentrations of 50 and 100 wt % of sulfuric acid. In the case of 100 wt % sulfuric acid, the conductivity reaches up to 10^{-3} S/cm within 30 min. The conductivity of sulfuric-acid- or aluminum-chloride-impregnated PAN film prior to the polymerization of thiophene is 10^{-13} – 10^{-14} S/cm. The conductivities of composite films synthesized with sulfuric acid are higher than those synthesized with corresponding concentrations of aluminum chloride. In order to investigate the cause of the difference in conductivities between two kinds of composites synthesized with sulfuric acid and aluminum chloride, the weight increments of PAN films after the polymerization of thiophene for one hour were measured and represented as the percent on the weight of PAN/PTP composite (Table I). From Table I it is certain that sulfuric acid has

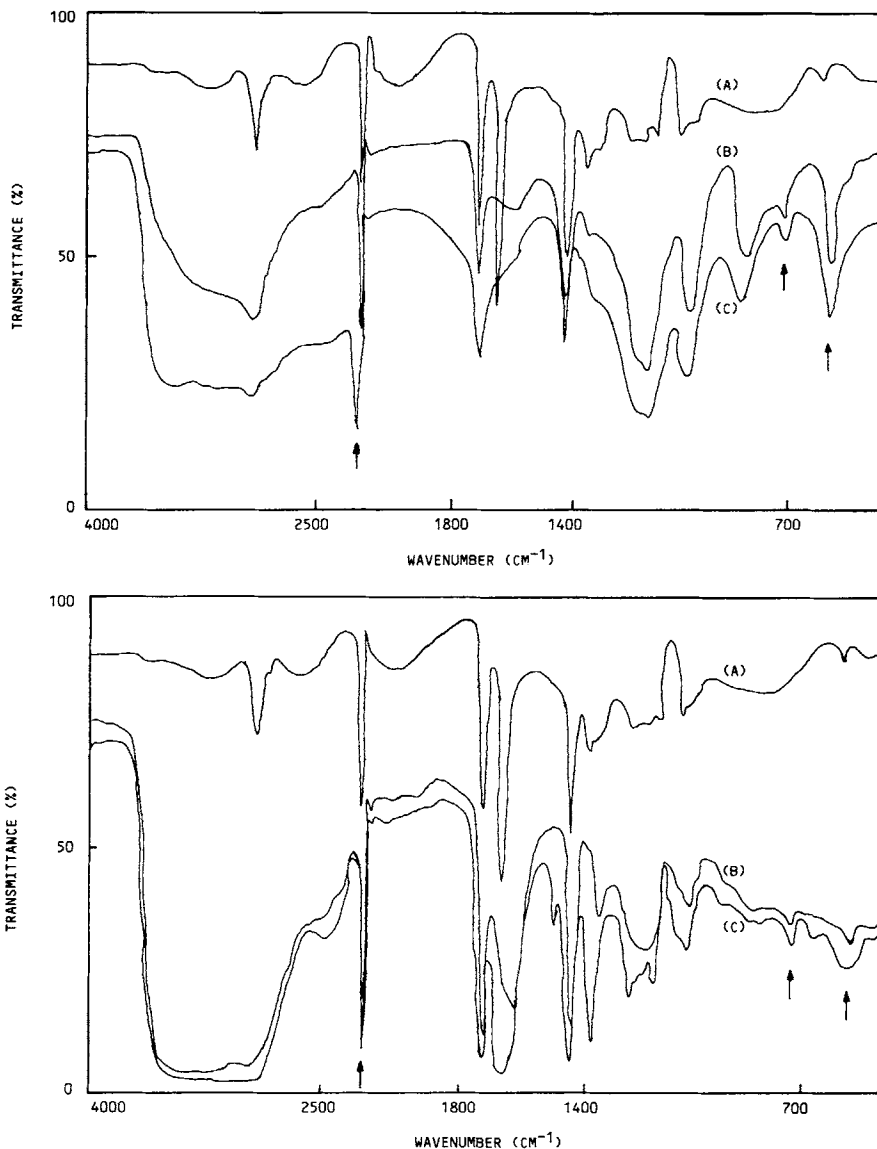


Fig. 2(a). IR spectra of (A) PAN, (B) PAN/PTP composite synthesized with 10 wt % H₂SO₄, and (C) PAN/PTP composite with 30 wt % H₂SO₄.

Fig. 2(b). IR spectra of (A) PAN, (B) PAN/PTP composite synthesized with 10 wt % AlCl₃, and (C) PAN/PTP composite with 30 wt % AlCl₃.

exerted a more profound effect as an initiator, and thus thiophene has been converted in higher yield to electroconductive polythiophene by sulfuric acid than by aluminum chloride. The increase of conductivity with the increase of the concentration of initiator or the weight fraction of polythiophene may be due to closer insulating gaps between conducting polythiophene particles, which were formed from denser initiator sites. From the data of Table I, the electrical

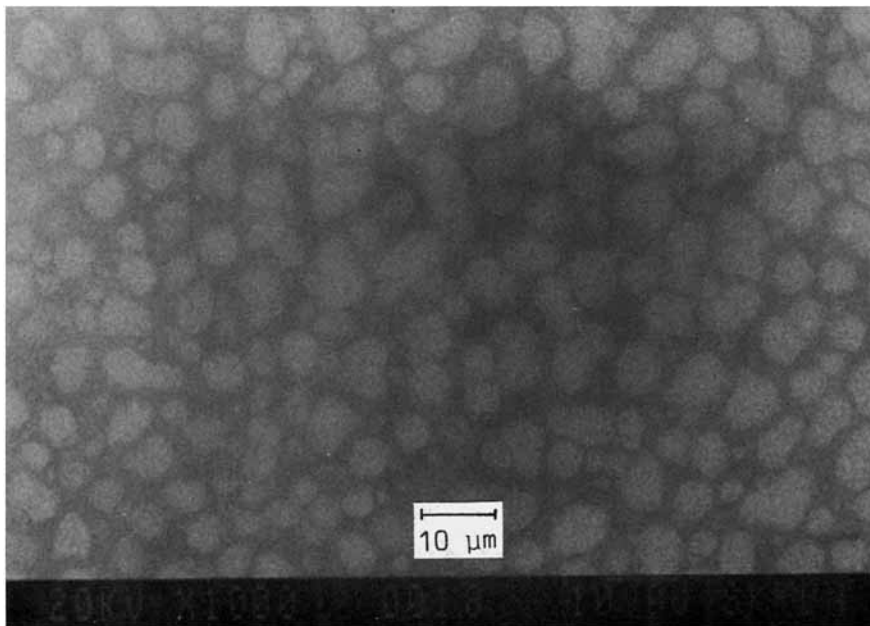


Fig. 3. Scanning electron micrograph of PAN/PTP composite (1 h) polymerization of thiophene with 30 wt % H_2SO_4 .

conductivity was plotted against the weight percent of polythiophene in PAN/PTP composites (Fig. 5). Note that the plot does not form a continuous curve but forms two different curves.

Figure 6 shows the electrical conductivity as a function of polymerization time at a given polymerization temperature of thiophene. As polymerization temperature increases at the constant initiator concentration, the conductivity reaches more rapidly to the maximum value and decreases also more rapidly from that. It may be explained as follows: the molecular mobility of PAN becomes higher, the diffusion of thiophene vapor to PAN matrix becomes easier, and consequently the conductivity reaches to the maximum value more rapidly, while the phase segregation between PAN and PTP becomes higher and thus the conductivity decreases more rapidly with the increases of polymerization temperature. Note that the maximum conductivity of the composites synthesized with an equal concentration of initiator are almost constant regardless of polymerization temperature.

For the examination of the thermal degradation of the conductivity, $\log R_t/R_0$ was plotted as a function of time in Figure 7. R_t represents the resistance of the sample at the temperature of the experiment at a given time. R_0 represents the resistance of the sample at the temperature of the experiment at time zero. The slope of the line implies the rate constant of the degradation of the conductivity. Note that the slope of the line increases with increasing temperature. The cause of the slope increase also seems to be due to the higher phase segregation between PAN and PTP as the temperature increases.

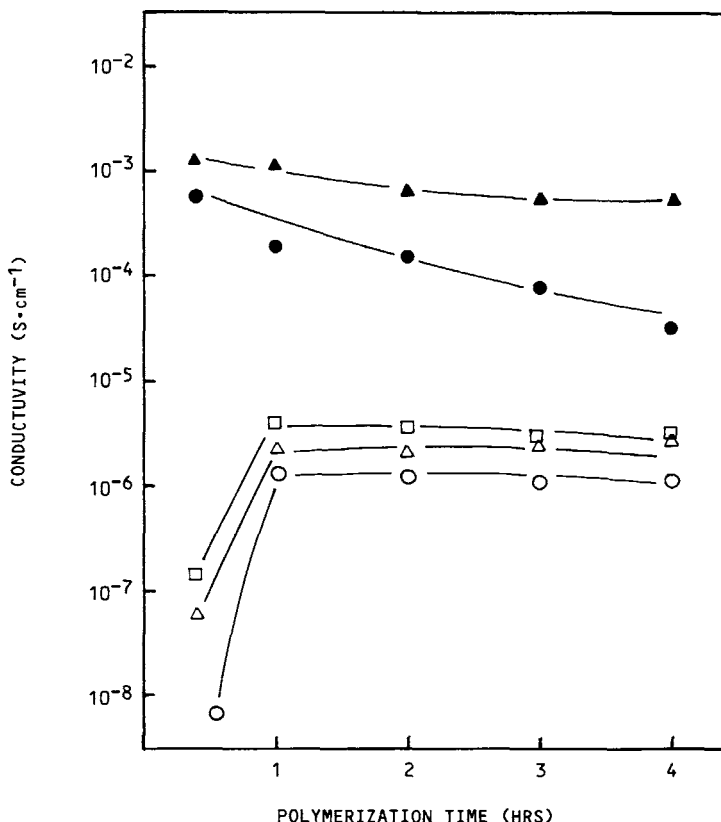


Fig. 4(a). Electrical conductivity of PAN/PTP composite vs. polymerization time at a given concentration of sulfuric acid, (○) 10; (△) 20, (□) 30; (●) 50; (▲) 100 wt %.

Figure 8 shows the electrical conductivity vs. time of ambient air exposure. The stability of conductivity to ambient air exposure is excellent, i.e., only about one order of magnitude drops on one month exposure.

Figure 9 shows the conductivity change brought about by exposure of the sample composite to humid air and its evacuation. The uptake of water vapor and gain of conductivity are reversible, but the gain of conductivity is only about one order of magnitude.

For the estimation of the transparency and the stability of transparency for composite films synthesized by varying the kind and the concentration of initiator, transmittance was measured with time of ambient air exposure at the maximum absorption wavelength of 593 nm. As shown in Figures 10a and 10b transmittances do not change for one month, which implies that the stability of transparency is excellent. The transmittances of composite films synthesized with sulfuric acid are higher than those with the corresponding concentration of aluminum chloride. The transmittance of composite film synthesized with 10% of sulfuric acid on the weight of PAN reaches as high as above 90%. It is indicated that sulfuric acid is more effective than aluminum chloride for the preparation of transparent conducting PAN/PTP composite films.

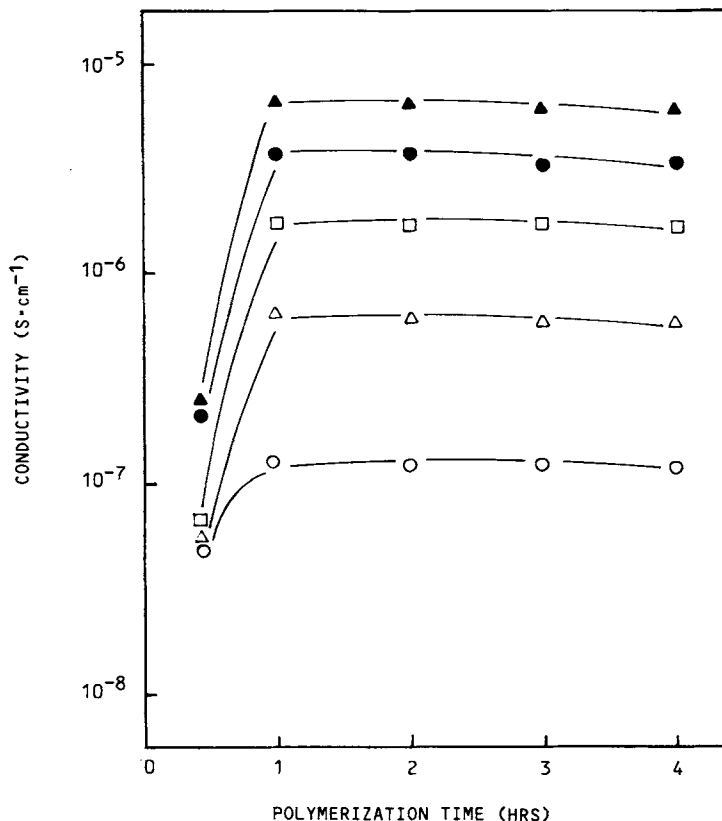


Fig. 4(b). Electrical conductivity of PAN/PTP composite vs. polymerization time at a given concentration of aluminum chloride, (○) 10; (△) 20; (□) 30; (●) 50; (▲) 100 wt %.

CONCLUSION

PAN/PTP composite films can be prepared by polymerizing thiophene vapor in PAN films impregnated with sulfuric acid or aluminum chloride as an initiator.

TABLE I
Effect of Kind and Concentration of Initiator on the Yield of PTP in PAN/PTP Composites

Initiator	Concentration of initiator (wt %)	Weight percent ^a of PTP	Conductivity (S/cm)
AlCl ₃	30	15.3	1.31 × 10 ⁻⁶
H ₂ SO ₄	30	21.3	5.39 × 10 ⁻⁶
AlCl ₃	50	17.4	3.43 × 10 ⁻⁶
H ₂ SO ₄	50	26.1	7.89 × 10 ⁻⁴
AlCl ₃	100	18.3	4.81 × 10 ⁻⁶
H ₂ SO ₄	100	40.8	1.86 × 10 ⁻³

^a The weight percent of polythiophene on the weight of PAN/PTP composite films.

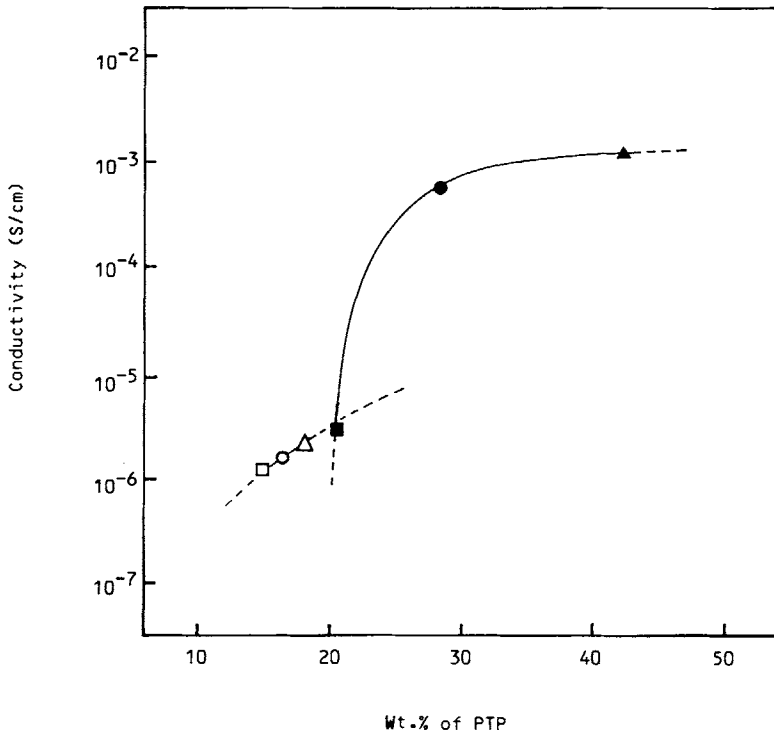


Fig. 5. Electrical conductivity vs. weight percent of PTP in PAN/PTP composites synthesized with 30 (□), 50 (○), and 100 wt % (△) AlCl₃ and 30 (■), 50 (●), and 100 wt % (▲) H₂SO₄.

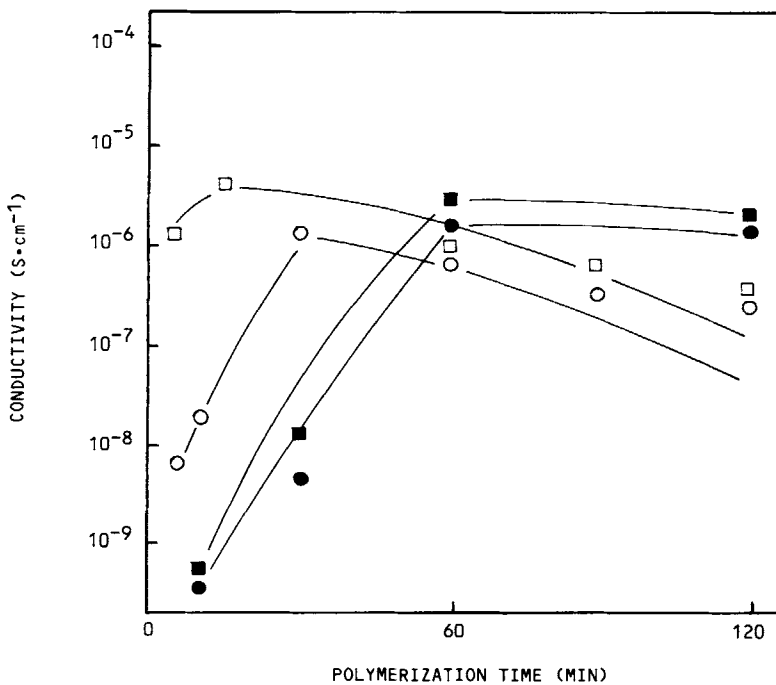


Fig. 6. Electrical conductivity vs. polymerization time at a given polymerization temperature of thiophene: (○) H₂SO₄ 10 wt % × 100°C; (●) H₂SO₄ 10 wt % × 25°C; (□) H₂SO₄ 30 wt % × 100°C; (■) H₂SO₄ 30 wt % × 25°C.

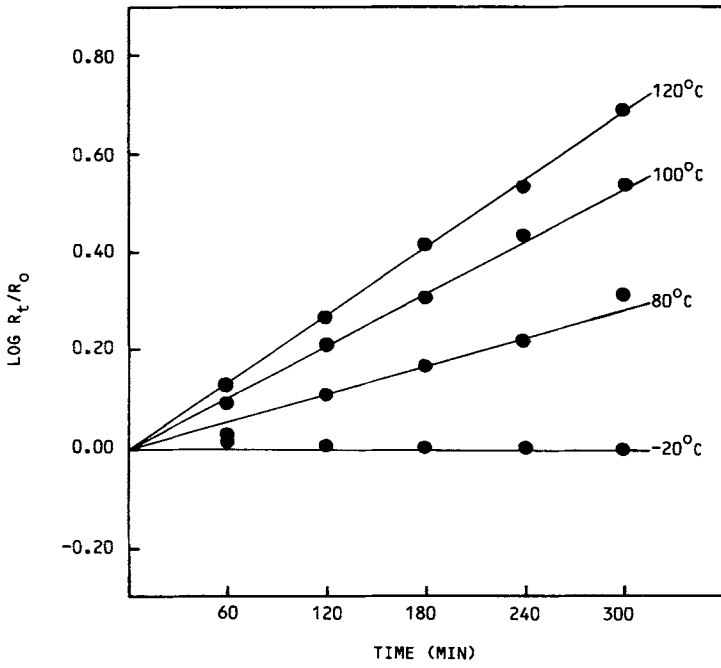


Fig. 7. $\log R_t/R_0$ vs. time at various temperature for PAN/PTP composite synthesized with 50 wt % H_2SO_4 (R_t = the resistance at the temperature of the experiment at a given time and R_0 = the resistance at time zero).

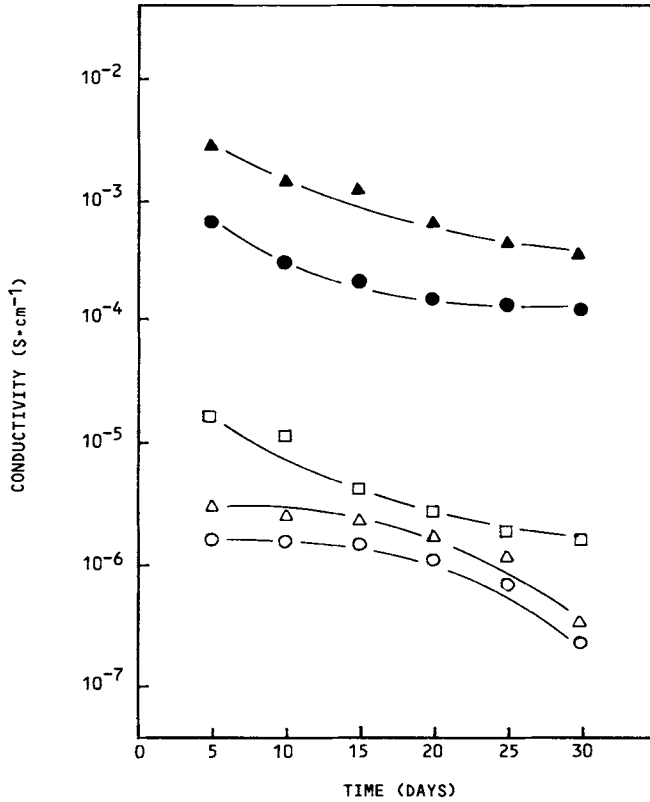


Fig. 8. Electrical conductivity vs. time of ambient air exposure for PAN/PTP composite synthesized with sulfuric acid: (○) 10, (△) 20; (□) 30; (●) 50; (▲) 100 wt % H_2SO_4 .

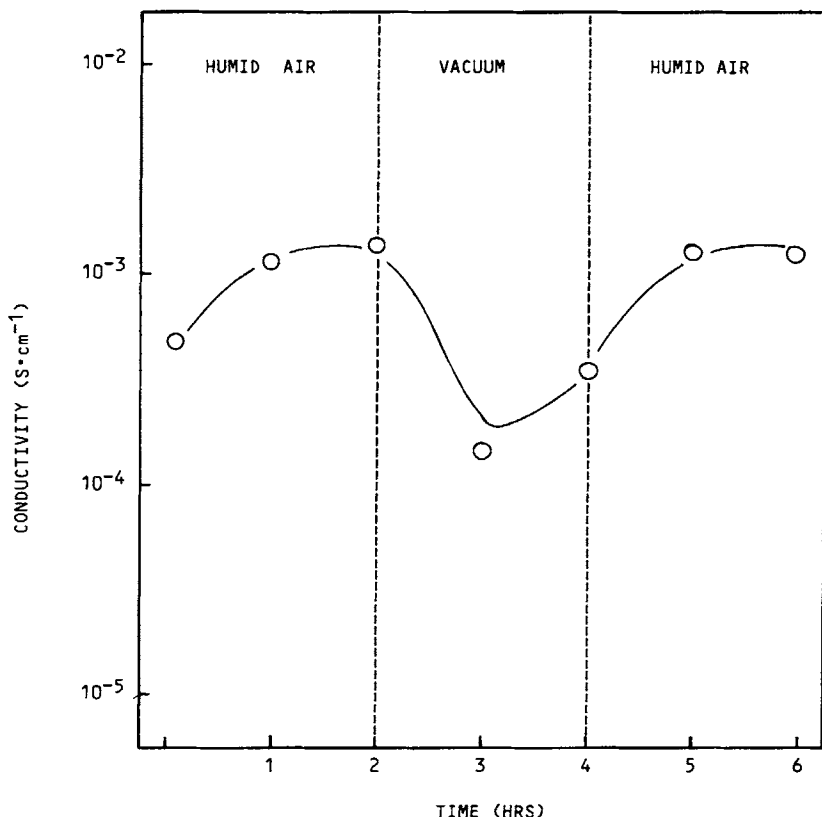


Fig. 9. Conductivity change of PAN/PTP composite exposed to humid air and vacuum (composite synthesized with 50 wt % H₂SO₄).

The IR spectra of composite films confirm that the material contains both PAN and PTP. The X-ray diffraction scans showed the absence of any reflections, thus the presence of crystallites in both PAN and PAN/PTP composite is negligible.

After polymerization of thiophene for 1 h, the electrical conductivities of composites reach in the range of 10⁻⁷–10⁻³ S/cm depending on the initiator and its concentration. The stability of conductivity to ambient air exposure is excellent, i.e., about one order of magnitude drops on one month exposure. The increasing rate of conductivity to the maximum value and the decaying rate of conductivity from that value increase with the polymerization temperature of thiophene, but the maximum values of conductivity are constant regardless of the polymerization temperature at a given concentration of initiator.

The transparency of composite films has been estimated by transmittance at the maximum absorption wavelength of 593 nm. The transmittance of composite film prepared with 10% sulfuric acid on the weight of PAN reaches above 90%. The transparency has been maintained for the period of experiment, i.e., one month under ambient air exposure. Sulfuric acid is more effective than aluminum chloride for the preparation of transparent conducting PAN/PTP composite films.

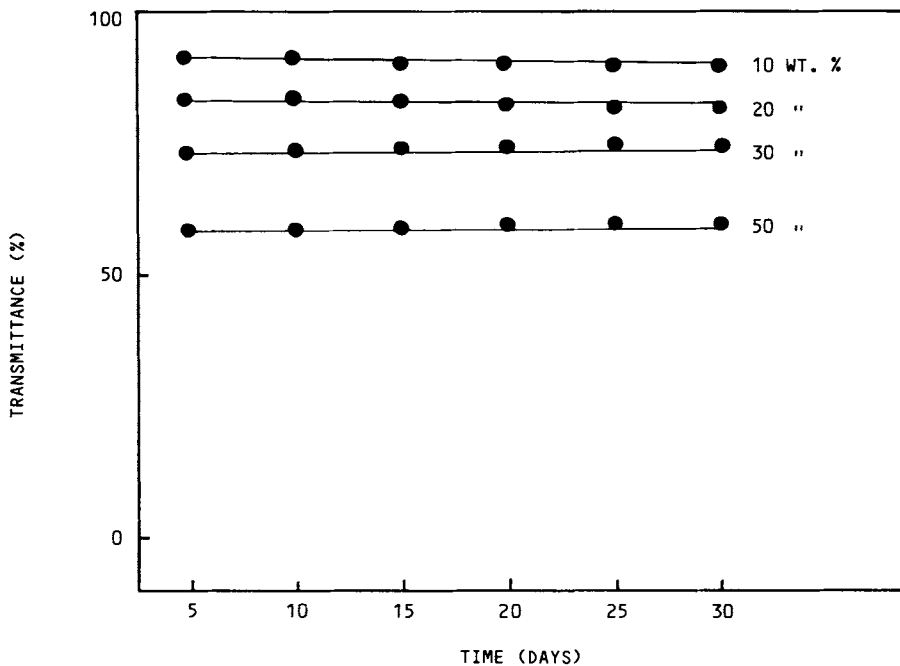


Fig. 10(a). Transmittance vs. time of ambient air exposure for PAN/PTP composite films synthesized by varying the concentration of H₂SO₄.

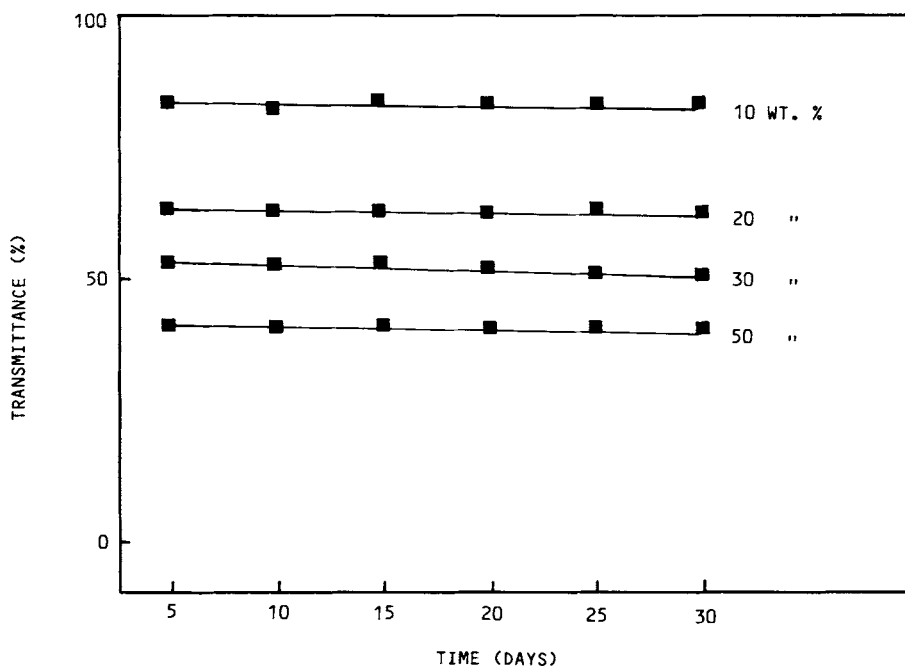


Fig. 10(b). Transmittance vs. time of ambient air exposure for PAN/PTP composite films synthesized by varying the concentration of AlCl₃.

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