

Structural and Electrical Behavior of Polyacrylonitrile–Polypyrrole Composite Film

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SYNOPSIS

Polyacrylonitrile–polypyrrole composite films were prepared by a vapor phase technique. The films obtained by this method have high conductivity and good mechanical properties. Growth of polypyrrole on the surface of polyacrylonitrile was investigated by electron microscopic studies. Electrical properties of composite films were investigated as a function of FeCl_3 content as well as polypyrrole uptake. The current–voltage characteristic suggest an ohmic conduction. The conductivity of these composite films was measured as a function of temperature yielding an activation energy of 0.16 eV.

INTRODUCTION

Electroactive conducting polymers have assumed great importance in recent years. Indeed, conducting polymers have emerged as a new class of materials to replace the inorganic semiconductors and metals.^{1–4} Among the wide range of conducting materials synthesized, conjugated organic polymers^{5–9} have been studied extensively as they are highly conducting materials. Of these, polypyrrole (PPy) has drawn considerable attention as it has better environmental stability. PPy is usually prepared electrochemically^{10,11} or chemically using a catalyst.^{12,13} However, films prepared by these methods have poor stability and are nonyielding. Though recently Diaz and Kanazawa¹⁴ had electrochemically polymerized free standing conducting films of PPy, films with improved flexibility and stability are desirable. Recently, high conducting polymer films having superior stability and flexibility were prepared by a composite/alloy technique.^{15–19} This was achieved by introducing high conducting PPy in the bulk of another high molecular weight polymer having superior flexibility and stability. The composite film prepared by the chemical phase method has an advantage over the electrochemically prepared one as in the former case there is no restriction on the

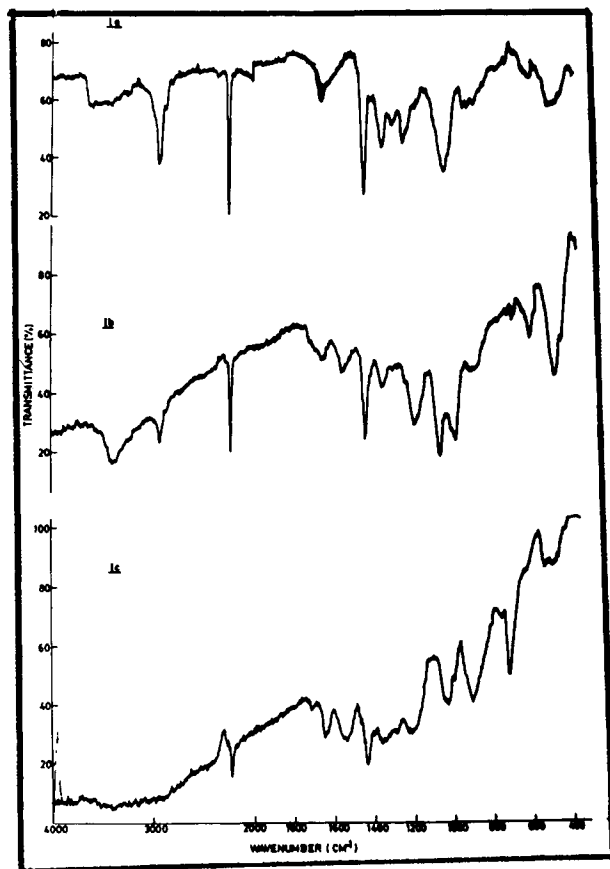


Figure 1 IR spectra of PAN and PAN–PPy composite films: (a) pure PAN; (b) 5 min exposed to pyrrole vapors; (c) 15 min exposed to pyrrole vapors.

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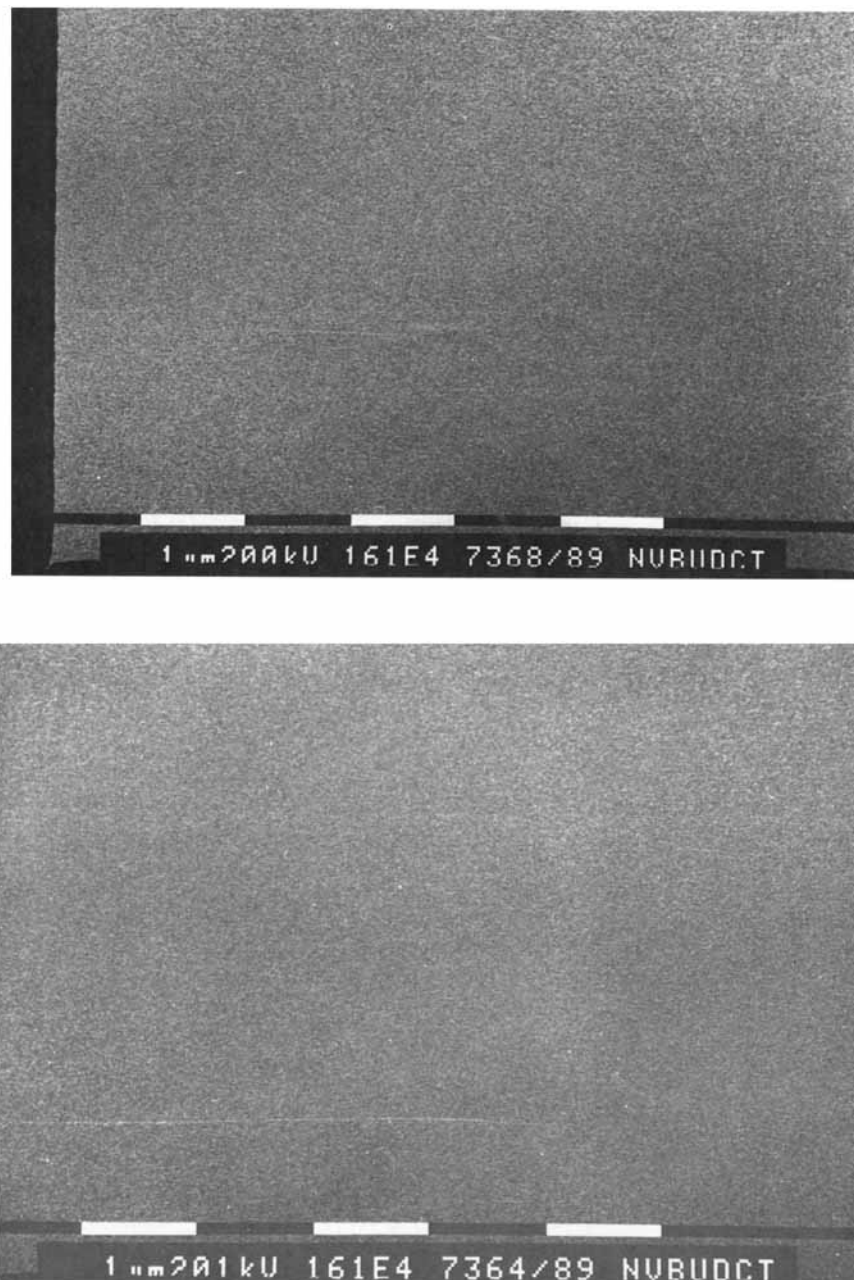


Figure 2 SEM micrograph of polyacrylonitrile: (a) pure PAN; (b) FeCl_3 -doped PAN.

surface area of the precursor film and the composite film need not be peeled off from the electrode. The PPy composite film prepared by this method has properties similar to the electrochemically polymerized one.

In our earlier report,²⁰ we successfully demonstrated the vapor phase polymerization of pyrrole on polyacrylonitrile (PAN). These composite films have remarkable thermal and mechanical stability and high conductivity, thus making practical utilization possible. In this paper, we report a detailed

investigation of the structure, morphology, and electrical conductivity of this composite film. This study was mainly undertaken to explore the possibilities of using such films for microelectronic applications.

EXPERIMENTAL

The conducting composite films of PAN-PPy were prepared as reported in our earlier publication.²⁰ A



Figure 3 SEM micrograph of FeCl_3 -doped PAN exposed for 15 min.

solution of polyacrylonitrile 2% (w/v) was made in dimethyl formamide (DMF). Anhydrous FeCl_3 was used as a doping agent as purchased without further purification. A required amount of FeCl_3 was added to the solution and stirred for 0.5 h. A few drops of this solution were poured on a glass plate floated on a mercury surface and dried under an infrared lamp for 0.5 h. The films thus cast were then peeled from the glass plate and washed with alcohol. These films

are brownish in color. In the present study PAN films doped with various percentages of FeCl_3 were made by adding 5, 10, 15, and 25% (w/w) of FeCl_3 to the polyacrylonitrile solution.

Pyrrole monomer used in the present study was purified by vacuum distillation. The preparation of polypyrrole-polyacrylonitrile composite films was carried out at room temperature by exposing FeCl_3 -doped PAN to pyrrole vapors. The time of exposure

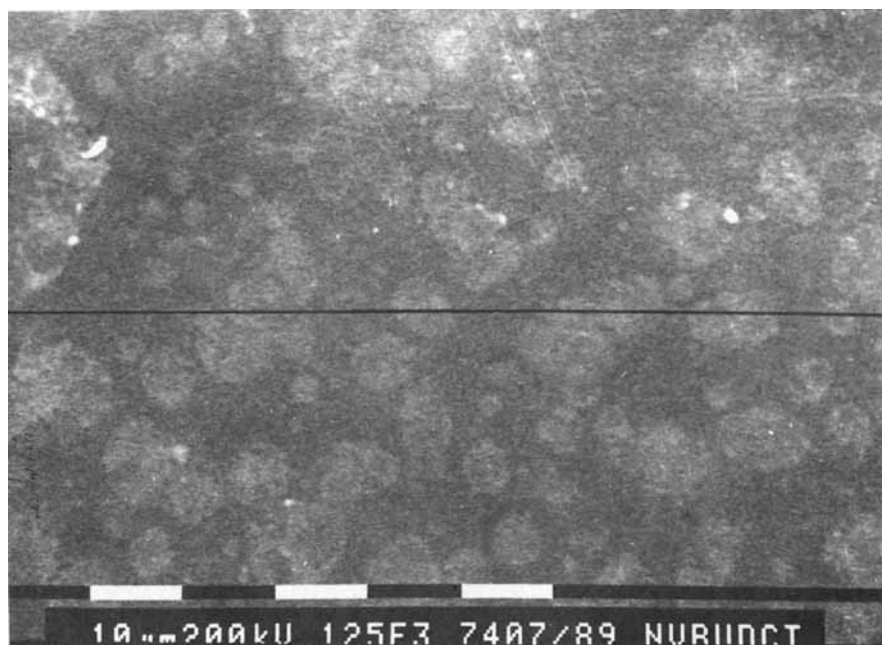


Figure 4 SEM micrograph of 10% FeCl_3 -PAN exposed for 30 min.

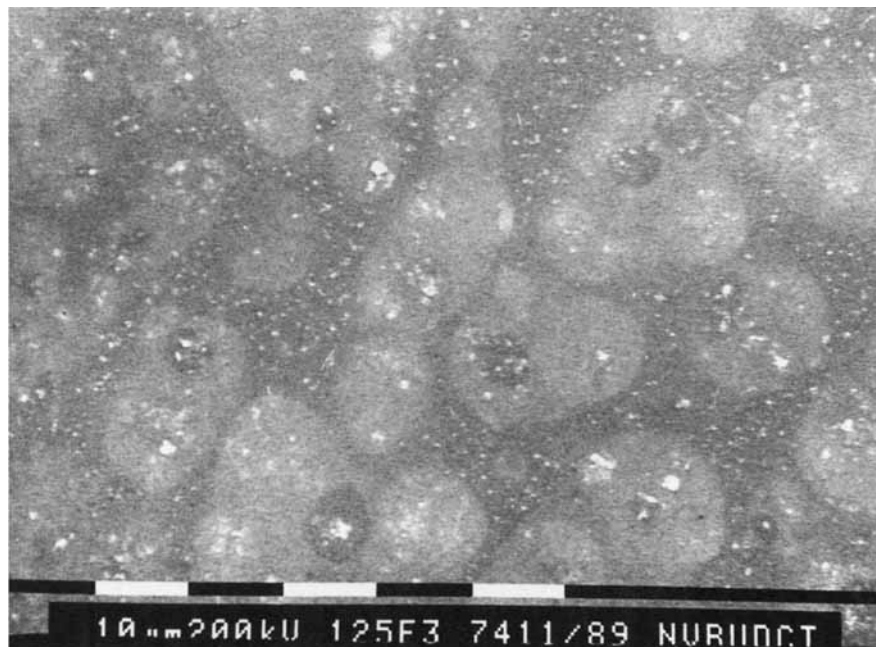


Figure 5 SEM micrograph of 15% FeCl₃-PAN exposed for 30 min.

was varied from a few minutes to several hours. The composite films were then washed with alcohol and dried under vacuum. The films are black in color.

Infrared spectra of PAN, as well as a PAN-PPy composite, were measured with a Perkin-Elmer Model No. 397 spectrophotometer.

Scanning Electron microscopic studies were car-

ried out with a Philips SEM 515. After the usual washing and drying the samples were sputter coated with gold of about 200 Å in thickness and observed under SEM at magnification of about 20,000×. Cross sections of the samples were observed by embedding the films in parafin wax and taking the cross section of thickness about 0.5 μm. These cross sections were

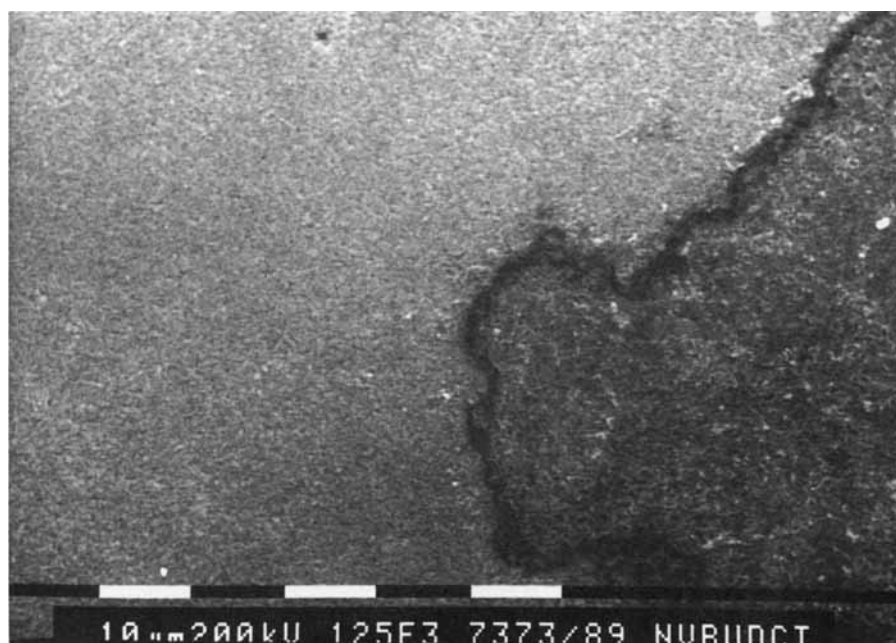


Figure 6 SEM micrograph of 15% FeCl₃-PAN exposed for 60 min.

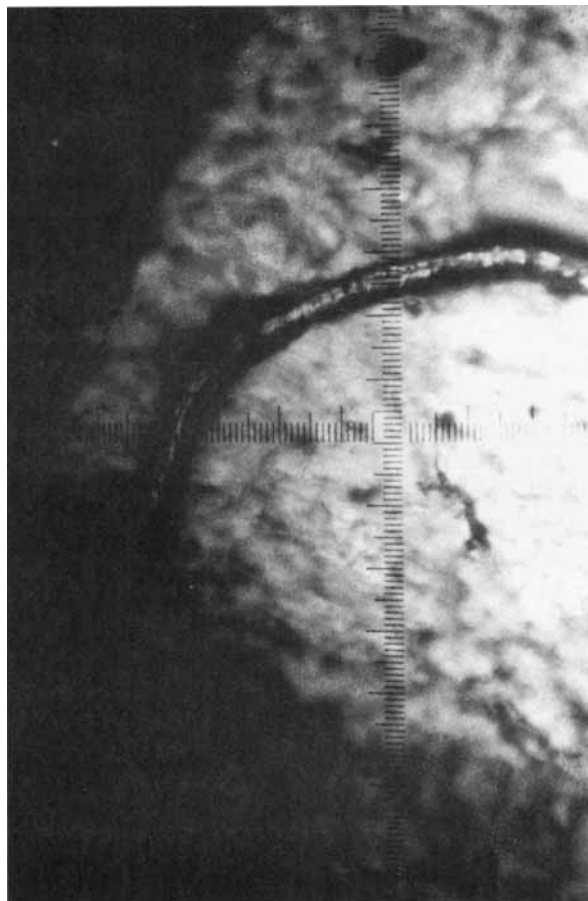


Figure 7 Cross-sectional photograph of 15% FeCl_3 -PAN exposed for 60 min.

then directly observed under a projection microscope at a magnification of about $250\times$.

Electrical measurements were carried out in a sandwiched configuration^{21,22} in a high vacuum cryostat. Heating of the sample was done at a rate of $1^\circ\text{C}/\text{min}$. The voltage was varied from 0 to 150 V, and sufficient time was allowed to elapse after the application of voltage to ensure steady state conduction.

RESULTS AND DISCUSSION

Structure and Morphology

The IR spectrum of PAN and PAN-PPy composite films are given in Figure 1. The IR spectrum of PAN film exposed to pyrrole vapour for a short interval [Fig. 1(b)] shows additional bands at 3400 , 1540 , 1180 , 1050 , and 900 cm^{-1} . On the other hand, the IR spectrum of the film exposed for a longer interval [Fig. 1(c)] show a featureless decrease in absorption

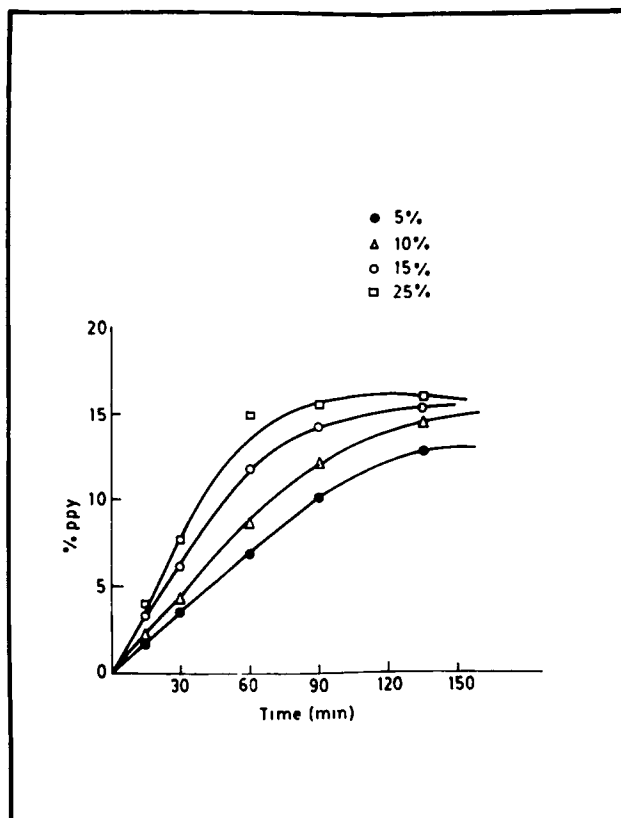


Figure 8 Variation of content of polypyrrole for different duration of exposure time.

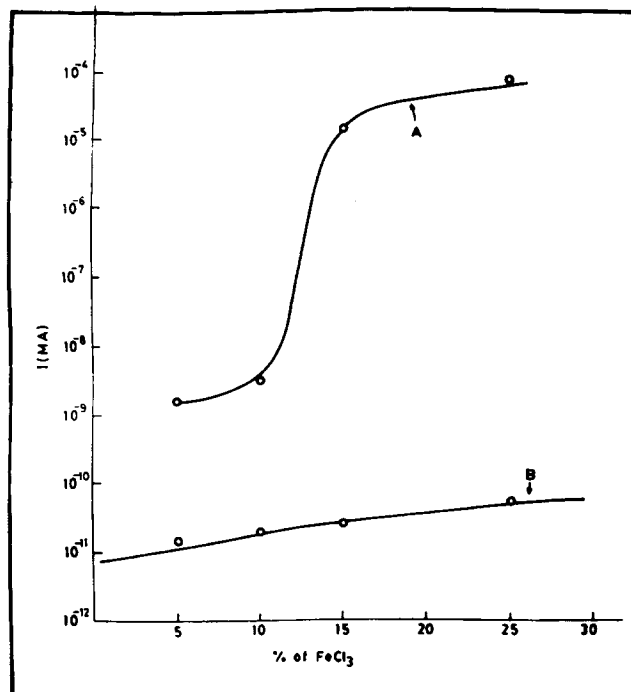


Figure 9 Variation of conductivity with FeCl_3 content.

from 4000 to 1800 cm^{-1} . This absorption tail suppresses the absorption of NH and CH stretching mode absorption at about 3400 and 2940 cm^{-1} . However, bands at about 1540, 1180, 1050, 900, and 720 cm^{-1} were observed. These are the characteristic bands of PPy.²³ This long absorption tail has been assigned to the tail of the absorption peak located in the near-IR for oxidized PPy.²⁴

In order to understand the morphology of films, it was thought interesting to investigate the growth morphology of the composite films using SEM. It can be seen from Figure 2(a) and (b) that pure undoped PAN, as well as FeCl_3 -doped PAN, shows a smooth surface structure. When the films containing FeCl_3 were exposed to pyrrole for 15 min, the morphology of the surface showed growth of a few globules of size 1 μm (Fig. 3). On the other hand, when all these films were exposed to pyrrole for 30 min, globular structures were well developed and formed islands. It was interesting to note from the micrographs that, with the increasing content of FeCl_3 , the size of these island structures increased from 1 μm to about 25 μm (Figs. 4 and 5). Electron micrographs further revealed that the islands later on merged to form continuous films on prolonged exposure (Fig. 6). SEM studies, however, do not give complete information on the composite in the interior of the blend. Therefore, the cross section of the film was studied. A typical micrograph of a cross section is shown in Figure 7. It may be seen that polypyrrole has penetrated into the bulk of the film from both surfaces. The depth of diffusion was found to increase with increasing time of exposure. In the case of film exposed to pyrrole for 60 min, the depth over which the diffusion is uniform was about 3 μm . It is also clear from the micrograph that polypyrrole has diffused deep into the entire film, though some regions in the interior are not heavily doped. The kinetics of the diffusion of polypyrrole were studied with various contents of FeCl_3 in the film. Figure 8 depicts the uptake of polypyrrole for different durations of time. It may be seen that the uptake of polypyrrole (PPy) increases initially and saturates at about 90 min. The amount of uptake of PPy also increases with an increased amount of FeCl_3 present in the sample.

Electrical Conduction

The electrical conduction of the samples was measured in the temperature range 25–100°C. The conductivity of the sample at room temperature was of the order of $10^{-8} \text{ S cm}^{-1}$. This value is in agreement with those reported for other composites of this cat-

egory.^{15,17} The variation of conductivity with FeCl_3 content and its accompanied polypyrrole uptake was studied. Figure 9 shows the variation of current as a function of FeCl_3 in the composite film for an applied voltage of 10 V at room temperature. The variation of conductivity with FeCl_3 alone in the film is also depicted in the same figure. It can be seen that the FeCl_3 does not increase the conductivity of the film appreciably. When the films were loaded with polypyrrole, the increase in the current is rather low up to a loading 9% of polypyrrole (10% FeCl_3 -doped film). However, the current increases drastically at 12% PPy loading (15% FeCl_3), after which further increase is again slow. This behavior shows that some threshold loading is required in order to get good conduction. This result is similar to that reported in other polymer composites.²⁵ This suggests that the diffusion of polypyrrole in PAN film gives probably a kind of continuous network which helps in the conduction process. The formation of such a network, either through particle contact or formation of polypyrrole islands separated from each other, leads to the enhancement in the conductivity. Microscopic investigation clearly reveals the for-

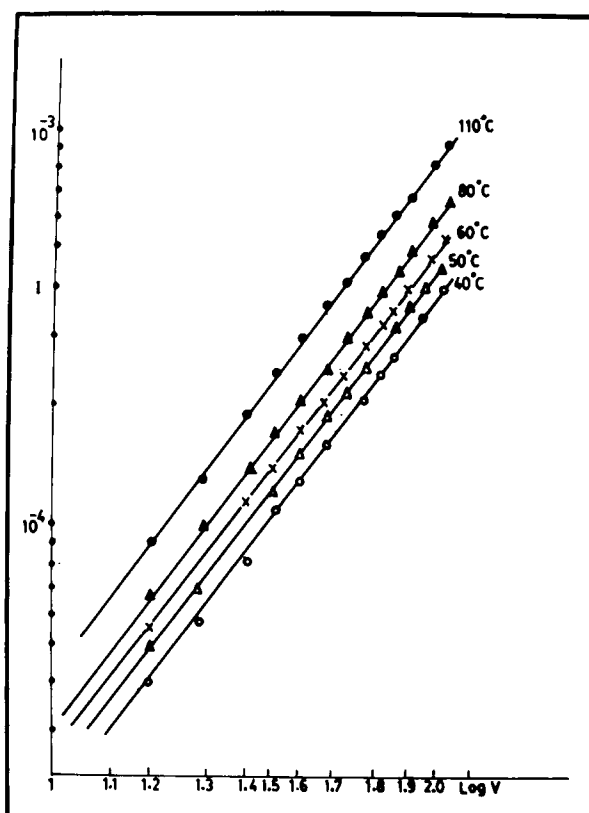


Figure 10 I-V characteristic for PAN-PPy composite film.

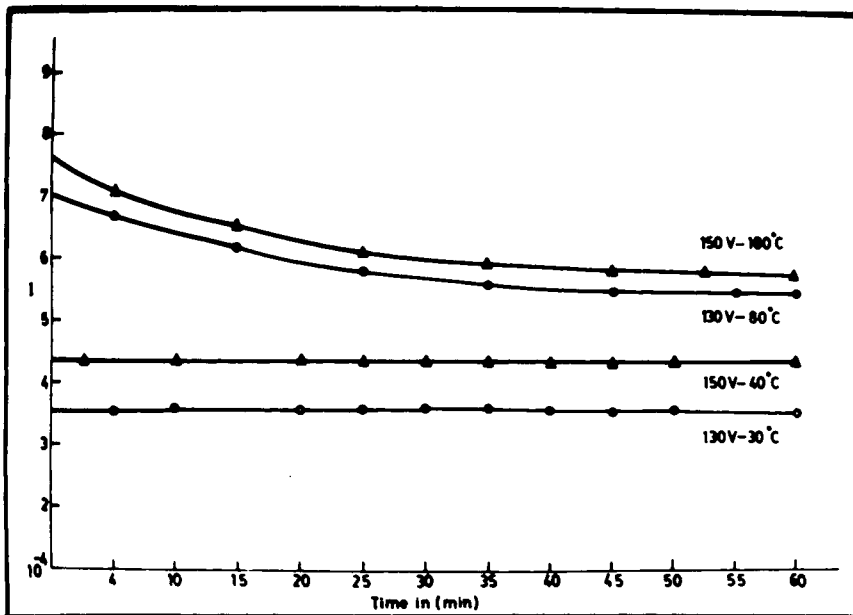


Figure 11 Time-dependent conductivity of PAN-PPy composite film.

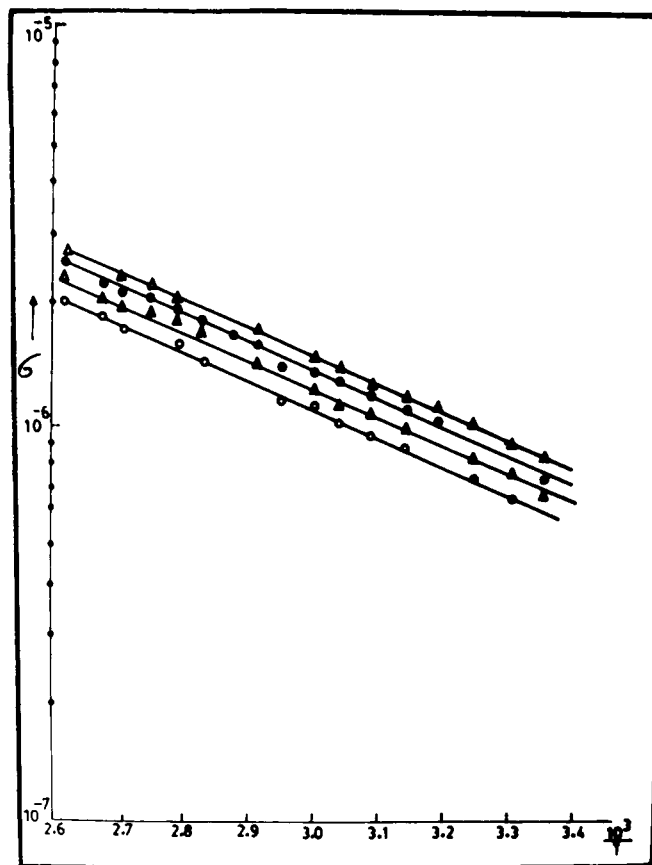


Figure 12 Arrhenius plot for PAN-PPy composite film.

mation of a network and the penetration of polypyrrole in the bulk of PAN.

Current-voltage characteristics for various films were studied at different temperatures. A typical one (15% doped FeCl₃-doped sample) is shown in Figure 10. The plot displays a linear variation of current with voltage having slope equal to unity. This suggests an ohmic behavior of PAN-PPy composite film. In order to understand the nature of the charge carrier, the time dependence of the current was recorded. If the conduction is due to ions, the current should decrease rapidly with time. When it is due to electrons the current does not change much. Figure 11 reveals that the current remains almost constant suggesting that the conduction is by electrons.^{26,27} Additional information on the conduction mechanism was derived by studying the variation of conductivity with temperature. Figure 12 represents log σ vs. $1/T$ plot for the composite film (15% FeCl₃-doped PAN exposed to PPy). This gives an Arrhenius plot from which the activation energy was calculated. The activation energy (ΔE) was found to be 0.16 eV. It must be pointed out that this value is much lower than that reported for chemically synthesized PPy.²⁸ This is probably due to the oxidized state of the polypyrrole in the presence of FeCl₃.

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