

Investigation of Structure of Polyacrylonitrile–Polypyrrole Composite Film

N. V. BHAT and E. SUNDARESAN, *Department of Chemical Technology, Matunga, Bombay 400019 India*

Synopsis

The structure of polyacrylonitrile–polypyrrole composite film, prepared using pyrrole in vapor and FeCl_3 as catalyst, was investigated using IR spectroscopy, DTA/TGA, and resistivity measurements. The films showed improved thermal stability and electrical conduction. The strength of the composite film decreased as compared to pure PAN and the growth structures of polypyrrole could be seen.

INTRODUCTION

The use of highly conductive polymers as electrical engineering material seems to be limited due to their lack of abundance, processibility, and stability. In recent years, the interest in forming polymer–polymer composites^{1–3} has taken place due to the fact that such materials possess improvement in mechanical properties, processibility, and stability in normal atmospheric conditions. Among these the electrochemically polymerized composites of pyrrole have attained much attention due to excellent flexibility, ease of doping, etc. Polymerization of pyrrole through chemical^{4–6} and electrochemical^{7–9} routes have been reported. However, the electrical properties vary from insulator to metal-like polymer, depending on the synthesis process. Free-standing stable and flexible films of polypyrrole have been produced using electropolymerization technique; however, these are nonyielding. It is, therefore, of great interest to make composite films of polypyrrole so that mechanical properties can be improved. Recently synthesis of conducting composite of polypyrrole^{10,11} at low temperature has been reported. In the present paper, we report the preparation of composite films of PAN–PPy at room temperature and discuss its growth and the mechanical properties.

EXPERIMENTAL

Polyacrylonitrile (PAN) was used as a polymeric matrix. Pyrrole monomer used in the present study was purified by vacuum distillation. Anhydrous FeCl_3 was used as an oxidizing agent. After dissolving PAN in dimethylformamide (2% w/v) a required amount of FeCl_3 (10% w/w) was added. A few drops of this solution was poured on a glass plate and dried under an infrared lamp. The films thus cast were further dried under vacuum for 0.5 h. These films are brownish yellow in color. The preparation of polypyrrole–PAN

composite films was carried out at room temperature by exposing FeCl_3 -PAN film to pyrrole vapor. The time of exposure was varied from few minutes to several hours. The composite films were then washed with distilled water and then dried under vacuum. The films are black in color.

RESULTS AND DISCUSSION

The IR spectrum of PAN and PAN-PPy composite are given in Figure 1. The IR spectrum of PAN films exposed to pyrrole vapor 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 spectra of the film exposed for a longer interval [Fig. 1(c)] show a featureless decrease in absorption 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} , respectively. However, the bands at about 1540, 1180, 1050, 900, and 720 cm^{-1} were observed. These are the characteristic bands of PPy.¹² This long absorption tail has been assigned to the tail of absorption peak located in the near-IR for oxidized PPy. The absorption peak at about 1700 cm^{-1} may be due to the substantial amount of the carbonyl group which can be present in the composite film. The polymerization of pyrrole by chemical oxidation always results in such a formation.^{6,13}

The densities of PAN and PAN-PPy composite films (exposed to pyrrole vapors for 60 min) were determined using floatation technique and were found to be 1.163 and 1.326, respectively. The fraction of PPy in the various films were determined from the weight difference before and after the exposure to pyrrole vapor. These values are given in Table I. The thermograms in nitrogen of PAN and PAN-PPy composites (60 min treated) are shown in Figures 2 and 3, respectively. The DTA scans of pure PAN show a sharp endothermic peak at about 298°C. In contrast, however, the PAN-PPy composite film show respective endothermic peak at about 310°C. The TGA scans of PAN show that it is stable to heat up to about 300°C, when it starts to lose weight suddenly. In comparison, the PAN-PPy composite loses weight gradually over the temperature range. Interestingly, the thermogravimetric scan of the polypyrrole-quinone complex also shows a similar thermogram as in the case of the PAN-PPy composite.⁴ In both the cases, more than half of their weight was retained when heated to a temperature of 450°C. From the nature of the two scans, it can be proposed that the endothermic peaks observed for the samples in DTA can be related to the decomposition of the samples. The resistivity of these films were determined at room temperature in the sandwich configuration.^{14,15} The resistivity of FeCl_3 -doped PAN films exposed to pyrrole vapor for different time intervals are given in Table I. The PAN-PPy composite shows a decrease in the resistivity by several orders of magnitude as compared with FeCl_3 -doped PAN films. It is interesting to note that films exposed to pyrrole vapors for 1 h shows maximum conductivity. This may be related to the surface structure of the composite films. Further, detailed investigation is necessary to confirm this correlation. The detailed investigation of conduction mechanism of this composite has been undertaken in our laboratory.

The mechanical properties of PAN films exposed to pyrrole for 1 h were studied using an Instron modulus testing machine. These values are given in

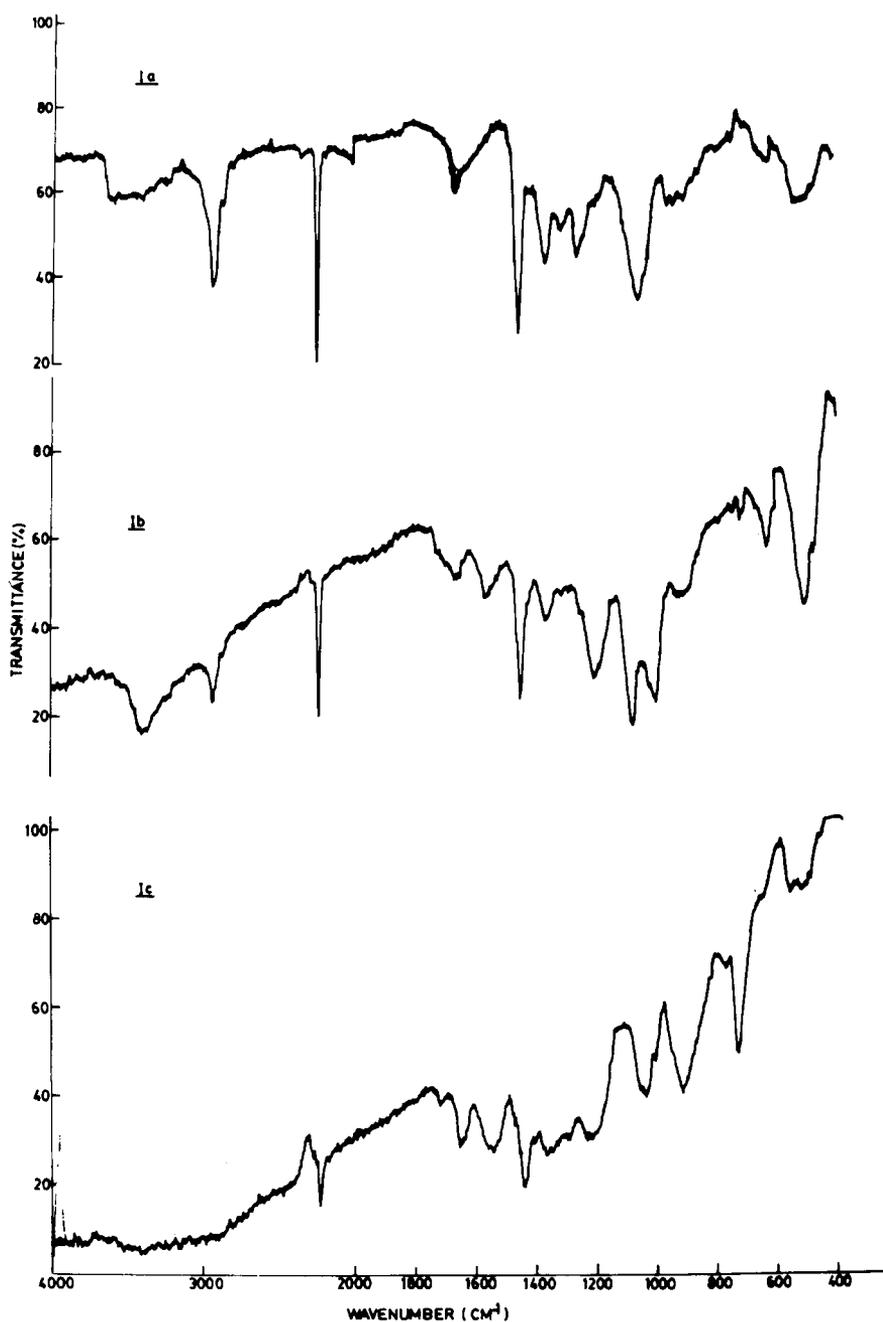


Fig. 1. Infrared spectra of (a) PAN film, (b) PAN-FeCl₃ film exposed to pyrrole vapor for 15 min, and (c) film exposed to pyrrole vapor for 30 min.

TABLE I
Electrical Resistivity after the Samples Exposed to Pyrrole
for Various Intervals

Sample	PPy (wt %)	Resistivity
PAN	—	16 M Ω cm
PAN + PPy (15 min)	4.0	1 M Ω cm
PAN + PPy (30 min)	5.2	25 K Ω cm
PAN + PPy (45 min)	5.5	5 K Ω cm
PAN + PPy (60 min)	5.8	2 K Ω cm
PAN + PPy (5 h)	5.8	20 K Ω cm

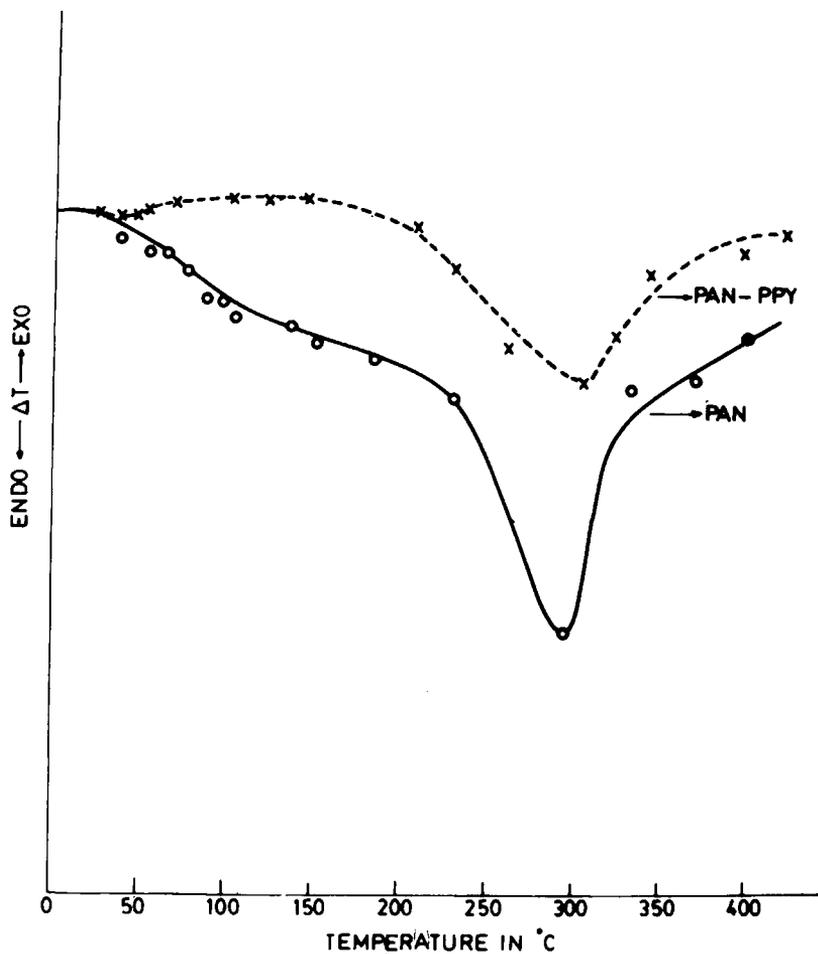


Fig. 2. DTA scans for PAN and PAN-PPy composite. Heating rate is 10°C/min.

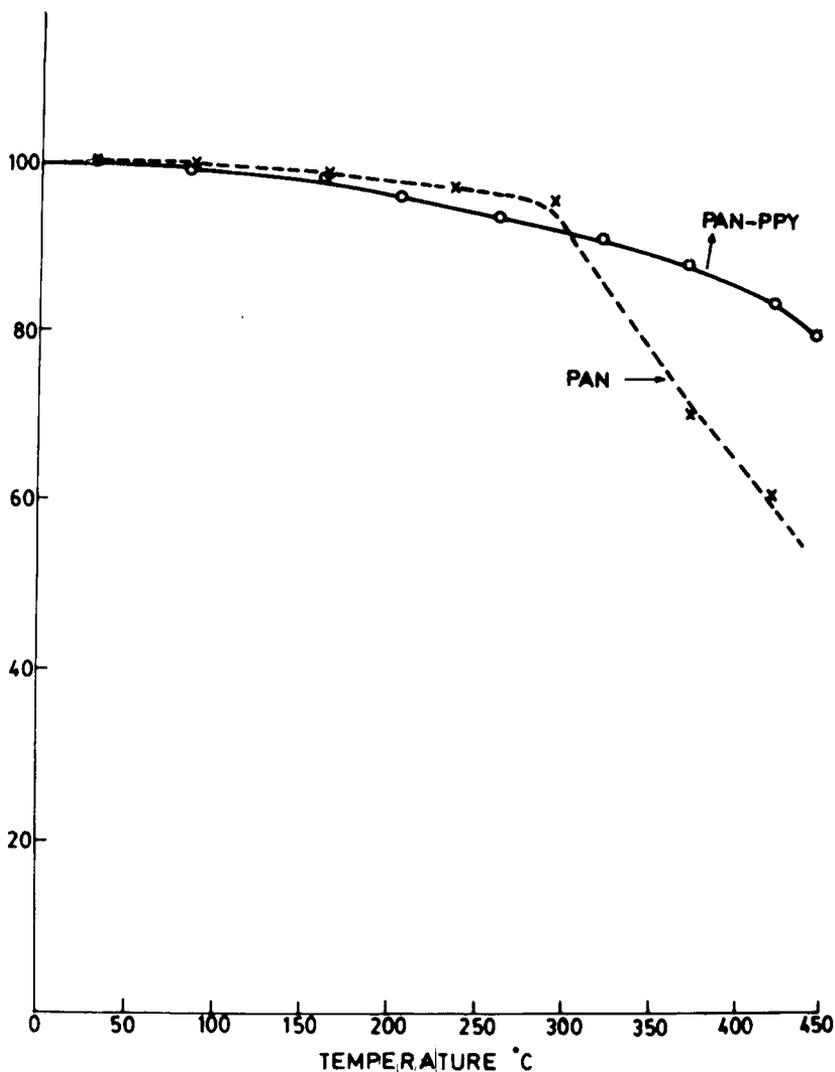


Fig. 3. TGA scans for PAN and PAN-PPy composite. Heating rate is 10°C/min.

Table II. It was observed that strength of PAN films decreases by about 25% after doping with FeCl_3 , but, on subsequent exposure to pyrrole, it increases slightly. Similarly, elongation at break of PAN decreases by about 30% on doping with FeCl_3 and, on subsequent exposure to pyrrole, it increases significantly. The surface morphology of these films was investigated. PAN and PAN- FeCl_3 films do not have any distinct surface structure. The PAN- FeCl_3 films exposed to pyrrole vapor for 1 h show uniform smooth structure. On the other hand, films exposed to pyrrole for 24 h shows rough and nonuniform surface structure.

TABLE II
Mechanical Properties of PAN and PAN-PPy Composite

Sample	Breaking strength (MPa)	Elongation (%)
PAN	16.2	15
PAN + FeCl ₃	12.16	10.5
PAN + PPy	12.9	13
Polypyrrole ^a	46.3	7

^a From Ref. 12.

References

1. K. I. Lee and H. Jopson, *Polym. Bull.*, **10**, 105 (1983).
2. O. Niwa, M. Hikita, and T. Tamamura, *Polym. Prepr. Jpn.*, **33**, 2515 (1984).
3. G. Ahlgren and B. Krische, *J. Chem. Soc. Chem. Commun.*, **14**, 946 (1984).
4. E. J. Kang, K. G. Neoh, T. C. Tan, and Y. K. Ong, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 2143 (1987).
5. Hari S. Nalwa, Larry R. Dalton, Werner F. Schmidt, and Johann G. Rabe, *Polym. Commun.*, **26**, 240 (1985).
6. M. Satmon, K. K. Kanazawa, A. F., Diaz and M. Krounbi, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 187 (1982).
7. W. Wernet, M. Monkenbusch, and G. Wegner, *Mol. Cryst. Liq. Cryst.*, **118**, 193 (1985).
8. A. F. Diaz and J. I. Castillo, *J. Chem. Soc. Chem. Commun.*, 397 (1980).
9. R. Qian and J. Qui, *Polym. J.*, **19**, 157 (1987).
10. T. Ogio and J. Miyata, *Polym. J.*, **18**, 95 (1986).
11. R. Qian and Y. Chem., *Proceedings, Plastic Conference*, Plastic and Rubber Institute, Singapore, 1986.
12. M. A. DePaoli, R. J. Waltman, A. F. Diaz, and J. Bargon, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 1687 (1985).
13. R. A. Jones and G. P. Been, *The Chemistry of Pyrroles*, Academic, San Francisco, 1977.
14. E. T. Kang, P. Ehrlich, A. P. Bhatt, and W. A. Anderson, *Macromolecules*, **17**, 1020 (1984).
15. I. K. Varma, S. Saxena, A. Tripathi, and D. S. Varma, *Polymer*, **29**, 559 (1988).

Received May 6, 1988

Accepted August 15, 1988