

Synthesis and Characterization of Polyacrylamide–Polyaniline Conductive Blends

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ABSTRACT: Conducting poly(acrylamide) films were synthesized by exposing the polyacrylamide films impregnated with ammonium peroxodisulphate, an oxidizing agent, to hydrochloric acid vapor and then to aniline vapor. The effects of varying the exposure time to aniline vapor and the resulting composite films of polyacrylamide–polyaniline were characterized by different methods. The mode of conduction has also been studied. The conductivity of the resulting composites reached up to 10^{-5} s/cm². © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 841–844, 1998

Key words: polyaniline; polyacrylamide; conductive blends; percolation percentage

INTRODUCTION

Among the conductive polymers, polyaniline (PANI) occupies a place of special interest. Aniline is a relatively cheap monomer. PANI can be easily synthesized in good yield by polymerizing aniline in protonic acid aqueous solution in the presence of an oxidant^{1–4} or electrochemically. These advantages, coupled with its chemical stability and high conductivity in the doped state, make its commercial application quite attractive.^{5–8} However, brittleness and lack of processibility are the main drawbacks hindering its better utilization. Attempts have been made to improve the poor mechanical properties and processibility of PANI by blending it with other polymers,^{9,10} or by substitution and copolymerization. Although blending of PANI with other polymers leads to a decrease of conductivity, it is conceivable that a composite with moderate conductivity and good mechanical properties can be obtained by the blending approach.^{11,12}

This article deals with synthesis of new composites of PANI with polyacrylamide (PAM) which forms the matrix of the blend. The change in conductivity of the blend system containing varying amounts of PANI have been studied in relation to its structure.

MATERIALS

Polyacrylamide (M_w 50,00000) was obtained from BDH (England). Aniline (E. Merck, Germany), ammonium peroxydisulphite (E. Merck, Germany), and hydrochloric acid (International, India) were used without further purification.

EXPERIMENTAL

Poly(acrylamide) was dissolved in water and ammonium peroxydisulphate was added and thoroughly mixed. PAM films were then cast on previously weighed glass plates and dried under vacuum at 50°C for 48 h until a constant weight. These films were exposed to HCl and then to aniline vapor and finally dried at 75°C under vacuum

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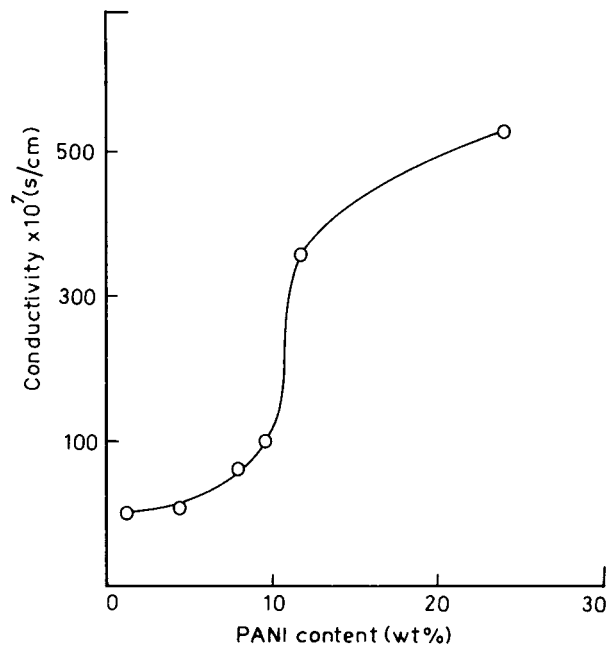


Figure 1 Plot of conductivity versus wt % of PANI.

to remove the excess aniline. The time of exposure over aniline was varied to vary the polyaniline content of the composites. The films having low percentages of polyaniline were translucent, but opacity increased with an increasing percentage of aniline.

The Fourier transform infrared (FTIR) spectra was obtained by using a FTIR spectrophotometer (Perkin-Elmer Model 1600). The thermogravimetric analysis (TGA) thermograms were obtained using a Shimadzu TGA-50 thermogravimetric analyzer.

RESULTS AND DISCUSSION

Conductivity Measurements

Conductivity measurements of the blended polymer films were performed by a Keithley electrometer (Model No. 236) ensuring that measurements were made as rapidly as possible to avoid absorption of moisture. The values of the conductivities of the blends were obtained (Fig. 1) at a fixed temperature of 27°C and a fixed potential difference of 3 V.

It was found that the conductivity of the blend system increased with an increase in percentage of polyaniline. At a certain percentage (the percolation percentage) of polyaniline, there is a sud-

den jump in conductivity, after which the increase in conductivity is not very significant. The percolation percentage for the present system was found to be 11.5%, a rather high value, which may be ascribed to poor dispersion and morphological features. Landauer¹³ treated the case of a random two-phase dispersion of a conductor in an insulating matrix. The theoretical model proposed by him predicts a sharp change in conductivity at the percolation threshold of 33%. Evidently, the present system does not conform to the Landauer model.

Figure 2 shows the temperature dependence of conductivity of the protonated PAM-PANI composite films. It was observed that the conductivity increased with the increase in temperature over a range of 90–300 K.

Figure 3 shows a plot of σ_T/σ_{RT} against $1/T^{1/4}$, where σ_T and σ_{RT} are the conductivities at a temperature T and room temperature (27°C), respectively. This behavior of the $\frac{1}{4}$ power temperature dependence of σ_T/σ_{RT} up to 270 K is consistent with the model of Mott and Davis¹⁴ of variable range hopping.

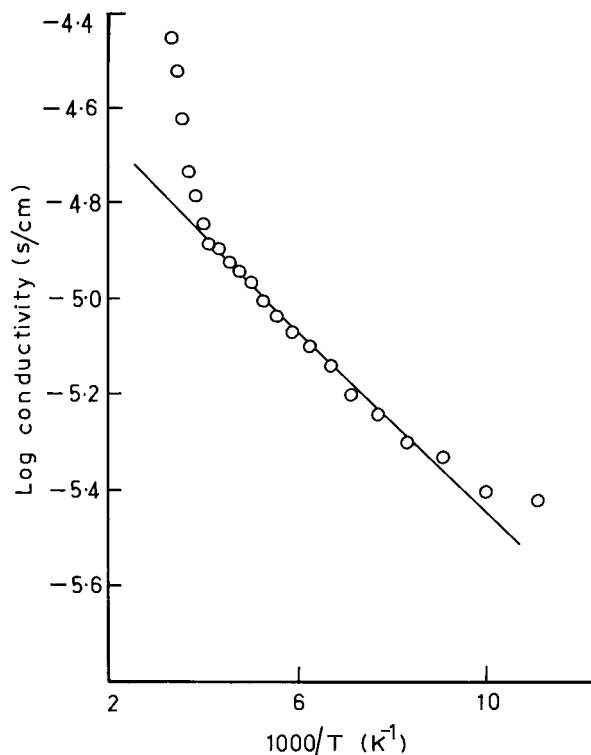


Figure 2 Plots of log conductivity versus reciprocal temperature for the PAM-PANI blend system (11.5% PANI).

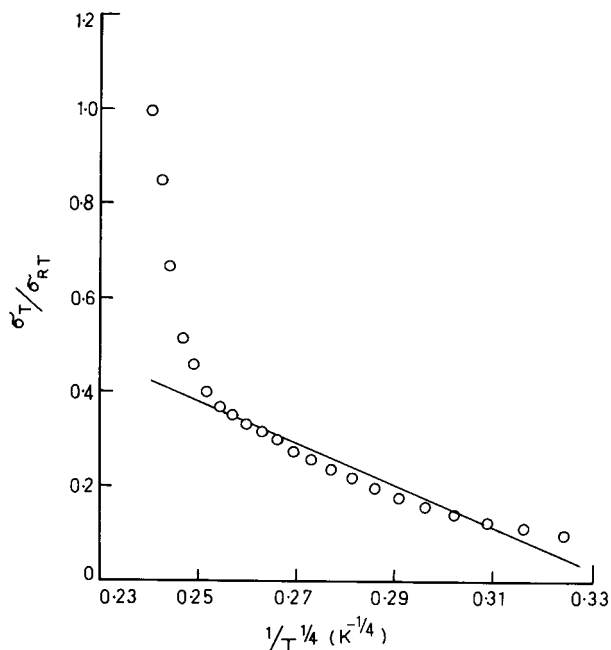


Figure 3 Plot of σ_T/σ_{RT} versus reciprocal of $1/T^{1/4}$ th power of temperature for the sample used in Figure 2.

Infrared Spectroscopy

Figure 4 represents the FTIR spectra of PAM, PANI, and PAM-PANI blend, and the significant peaks are shown in Table I. The peaks at 3437.5 and 1654 cm^{-1} in the blend system correspond to that of 3449 and 1655.2 cm^{-1} , respectively, in

PAM. The first peak is due to the amide —N—H stretching vibration. The latter peak corresponds to the —C=O stretching vibration of the amide in the solid phase. The intensity of both the bands decreased in the blend.

The peak at 2367.6 cm^{-1} in the blend corresponds to that of 2588 cm^{-1} in PANI. This is due to NH_2^+ , NH^+ stretching. The peak of PANI at 1492.4 cm^{-1} due to C=C stretching vibration in aromatic ring system shifts at 1400.7 cm^{-1} in the blend. The peak at 1294 cm^{-1} in PANI due to —C—N stretching vibration with aromatic conjugation becomes very weak in the blend.

The band at 743–682 cm^{-1} in PANI is due to the vibration of symmetrically substituted benzene. This band is absent in the blend system as the symmetrical environment of the PANI structure is lost. This indicates the presence of some interaction, presumably H-bonding, between the two polymers PAM and PANI in the blend system.

Thermal Analysis

In Figure 5, we present the thermogravimetric curves for PAM, PANI, and PAM-PANI blends. The pure PAM exhibited a process of mass loss at 260°C and another at 500°C, leaving practically no residue. PANI presents a mass loss, probably due to loss of water, at 100°C, and another at 225°C, leaving a residue of (50.9%) at 800°C. The blend presents a thermogram showing a mass loss

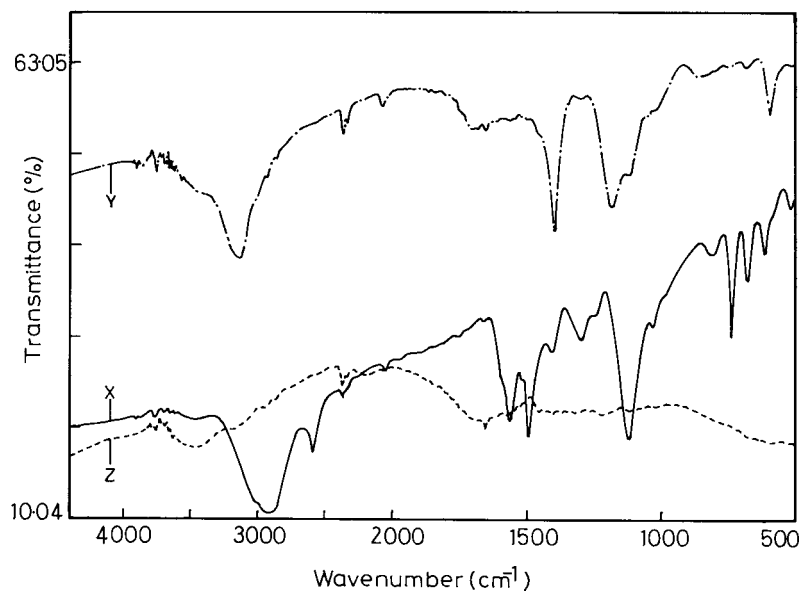


Figure 4 FTIR spectra of (X) PANI, (Y) Blend, and (Z) PAM.

Table I Characteristics Peaks (cm^{-1}) of the FTIR Spectrum (Figure 4) of PAM, PANI, and PAM-PANI Blend

PAM	PANI	PAM-PANI	Functional Group
3449		3437.5	Amide —N—H stretching vibration
	2588		NH_2^+ , NH^+ stretching
1655.2		1654	—C=O stretching of amides in the solid phase
	1492	1400.7	C—C stretching vibration
	1294		C—N stretching vibration with aromatic conjugation
	743–682		Vibration of symmetrically substituted benzene ring

Characteristic peaks (cm^{-1}) of the FTIR Spectra (Figure 4).

at 250°C and leaving a residue of (15.1%). This is presumably due to the incorporation of PANI in PAM and H-bonding between the two, leading to a higher degree of heat stability.

CONCLUSION

Conducting polymer blends can be synthesized using a nonconducting matrix PAM and blending it with PANI, after protonating the PAM films impregnated with $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The conductivity of the films is in the range 10^{-5} s/cm. The percolation percentage of PANI has also been calculated. It is also presumed that the conductivity of the film is due to the protonated PANI and the long

fibrils of PANI. The stability of conductivity to the ambient air temperature is very good.

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REFERENCES

1. M. Jozefowicz, J. H. Perichon, L. T. Yu, and R. E. Buvet, *Brit. Pat.* 1,216,569 (1970).
2. J. C. Chiang and A. G. MacDiarmid, *Synth. Met.*, **13**, 193 (1986).
3. J. P. Travers, J. Chroboczek, F. Devreux, F. Genoud, N. Nechtschein, A. Syed, E. M. Genies, and C. Tsintavis, *Mol. Cryst. Liq. Cryst.*, **121**, 195 (1985).
4. A. G. MacDiarmid, J. C. Chiang, M. Halpern, W. S. Huang, S. L. Mu, N. L. D. Somasiri, W. Wu, and S. I. Yaniger, *Mol. Cryst. Liq. Cryst.*, **121**, 173 (1985).
5. R. DeSurville, M. Jozefowicz, J. Perichon, and R. Buvet, *Electrochem. Acta*, **13**, 1451 (1968).
6. E. M. Genies, G. Pierre, C. Santier, and C. Tsintavis, *Fr. Pat.* E.N. 83,07,958 (1983).
7. T. Kobayashi, H. Yoneyama, and H. Tamura, *J. Electroanal. Chem.*, **161**, 281 (1984).
8. F. Zuo, R. P. MacCall, J. M. Ginder, M. G. Roe, J. M. Leng, A. J. Epstein, G. E. Astunias, S. P. Ermer, A. Ray, and A. G. MacDiarmid, *Synth. Met.* **29**, E445 (1989).
9. M. A. Paoli, E. A. Duek, and M. A. Rodrigues, *Synth. Met.*, **41**, 973 (1991).
10. Un Heum Park, Sang Hoon Choi, Suk Kyu Song, and Seijo Miyata, *J. Appl. Polym. Sci.*, **45**, 843 (1992).
11. Show An Chen and Woei Guwn Eang, *Macromolecules*, **24**, 1242 (1991).
12. J. Anon, *Appl. Polym. Sci.*, **51**, 1347 (1994).
13. R. Landauer, *J. Appl. Phys.*, **23**, 779 (1952).
14. N. F. Mott and E. A. Davis, *Electronic Process in Noncrystalline Materials*, 2nd ed., Clarendon, Oxford, 1979, p. 34.

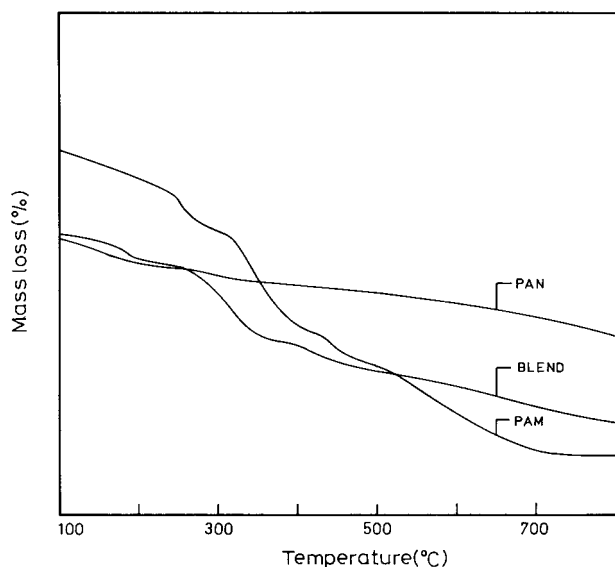


Figure 5 Thermogravimetric curves of PAM, PANI, and the Blend.