NOTES

Preparation and Characterization of Polyaniline–PVC Polymer Composite Film

INTRODUCTION

Conducting polymers have attracted considerable attention recently. Among them, polyaniline (PAn) occupies an important place because of its unique properties like ease of preparation, simplicity of the doping process, good stability, good electronic properties, and electrochromic effects.[1] However, one of the major problems associated with PAn is its poor processibility. Several methods have been reported to overcome this shortcoming. These include (a) structural modification of PAn by ring or N-substitution,[2,3] (b) electrochemical polymerization of aniline in a polymer matrix,[4,5] (c) synthesis of PAn in the presence of preformed stable colloidal particles to give a conducting polymer,[6] (d) preparation of colloidal dispersion,[7,8] and (e) blending with other polymers in a cosolvent.[9]

In this article, we have described a new method of preparation of conducting polymer composite from PAn. The undoped form of PAn was used for the preparation of PAn–PVC composite films. These films were successfully doped by diffusing gaseous hydrogen chloride into the composite.

EXPERIMENTAL

The solubility of the undoped form of PAn (i.e., the base form) is higher in a number of organic solvents than that of the doped (salt) form. Therefore, emeraldine hydrochloride was initially converted to the free-base form.

Emeraldine hydrochloride, 0.12 g, was placed in a 100 mL round-bottom flask. A 3% solution of NH_4OH was added and the suspension was stirred for 2 h. Then, it was filtered and dried under suction. A dark blue powder thus obtained was the emeraldine base.

About 0.06 g of this emeraldine base was dissolved in 12 mL of dimethylacetamide (DMAc) by vigorous shaking. The undissolved portion was removed by filtering the dark blue solution. A solution of 0.26 g of PVC powder in 8 mL

DMAC was prepared separately. The solution was then mixed thoroughly and a film was cast on a smooth glass plate. The solvent from the cast film was evaporated by keeping it in an oven at 80°C and then the film was removed carefully. A thin transparent bluish film was thus obtained. This film has been designated as sample I and it contained 18% PAn. A thicker film containing 28% PAn was designated as sample II and was prepared by the same method. The doping of the PAn, which is present in the film in the form of its emeraldine base, was accomplished using hydrogen chloride gas. The film, which was blue in color, turned green after the HCl treatment.

Thermal characterization was done using a DuPont 1090 thermal analyzer having a 951 TG module. The electrical conductivity was measured by a two-probe method using a Keithley 610C electrometer and a regulated power supply (Aplab 7332).

RESULTS AND DISCUSSION

Figure 1 shows the TG traces of doped PAn and the PAn–PVC composite film. No weight loss was observed up to 260°C in the case of the composite film. This is in contrast to the pure PAn sample where some weight loss was observed in this range. The observed difference in weight loss may be purely a diffusion-controlled phenomena whereby HCl is not volatalized easily from the PVC matrix. This gives high-temperature conductive properties to the composites, e.g., the conductivity of the PAn–PVC composite films does not change even at 150°C, unlike pure PAn, whose conductivity changes irreversibly above 100°C.

The dependence of electrical conductivity on temperature is given by

$$\sigma = \sigma_0 \exp(-A/kT)$$

where A is the activation energy, and k, the Boltzmann constant. The variation of log σ with inverse of temperature for samples I and II are shown in Figure 2. These
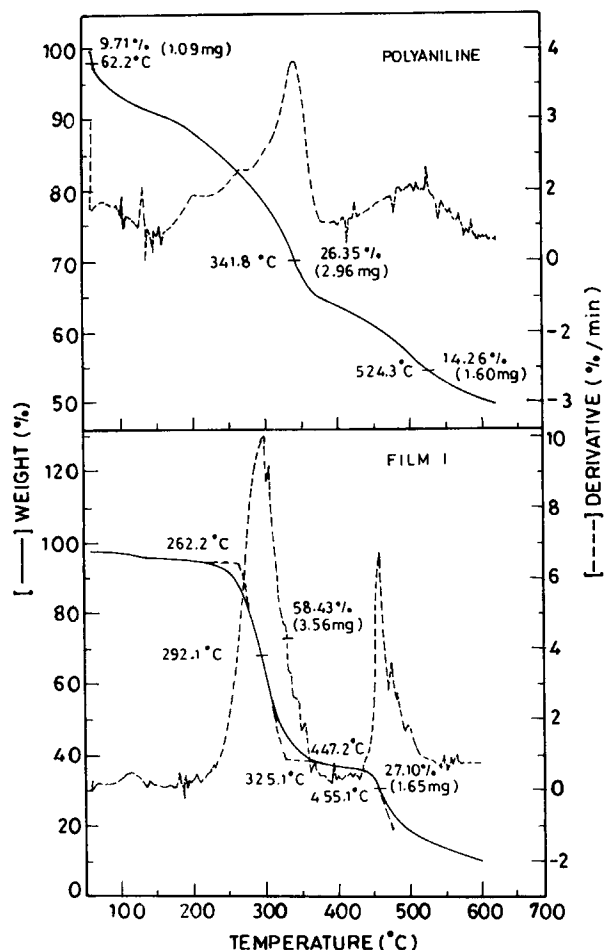
1347

Figure 1 TG traces of doped PAn and doped PAn/PVC composite (film I).

curves indicate two different slopes in the lower- and higher-temperature regions. The transition takes place at about 70°C, which corresponds to the T_g of the matrix, i.e., PVC. The two slopes indicate that the energy associated with the conduction process is not the same in the temperature ranges studied. The activation energies, calculated from these plots, are given in Table I.

These values are comparable to those reported for the nylon 6–PAn composite.[10] This type of change in activation energy with temperature is common in polymers irrespective of the nature of charge carriers (electronic or ionic). But, in case of ionic conduction, the activation energies are large. However, in our case, a low activation energy was noticed at lower temperatures, i.e., below T_g; this suggests that electronic conduction dominates at lower temperatures. Studies are in progress to establish the conduction mechanism at higher temperatures in the film.

CONCLUSIONS

A thin, transparent PAn/PVC composite film was successfully developed. This was obtained by a solution-blending technique using DMAc as a solvent. The doping was carried out by gaseous HCl. The conductivity was measured as a function of temperature and activation energy was calculated. Activation energy is found to be low in the low-temperature region up to 70°C and, subsequently, it increases.

The conductivity of these films does not change irreversibly even at 150°C, unlike pure PAn, whose conductivity decreases irreversibly even at 100°C. This conducting composite film may be used in applications like electromagnetic interference shields, packaging materials for
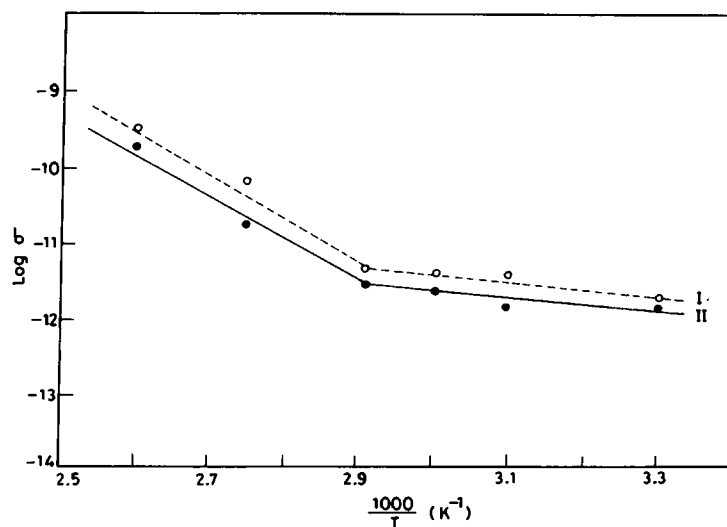

Figure 2 Plot of log σ vs. $1000/T$ for PAn/PVC films (I and II).

Table I   Activation Energy of PAn/PVC Composite

| Sample | Activation Energy (eV) in the Temperature Range | |
	30–70°C	70–125°C
I	0.0861	0.502
II	0.0662	0.469

sensitive electronic equipment, electrochromic devices, and rechargeable batteries.

References

1. W. Salamedi, I. Lundstrom, W. S. Huang, and A. G. Mac Diarmid, *Synth. Met.*, **13**, 291 (1986).
2. J. Yue and A. J. Epstein, *J. Am. Chem. Soc.*, **112**, 2800 (1990).
3. L. Wang and F. Wang, *Polym. Commun.*, **30**, 123 (1989).
4. S. A. Chen and W. G. Fang, *Macromolecules*, **24**, 1242 (1991).
5. G. Bidan and B. Ehui, *J. Chem. Soc. Chem. Commun.*, 1568 (1989).
6. P. Beadle, S. P. Armer, G. Gottesfeld, C. Mombour-guette, and S. F. Agnew, *Macromolecules*, **25**, 2526 (1992).
7. S. P. Armer and M. J. Aldirsi, *J. Chem. Soc. Chem. Commun.*, 88 (1989).
8. B. Vincent and J. Waterson, *J. Chem. Soc. Chem. Commun.*, 683 (1990).
9. A. Andreatta and A. J. Heager, *Polym. Commun.*, **31**, 275 (1990).
10. Y. H. Park, *J. Polym. Sci. Polym. Chem. Ed.*, **40**, 846 (1992).

M. Thangarathinavelu
A. K. Tripathi
T. C. Goel
I. K. Varma*
Centre for Materials Science and Technology,
Indian Institute of Technology, Delhi,
New Delhi 110016, India

* To whom correspondence should be addressed.