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ELECTRICALLY CONDUCTIVE INTERPENETRATING NETWORK COMPOSITES OF POLYANILINE AND CARBOXYMETHYLCELLULOSE

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Abstract—Conductive polyaniline composite films formed by chemical oxidative polymerization of aniline inside carboxymethylcellulose matrix films have been studied. The composite shows extremely low percolation threshold ($f_c \approx 1.12 \times 10^{-3}$). The UV-visible absorption spectra of the composite materials are affected by acid/base treatment in the same manner as pure polyaniline. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The principal problem encountered with the potential utilization of conducting polymers is their poor processability and environmental stability. Incorporating plastics or rubber with conducting polymer is an attractive route for improving processability without losing mechanical properties. In the literature, several works have been reported on the preparation of interpenetrating composites of polyaniline (PANI) with several matrix polymers e.g. with poly(methyl methacrylate) [1], Naffion [2, 3], Nylon6 [4–6], poly(ethylene imine) [7], poly(vinyl alcohol) [8], nitrile rubber [9] etc. Both electrochemical and chemical methods of polymerization have been used. The former uses a working electrode coated with the matrix polymer. The conducting polymer grows from the electrode surface, and gradually pervades the coated film, which gets swollen by solvents containing dopant anions as electrolytes. In the chemical method an oxidizing agent is incorporated into a polymer film. The film is then exposed either to the monomer vapor [5] or to a solution of the monomer in the appropriate liquid [8].

Interactions between the two blended polymers can greatly influence the conductivity and physical properties of the films. In terms of percolation theory, at sufficiently low concentration where there is no connected path, the conductivity is very small. As the concentration of the conducting polymer (CP) is increased, the conductivity shows a sharp increase at a certain concentration of CP. This concentration is called the percolation threshold. At further higher concentration, conductivity increases slowly. Classical percolation theory for conducting polymer globular aggregates in an insulating medium predicts a percolation threshold at a volume fraction of 0.16 [10]. For rod like structures the percolation threshold depends on the excluded volume per fibril and the former can be lower than the value for globular morphologies [11, 12].

The present work reports the results of a study on interpenetrating composites of PANI using carboxymethyl-cellulose (CMC) as the matrix polymer. The composites were prepared by polymerizing aniline oxidatively inside the matrix polymer which was embedded with $K_2Cr_2O_7$ oxidant. The composites are found to have very low percolation thresholds.

EXPERIMENTAL SECTION

Aniline (E. Merck, India) was distilled under vacuum over zinc granules before use and stored under Argon atmosphere at −10°C. Water was distilled over alkaline $KMnO_4$. Potassium dichromate (E. Merck) and hydrochloric acid (E. Merck) and carboxymethylcellulose (CMC) (BDH, England) were used as received.

Apparatus

Standard four-probe conductivity measurements were done at room temperature using a Keithley (model 220) constant d.c. source and a Keithley (model 181) nanovoltmeter. UV-visible spectra of the films were recorded using a Shimadzu UV-2100 UV-visible spectrophotometer. Conducting polymer in the matrix was determined from the nitrogen content estimated by a semimicro Kjeldahl technique [13]. The Cl content was estimated by burning the samples in an oxygen flask (Heraeus, Germany) followed by absorption of gases and titration according to the standard method [14].

Polymerization

In a typical reaction 5% aqueous solution of CMC was mixed with varying amounts of potassium dichromate. Films were cast from the admixture in polyethylene petridishes and allowed to dry for 3–4 days at room temperature. The resulting orange yellow transparent films were then dipped into an aqueous solution of 0.1 M aniline and 1.2 M HCl. Aniline that diffused into the films was polymerized to PANI. Within a few minutes the color of the films changed from blue to deep green which grew deeper as the reaction proceeded further for 4 h. The IPN composite films were then dipped into aqueous 1.2 M HCl solution for one day to remove excess oxidant and dried under vacuum at room temperature for 48 h. The PANI content was determined by nitrogen analysis.

RESULTS AND DISCUSSION

During the preparation of the composite film the concentration of aniline used was such that no polymerization occurred inside the solution. All polymerization occurs inside the matrix films of aniline monomer that diffused into the oxidant embedded matrix. The as formed PANI contains Cl, signifying the presence of Cl^- as dopant anions. The Cl/N atom ratio is ≈ 0.5 in all cases which indicates that the PANI is in the half-oxidized emeraldine salt state.

The conductivity of the films was measured on both sides in all cases and the resulting conductivity values were taken as average of the respective both side values. For each film the conductivity value of both sides was of the same order of magnitude. The composite film thicknesses were in between 0.5 μm to 1 μm. The same conductivity data on both sides implies that the composition of each film is the same through out the film.

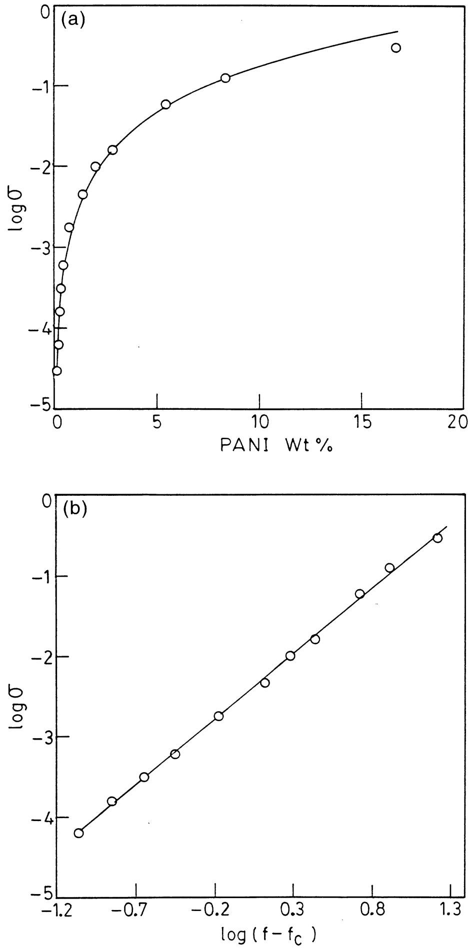

Fig. 1. (a) Plot of log electrical conductivity vs PANI concentration in PANI/CMC composite films, (b) Plot of log (conductivity) vs log $(f - f_c)$.

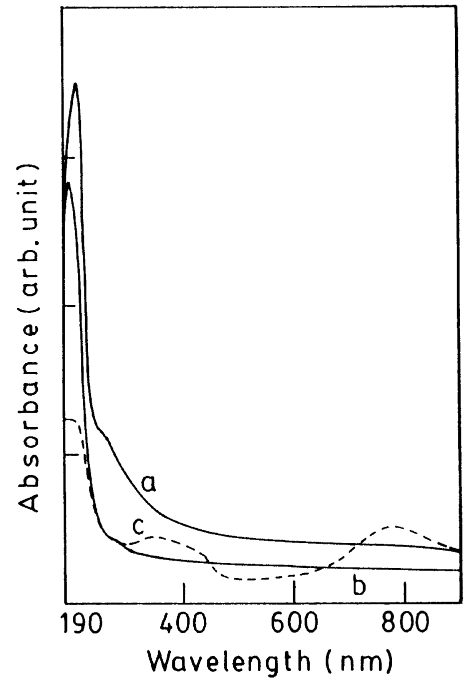

Fig. 2. UV-vis spectra of (a) CMC film, (b) $K_2Cr_2O_7$ embedded CMC acid washed film and (c) freshly made PANI/CMC film.

Figure 1(a) shows the variation of conductivity with PANI concentration. Figure 1(b) shows the fitting of the conductivity vs composition data to the scaling law of percolation theory

$$\sigma(f) = c(f - f_c)^t \qquad (1)$$

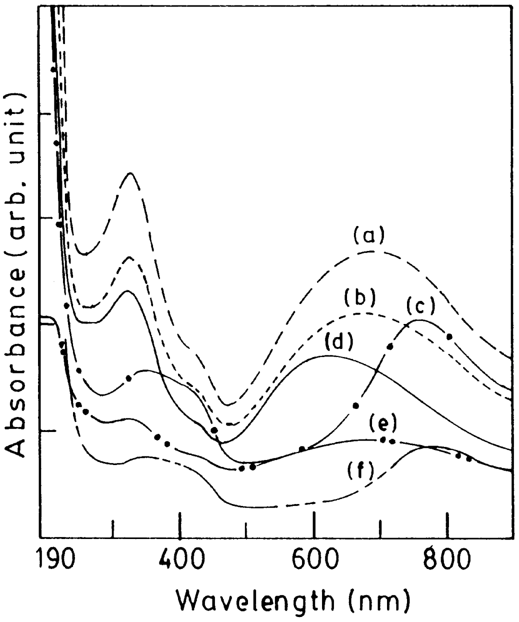

Fig. 3. UV-vis spectra of PANI/CMC film at pH 1.5 (f), pH 1.99 (c), pH 3.70 (a), pH 4.98 (e), pH 5.93 (b) and pH 6.5 (d).

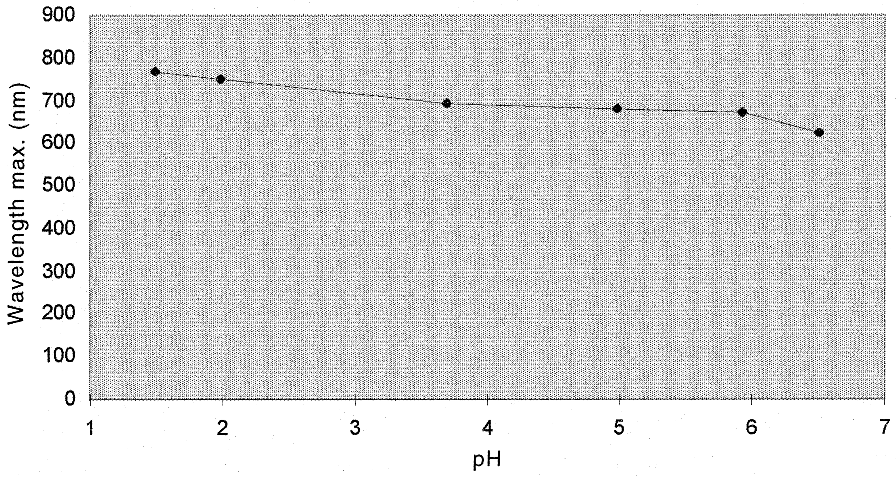

Fig. 4. Relationship between the wavelength maximum of the broad peaks vs pH.

where $\sigma(f)$ is the experimentally obtained conductivity measured at room temperature, c is a constant, t is the critical exponent and f is the volume fraction of filler particles. The method yields a value of percolation threshold (f_c) which is exceptionally low $\approx 1.12 \times 10^{-3}$ and $t \approx 1.63$. These values are much lower than the theoretically predicted value of $f_c \approx 0.16$ for spherical conducting particles dispersed in a nonconducting matrix in three dimensions [10]. Earlier, Makhlouki *et al.* [15] reported similar low percolation threshold (PVA/PPy molar ratio of 5.3×10^{-3}) for PPy–PVA composite Rubner *et al.* [16] reported a low f_c ($=0.028$) and $t = 3.2$ for semi-IPN composite of poly(3-octyl thiophene)–polystyrene. For most of the composites a value of $t \approx 2$ has been reported [17–26]. Also for polyaniline blends, which have exhibited extremely low f_c due to self-assembly of PANI molecules or nanoparticles, a value of $t \approx 2$ has also been reported [17, 25, 26]. Fernandez *et al.* [27, 28] have attributed low f_c (≈ 0.1) to the better dispersion of PPy in the matrix caused by hydrogen bonding. But no such hydrogen bonding is present in the present system although it shows a very low value of f_c. The low f_c may be explained as follows. Bargon *et al.* [29] explained that the polymer matrix swells under the action of solvents resulting in the dendritic formation of solvent channels into which monomer diffuses. Polymer formed in these solvent channels retains the tree-like structure of the solvent channels. This type of growth allows percolation threshold to reach earlier than in the case of isotropic growth.

The UV-visible absorption spectra of freshly made films of PANI/CMC, CMC and $K_2Cr_2O_7$ embedded CMC acid washed films are shown in Fig. 2. CMC is an excellent matrix material for optical studies as it does not absorb in the visible region, but exhibits a sharp cut off at 215 nm (CMC film) and 202 nm ($K_2Cr_2O_7$ embedded CMC acid washed film). The spectra of the composite films is qualitatively similar to the spectra of the emeraldine salt form of PANI which have been reported previously [30–32].

The change in the optical response of these films with pH is shown in Fig. 3. To obtain these spectra PANI/CMC films were treated as follows. First, they were dipped into 0.1 mol dm^{-3} KOH solution. The solution was stirred for about 10 min thereby converting the emeraldine salt form to the emeraldine base form. The composite films were then soaked for 24 h in solutions of different pH (over the range of pH 1–7) which were prepared by adjusting the pH (KCl + HCl), using dilute HCl, thereby converting a fraction of the base form back to the salt form. The films were then removed from solution, blotted dry and UV-vis spectra were recorded using air as a reference.

It can be seen from examination of Fig. 3 that the short wave length peak shifts about 20 nm and the trough at 435 nm shifts about 40 nm over the pH range whereas the more dramatic pH effect, i.e. a shift of about 160 nm of the 784 nm peak (approximately 25 nm/pH) occurs over the pH range 1.5–8.5. The shift of this broad transition is primarily responsible for the observed color change of the film (blue to green) associated with changing pH. The maximum absorption wavelength of this transition obeys a nearly linear relation with pH (Fig. 4).

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REFERENCES

1. Lacroix, J. C. and Diaz, A. F., *Makromol. Chem. Macromol. Symp.*, 1987, **8,** 17.
2. Orata, D. and Buttry, D. A., *J. Electroanal. Chem.*, 1988, **257,** 71.
3. Bidan, G. and Ehui, B., *J. Chem. Soc. Chem. Commun.*, 1989, 1588.
4. Gregory, R. V., Kimbrell, W. C. and Kuhn, H. H., *Synth. Met.*, 1989, **28,** C823.
5. Park, Y. H., Choi, S. H., Song, S. K. and Miyata, S., *J. Appl. Polym. Sci.*, 1992, **45,** 843.
6. Byun, S. W. and Im, S. S., *Synth. Met.*, 1995, **69,** 219.

7. Akhtar, M., Weakliem, H. A., Paiste, R. M. and Gaugham, G., *Synth. Met.*, 1988, **26,** 203.
8. Chen, S. A. and Fang, W. G., *Macromolecules*, 1991, **24,** 1242.
9. Tassi, E. L. and De-Paoli, M. A., *Polymer*, 1992, **33,** 2427.
10. Zallen, R., *The Physics of Amorphous Solids*. John Wiley, New York, 1983, Ch. 4.
11. Andreatta, A., Heeger, A. J. and Smith, P., *Polym. Commun.*, 1990, **31,** 275.
12. Balberg, I., Anderson, C. H., Alexander, S. and Wagner, N., *Phys. Rev. B.*, 1984, **30,** 3933.
13. Cole, J. O. and Parks, C. R., *Ind. Eng. Chem.*, 1946, **18,** 61.
14. Dirscherl, A., *Mikrochim. Acta*, 1968, 316.
15. Makhlouki, M., Morsli, M., Bonnet, A., Conan, A., Pron, A. and Lefrant, S., *J. Appl. Polym. Sci.*, 1992, **44,** 443.
16. Wang, Y. and Rubner, M. F., *Macromolecules*, 1992, **25,** 3284.
17. Reghu, M., Yoon, C. O., Yang, C. Y., Moses, D., Cao, Y. and Heeger, A. J., *Macromolecules*, 1993, **26,** 7245.
18. Fiazzi, A., Moulton, J., Pakbaz, K., Rughooputh, S. D. D. V., Smith, P. and Heeger, A. J., *Phys. Rev. Lett.*, 1990, **64,** 2180.
19. Hotta, S., Rughooputh, S. D. D. V. and Heeger, A. J., *Synth. Met.*, 1987, **22,** 79.
20. Michels, M. A. J., Brokken-Zijp, J. C. M., Groenewoud, M. M. and Knoester, A., *Physica A.*, 1989, **157,** 529.
21. Song, Y., Noh, T. W., Lee, S. I. and Gaines, J. R., *Phys. Rev. B.*, 1986, **33,** 904.
22. Balberg, I. and Bozowski, S., *Solid State Commun.*, 1982, **44,** 551.
23. Medalia, A. I., *Rubber Chem. Tech.*, 1986, **59,** 433.
24. Benguigui, L., Narkis, M. and Yacubowich, J., *J. Polym. Sci. B.*, 1987, **25,** 127.
25. Banerjee, P. and Mandal, B. M., *Macromolecules*, 1995, **28,** 3940.
26. Banerjee, P. and Mandal, B. M., *Synth. Met.*, 1995, **74,** 267.
27. Wang, H. L., Toppare, L. and Fernandez, J. E., *Macromolecules*, 1990, **23,** 1053.
28. Wang, H. L. and Fernandez, J. E., *Macromolecules*, 1992, **25,** 6179.
29. Bargon, J., Zimmermann, A. and Rowekamp, M., *Mater. Sci. Forum*, 1989, **42,** 233.
30. Salanek, W. R., Liedberg, B., Inganas, O., Erlandsson, R., Lundstrom, I., MacDiarmid, A. G., Halpernn, M. and Somasiri, N. L. D., *Mol. Cryst. Liq. Cryst.*, 1985, **121,** 191.
31. Wudl, F., Angus, R. O., Lu, F. L., Allemand, D. M., Vachon, D. J., Nowak, M., Liu, Z. X. and Heeger, A. J., *J. Am. Chem. Soc.*, 1987, **109,** 3677.
32. Li, Y., Yan, B., Yang, J., Cao, Y. and Qian, R., *Synth. Met.*, 1988, **25,** 79.