

Freestanding conducting polyaniline film for the control of electromagnetic radiations

K.K. Satheesh Kumar, S. Geetha, D.C. Trivedi *

Centre for Studies in Conducting Polymers, Electrochemical Materials Science Division, Central Electrochemical Research Institute, Karaikudi 630 006, Tamilnadu, India

Received 20 February 2004; received in revised form 24 June 2004

Available online 7 October 2004

Abstract

Electromagnetic interference is pollution generated due to dense nature of circuitry in electronic devices and is required to be control at its source. Polyaniline is an environmentally stable conducting polymer which can be cast as thin film, which can replace the corrosive metals as a shield for the control of electromagnetic radiations. In this communication we discuss our results on the preparation of flexible freestanding conducting polyaniline film of varied thickness using either *p*-toluenesulphonic acid (PTSA) or camphor-10-sulphonic acid as a primary dopant and 4-chloro-3-methyl phenol (CMC) as a secondary dopant. The resulting films were characterized by conductivity, scanning electron micrograph and shielding effectiveness measurements (SE). The SE measurements were carried out using co-axial transmission line method in the frequency range of 0.1–1000 MHz. We noticed that only the change of 2% in the shielding effectiveness of these films over the period of 3 years indicating the environmental stability of polyaniline films.

© 2004 Elsevier B.V. All rights reserved.

PACS: 71.20; 71.38

Keywords: Conducting polymers; Polyaniline; Flexible film; Electromagnetic interference; Shielding effectiveness

1. Introduction

Electromagnetic interference (EMI) is the electromagnetic radiation emitted by electrical and electronic equipments. This interference has increased by many folds due to increasing complexity of electronic devices and higher packing density [1]. The compatibility of a component function in close proximity of another component is known as electromagnetic compatibility (EMC). If these twin problems of EMI and EMC are left

unattended can cause severe damage to communication system and safety operation of many devices.

To prevent malfunctioning, electronic devices must be shielded in such a way that both incoming and outgoing interferences are filtered away. Shielding has the effect of both reducing undesirable emissions and protecting delicate components from possible interference due to stray external signals. In the past, metal shrouds were conveniently used in many occasions for EMI shielding. When laptop and notebook computers are designed, internal metal shrouds are disadvantageous in weight consideration. They demand low-cost, low-weight, high-strength, and easily fabricable plastics that can withstand both processing and end use environments. At present the EMI is controlled by using various types of conducting composites having conductive fillers such as metal fibres, metal particulates, carbon black and graphite fibre [2,3].

* Corresponding author. Tel.: +91 4565 227775; fax: +91 4565 227779/227713.

E-mail address: trivedi_dc@rediffmail.com (D.C. Trivedi).

The EMI shield is a barrier placed between an emitter and a susceptor that diminishes the strength of the interference. How best this shield attenuates the electromagnetic field is referred to as shielding effectiveness (SE) and is measured in decibel (dB). The losses in field strength from a shielding barrier are a function of the barrier material (permeability, conductivity and thickness), frequency and distance from the EMI source to the shield.

Conducting polymers are the organic conjugated materials which exhibit electronic conductivity and are non-corrosive, light weight material whose electronic conductivity can be tailored for most suitable material to replace corrosive metals and carbon to control electromagnetic radiations. Polyaniline (PAn) is an amorphous powdery material and is categorized as an intractable polymer with poor mechanical properties. A number of investigations have shown that using functionalized dopant it is possible to obtain a homogeneous dispersion [4–12]. Recently it has been reported that PAn can yield a freestanding film from solvents like xylene and chloroform in presence of *m*-cresol and D,L-camphorsulphonic acid or dodecylbenzenesulphonic acid as dopants with conductivities in the range of 100–400 S/cm [13]. The value is approximately two orders of magnitude larger than that of (non-oriented) PAn films obtained from NMP solution doped with aqueous HCl [14]. The influence of *m*-cresol on conductivity of PAn is known as a secondary doping, which in presence of a primary dopant enhances the conductivity of the system but can not induce any conductivity on its own.

Secondary doping concept is one of the most simple and interesting methods to induce changes in physico-chemical properties of PAn via the formation of ternary system. Phenomenologically, a primary dopant for a conducting polymer is an ion, whose relatively small amount drastically alters the electronic, optical, magnetic, morphology and structural properties of the polymer and is accompanied by a large increase in electronic conductivity. Dedoping results in a reversal of the newly induced properties. Phenomenologically, a secondary dopant is an “inert substance” which when is added to a primary doped polymer, induces further changes in the aforesaid properties. It differs from a primary dopant in that the newly enhanced properties may persist even upon complete removal of the secondary dopant. This effect of secondary doping is due to change that occurs at molecular level. Thus PAn molecular conformation changes from ‘coiled’ to ‘uncoil’. Attainment of the uncoiled state i.e. expanded molecular conformation acts to reduce-conjugation defects arises out of ring twisting in the polymer backbone. The opening up of the coil tends to promote the linear conformation necessary for crystalline structure thus increasing the crystallinity of the polymer [15–17]. Recently, a new

protonating agent 1,2-benzenedicarboxylic acid, 4-sulpho, 1,2-di (2-ethylhexyl) ester [DEHEPSA] for PAn has been reported [18] that combined doping and plasticizing properties.

Makela et al. [19,20] measured the electromagnetic interference shielding efficiency for a two-layered structure of electrically conducting PAn-camphor sulphonic acid. The polymer is spin coated from *m*-cresol solution on an electrically insulating substrate as a 1–30 μm thick layer having a conductivity of 10–100 S/cm and the shielding effectiveness have been measured in the near-field with a dual-chamber box and in the far-field with a transmission line method. The SE was found to be 39 dB.

In this communication we present our results on EMI shielding of flexible free standing conducting PAn film of thickness 0.05, 0.3 and 0.6 mm obtained by using *p*-toluenesulphonic acid (PTSA) and camphor-10-sulphonic acid (CSA) as a primary dopant and 4-chloro-3-methyl phenol (CMC) as a secondary dopant by solution casting. We observed that film of thickness more than 0.3 mm cracks at the surface. The thicker film of 0.6 mm was prepared by pasting 0.3 mm films using the casting solution.

2. Experimental

All the chemicals used were of AnalaR grade. Aniline was freshly distilled before use. Distilled water was employed.

Polyaniline powder was synthesized chemically by oxidative polymerization of aniline in an aqueous HCl solution [4]. Aniline (0.1 M) was dissolved in 1 M aqueous solution of HCl below 5°C and an aqueous solution of ammonium peroxydisulphate (0.1 M), was added to the above solution over a period of 30 min with vigorous stirring. The mixture was stirred continuously for 2 h. The precipitate was collected by filtration and then washed repeatedly with distilled water. Polyaniline base was obtained when the polyaniline was treated with aqueous solution of ammonia (pH \sim 9) under stirring for 6–8 h and washed with distilled water till washings were neutral to a pH indicator paper. The blue emeraldine base powder, obtained after filtration, was purified by refluxing with methyl alcohol, benzene and acetone. This process of treatment with organic solvents was repeatedly done till the filtrate was colorless. Finally, the blue emeraldine base obtained was dried under dynamic vacuum at 60–80°C for 8 h. This emeraldine base is the starting material for the preparation of flexible and freestanding conducting PAn film.

PAn–CSA/CMC film was prepared by mixing 1 g (3 mmol) emeraldine base powder, 1.32 g (6 mmol) camphor-10-sulphonic and 2 g (14 mmol) CMC are ground thoroughly in a homogeniser in presence of any one of

the solvents such as benzene, chloroform, toluene or xylene for 1–2h. The thick solution obtained was casted and cured for 12h under ambient condition. This on drying under dynamic vacuum at 50–70°C for 4h yielded a flexible freestanding film. The thickness obtained by this method was 0.05 and 0.3mm.

Similarly, PAN–PTSA/CMC film was prepared by mixing 1g (3mmol) emeraldine base powder, 1.045g (5mmol) *p*-toluenesulphonic acid and 4.09g (28mmol) CMC are ground thoroughly in a homogeniser in presence of any one of the solvents such as benzene, chloroform, toluene or xylene for 1–2h. The thick solution obtained was casted and cured for 12h under ambient condition. This on drying under dynamic vacuum at 50–70°C for 4h yielded a flexible freestanding film. The thickness obtained by this method was 0.05 and 0.3mm.

Various methods are available for the measurement of shielding effectiveness (EMI SE). Among these methods co-axial transmission line method is most preferred because results from various laboratories are comparable. Tests were carried out on a small torus shaped cell. The round coupon of the sample of internal dia. 43mm and outer dia of 120mm was cut and silver ink was applied on the periphery of the sample to reduce the contact resistance between sample and a holder to 0.2Ωcm. The measurements were made at specific frequencies using a signal generator 8642 B (Hewlett Packard) and field intensity meters (NM17/27A for 0.01–32MHz and NM37/57A for 30–1000MHz) with point-by-point method with and without specimen. SEM studies were carried out after gold sputtering on the freestanding film. The scanning electron micrographs were recorded using Hitachi S-3000H. All SEM studies on freestanding film of conducting PAN were carried out after removal of solvent and excess of secondary dopant by heating at 60–70°C under dynamic vacuum for at least 4h. The thickness of the flexible and freestanding conducting polyaniline films was measured by using magnetic coating thickness gauge (MIKRO TESTER 1V, Model No. F171/100). The conductivity of the flexible and freestanding films was measured by four-probe method (Model No. DFP-02).

3. Results and discussion

Hitherto thick conducting PAN films of 0.05, 0.3 and 0.6mm have not been reported. The maximum thickness reported till now is not more than 30μm. Though these films exhibit high conductivity for a practical application for use as shielding material, slightly thicker films are required in view of all practical difficulties arising out of handling at large scale. We believe that film formation property in PAN in presence of primary dopant in combination with secondary dopant uncoils the structure to an extended structure to yield a material, which has film formation property. This effect depends upon the ratio of emeraldine base, primary dopant and secondary dopant. This ratio is not constant and essentially is the function of an orientation, functionality and electronegativity of the primary dopants. We have failed to observe any film formation property when unfunctionalized dopants like hydrochloric acid, acetic acid, sulphuric acid and organic acids like sulphamic and 5-sulphosalicylic acid. The interaction of a primary dopant with secondary dopant in presence of PAN gives rise to meta-para type of interaction in a ternary system. This type of meta-para interaction gives the two dimensional structure going towards three-dimensional network, which stabilizes PAN molecular moieties in a chain structure to yield a freestanding film. Basically PAN has a pseudo-one-dimensional structure and is amorphous.

The micrograph of the PAN–PTSA/CMC film shows the crystallite structure. The maximum size of a crystallite is around 5μm and smallest is 1μm embedded between large size crystallites of various shapes and PAN–CSA/CMC film shows fibrillar morphology having fibril width of around 0.5μm running to the full length of the structure. These fibrils form a well-knitted network and the micrographs are shown in Fig. 1.

The conductivity of as obtained 0.05 and 0.3mm films and 0.6mm film by pasting were measured by four-probe technique [21]. The method developed by Van der pauw for measuring the conductivity was used, by using the formula as given in Eq. (1):

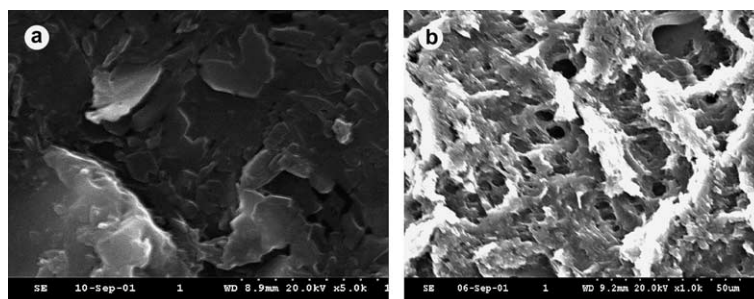


Fig. 1. SEM micrograph of freestanding. (a) PAN–PTSA/CMC. (b) PAN–CSA/CMC film.

Table 1
EMI SE studies on freestanding conducting PAN–PTSA/CMC film

Sample (thickness, mm)	Conductivity (S/cm)	SE (dB) at				
		0.1 MHz	1 MHz	10 MHz	100 MHz	1000 MHz
PAN–PTSA/CMC film (0.05)	0.2	22	17	16	16	21
PAN–PTSA/CMC film (0.3)	2.2	31	33	34	34	39
PAN–PTSA/CMC film (0.6)	10	33	37	39	37	45

Table 2
EMI SE studies on freestanding conducting PAN–CSA/CMC film

Sample (thickness, mm)	Conductivity (S/cm)	SE (dB) at				
		0.1 MHz	1 MHz	10 MHz	100 MHz	1000 MHz
PAN–CSA/CMC film (0.05)	0.04	18	15	10	10	10
PAN–CSA/CMC film (0.3)	0.1	22	17	16	15	14
PAN–CSA/CMC film (0.6)	0.3	17	18	18	16	19

$$\sigma = \ln 2 / \pi d x i / v, \quad (1)$$

d is the sample thickness.

The conductivity of the film obtained by using CSA and PTSA as a primary dopant and CMC as a secondary dopant measured using Eq. (1) are tabulated in Tables 1 and 2.

The shielding effectiveness (SE) for EMI control is largely a function of conductivity of the material. Materials having a resistivity below $10 \Omega\text{cm}$ are suitable as a shield for electromagnetic interference (EMI) while higher resistivity materials are suitable for anti-static applications. Thus, EMI shielding effectiveness (EMI SE) is described as the attenuation of an electromagnetic

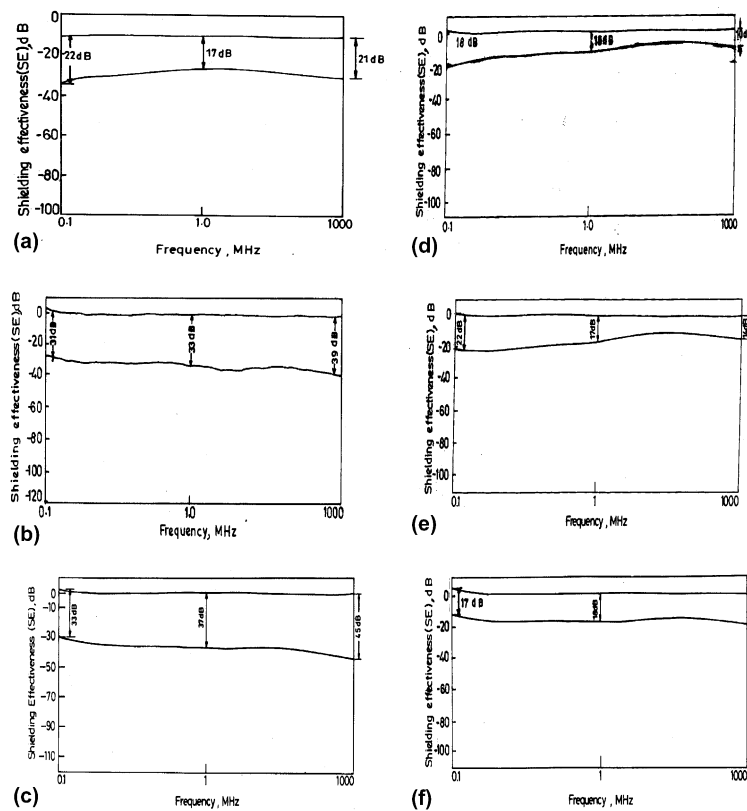


Fig. 2. EMI SE curves of freestanding. (a) PAN–PTSA/CMC film ($t = 0.05$ mm), (b) PAN–PTSA/CMC film ($t = 0.3$ mm), (c) PAN–PTSA/CMC film ($t = 0.6$ mm), (d) PAN–CSA/CMC film ($t = 0.05$ mm), (e) PAN–CSA/CMC film ($t = 0.3$ mm) and (f) PAN–CSA/CMC film ($t = 0.6$ mm).

wave produced by its passage through a shield and is measured as the ratio of the shield strength before and after attenuation and is expressed in decibel, dB calculated according to the following Eq. (2) [22].

$$SE = 20 \log E_i/E_t, \quad (2)$$

where SE is the Shielding Effectiveness, E_i is the incident electrical field strength in Vm^{-1} (before attenuation), E_t is the transmitted electrical field strength in Vm^{-1} (after attenuation).

The EMI SE curves of freestanding PAN–PTSA/CMC film and PAN–CSA/CMC film measured by co-axial transmission line method in the frequency range of 0.1–1000 MHz are shown in Fig. 2 and the EMI SE results are recorded in Tables 1 and 2.

The perusal of Tables 1 and 2 reveals that the shielding effectiveness on freestanding film of PAN–PTSA/CMC is more compared to freestanding film of PAN–CSA/CMC. Our study indicates that 0.6 mm thick film of conductivity 10 S/cm of PAN–PTSA/CMC offers shielding effectiveness of 33 dB at 0.1 MHz and 45 dB at 1000 MHz and 0.6 mm thick film of conductivity 0.3 S/cm of PAN–CSA/CMC offers shielding effectiveness of 17 dB at 0.1 MHz and 19 dB at 1000 MHz. The reason for better shielding effectiveness of PAN–PTSA/

CMC film is attributed to the closely packed structure, which is pore free as can be seen in SEM micrographs (Fig. 1a).

Effect of SE on the thickness and conductivity of PAN–PTSA/CMC film and PAN–CSA/CMC film is shown in Fig. 3a and b. The results showed that SE is increased with increase in thickness and conductivity.

4. Conclusion

In this work we have shown that it is possible to achieve uniform shielding against electromagnetic radiation using PAN free standing film obtained by secondary dopant concept which are pore free and are easy to synthesize and are flexible. The work is in progress to study their utility up to 40 GHz.

Acknowledgments

Authors wish to thank Dr. D.C. Pandey, Scientist EMI/EMC, Electronics and Radar Development Establishment (LRDE), Bangalore (India) for his help in carrying out the study on EMI Shielding Effectiveness. Two of us (K.K.S and S.G) thank Council of Scientific and Industrial Research (C.S.I.R), New Delhi for the award of Senior Research Fellowship.

References

- [1] M. Mordiguine, Interference Control in Computer and Microprocessors Based Equipments, Don White Consultant Inc., Virginia, 1984.
- [2] J.M. Chion, O. Zheng, D.D.L. Chung, Composites 20 (1989) 379.
- [3] Z. Osawa, K. Kobayashi, J. Mater. Sci. 22 (1987) 4387.
- [4] D.C. Trivedi, in: H.S. Nalwa (Ed.), Handbook of Organic Conductive Molecules and Polymers, vol. 2, Wiley, New York, 1997, pp. 505–572.
- [5] D.C. Trivedi, J. Solid State Electrochem. 2 (1998) 85.
- [6] D.C. Trivedi, Bull. Mater. Sci. 22 (1999) 447.
- [7] M. Angelpoulos, A. Ray, A.G. MacDiarmid, Synth. Met. 21 (1987) 21.
- [8] M. Angelpoulos, G.E. Asturias, S.P. Ermer, A. Ray, E.M. Scherr, A.G. MacDiarmid, M. Akhtar, Z. Kiss, A.J. Epstein, Mol. Cryst. Liq. Cryst. 160 (1988) 151.
- [9] A. Andreatta, Y. Cao, J.C. Chiang, A.J. Heeger, P. Smith, Synth. Met. 26 (1988) 383.
- [10] M. Vijayan, D.C. Trivedi, Synth. Met. 107 (1999) 57.
- [11] M. Abe, A. Ohtani, Y. Umemoto, S. Akizuki, M. Ezoe, H. Higuchi, K. Nakamoto, A. Okuno, Y. Noda, J. Chem. Soc. Chem. Commun. (1989) 1736.
- [12] S.A. Chen, H.T. Lee, Macromolecules 26 (1993) 3254.
- [13] (a) Y. Cao, A.J. Heeger, Synth. Met. 52 (1993) 1993; (b) Y. Cao, P. Smith, Polymer 34 (1993) 3139.
- [14] (a) A.G. MacDiarmid, J.C. Chiang, A.F. Richter, A.J. Epstein, Synth. Met. 18 (1987) 285; (b) J.C. Chiang, A.G. MacDiarmid, Synth. Met. 13 (1986) 193.

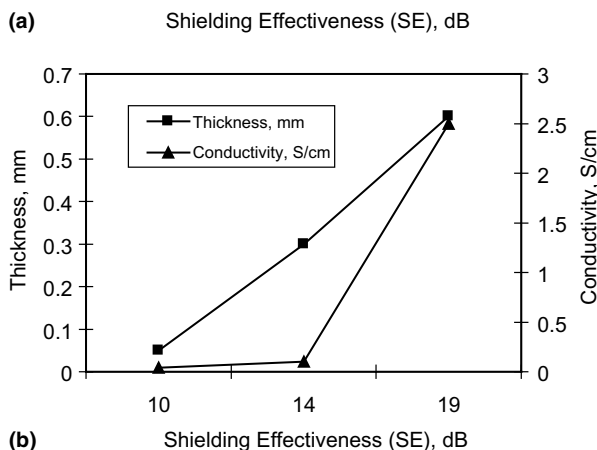
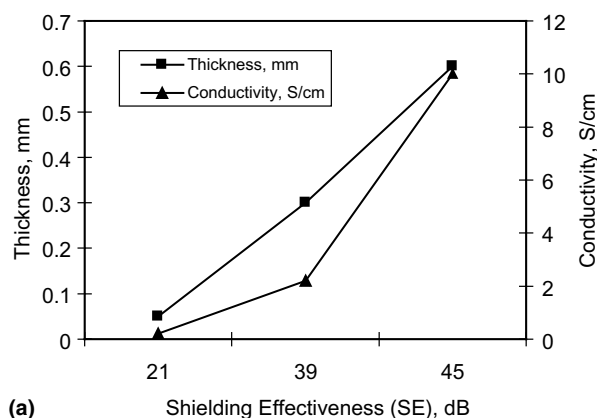


Fig. 3. Effect of SE on the thickness and conductivity of free standing. (a) PAN–PTSA/CMC. (b) PAN–CSA/CMC film.

- [15] A.G. MacDiarmid, A.J. Epstein, *Synth. Met.* 65 (1994) 103.
- [16] A.G. MacDiarmid, A.J. Epstein, *Synth. Met.* 69 (1995) 85.
- [17] O.T. Ikkala, L.O. Pietila, L. Ahjopalo, H. Osterholm, P.J. Passiniemi, *J. Chem. Phys.* 103 (1995) 9855.
- [18] T.E. Olinga, J. Fraysse, J.P. Travers, A. Dufresne, A. Pron, *Macromolecules* 33 (2000) 2107.
- [19] T. Makela, S. Pienimaa, T. Taka, S. Jussila, H. Isotala, *Synth. Met.* 85 (1997) 1335.
- [20] T. Makela, J. Sten, A. Hujanen, H. Isotala, *Synth. Met.* 101 (1999) 707.
- [21] R.L. Elsenbaumer, L.W. Shacklette, in: T.A. Skotheim, (Ed.), *Handbook of Conducting Polymers*, Vol. 1, Marcel Dekker, New York, 1986, p. 213.
- [22] *Tech.Trends III – International Reports on Emerging technologies – EMI Shielding, Conductive Plastics and Elastomers*, INNOVATION 128, S.A. Paris 1987.