Polyaniline reinforced conducting E-glass fabric using 4-chloro-3-methyl phenol as secondary dopant for the control of electromagnetic radiations

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

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

Abstract

A method is described to increase the shielding effectiveness (SE) of polyaniline grafted E-glass fabric to control electromagnetic radiations. This process involves the pretreatment of glass fabric with aqueous solution of 10% maleic anhydride prior to grafting of polyaniline by in situ polymerization of aniline. The polyaniline grafted E-glass fabrics treated with polyaniline solution in chloroform is prepared using either *p*-toluene sulphonic acid (PTSA) or camphor-10-sulphonic acid (CSA) as dopants and 4-chloro-3-methyl phenol (CMC) as secondary dopant to get pore free polyaniline coating of thickness of 100 μm. The resulting pore free conducting fabric of 3 mm thick offered maximum SE of 54 dB at 1000 MHz. The conducting fabrics were characterized by UV–Vis spectroscopy, Conductivity, SEM, XRD, TGA and shielding effectiveness measurements. The SE measurements were carried out using co-axial transmission line method in the frequency range of 0.1–1000 MHz. The study indicates that SE increases with increase in thickness and conductivity of test coupons.
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1. Introduction

The increasing complexity of electronic devices and systems in the form of higher packing density, quick response has generated pollution in the form of electromagnetic interference (EMI) [1]. Electromagnetic radiation is one of the unfortunate byproducts of the rapid proliferation of electronic devices. If this problem is left unattended can cause severe damage to system and therefore, has to be controlled. At present EMI is controlled by use of metal and carbon fiber composites such as Al, Cu, Ag-epoxy matrix [2], Ni–carbon fiber/ABS [3], Ni–carbon fiber/PC/ABS [4], Ni–carbon fiber/PC/ABS /coupling agent [5] and electroless nickel carbon fiber/ABS [6,7]. These shielding materials based on metal/carbon suffer from limited mechanical flexibility, heavy weight and corrosion.

Conducting polymers are new materials based on carbon–carbon bond with a conjugation thus are flexible and free from corrosion with advantage that their electronic conductivity can be tuned depending upon the need of its application and hence have been predicted to replace existing metal/carbon/graphite based material. If they replace them the reduction in weight can be achieved and due to non-corrosive nature can be advantage under hostile environmental condition.

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* Corresponding author. Tel.: +91 4565 227775; fax: +91 4565 227779/227713.
E-mail address: trivedi_dc@rediffmail.com (D.C. Trivedi).

Among all conducting polymers, polyaniline is important because of its easy synthesis and environmental stability. Conducting polyaniline composites are mainly used in EMI shielding purposes. Kathirgamanathan [8] has described that the 3 mm thick, 3:1, polyaniline coated nickel (spheres) carbon black, composite in copoly (ethylene–propylene) host offers SE > 20 dB in the frequency range 10 KHz–100 MHz is suitable for most shielding applications and high SE ≥ 60 dB in the range 10 KHz–1 MHz is suitable for high performance applications at low frequencies. Lee et al. [9] observed the EMI shielding efficiency of the mixtures of PAn and conducting powders such as silver, graphite and carbon black in the frequency range from 10 MHz to 1 GHz. The SE of emeraldine salt (ES)/graphite and ES/Silver are ∼27 and ∼46 dB respectively, while PAn–ES without mixing of conductive powder is only ∼17 dB. The SE of the mixture of doped PAn and silver powder (ES/Ag) is ∼46 dB at room temperature. They observed that the SE increases with increasing DC conductivity and they also observed that the SE against electromagnetic radiation increases through chemical doping and mixing with conducting powder. Wessling [10] reported that by dispersing PAn in a matrix polymer like PVC, PMMA and polyester, conductivity values of around 20 S/cm and in some cases up to 100 S/cm can be achieved. Such values, which are higher than those so far achieved by incorporating carbon black into polymers, promise a very high standard of EMI shielding. The shielding effect is up to 25 dB higher than with carbon black compounds and lies, depending on the frequency of the EMI, in the region of 40–75 dB for both near and far field. But still a considerable improvement in mechanical values is needed and preferably, conductivity levels that are higher by one or two orders of magnitude and hence these blends are not used for commercial purposes. PAn–CSA cast film using *m*-cresol as the secondary dopant offers a shielding efficiency of 39 dB at 1 GHz [11,12].

In a previous publication from this laboratory a method was described to graft polyaniline on flexible substrates like E-glass fabric and nylon in presence of 5-sulphosalicylic acid, benzene sulphonic acid and *p*-toluene sulphonic acid. However, due to porous nature of a substrate the conductivity of the PAn-grafted fabric were not upto expectation and SE were low [13–15].

In this report we discuss the pretreatment of glass fabric prior to grafting of polyaniline by in situ polymerization of aniline under aqueous acidic conditions. The use of secondary dopant, CMC to prepare a conductive paste, which can be coated on the PAn grafted fabric to achieve pore free reinforced PAn flexible surfaces to make it as a viable material for the control of EMI is also described.

2. Experimental

2.1. Reagents

All the chemicals used were of AnalaR grade. Aniline was freshly distilled before use. Distilled water was employed. The blue emeraldine base is obtained from procedure as discussed earlier [16].

2.2. Grafting of PAn on E-glass fabric

The E-glass fabrics were subjected to thorough cleaning using sodium carbonate solution to remove foreign materials. Then these E-glass fabrics were treated with 10% maleic anhydride solution in ethyl methyl ketone, methanol, or acetone solution for half an hour to one hour and dried at room temperature. This pretreatment yields the fabric with large number of active sites due to carbonyl group, to act as an anchor for PAn chain, whose formation is via the generation of free radicals. This way even in interstices of the fabric, PAn gets anchored to enhance the electronic conductivity of a grafted E-glass fabric and reduces its porosity.

The maleic anhydride treated E-glass fabrics are immersed in 0.1 M solution of aniline in 1 M aqueous solution of organic sulphonic acid (CSA/PTSA) at pH 1. The grafting was carried out using double walled tray (30 × 40 cm) with provision to circulate chilled water (∼2–4 °C) to maintain the temperature. The substrates were rotated continuously on a mechanical shaker to ensure the uniformity of reaction at the solid/liquid interface. Stiochiometric amount of 0.1 M chilled aqueous solution of ammonium peroxydisulphate was added slowly to the reaction mixture containing substrate. After an hour the substrates were removed and rinsed thoroughly with distilled water. The grafting experiments were carried out twice to achieve good conductivity and to achieve deposition of conducting phase in the interstices of the fabric. At the end of two graftings, dedoping was carried out in 1 M ammonia solution to remove all oligomeric impurities. After thorough washings with distilled water the dedoped fabrics were dipped in the doping acid solution of 1 M strength and agitated for an hour to ensure uniform doping and were finally dried at 50 °C under vacuum for 2 h.

2.2.1. Preparation of PAn–CSA/CMC reinforced conducting E-glass fabric

PAn paste is prepared by mixing 2.5 g (6.9 mmol) emeraldine base powder, 3.2 g (13.8 mmol) CSA and 4 g (28.05 mmol) CMC are ground thoroughly in a homogeniser in presence of any one of the solvents such as benzene, chloroform, toluene or xylene for 1–2 h. PAn–CSA grafted E-glass fabric reinforced with PAn–CSA/CMC is prepared by applying this paste on the surfaces of the PAn–CSA grafted E-glass fabric using

an applicator. After applying this coating coupons were cured for 12 h at room temperature and later dried under vacuum for 4 h at 60 °C.

2.2.2. Preparation of PAn–PTSA/CMC reinforced conducting E-glass fabric

PAn paste is prepared by mixing 2.5 g (6.9 mmol) emeraldine base powder, 2.6 g (13.7 mmol) PTSA and 10 g (70.13 mmol) CMC are ground thoroughly in a homogeniser in presence of any one of the solvents such as benzene, chloroform, toluene or xylene for 1–2 h. PAn–PTSA grafted E-glass fabric reinforced with PAn–PTSA/CMC is prepared by applying this paste on the surfaces of the PAn–PTSA grafted E-glass fabric using an applicator. After applying this coating coupons were cured for 12 h at room temperature and later dried under vacuum for 4 h at 60 °C.

2.3. Characterization

The electronic spectra of the PAn grafted E-glass fabric reinforced with PAn/CMC was recorded on a UV–VIS–NIR Varian Cary-500 Spectrophotometer. The conductivity data of the grafted samples were measured by four-probe method (Model No. DFP–02). The scanning electron micrographs of these materials were recorded on a Hitachi S-3000H. The X-ray diffraction patterns were recorded using (Cu Kα, $\lambda = 1.5418$ Å) Jeol JDX 8030 X-ray diffractometer. The thermogravimetric analysis data were recorded on Perkin–Elmer 7 series thermal analysis system from room temperature to 800 °C at a rate of 10 °C/min under atmospheric air.

2.4. Shielding effectiveness measurements

The various methods are available for the measurement of shielding effectiveness (SE). Among these methods co-axial method is most preferred because results from various laboratories are comparable. The co-axial transmission line method was used to measure the shielding effectiveness (EMI SE). Tests were carried out on a small torus shaped cell. The round coupon of the sample of internal dia. 43 mm and outer dia. of 120 mm was cut and on periphery of the sample the silver ink was applied to reduce the contact resistance between sample and a holder to 0.2 Ω cm. The measurements were made at specific frequencies using a signal generator 8642 B (Hewlett–Packard) and field intensity meters (NM17/27A for 0.01–32 MHz and NM37/57A for 30–1000 MHz) with point-by-point method with and without specimen.

3. Results and discussion

The formation of conducting polymers occurs via the generation of a cation radical of intermediate stability,

which on further coupling builds up a polymer chain. We have utilized this intermediate stability of cation radicals to carry out in situ coating of conducting polymers on insulating surfaces like E-glass fabric using different dopants. These cations of intermediate stability get adsorbed on the surface interstices of fabrics, and these cations on further coupling reaction, lead to the formation of stable, adherent and uniform electrically conductive coating. We have named this conducting coating as grafting because these coating do not exhibit electrochromic response as observed for deposition on metal surfaces suggesting that π-electrons of the aromatic nucleus are involved in strong adsorption on the fabric and hence the transition of structure from benzenoid to quinoid gets hampered. The mechanism of PAn synthesis can be written as in Scheme 1.

The electronic spectra of PAn–PTSA/CMC reinforced conducting E-glass fabric exhibits two absorption peaks at 369 and 772 nm. In the absence of secondary dopant PAn–PTSA grafted fabric has absorption peaks at 328 and 682 nm. Similarly the electronic spectra of PAn–CSA grafted fabric exhibits absorption peaks at 340, 416 and 698 nm and PAn–CSA/CMC reinforced conducting E-glass fabric exhibits absorption peaks at 320, 405 and 706 nm and the spectrum is shown in Fig. 1 and the absorption peak maxima are shown in Table 1.

The band due to charge carrier observed at 682 nm for PAn–PTSA grafted E-glass fabric shifts to higher wavelength ∼772 nm extending to IR region in presence of a secondary dopant, CMC. Similarly the band due to charge carrier observed at 698 nm for PAn–CSA grafted E-glass fabric shifts to higher wavelength ∼706 nm extending to IR region in presence of a secondary dopant, CMC. This shows that secondary dopant not only favours formation of charge carriers, bipolarons, but also induces processibility in polymer system by its plasticizing effect which yields a closely packed polymer matrix by "straightening-out" the polymer chain from its coiled structure to uncoiled structure and becomes more expanded with concomitant reduction in π-defects
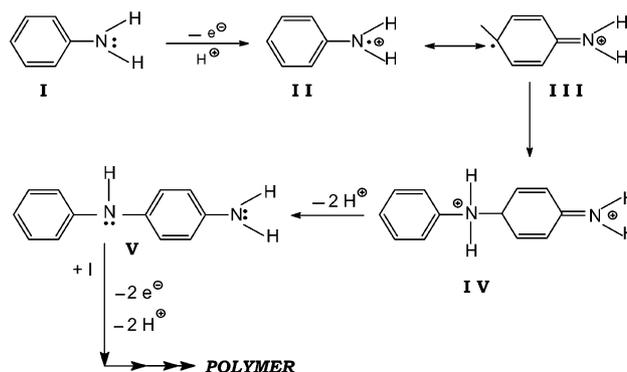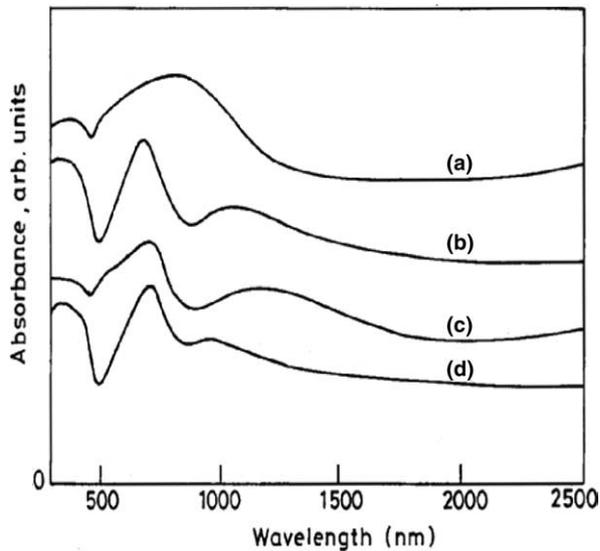
Scheme 1. Mechanism of polyaniline synthesis.

Fig. 1. UV–Vis–NIR absorption spectra of: (a) PAn–PTSA/CMC reinforced conducting E-glass fabric; (b) PAn–PTSA grafted E-glass fabric; (c) PAn–CSA/CMC reinforced conducting E-glass fabric; (d) PAn–CSA grafted E-glass fabric.

caused by ring twisting as suggested by MacDiarmid and Epstein [17,18].

The conductivity of PAn grafted E-glass fabric reinforced with doped PAn/CMC is measured by four-probe method and the data is concluded in Tables 3 and 4. By this method the conductivity of the PAn–PTSA/CMC reinforced conducting E-glass fabric is found to be 0.2 S/cm ($t = 0.15$ mm), 0.5 S/cm ($t = 1.4$ mm), 0.8 S/cm ($t = 3$ mm) and PAn–CSA/CMC reinforced conducting E-glass fabric is found to be 0.04 S/cm ($t = 0.15$ mm), 0.1 S/cm ($t = 1.4$ mm), 0.3 S/cm ($t = 3$ mm).

The SEM study of PAn–PTSA/CMC reinforced conducting E-glass fabric indicates the regularity of PAn without any morphological defect (Fig. 2(a)) and PAn–CSA/CMC reinforced conducting E-glass fabric indicates the honeycomb morphology at a regular interval (Fig. 2(b)).

The PAn–PTSA grafted E-glass fabric gives XRD peaks at $2\theta = 5.7°$, $7.2°$, $8.7°$, $10.6°$, $12.1°$ and $14.5°$ and these peaks are broader indicating amorphous nature of the cloth. The XRD patterns of PAn–PTSA/CMC reinforced conducting E-glass fabric exhibit peaks at $2\theta = 5.0°$, $6.0°$, $6.8°$, $7.9°$, $10.9°$, and $12.1°$. Similarly PAn–CSA grafted E-glass fabric gives XRD peaks at $2\theta = 5.2°$, $6.8°$, $8.6°$, $9.9°$, $12.1°$, $11.5°$, $13.5°$ and $14.4°$ and these peaks are broader indicating amorphous nature of the cloth. The XRD patterns of PAn–CSA/CMC reinforced conducting E-glass fabric exhibit peaks at $2\theta = 5.1°$, $6.4°$, $11.4°$, $15.0°$ and $16.4°$.

Table 1
Absorption peak maxima of PAn-grafted E-glass fabric in presence and absence of secondary dopant

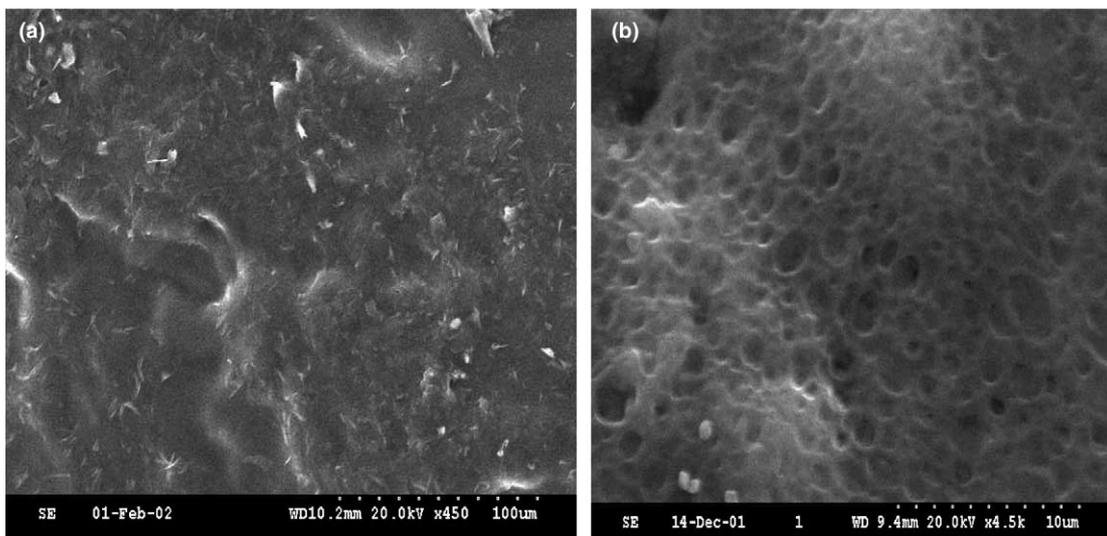| PAn-grafted E-glass fabric	λ_{max} in nm	
	In absence of CMC	In presence of CMC
PAn–PTSA grafted E-glass fabric	328, 682	369, 772
PAn–CSA grafted E-glass fabric	340, 416, 698	320, 405, 706

Fig. 2. SEM micrograph of: (a) PAn–PTSA/CMC reinforced conducting E-glass fabric; (b) PAn–CSA/CMC reinforced conducting E-glass fabric.

As can be observed in the presence of CMC as a secondary dopant the XRD peak is sharper indicating that the amorphous material has developed some crystallinity in its structure. The 2θ and d values of PAn grafted E-glass fabrics and PAn/CMC reinforced conducting E-glass fabrics are tabulated in Table 2 and the patterns are recorded in Fig. 3.

The TGA of PAn–PTSA/CMC reinforced conducting E-glass fabric shows the first weight loss of $\sim$1.5% at 100 °C due to loss of moisture. The second weight loss occurs in two steps; in the first step weight loss of $\sim$7% is observed between 126 and 330 °C, which is equivalent to the weight of the dopant, i.e., PTSA. In the second step, weight loss of $\sim$14% is observed between 330 and 589 °C, which is equivalent to the secondary dopant, i.e., CMC. The final degradation of the polymer starts at 680 °C and the substrate is found to be stable up to 800 °C.

Similarly the TGA of PAn–CSA/CMC reinforced conducting E-glass fabric shows the first weight loss of $\sim$1.5% at 100 °C due to loss of moisture. The second weight loss occurs in two steps, in the first step weight loss of $\sim$11.5% is observed between 254 and 479 °C, which is equivalent to the weight of the dopant, i.e., CSA. In the second step weight loss of $\sim$18.8% is observed between 479 and 633 °C, which is equivalent to the secondary dopant, i.e., CMC. The final degradation of the polymer starts from $\sim$669 °C and is found to be stable upto 800 °C. These data suggests that the thermal stability of the PAn/primary dopant/secondary dopant ternary system increases in presence of CMC perhaps due to cross-linking.

The shielding effectiveness for EMI control is largely a function of surface conductivity of the material. Materials having a surface resistivity below 10 Ω cm are suitable as a shield for 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 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. (1) [1]
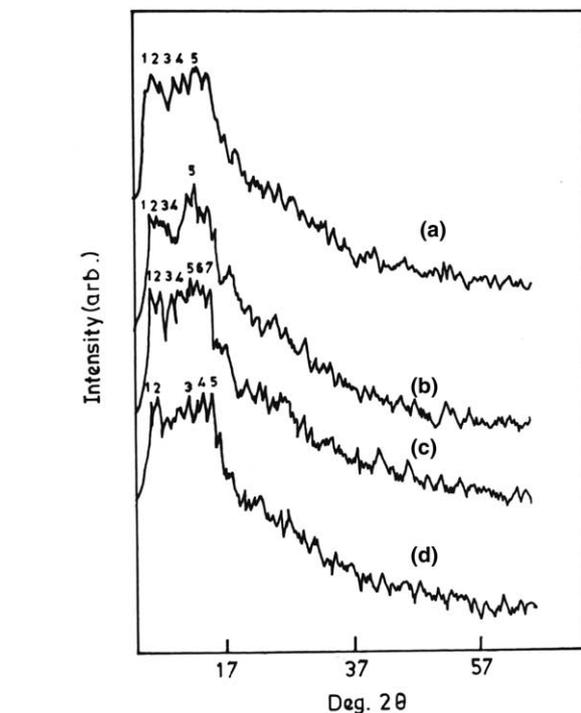

Fig. 3. X-ray diffraction powder pattern (Cu Kα, $\lambda = 1.5418$ Å) of: (a) PAn–PTSA grafted E-glass fabric; (b) PAn–PTSA/CMC reinforced conducting E-glass fabric; (c) PAn–CSA grafted E-glass fabric; (d) PAn–CSA/CMC reinforced conducting E-glass fabric.

$$SE = 20 \log E_t/E_i, \tag{1}$$

where SE is the shielding effectiveness, E the electrical field strength in V m^{-1}, i the incident, t the transmitted.

The EMI SE measurements were carried out using co-axial transmission line method in the frequency range of 0.1–1000 MHz and the curves are shown in Fig. 4 and the results are tabulated in Tables 3 and 4. The study also indicates that the SE of these samples has a strong dependence on:

(1) Placement of sample.
(2) Anisotropy of the sample.
(3) Thickness of coating.
(4) Level of doping and type of dopant.
(5) Orientation of the dopant.
(6) Magnetic properties.

Table 2
Powder X-ray diffraction data (Cu Kα, $\lambda = 1.5418$ Å) of PAn/CMC reinforced conducting E-glass fabric

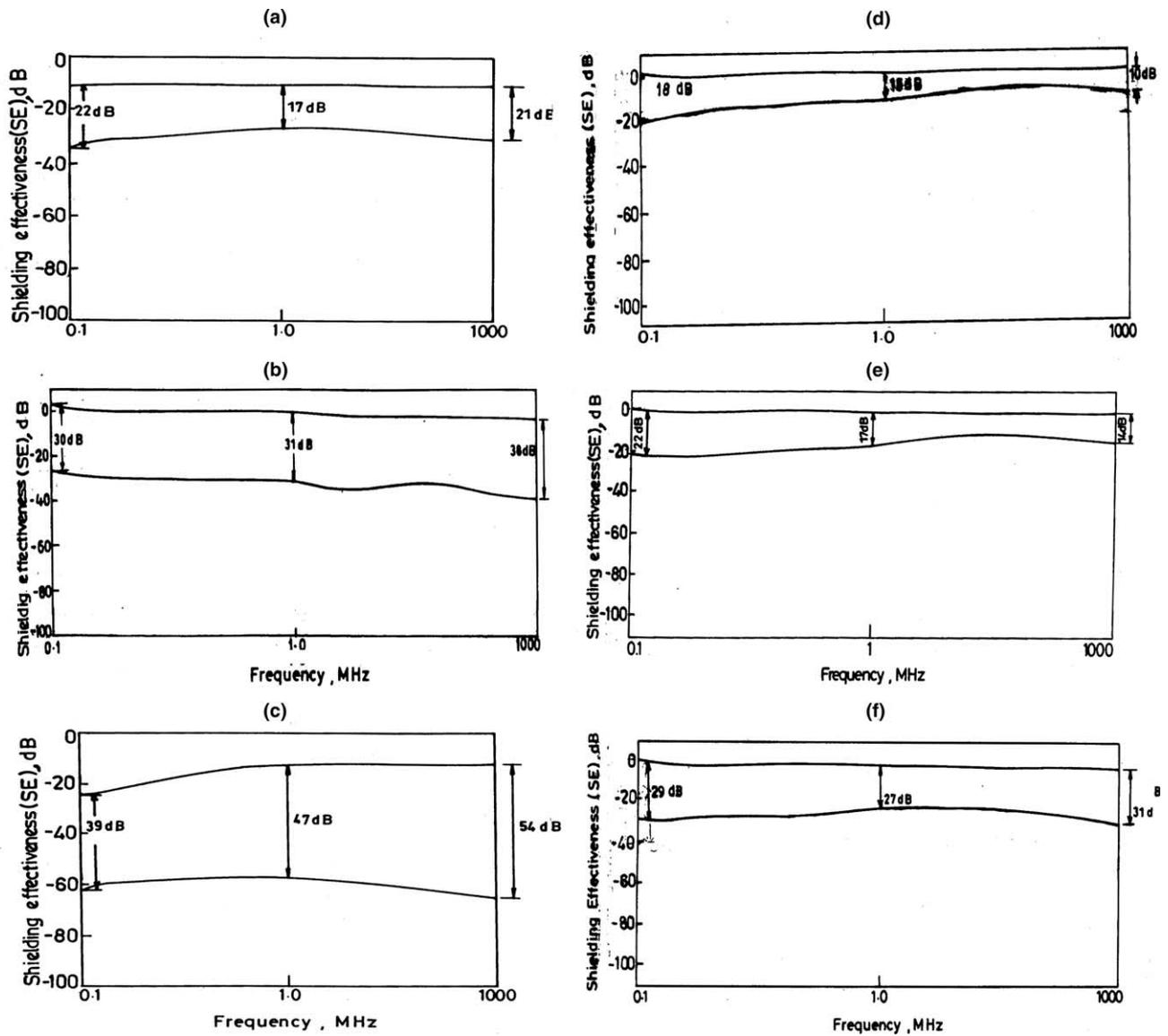| PAn–PTSA grafted E-glass fabric		PAn–PTSA/CMC reinforced conducting E-glass fabric		PAn–CSA grafted E-glass fabric		PAn–CSA/CMC reinforced conducting E-glass fabric	
2θ	d	2θ	d	2θ	d	2θ	d
5.7	15.4	5.0	17.6	5.2	16.9	5.1	17.3
7.2	12.2	6.0	14.7	6.8	12.9	6.4	13.7
8.7	10.1	6.8	12.9	8.6	10.2	11.4	7.7
10.6	8.3	7.9	11.1	9.9	8.9	13.5	6.5
12.1	7.3	10.9	8.1	11.5	7.6	15.0	5.9

Fig. 4. EMI SE curves of PAn reinforecd conducting E-glass fabric: (a) PAn–PTSA/CMC (t = 0.15 mm) ;(b) PAn–PTSA/CMC (t = 1.4 mm); (c) PAn–PTSA/CMC (t = 3 mm); (d) PAn–CSA/CMC(t = 0.15 mm); (e) PAn–CSA/CMC (t = 1.4 mm); (f) PAn–CSA/CMC (t = 3 mm).

Table 3
Data on EMI SE studies on PAn–PTSA/CMC reinforced conducting E-glass fabric

Sample	Conductivity (S/cm)	Frequency in MHz				
		0.1	1	10	100	1000
Pan–PTSA/CMC reinforced conducting E-glass fabric (t = 0.15 mm) (observed in dB)	0.2	22	17	16	16	21
Pan–PTSA/CMC reinforced conducting E-glass fabric (t = 1.4 mm) (7 coupons together) (observed in dB)	0.5	30	31	35	32	38
Pan–PTSA/CMC reinforced conducting E-glass fabric (t = 3 mm) (15 coupons together) (observed in dB)	0.8	39	47	46	47	54

t = thickness.

The perusal of Tables 3 and 4 reveals that increasing sample thickness and conductivity enhances the SE of the material. Our study indicates that 3 mm thick sample of conductivity 0.8 S/cm of PAnPTSA/CMC reinforced conducting E-glass fabric SE of 39 dB at 0.1 MHz and 54 dB at 1000 MHz and PAn–CSA/CMC

Table 4
Data on EMI SE studies on PAn–CSA/CMC reinforced conducting E-glass fabric

| Sample	Conductivity (S/cm)	Frequency in MHz				
		0.1	1	10	100	1000
PAn–CSA/CMC reinforced conducting E-glass fabric (t = 0.15 mm) (observed in dB)	0.04	18	15	10	10	10
PAn–CSA/CMC reinforced conducting E-glass fabric (t = 1.4 mm) (7 coupons together) (observed in dB)	0.1	22	17	16	15	14
PAn–CSA/CMC reinforced conducting E-glass fabric (t = 3 mm) (15 coupons together) (observed in dB)	0.3	29	27	26	26	31

t = thickness.
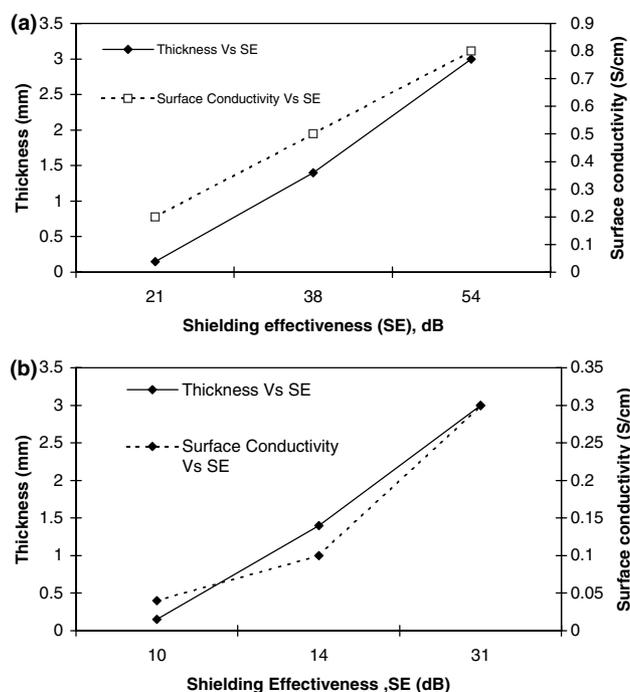
Fig. 5. (a) Effect of SE on the thickness and surface conductivity of PAn–PTSA/CMC reinforced conducting E-glass fabric. (b) Effect of SE on the thickness and conductivity of PAn–CSA/CMC reinforced conducting E-glass fabric.

reinforced conducting E-glass fabric of conductivity 0.3 S/cm, offers SE of 29 dB at 0.1 MHz and 31 dB at 1000 MHz. The reason for better SE of PAn–PTSA/CMC reinforced system is ascribed to the featureless structure, which is pore free as can be seen in SEM micrographs.

As can be seen in Fig. 5(a) and (b), SE increases with thickness and conductivity.

4. Conclusions

We have shown that SE of PAn grafted E-glass fabric can be enhanced by coating conducting PAn paste using CMC as a secondary dopant and PTSA and CSA as a primary dopant. The advantage of using these PAn grafted surfaces is that they withstand any level of acidic fumes and high humidity levels without any degradation.

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