

Conducting polyaniline composite for ESD and EMI at 101 GHz

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Abstract

Conducting polyaniline forms an important family of electronic polymers with a developed potential application for a number of areas because of their flexible chemistry, processibility, environmental stability and ease of forming composites. The electromagnetic interference shielding effectiveness of conducting polyaniline (PANI)–ABS composites was studied at 101 GHz. It was observed that shielding effectiveness of the PANI–ABS composites increases with the increase in the loading levels of the conducting polymer doped with hybrid dopants. The lower loading of PANI doped with hybrid dopants in the moulded conducting composites can be effectively used for the dissipation of electrostatic charge. However, with higher loadings, a shielding effectiveness of 60 dB has been achieved which makes the conducting composites a potential EMI shielding material for its application in encapsulation of electronic equipments in electronic and in high tech applications. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyaniline; Electrostatic dissipation charge (ESD); Electromagnetic Interference (EMI)

1. Introduction

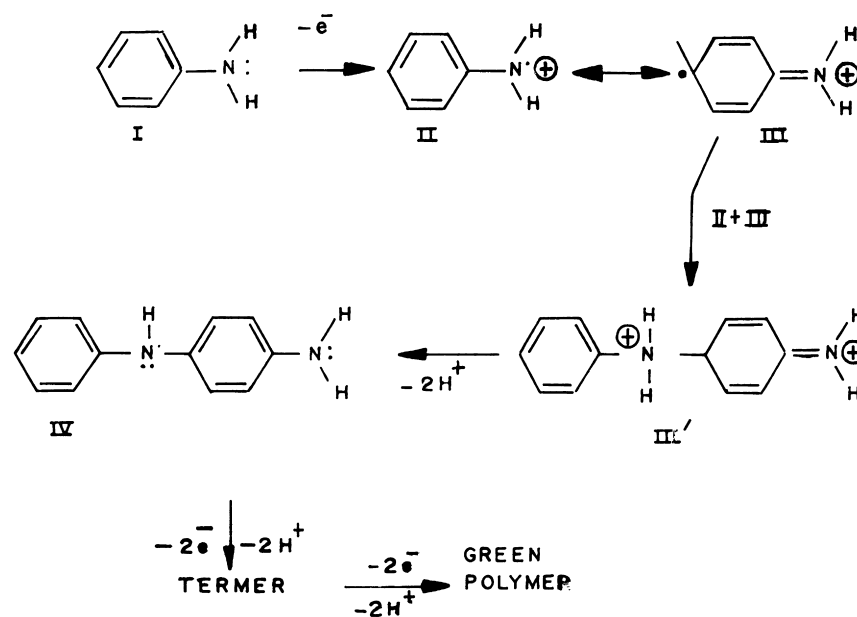
Ever since the successful synthesis of conducting polyacetylene in 1977 by Shirakawa et al. [1], electrically conducting polymers have generated a tremendous interest due to their potential applications in batteries [2,3], electrochromic devices [4,5], sensors [6–9], light emitting diodes [10–13]. Electrically conducting organic polymers or synthetic metals are the materials that combine the chemical and mechanical properties of polymers with the electronic properties of metals and semiconductors. These polymers become conductive upon partial oxidation or reduction and the electrical conductivity in these materials ranges from 10^5 to 10^{-8} S/cm depending upon the doping level and the extent of doping. The electrical properties of conducting polymers can be reversibly changed over the full range from an insulator to a metallic conductor. However, the major drawback of these polymers is the unprocessibility and intractability which has made their processing into the desired form rather difficult. Electrically conducting composites are a novel class of materials that combine the mechanical properties of the conventional polymers and electrical properties of the conducting polymers. Their use as new materials has opened up entirely new field for polymeric

materials. These novel conductive composites are under intense research world wide both in research institutions and in electronic industries.

Among the conducting polymers, conducting polyaniline (PANI) has attracted a great deal of attention from chemists, polymer technologists and material scientists because of its environmental stability and unique proto-electronic conduction mechanism. PANI's conductivity can be reversibly controlled either electrochemically (by oxidation–reduction) or chemically (by protonation/deprotonation), and conductivity increases with doping from the undoped insulating base form to fully doped conducting acid form. PANI with different forms find different uses like leucoemeraldine—the completely reduced form find applications in electrochromic devices and in Li–PANI batteries; pernigraniline is used for non-linear optics while emeraldine base consisting of 50% reduced and 50% oxidised moieties is used in HCl sensors and for making thin films. Other applications of conducting PANI include electrostatic charge dissipation, electromagnetic interference, anticorrosion coating, light emitting diodes and batteries. Recently the protonation of PANI with organic sulphonic acids and macromolecules has been reported for the preparation of electrically conducting polymers with improved processibility [14–16] for making conductive blends and composites for various applications. Polymerisation of PANI in the presence of a functionalised protonic acid like

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dodecylbenzene sulphonic acid (DBSA) and dinonylnaphthalene sulphonic acid (DNNSA) has been produced with high molecular weight through emulsion polymerisation [17]. Polymer produced by this procedure results in highly processible conducting polymer with fibrillar like morphology. While Shacklette et al. [18] have developed a surface–core doping process in which PANI is predominately doped with one acid at the core of a particle and a second dopant predominately at the surface just to achieve increased compatibility between the PANI particles and a second polymer matrix e.g. Nylon, polystyrene (PS), low density polyethylene (LDPE). However, the present investigation reports the synthesis of PANI in the presence of mixed organic dopants, preparation of blends of PANI with conventional thermoplastic acrylonitrile–butadiene–styrene (ABS) and studying the EMI/ESD response of conducting composite in at 101 GHz.

EMI (electromagnetic interference) can be defined as spurious voltages and currents induced in electronic circuitry by external sources. In recent years, EMI problem or electromagnetic pollution has received wide attention because of the malfunctioning of the electronic equipments from the radiations generated from the source or emanating from other electronic equipments. Research in the past decade has established the ability of polymer composites made with electrically conducting polymers to be suitable as a shield against the electromagnetic interference [19–27]. So far conducting composites were made by adding metallic fillers, C-black or metallic powders. However because of certain disadvantages like labour intensity, relatively high cost and time consuming besides the galvanic corrosion phenomenon observed when dissimilar metals are joined, conducting polymer composites were being made which

were found suitable for EMI shielding and for the dissipation of electrostatic charge.

2. Experimental

The polymerisation of aniline to polyaniline was carried out by chemical oxidative polymerisation of aniline (0.1 mol) in the presence of inorganic protonic acid like 1.0 N HCl using ammonium peroxydisulphate (0.1 mol) as oxidant at 3–8°C. The stirring was carried out for 4–6 h. The polymer so obtained was filtered and undoped with aqueous ammonia resulting in the formation of emeraldine base. This polymer was doped with a specific ratio of mixed organic dopants consisting of DBSA and PTSA, the dopant ratio being varied from 5:5 to 9:1. For making conductive blends, insulating polymer (ABS) grade no. 120, obtained from ABSOLAC Pvt India Ltd, Gujarat was used. Because of the terblend nature, ABS offers a wide compatibility for conducting polymer PANI which helps in making a conductive composite. Blending of conducting PANI with ABS was carried out in Nuchen Extruder at a temperature ranging from 180–190°C. Two zones of heating along with the vacuum zone results in the formation of conductive composite in the form of hard rod shape from where composite sheets were made in a compression moulding machine 30 T, BH1, Nuchen Limited with maximum working pressure of 150 kg/cm². The composite sheets were made as per the standard procedure.

The characterisation of the conducting polymer PANI doped with mixed dopants was carried out by UV–visible, FTIR and thermogravimetric analysis. The isothermal studies of the polymer was carried at different temperatures in order to see the thermal stability of the polymer with

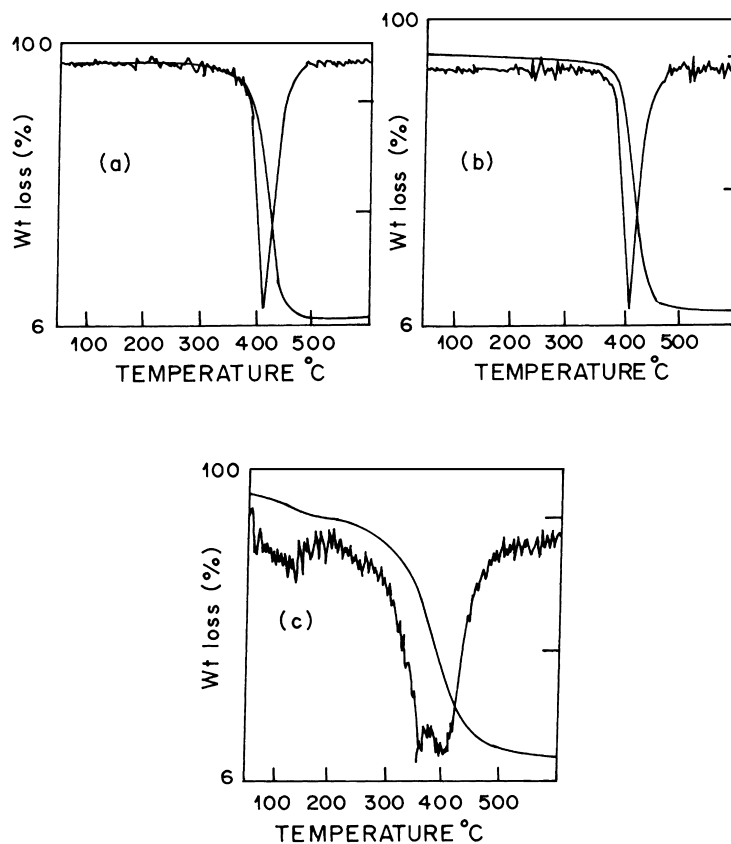


Fig. 1. Thermogravimetric analysis curve of: (a) Blank ABS; (b) ABS:PANI::9:1 composite; and (c) ABS:PANI::5:5 composite at a heating rate of 10°C/min under N₂.

respect to time. The isothermal conductivity measurements of the polymer at different temperatures were also carried out to see the electrical conductivity stability of the polymer with temperature. The electrical resistivity measurement of the conducting composite was done by four probe method using Keithley 332/LCZ electrometer.

2.1. Static charge measurements

The static charge on the insulating and conducting PANI composite blend was carried out using Static Charge Meter, model SCM-1, Para Electronics, Bombay mounted on an energy stand at a distance of 2.5 cm from energy dish whose capacitance at this distance was 25 pF. The meter works on capacitance principle. The capacitance is formed between charged surface and the probe. The capacitance is inversely proportional to the distance between the two surfaces.

2.2. EMI measurements at 101 GHz

The electromagnetic interference measurements at 101 GHz were carried out using a phase log oscillator of 101 GHz frequency generator, Model No. 956 W4-010-101, S/N 033 using conical horned antenna, Model No. 458264-1031, S/N 012 and mm wave power receiving set up consisting of pyramidal horned antenna, Model No. 861W/387, S/

N 483. The shielding effectiveness was measured by noting the power with and without the samples by placing them near to the surface of the antenna.

3. Results and discussion

3.1. Mechanism of oxidative polymerisation of conducting PANI

The polymerisation of aniline to conducting PANI proceeds through the formation of a radical cation by an internal redox reaction which causes the reorganisation of electronic structure to give two semiquinone radical cations. The chemical oxidative polymerisation of monomer to polymer is shown in Scheme 1. In the chemical oxidative polymerisation, the chemical oxidant initiates the formation of anilinium radical cation and these radical cations through the coupling reaction leads to the formation of stable electrically conducting polymer. Emeraldine base polymer obtained by undoping the polymer was doped with different ratios of mixed dopants consisting of DBSA and PTSA. From the electrical conductivity measurements of PANI doped with different ratios of DBSA and PTSA, we observed that the best results are obtained when DBS:PTS

Table 1
Mechanical and electrical properties of ABS–PANI composite

| S. No. | Composition of composite ABS:PANI | Tensile strength (Mpa) | Electrical resistivity (Ω cm) |
|--------|-----------------------------------|------------------------|---------------------------------------|
| 1 | Blank ABS | 41.73 | $>10^{12}$ |
| 2 | 90:10 | 26.60 | $>3.0 \times 10^8$ |
| 3 | 80:20 | 23.88 | 1.31×10^7 |
| 4 | 70:30 | 18.59 | 1.24×10^6 |
| 5 | 60:40 | 17.21 | 7.87×10^4 |
| 6 | 50:50 | 14.14 | 10.08 |

ratio was kept at 5:5 and 9:1 and hence these ratios were selected for making blends of PANI with ABS.

3.2. Thermogravimetric analysis of PANI doped with DBS/PTS and its composite with ABS

TGA analysis of undoped PANI shows that PANI is stable up to 434°C. PANI doped with a mixed ratio of (DBS:PTS::5:5) shows a thermal stability up to 251°C. A weight loss is observed from 251 to 414°C which corresponds to 62% and is possibly due to the leaching of dopant moiety from the polymeric matrix, whereas a weight loss of about 18% is observed from 414 to 700°C which is contributed due to the degradation of polymeric backbone. The TGA analysis of blank ABS insulating polymer (Fig. 1, curve a) shows no appreciable loss up to 405°C and then a sharp loss is observed up to 475°C indicating the breakdown of the polymer matrix. TGA curve of conducting composite (ABS:PANI::90:10) (Fig. 1, curve b) shows no weight loss% up to 347°C indicating the thermal stability of the polymer up to 347°C. From 347 to 447°C a sharp fall in weight loss is observed. However, the conducting composite with insulating and conducting polymer present in the ratio of 1:1 (ABS:PANI::50:50) shows a weight loss of the order

of 2.04% up to 180°C. From 180 to 300°C, weight loss of about 18.4% is observed which is accounted for the loss of the dopant moiety present in the conducting polymer composite (Fig. 1, curve c). A weight loss of the order of 60.29% is observed from 300 to 550°C which is possibly due to the degradation of the polymeric backbone. This implies that by increasing the percentage of the PANI in the composite makes the conducting composite thermally less stable.

3.3. Mechanical and electrical properties of conducting composites

The tensile strength of the PANI–ABS composite with different loading levels of PANI is tabulated in Table 1. It can be seen that the tensile strength of the composite progressively decreases with the increasing PANI ratio in ABS. Experiments revealed that maximum loading beyond equimolar ratio of PANI brings to the breakdown of the composite. The electrical resistivity of the conducting composite increases with the increase in the loading level of doped PANI and shows a marked increase to 10.08 Ω cm for the PANI–ABS composite having composition [ABS:PANI::5:5].

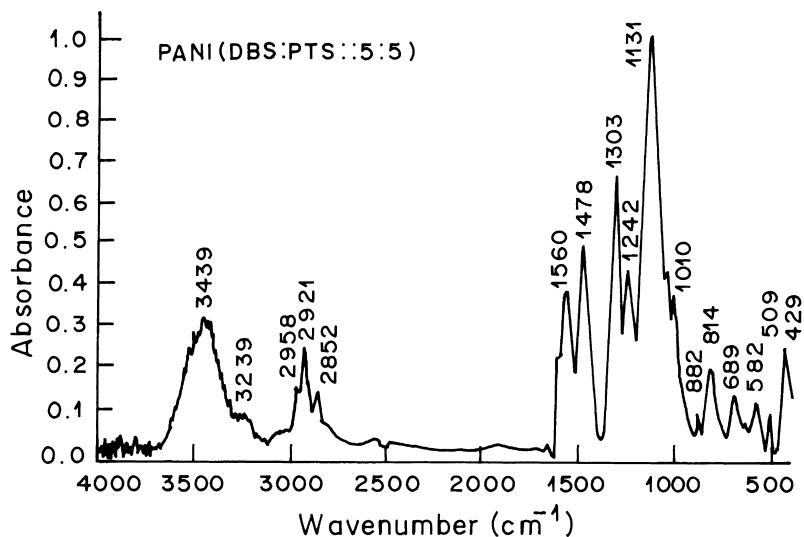


Fig. 2. FTIR spectra of PANI doped with DBS and PTS (5:5) in KBr.

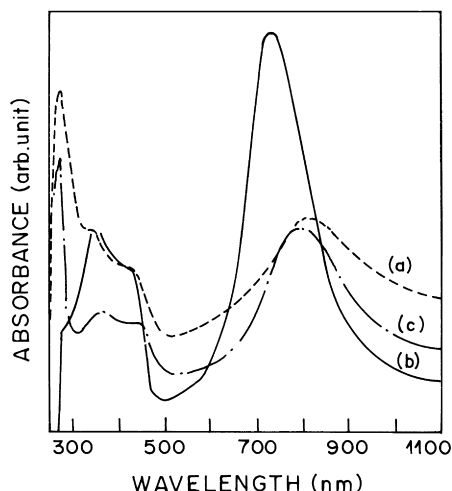


Fig. 3. UV-visible spectra of: (a) PANI doped with PTSA in DMSO; (b) PANI doped with DBSA in CHCl_3 ; and (c) PANI doped with DBS:PTS::5:5.

3.4. FTIR analysis

The principal absorption bands observed in the FTIR spectra of PANI powder (in KBr) doped with DBS:PTS is given in [Fig.2]. In the region $1650\text{--}1400\text{ cm}^{-1}$, bands due to the aromatic ring breathing, N–H deformation and C–N stretching are observed. Bands at 1583 and 1493 cm^{-1} are the characteristic bands of nitrogen benzenoid and quinoid form and are present due to the conducting state of the polymer. The band at 1155 cm^{-1} (v.s.) is assigned to be present due to the charge delocalisation on the polymer backbone. The presence of the bands at 1182 and 1070 cm^{-1} are characteristic of the asymmetric and symmetric –OSO– stretching vibrations. In case of ABS, presence of peaks vary with the monomeric ratios but the characteristic peaks which appear always due to strong structural bonding are found at 966 and 912 cm^{-1} which is attributed due to the presence of double bond in butadiene moiety. Peak values at 1603 and 1637 cm^{-1} are due to the C=C conjugated system and due to the presence of aromatic C–H out of plane band. The absorption peak at 2924 cm^{-1} indicates the asymmetric stretching of –CH and

the band at 3026 cm^{-1} shows the stretching pattern of HC=C along the polymeric chain. The characterisation absorption band in ABS is present due to C=N appear at 2237 cm^{-1} .

3.5. UV-Visible absorption spectra

The UV-Visible absorption spectra of PANI doped with PTS, DBS and mixed ratio of PTS/DBS are shown in (Fig. 3). Undoped PANI in DMSO showed absorption bands at 320 and 620 nm present due to the $\pi\text{--}\pi^*$ transition of the benzenoid ring and exciton band. In the presence of PANI doped with PTS, UV-visible absorption bands in DMSO appear at 335 , 442 and 817 nm . PANI doped with DBS in chloroform show bands at 351 , 428 and 734 nm . All these bands show a slight shifting when PANI is doped with DBS:PTS::5:5 ratio. In this case absorption bands appear at 360 , 440 and 765 nm which are present due to the $\pi\text{--}\pi^*$ transition and metallic polaron band transitions in the polymer matrix. No bifurcating peaks due to PTS and DBS appear in the electronic spectra and only single peak due to mixed dopant appear in the polyaniline DBS:PTS system which shows the equal contribution of both the dopants in the doped PANI matrix.

3.6. Static charge results

The static charge of the insulating ABS polymer and conducting PANI/ABS composite was measured using static charge meter SCM-1. Static potential in coulombs was measured using relationship

$$Q = CV$$

where C is the capacitance of the base plate; and V , the voltage indicated on the static charge meter.

Static energy is calculated using the relationship

$$E = \frac{1}{2} CV^2$$

(in Joules) For blank ABS sample, SCM meter reading lies at 0.4 kV .

Using the Multiplier table, static potential = 400 V , capacitance = 25 pF .

Table 2
Shielding effectiveness of PANI-ABS conductive composite at 101 GHz

| Nature of ABS-PANI composite | Input power | Output power | Attenuation value SE (dB) = $10 \log_{10} p_i/p_o$ |
|------------------------------|-------------|-----------------------|--|
| 100:0 | 1.092 mW | 0.7 mW | 0 (0) ^a |
| 98:2 | | 0.28 mW | 5.91 (3.5) ^a |
| 95:5 | | 0.26 mW | 6.23 (7.2) ^a |
| 90:10 | | 80 μW | 11.35 (11) ^a |
| 80:20 | | 12 μW | 18.42 (18) |
| 70:30 | | 33 nW | 45.19 (36) ^a |
| 60:40 | | 30 nW | 45.61 (42) ^a |
| 50:50 | | Beyond limit (< 0 nW) | > 60 (>60 dB) ^a |

^a These values represent the shielding effectiveness reading measured directly with the EMI equipment set up.

On applying the formula $Q = CV$.

For ABS $Q = 25 \times 10^{-12} \times 400 = 10 \times 10^{-9} \text{ C}$ and static energy $E = 0.5CV^2$

Therefore for ABS $E = 200 \times 10^{-8} \text{ J}$.

However, on keeping the compounded composite mould of ABS:PANI::90:10 in the energy pan, no static charge was observed. This implies that there is a complete dissipation of static charge from the compounded conducting blend sample of PANI–ABS.

3.7. EMI measurements at 101 GHz

Shielding effectiveness is measured as the ratio of the field strength before and after attenuation and is expressed in decibels (dB) calculated according to formula as:

$$SE = 10 \log p_i/p_t$$

where SE is the shielding effectiveness; p_i , power in watts (i stands for incident wave, t for transmitted wave).

The values of the shielding effectiveness as measured using 101 GHz transmitter set up is given in Table 2.

The results of Table 2 show that higher loading levels of PANI in the composite matrix gives a higher shielding effectiveness of the order of 60 dB whereas lower loadings of PANI in the composite (PANI/ABS::10:90) shows a shielding effectiveness of 11.35 dB. A loading level of 5% PANI in ABS gives a shielding effectiveness of the order of 6.23 dB which cannot be effectively used for the controlling of interference in the mm range but can be used for the dissipation of static charge.

4. Conclusions

It has been shown that the polyaniline doped with a specific ratio of mixed dopant like *p*-toluene sulphonate and dodecylbenzene sulphonate can be melt blended with an insulating polymer like acrylonitrile–butadiene–styrene resulting in the formation of conducting composite. Low loading levels of polyaniline in the composite can be used for the dissipation of electrostatic charge whereas high loading levels can be used for the shielding of electromagnetic interference at 101 GHz.

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