Improved Method to Graft Polyaniline on E-Glass Fabric to Enhance Its Electronic Conductivity

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ABSTRACT: A method to enhance the electronic conductivity of polyaniline grafted E-glass fabric is described. The influence of substituted aromatic sulfonic acids as primary dopants on conductivity of the grafted polyaniline–E-glass fabrics is studied. The conducting fabrics obtained in this method were characterized by UV-vis spectroscopy, scanning electron microscopy, X-ray diffraction study, thermogravimetric analysis , and conductivity. Shielding effectiveness measurements on these Pan–E-glass fabrics showed that the performance is improved (i.e., 0.01 MHz = 49 dB, 1000 MHz = 7 dB) compared to earlier studies (i.e., 0.05 MHz = 37 dB, 1000 MHz = 1 dB) without pretreatment of fabrics. Possible application of these fabrics, e.g., for dissipation of electrostatic charge, is suggested. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 2316–2323, 2005

Key words: polyaniline; grafting; aromatic sulfonic acid; shielding effectiveness

INTRODUCTION

The increasing complexity of electronic devices and systems in the form of higher packing density and quick response has generated pollution in the form of electromagnetic interference (EMI). Electromagnetic radiation is one of the unfortunate by-products of the rapid proliferation of electronic devices.[1] If this problem is left unattended it can cause severe damage to the communication systems and safety operation of many devices. Owing to their more esthetic appeal, plastics have replaced metal cabinets for much electronic equipment and, unlike metals, plastics are transparent to electromagnetic radiation and cannot be earthen to provide electrostatic control. At present the most cost-effective means of controlling EMI and electrostatic charge dissipation (ESD) is to use various types of conducting composites with conductive fillers such as metal fibers, metal particulates, carbon black and graphite fiber, and carbon-fiber and metal-fiber filled polyolefine composites.[2] The metal-based composites are prone to corrosion and carbon based composites are brittle in nature and lack esthetic appeal.

Materials that have the ability to dissipate charges formed, by any means including tribocharging and induction, on the material are referred to as static dissipative. An antistatic agent is generally used to describe a substance that is added to a material to make that material static dissipative.

The ESD can be minimized by adding antistatic agents. These agents can function by reducing the generation of charge, by increasing the rate of charge dissipation, or by both mechanisms. Substances of high electrical conductivity are effective antistatic agents and these include nitrogen compounds such as long-chain amines, amides and quaternary ammonium salts, esters of fatty acids and their derivatives, sulfonic acids and alkyl aryl sulfonates, polyoxyethylene derivatives, polyglycols and their derivatives, polyhydric alcohols and their derivatives, phosphoric acid derivatives, solutions of electrolytes in liquids with high dielectric constants, molten salts, metals, carbon black, and semiconductors.[3]

Polyaniline, an environmentally stable polymer, can be used for grafting so that the flexible grafted surfaces can be used as a new material for the control of ESD. These materials may show better performance than metal fiber/powder filled composites, which are susceptible to galvanic corrosion and loss of conductivity due to friction or, as in the graphite reinforced composites, to brittleness. The electrolyte for ESD purpose cannot be used for obvious reasons.

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-sulfosalicylic acid, benzene sulfonic acid, and *p*-toluene sulfonic acid. However, due to the porous nature of a substrate the conductivities of the polyaniline-grafted fabric were not up to expectations and shielding effectiveness was low.[4–7]

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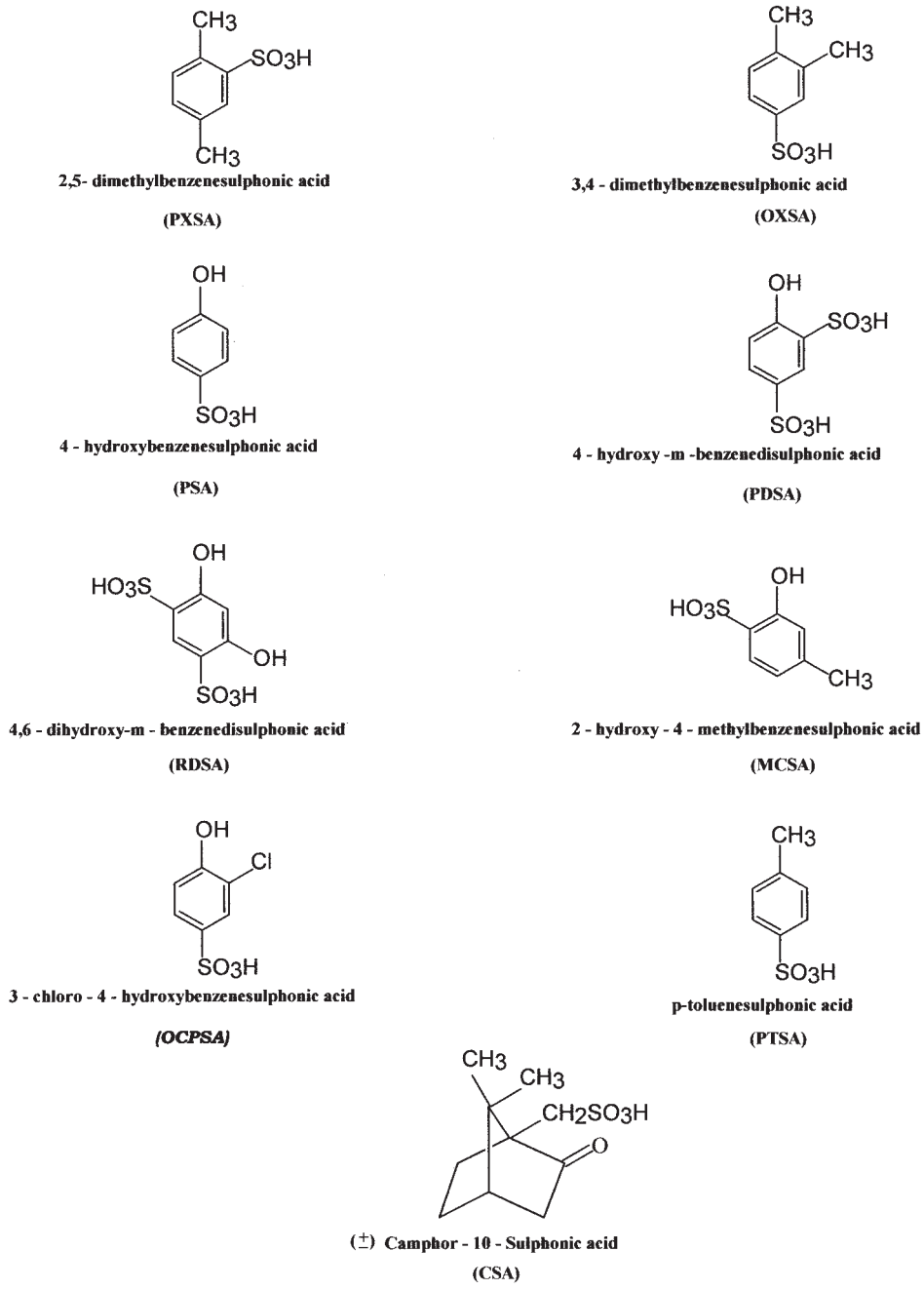


Figure 1 Structure of various doping acids.

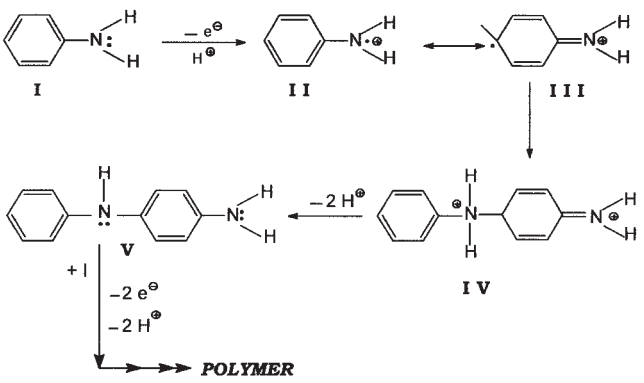
In this article, we discuss the pretreatment of E-glass fabrics and grafting of polyaniline on it in the presence of nine aromatic sulfonic acids as dopants, viz. 2,5-dimethylbenzenesulfonic acid, 3,4-dimethylbenzenesulfonic acid, 4-hydroxy benzenesulfonic acid, 4-hydroxy-*m*-benzenedisulfonic acid, 4,6-dihydroxy-*m*-benzenedisulfonic acid, 2-hydroxy-4-methylbenzenesulfonic acid, 3-chloro-4-hydroxybenzenesulfonic acid, *p*-toluenesulfonic acid, and camphor-10-sulfonic acid. In the presence of these dopants polyaniline gets deposited on the surface and interstices of fabric to impart electronic conductivity to the fabric so that it can be used as an antistatic material for the dissipation of electrostatic charge.

EXPERIMENTAL

All chemicals used were of AnalaR grade. Aniline was freshly distilled before use. Distilled water was employed. E-glass fabric was purchased from John R. Sweet Co. (Mustoe, VA).

Instrumentation

The surface resistivity data of the conductive grafted samples were measured using the two-probe method by holding the sample between two thin metallic foils (platinum or copper), placing them 1 cm apart, and is expressed as Ω cm.



Scheme 1

The diffuse reflectance spectra of the Pan-grafted E-glass fabrics were recorded on a UV-vis-NIR Varian Cary-500 spectrophotometer. The X-ray diffraction pattern of polyaniline grafted surfaces was recorded using Cu Kα radiation (λ = 1.5418^0 A) on Jeol JDX 8030 X-ray diffractometer. The fiber diameter and polymer morphology of PAn-grafted E-glass fabric were determined using scanning electron microscopy (SEM). A small fiber was placed on the SEM holder and gold sputtering was done on it. The scanning electron microscopy was recorded at magnification 450 K using a Hitachi SEM machine [*S*-3000H]. The thermogravimetric analysis data of the polyaniline grafted on E-glass fabrics were recorded on a Perkin–Elmer 7 series thermal analysis system under atmospheric nitrogen at 10°C/min.

Shielding effectiveness measurements

Various methods are available for the measurement of shielding effectiveness (SE). Among these methods, the coaxial method is the most preferred because results from various laboratories are comparable. The coaxial transmission line method (ASTM-S7) was used to measure the SE. Tests were carried out on a small torus-shape cell. The round coupon of the sample of internal diameter 43 mm and outer diameter of 120 mm was cut and on the periphery of the sample silver ink was applied to reduce the contact resistance between the sample and a holder to 0.2 Ω cm. The measurements were made at specific frequencies using a signal generator 8642 B (Hewlet-Packard) and field intensity meters (NM17/27A for 0.01–32 MHz and NM37/57A for 30–1000 MHz) using the point-by-point method with and without the specimen.

Pretreatment on E-glass fabric

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 either ethyl methyl ketone, methanol, or acetone solution for half an hour

TABLE I
Absorption Peak Maxima of PAn-Grafted E-Glass Fabric with Different Dopants

S. No	Dopants	Absorption bands	Assignments
1	PXSA	328	π–π* transition in benzenoid ring
		434	Cation–radicals
		666	(localized) trapped excitons–bipolarons
2	OXSA	340	π–π* transition in benzenoid ring
		456	Cation–radicals
		698	(localized) trapped excitons–bipolarons
3	PSA	333	π–π* transition in benzenoid ring
		439	Cation–radicals
		670	(localized) trapped excitons–bipolarons
4	PDSA	340	π–π* transition in benzenoid ring
		439	Cation–radicals
		657	(localized) trapped excitons–bipolarons
5	RDSA	320	π–π* transition in benzenoid ring
		439	Cation–radicals
		658	(localized) trapped excitons–bipolarons
6	OCPSA	328	π–π* transition in benzenoid ring
		439	Cation–radicals
		674	(localized) trapped excitons–bipolarons
7	MCSA	352	π–π* transition in benzenoid ring
		439	Cation–radicals
		690	(localized) trapped excitons–bipolarons
8	PTSA	328	π–π* transition in benzenoid ring
		439	Cation–radicals
		682	(localized) trapped excitons–bipolarons
9	CSA	340	π–π* transition in benzenoid ring
		416	Cation–radicals
		698	(localized) trapped excitons–bipolarons

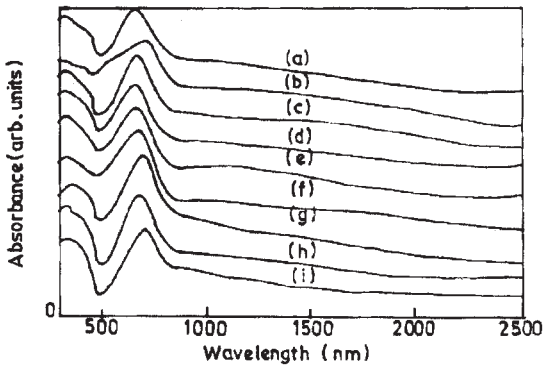


Figure 2 UV-vis absorption spectra of PAn-grafted E-glass fabric with different dopants: (a) PXSA; (b) OXSA; (c) PSA; (d) PDSA; (e) RDSA; (f) OCPSA; (g) MCSA; (h) PTSA; (i) CSA.

to 1 h and dried at room temperature. We speculate that this pretreatment yields fabric with a large number of active sites due to the carbonyl group, to act as an anchor for the PAn chain, the formation of which is via the generation of free radicals. This way even in the interstices of the fabric, PAn gets anchored to enhance the electronic conductivity of a grafted E-glass fabric and reduces its porosity.

Grafting of polyaniline on E-glass fabric

Maleic anhydride treated E-glass fabrics were immersed in 0.1 *M* solution of aniline in aromatic sulfonic acid at pH 1–2. The grafting was carried out using a double-wall tray (30 × 40 cm) with the 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. A stoichiometric 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 along with benzoquinone, benzidine formed during the course of the reaction. The low-molecular-weight oligomeric polyaniline will not get grafted on fabric. 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. They were finally dried at 50°C under vacuum for 2 h.

The dopants used were 2,5-dimethylbenzenesulfonic acid (PXSA), 3,4-dimethyl benzenesulfonic acid (OXSA), 3-chloro-4-hydroxybenzenesulfonic acid (OCPSA), 2-methyl-4-hydroxybenzenesulfonicacid (MCSA), 4,6-dihydroxy-*m*-benzene disulfonic acid (RDSA), 4-hydroxy-*m*-benzenedisulfonic acid (PDSA), and 4-hydroxybenzenesulfonic acid (PSA), *p*-toluenesulfonic acid (PTSA), and camphor-10-sulfonic acid (CSA). The structure of the dopants is shown in Figure 1.

Synthesis of aromatic sulfonic acids

Aromatic sulfonic acids used in these studies were synthesized and purified as per standard procedures available in literature.[8–14]

RESULTS AND DISCUSSIONS

The formation of conducting polymer 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

TABLE II
Comparison of Resistivity Data of PAn-Grafted E-Glass Fabrics and PAn Pellets Using Nine Aromatic Sulfonic Acids as Dopants

S. No	Dopant	Resistivity of pressed pellets [1 mm thick] (Ω cm)	Resistivity (Ω cm) PAn thickness on grafted fabric 6 μm as indicated by SEM studies			
			Surface			
			Direction 1	Direction 2	Average	Bulk
1	PXSA	1.1	310	550	430	15
2	OXSA	1.1	350	400	375	10
3	PSA	0.8	400	650	525	25
4	PDSA	1.0	400	630	515	25
5	RDSA	1.0	200	250	225	20
6	OCPSA	0.62	500	650	575	25
7	MCSA	0.66	500	600	550	15
8	PTSA	1.0	250	350	300	15
9	CSA	0.5	200	300	250	10

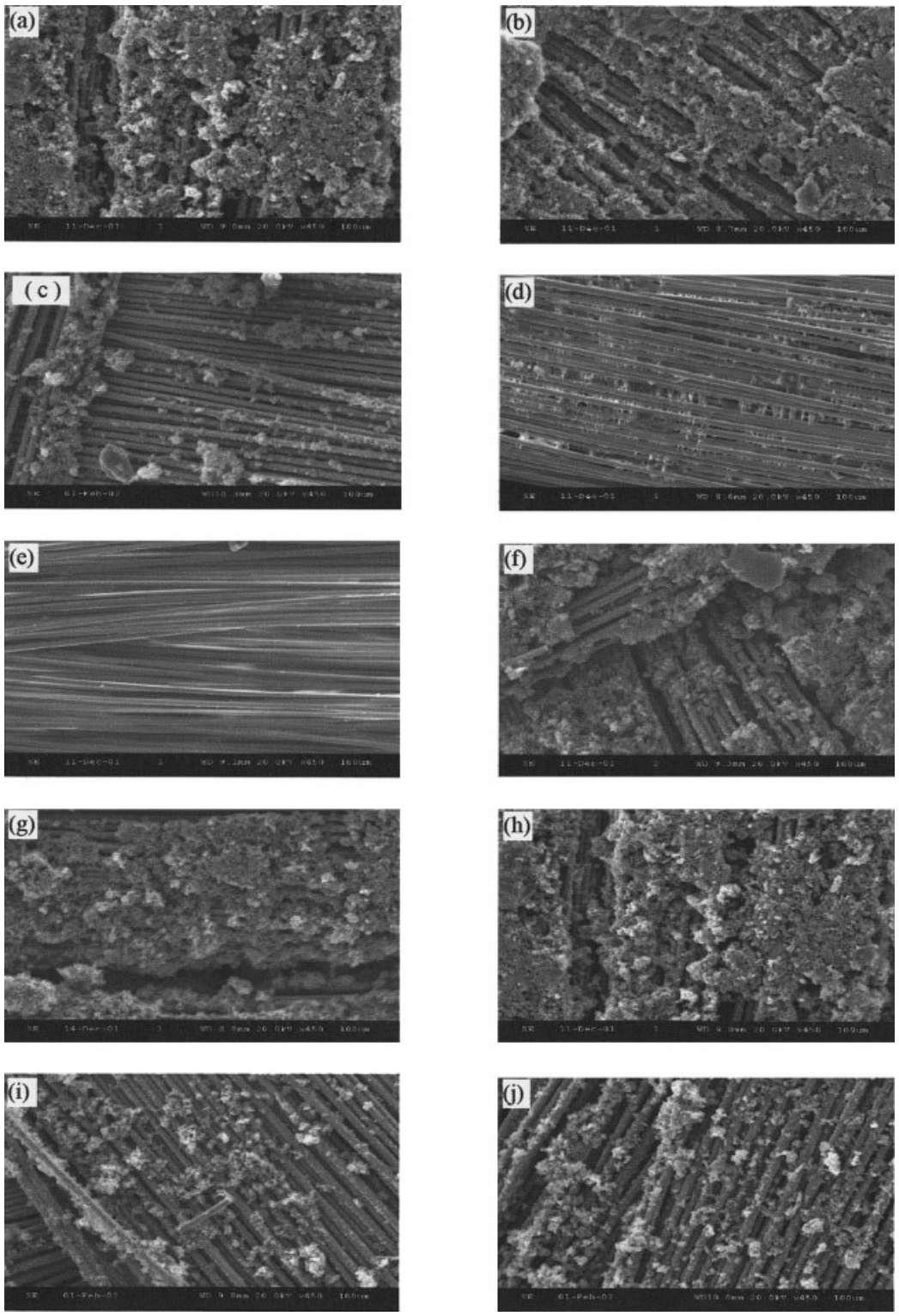


Figure 3 Scanning electron micrographs of PAn-grafted E-glass fabric with different dopants: (a) Maleic anhydride treated E-glass fabric; (b) PXSA; (c) OXSA; (d) PSA; (e) PDSA; (f) RDSA; (g) OCPSA; (h) MCSA; (i) PTSA; (j) CSA.

using different dopants. These cations of intermediate stability get adsorbed on the surface interstices of fabrics, and, upon further coupling reaction, lead to the formation of stable, adherent, and uniform electrically conductive coating.[15] We have named this conducting coating grafting because these coatings 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

TABLE III
Data on X-Ray Diffraction Pattern (Cu, Kα, λ = 1.5418 A^0) of PAn-Grafted E-Glass Fabric with Different Dopants

PAn-PXSA grafted E-glass fabric		PAn-OXSA grafted E-glass fabric		PAn-PDSA grafted E-glass fabric		PAn-RDSA grafted E-glass fabric		PAn-MCSA grafted E-glass fabric		PAn-OCPSA grafted E-glass fabric		PAn-PSA grafted E-glass fabric		PAn-CSA grafted E-glass fabric		PAn-PTSA grafted E-glass fabric	
2θ	d	2θ	d	2θ	d	2θ	d	2θ	d	2θ	d	2θ	d	2θ	d	2θ	d
5.6	15.7	5.8	15.2	5.6	15.7	5.6	15.7	4.9	18.0	5.0	17.6	4.9	18.0	5.2	16.9	5.7	15.4
6.5	13.5	6.7	13.1	6.3	14.0	6.8	12.9	6.5	13.5	6.6	13.3	6.3	14.0	6.8	12.9	7.2	12.2
8.9	9.9	11.0	8.3	10.0	8.8	10.2	8.6	9.3	9.5	10.0	8.8	7.4	11.9	8.6	10.2	8.7	10.1
10.2	8.6	12.2	7.2	11.5	7.6	12.5	7.0	11.2	7.8	11.8	7.4	13.4	6.6	9.9	8.9	10.6	8.3
12.1	7.3	—	—	14.0	6.3	14.6	6.0	12.7	6.9	14.5	6.1	—	—	11.5	7.6	12.1	7.3
13.8	6.4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

from benzenoid to quinoid gets hampered. The polymerization reaction mechanism can be written as shown in Scheme 1.

The absorption peak maxima of Pan-grafted E-glass fabric with different dopants and its possible assignments are tabulated in Table I and the curves are shown in Figure 2. The peak observed at the 320–352 nm range is assigned due to the π–π^* transition associated with the benzenoid ring. The peak due to cation radicals lies at the 416–456 nm range. The band observed at 657–698 nm range is due to charge carriers.

The resistance of the grafted fabric was measured using the two-probe method and the data are presented in Table II. The resistivity data suggest that there is very little anisotropy in electrical conductivity in in situ polymerization of aniline on fabric. This anisotropy is not due to the substrate material, as is evident from the fact that when PAn is coated on fabric from NMP solution there is no anisotropy.[4] From Table II, it is clear that the conductivity of pressed pellets is more than the conductivity of grafted fabric. This is assigned due to restricted orientation of a polymer on grafted fabric. The resistivity for the pressed pellets varied from 0.5 to 1 Ω cm. The bulk resistivity for grafted fabrics varied from 10 to 25 Ω cm. Thus, not much variation is observed in the conductivities of the pellets or grafted fabrics when sulfonic acid is changed. This shows that all sulfonic acids orient in a similar fashion in the doped state.

From the SEM study, the thickness of the maleic anhydride treated E-glass fiber was found to be 5 μm. The SEM study of doped Pan-grafted E-glass fabric with different dopants shows the regularity of PAn deposit on the fabric (Fig. 3). The thickness of PAn doped grafted E-glass fabric with different dopants is calculated by subtracting from the thickness of the blank fiber to find out the thickness of the PAn on a grafted E-glass fabric. The thicknesses of the doped Pan-grafted E-glass fabrics are 5.7, 3.1, 2.8, 2.3, 4.7, 3.2, 4.7, 3.6, and 3.6 μm for dopants PXSA, OXSA, PSA, PDSA, RDSA, OCPSA, MCSA, PTSA, and CSA, respectively.

The 2θ and d values of PAn-grafted E-glass fabric doped with nine dopants as obtained from X-ray diffraction pattern are calculated in Table III and the pattern is shown in Fig. 4. The pattern shows that peaks are broader, indicating amorphous nature of the grafted PAn on glass fabric.

The grafted fabrics using the above dopants are subjected to thermogravimetric analysis and in all

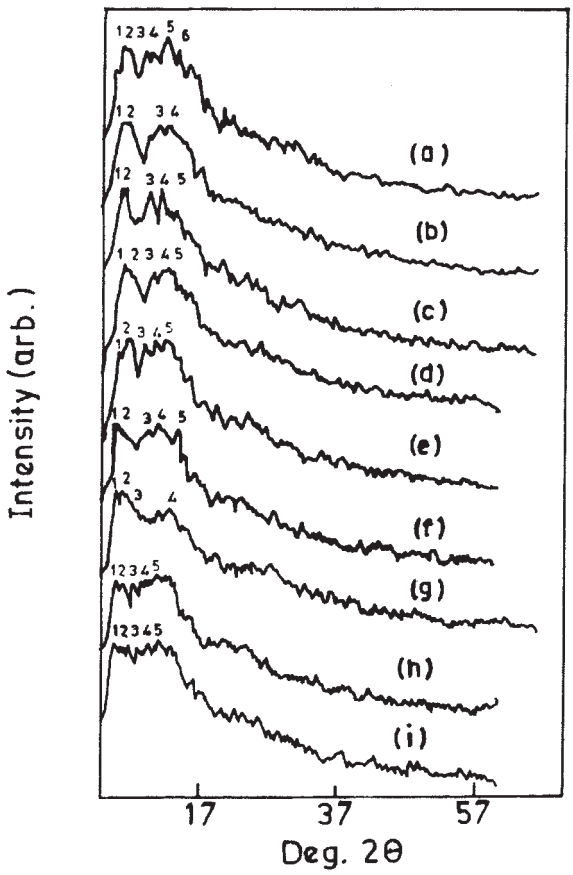


Figure 4 X-ray diffraction patterns (Cu Kα radiation (λ = 1.5418^0 A) of PAn-grafted E-glass fabric doped with nine dopants: (a) PXSA; (b) OXSA; (c) PDSA; (d) RDSA; (e) MCSA; (f) OCPSA; (g) PSA; (h) CSA; (i) PTSA.

TABLE IV
Thermal Stability of PAn-Grafted E-Glass Fabric with Various Dopants

Dopants	Moisture (weight %)	% of doped PAn on grafted E-glass fabric (dopant %)	Dopant expulsion temperature (°C)	Decomposition temperature (°C)
PXSA	1	27.2 (7.8)	295	585
OXSA	1	21.5 (5.6)	333	578
PSA	1	26.7 (8)	243	552
PDSA	1	20.5 (5.6)	305	556
RDSA	1.5	21.9 (7)	153	520
OCPSA	1	24.0 (7)	233	561
MCSA	2	29.7 (9.8)	278	564
PTSA	1	25.0 (7.8)	206	520
CSA	1	23.5 (8)	302	574

cases the first weight loss (1–2%) occurs at ~100°C due to loss of absorbed moisture. The second weight loss (5.6–9.8%) is observed at ~153–302°C and this was equivalent to the doping level of the dopant in the polymer (20.5–29.7%) and confirmed by doping and dedoping experiments. The degradation of the polymer occurs at 520–585°C. The substrate was found to be stable up to 700°C. The values are recorded in Table IV.

The SE for EMI control is largely a function of surface conductivity of the material. For antistatic applications, the typical resistivity recommended is 10^2–10^6 Ω cm. Materials having a surface resistivity below 10 Ω cm are suitable as a shield for EMI. Thus, EMI shielding effectiveness 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 decibels, calculated according to the equation[1]

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

where SE = shielding effectiveness, E_i = electrical field strength in $V\ m^{-1}$ for the incident wave, and E_t = electrical field strength in $V\ m^{-1}$ for the transmitted wave.

The SE measurements were carried out using the coaxial transmission line method in the frequency range of 0.01 to 1000 MHz. The study also indicates that the SE of these samples has a strong dependence on the following:

(1) placement of sample;
(2) anisotropy of the sample;
(3) thickness of the coating;
(4) level of doping and type of dopant;
(5) orientation of the dopant;
(6) magnetic properties.

The shielding effectiveness as measured by coaxial transmission line is recorded in Table V. PAn grafted on the E-glass fabric offers comparatively better shielding effectiveness up to 1 MHz, and after that shielding effectiveness falls in the range of 2 to 7 at 1000 MHz, indicating that these grafted fabrics (0.1 mm thick) can find application as antistatic curtains for housing sophisticated equipments. Our present study shows that the performance of grafted PAn on maleic anhydride modified fabric is improved (i.e., 0.01 MHz = 49 dB, 1000 MHz = 7 dB) compared to earlier studies (i.e., 0.05 MHz = 37 dB, 1000 MHz = 1 dB) without pretreatment of fabrics.

In this work we have shown that the adherent conducting polyaniline of a moderate electronic conductivity can be coated on E-glass fabric after pretreatment with maleic anhydride, a surface active reagent, to impart the conductivity in the interstices of the fabric. This process reduces the amount of porosity, so that these fabrics can be used as an antistatic curtain for housing sophisticated equipment, carpets, and various applications such as armrests. We believe that our process of imparting an electronic conductivity to the fabric is highly economic and commercially viable. Study is in progress to obtain pore-free polyaniline reinforced E-glass fabric using the secondary doping concept.

TABLE V
Data on SE Studies on PAn-Grafted E-Glass Fabric in dB by Coaxial Transmission Line Method in the Presence of Nine Aromatic Sulfonic Acids as Primary Dopant (Thickness = 0.1 mm)

	SE (dB) at					
Dopants	0.01 MHz	0.1 MHz	1 MHz	10 MHz	100 MHz	1000 MHz
PXSA	26	26	25	11	5	5
OXSA	33	32	26	10	8	7
PSA	20	17	13	6	6	5
PDSA	17	17	16	9	6	5
RDSA	29	18	28	15	6	6
OCPSA	18	18	17	8	8	2
MCSA	49	45	20	10	9	5
CSA	30	30	25	14	13	7
PTSA	37	35	30	14	10	6

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