EMI Shielding: Methods and Materials—A Review

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Received 3 August 2007; accepted 19 October 2008
DOI 10.1002/app.29812

ABSTRACT: The growth in the application of electronic devices across a broad spectrum of military, industrial, commercial and consumer sectors has created a new form of pollution known as noise or radio frequency interference (RFI) or electromagnetic radiation or electromagnetic interference (EMI) that can cause interference or malfunctioning of equipment. Therefore, there is a greater need for the effective shielding of components from its adverse effects. This review surveys the shielding materials like metals, conducting plastics and conducting polymers for the control of electromagnetic radiations. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2073–2086, 2009

Key words: shielding materials; composites; conducting polymers; electromagnetic interference

INTRODUCTION

The increasing complexity of electronic devices/systems in the form of higher packing density for quick response has resulted in electromagnetic interference.[1] EMI consists of many unwanted radiated signals which can cause unacceptable degradation of system or equipment performance.[2] These problems if left unattended can cause severe damage to communication system and safety operation of many electronic devices. The most common cause of EMI is electrostatic discharge (ESD). It is a common phenomenon that is readily recognized by even a nontechnical person as radio static, distorted television reception in the form of flashes on the screen and click heard on audio systems when a light is switched on. EMI also causes health hazards such as symptoms of languidness, insomnia; nervousness and headache on exposure to electromagnetic waves.[3–5] High frequency signals are used in the operation of microprocessor-controlled devices and can be transmitted out of the device to the surrounding environment to cause the malfunctioning of nearby equipment. To prevent malfunctioning, electronic devices must be shielded in such a way that both incoming and outgoing interferences are filtered.[6] The present review discuss on various methods and materials for the control of EMI shielding.

THEORY ON SHIELDING OF ELECTROMAGNETIC INTERFERENCE

Shielding effectiveness is the ratio of impinging energy to the residual energy. When an electromagnetic wave pass through a shield, absorption and reflection takes place. Residual energy is part of the remaining energy that is neither reflected nor absorbed by the shield but it is emerged out from the shield. All electromagnetic waves consist of two essential components, a magnetic field (H) and an electric field (E) as shown in Figure 1. These two fields are perpendicular to each other and the direction of wave propagation is at right angles to the plane containing the two components. The relative magnitude depends upon the waveform and its source. The ratio of E to H is called wave impedance. The intrinsic impedance of free space is 377 Ω.[7] EMI shielding consists of two regions, the near field shielding region and far field shielding region. When the distance between the radiation source and the shield is larger than $\lambda/2\pi$ (where λ is the wavelength of the source), it is in the far field shielding region. The electromagnetic plane wave theory is generally applied for EMI shielding in this region. When the distance is less than $\lambda/2\pi$, it is in the near field shielding and the theory based on the contribution of electric and magnetic dipoles is used for EMI shielding.[8]

Shielding effectiveness (SE) is the ratio of the field before and after attenuation of electric and magnetic field and can be expressed as

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

$$SE = 20 \log (H_t/H_i) \tag{2}$$

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Contract grant sponsor: Department of Science and Technology (DST), New Delhi.

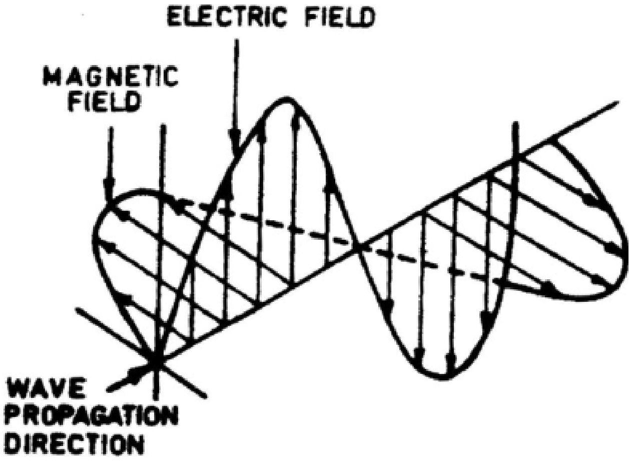

Figure 1 Electromagnetic radiation vector.

where E and H are electric and magnetic fields and the subscripts t and i refer to the transmitted and incident waves. E is measured in volts/m and H in amps/m. SE is a function of frequency.[2,7]

The attenuation of an electromagnetic wave occurs by three mechanisms as shown in Figure 2.

Absorption (A)
Reflection (R)
Multiple reflections (B)

Thus shielding effectiveness is the sum of all the three terms

SE = A + R + B

EMI SHIELDING EFFECTIVENESS MEASUREMENT (EMI SE)

The following are the four test methods commonly used to measure EMI Shielding Effectiveness of a given shielding material.[2,4]

1. Open Field or Free Space Method
2. Shielded Box Method
3. Shielded Room Method
4. Coaxial Transmission Line Method

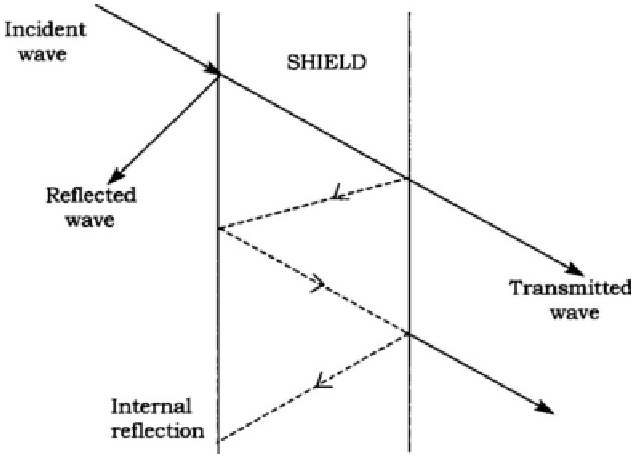

Figure 2 Attenuation of an electromagnetic wave by a shield.

Open field or free space method

The open field or free space method is used to evaluate the practical shielding effectiveness of a complete electronic assembly. Thus, this test measures the radiated emissions that escape from a finished product. The test does not measure the performance of any specific material and is subject to wide variations due to differences in the assembly of individual finished products. This is a true test of the service performance of the designed shielding of the finished product. The test method involves mounting the device at a distance of 30 m from a receiving antenna and recording the radiated emissions as shown in Figure 3. In the same test, the conducted emissions transmitted down the power line are also recorded.

Shielded Box method

The shielded box method is widely used for comparative measurements of test specimens of different shield materials. The test comprises of a metal box and an electrically tight seam that has a sample port in one wall and is fitted with a receiving antenna. A transmitting antenna is placed outside the box and the intensity of signals received by the antenna is recorded both through the open port and with a test specimen fitted over the port. This aspect is illustrated in Figure 4. The drawback of this method is that an adequate electrical contact between test specimens and the shielded box is difficult to achieve. The other concern is its limited range of frequency of about 500 MHz. The results from different laboratories show poor correlation.

Coaxial transmission line method

The coaxial transmission line method for the measurement of shielding effectiveness overcomes the limitations

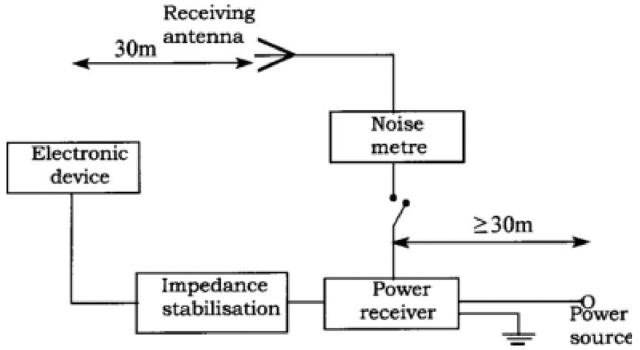

Figure 3 Open field SE measurement (Adapted from reference 2).

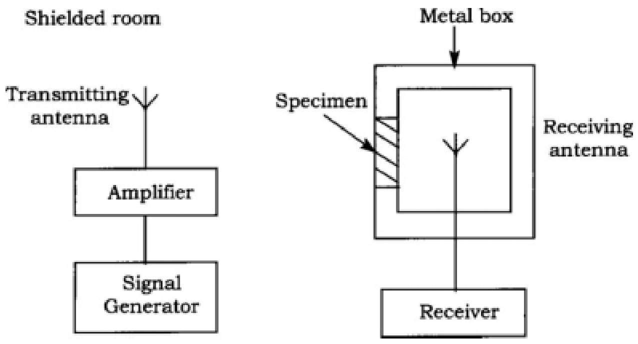

Figure 4 Shielded box SE measurement (Adapted from reference 2).

of shielded box technique and is now the preferred method. The major advantage of this technique is the fact that the results obtained in different laboratories are comparable. In addition, the coaxial transmission line can also be used to resolve the data into the reflected, absorbed and transmitted components. This is illustrated in Figure 5. Tests are carried out on small doughnut shaped samples. The measurements can be made at specific frequencies using a modulated signal generator, crystal detector and tuned amplifier or alternatively, in a swept mode using a tracking generator and spectrum analyzer as receiver. In the point-by-point mode, the system is first set up at a given frequency without the specimen holder in the line. The variable attenuator is set to maximum and the signal level is recorded. The specimen holder is then inserted into the line and the attenuator reduced until the same reading as before is recorded. The attenuation of the signal obtained is a direct measure of the shielding effectiveness of the specimen. To obtain the spectrum of responses the procedure is repeated at a series of different frequencies. Obviously, this point-by-point approach is time consuming, typically requiring several hours to produce a spectrum. In the swept mode a tracking generator driven by a spectrum analyzer replaces the generator. The spectrum analyzer presents the response of the system as a single curve on a display screen in a few minutes. A dynamic range of about 80 dB can be obtained with standard coaxial cables.

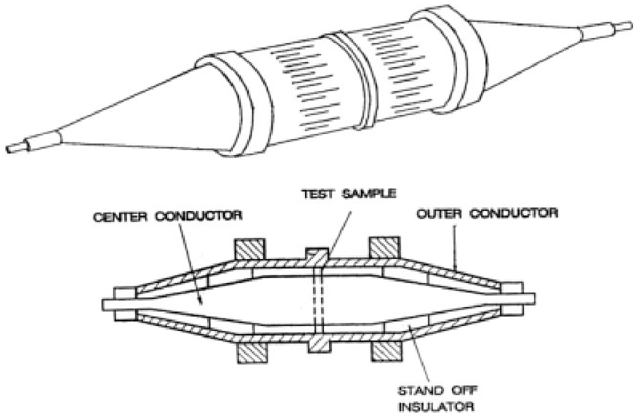

Figure 5 Coaxial transmission line spectrum.

The equipment used consists of small torus shaped cell with an internal diameter of 50 mm and outer diameter of 125 mm. The round coupon of the samples of thickness 1 mm are cut, the contact resistance between sample and holder should be less than 0.2 Ω cm. The measurements are taken at specific frequencies using a signal generator 8642 B (HEWLETT PACKARD) and field intensity meters (NM 17/27A for 0.01–32 MHz and NM 37/57A for 30 MHz to 1000 MHz) with point-by-point method with and without specimen. The observations are recorded from 0.01 MHz to 1000 MHz. The American Society for Testing and Materials, ASTM D4935-99, has adopted coaxial transmission line technique[9] as recognized standard method for measurement of the shielding effectiveness of planar specimens.

Shielded room method

The shielded room method is the most sophisticated one and has been developed to overcome the limitations of the shielded box method. The general principle is the same as the shielded box method except that each of the components of the measuring system, signal generator, transmitting antenna, receiving antenna and recorder are isolated in separate rooms to eliminate the possibility of interference. In addition, the antennas are located in room sized anechoic chambers and the test specimen size is greatly increased, typically of the order of 2.5 m^2 in area. This is illustrated in Figure 6 compared with the shielded box method, the frequency range over which reliable results can be obtained is greatly extended and the reproducibility of the data is significantly improved.

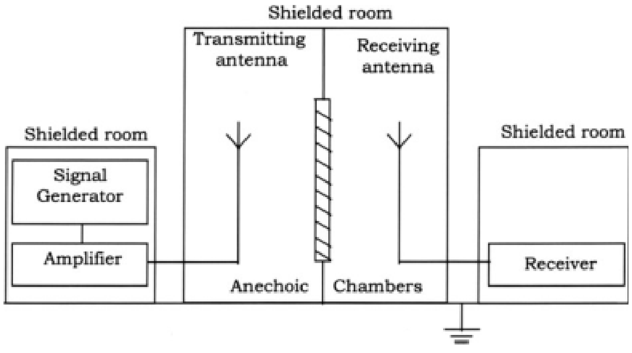

Figure 6 Shielded Room SE Measurement (Adapted from reference 2).

TABLE I
Electrical Conductivity of Metals
(Adapted from reference 6)

Metals	Conductivity (S/cm)
Silver	6.8×10^5
Copper	6.4×10^5
Aluminum	4.0×10^5
Brass	1.7×10^5
Nickel	9.7×10^4
Steel	6.3×10^4
Stainless steel	1.8×10^4
Electroless Nickel	1.8×10^4
Graphite	5.0×10^2

LITERATURE SURVEY

Metals used in EMI shielding

Metals are excellent conductors of electricity and can absorb, reflect and transmit electromagnetic interference. The electrical conductivity of metals is shown in Table I. Rubbers and plastics are nonconducting and are transparent to EMI. The ability to conduct both electricity and heat by metals is the major reason for their use in many applications. Electrical equipments, where there is high build up of static charges, high speed machinery where heat is generated are generally protected by grounding them by metal conductors so that the static charges and heat are dissipated. In a similar manner, high frequency electromagnetic radiation is either prevented from escaping from the equipment or the equipment is shielded from stray radiation by metal shields and covers.[10]

The common material used for construction of enclosures for shielding is mumetal, a high permeability alloy of 14% iron, 5% copper, 1.5% chromium and 79.5% nickel. The other metals/materials used as a shield are brass, aluminum, silver, nickel, stainless steel, metalized plastics and conductive carbon/graphite composites. These conductive composites have certain limitations, for example carbon/graphite suffer from brittleness, aluminum based has low impact resistance, and stainless steel has high density. The metal shield is susceptible for corrosion, which leads to Rusty Bolt Effect of nonlinearity to cause intermodulation problem especially in sea environment. The use of two different metals for shield and gasket causes galvanic corrosion which leads to nonlinearity and decrease in SE of the metallic shields.[11,12]

For shielding applications based on reflection, the weight saving benefit of magnesium enclosures extends over the full frequency spectrum. For shielding based on absorption, die cast enclosures of magnesium and aluminum provide nominally equivalent shielding effectiveness on an equal weight basis. The lower density of magnesium offsets the higher conductivity of the aluminum. Die cast magnesium alloy enclosures for EMI shielding provide significant advantages over both plastic and alternative metal housings.[13]

Plastic materials in EMI shielding—Embedded metal foil as a shield

The embedded thin metal foils of aluminum, copper or silver in the polymer matrix are in vogue with suitable provision for grounding. The extent of shielding achievable depends on the material of the foil, thickness of the foil embedded and the effectiveness of grounding arrangement. Samples have been evaluated for their shielding effectiveness with aluminum and copper foils using ASTM Std. D 4935-89 method. The SE measured was found to 40 dB in the frequency range of 100 MHz to 1000 MHz.[7] Plastic housings are natural insulators and do not reflect or absorb EMI. Most of the energy waves are not obstructed by thermoplastics and enter or leave the housing readily, which causes interference problems. To shield EMI, technical approaches have been extensively considered to modify electrical conductivity of the plastics by the way of

1. Conductive Coating on Plastics
2. Compounding with Conductive Fillers
3. Intrinsically Conductive Polymers - ICP

Conductive coating on plastics

Metallic plating[6,7] and coating on plastics are well-established techniques for decorative, automotive appliance and plumbing products. However, metallized plastics are also used for conductive applications. For EMI shielding purpose following methods are used for metalizing the plastic surface.[14–17]

The different coating techniques are:

- Foil laminates and tapes
- Ion plating
- Vacuum metallization
- Zinc flame spraying
- Zinc arc spraying
- Cathode sputtering
- Conductive paints
- Electroless plating
- Electroplating

Disadvantages of conductive-coatings:

All the above operations are secondary to the molding operation and hence demand additional surface preparation and special equipment.

Compounding with conductive fillers

Conventional plastic materials are excellent electrical insulators having resistivity in the range of 10^{15}–10^{18} Ω cm and made conducting by incorporation of a conducting material. One of the first materials used for this purpose was carbon black.

Carbon black/fibers. Carbon black has a long established association with the rubber industry as the principle reinforcement for mechanical goods and with the plastics industry as filler in wire and cable sheathing. However, because of its graphitic nature, carbon black is a semiconductor, typically the dry resistivity is in the range of 20–0.5 Ω cm and when used as filler in rubbers and plastics it endows the compound with antistatic/conductive properties. Conductive carbon filled compounds finds their principle application in areas that demand antistatic protection (i.e., ESD).

Bowyer and Bader[18] reported the composites of very high specific strength and stiffness produced by incorporating continuous aligned filaments of glass and carbon into matrices of thermosetting plastics like epoxy or polyester. Calleja et al.[19] studied the electrical conductivity of high-density polyethylene (HDPE)—Carbon fiber composites mixed with different concentrations of carbon black. The use of these two filler types in HDPE composites combines the conducting features of both. Carbon fibers provide charge transport over large distances and carbon black particles improve the inter fiber contacts. It is shown that for composites in which the segmented carbon black - HDPE component lies above the percolation threshold the electrical interfiber contacts are activated through carbon black particle bridges, leading to a conductivity rise. Ramadin et al.[20] reported the electrical properties of laminated epoxy-carbon fiber composites. The electromagnetic losses as a function of frequency and specimen spacing are also studied. They observed optimum SE of the laminated epoxy composite ($\sim$ 62 dB) occurs at about 30 mm specimen spacing and frequency $\sim$ 9 GHz. Das et al.[21] reported that the EMI shielding characteristics of natural rubber and Ethylene-vinyl acetate (EVA) filled with conductive carbon black (Vulcan XC-72) and short carbon fiber (SCF). The EVA based composites are found to be the more effective in EMI shielding particularly when SCF is used as the conductive filler. The SCF filled composites exhibit higher SE at lower filler loading compared to carbon black filled ones. The SE of these composites is found to be higher at X - band frequency range (8–12 GHz) compared to that at microwave frequency range (100–2000 MHz). The composites containing SCF are technically useful material (SE $\geq$ 20dB) in X-band region.

Graphite fibers are used with greater frequency in high performance applications, usually for their reinforcing properties. Simon[22] reported that resins with 30% graphite fibers exhibit high modulus (15 to 20 MPa) and enough electrical conductivity for some EMI shielding applications. Padma[23] studied the shielding effectiveness of carbon and Kevlar composite panels and has shown that they offer sufficiently good EMI SE. Sau et al.[24] reported that the electrical and mechanical properties of conductive rubber composites based on Ethylene - Propylene - Diene Rubber (EPDM), Acrylonitrile butadiene rubber (NBR) and 50/50 (w/w ratio) blends of EPDM/NBR containing different loading of short carbon fiber (SCF). The volume resistivity of all fiber - rubber composites increases with the increase in temperature, and the rate of increase in resistivity against temperature depend on the loading of carbon fiber and the nature of the base polymer.

Luo and Chung[25] reported that composites with continuous carbon fibers have better EMI SE than those with discontinuous fillers. Continuous carbon-fiber composite with a carbon-matrix is more effective for shielding, more reflective and more conductive when compared to an epoxy matrix reaching EMI SE of 124 dB at 0.3 MHz–1.5 GHz. The introduction of discontinuous carbon filaments to an epoxy matrix composite with continuous carbon fibers degrades the EMI SE. The dominant mechanism of EMI shielding for these continuous carbon-fiber structural composites is reflection.

Bigg[26] reported the influence of chemical environment on the conductive properties of composites. It is evident that chemical exposure has a significant effect on the bulk electrical conductivity of some filled polymer matrix compositions. The polymers mainly used are ABS, polyphenylene oxide polystyrene blend, nylon 6,6 and polyphenylene sulfide (PPS) and the fillers used are PAN based carbon fiber, aluminum flakes, stainless steel fibers and aluminum-coated glass fibers and examined the SE studies at different exposure conditions in the 1 GHz region. He found that compounds obtained their electrical conductivity from either conductive carbon black or carbon fibers were generally unaffected by the chemical exposures.

Shiratori et al.[27] reported the encapsulation of exfoliated graphite - PMMA composite. This encapsulated exfoliated graphite composite can be directly molded by hot pressing. The electrical conductivity and the EMI SE of this molded product were superior to those of the exfoliated graphite-PMMA composite made by mechanical mixing. This is due to homogeneous dispersion of exfoliated graphite in the encapsulated composite.

Luo and Chung[28] reported the electromagnetic interference shielding effect of flexible graphite. The SE is exceptionally high 130 dB at 1–2 GHz higher than that of solid copper. In addition to conventional shielding applications, flexible graphite can serve as

TABLE II
EMI SE Values of Carbon Black/Fiber Composites

Materials	Frequency range	Shielding effectiveness (dB)	References
Laminated epoxy carbon fiber	~ 9 GHz	~ 62	19
Natural rubber/ethylene-vinyl acetate/carbon black/short carbon fiber	8–12 GHz	≥ 20	20
Continuous carbon fiber composite/carbon matrix	0.3 MHz-1.5 GHz	124	24
Flexible graphite	1–2 GHz	130	27

a shielding gasket material, due to its resilience. The EMI SE values of carbon black/fiber composites are summarized in Table II.

Stainless steel fibers. Stainless steel fibers filled thermoplastics are ABS, nylon 6.6 (PA 6.6), and polycarbonate and polyphenylene oxide, filled with 7% (w/w) steel fibers. The shielding effectiveness of these compounds is typically 36–42 dB. The results are shown in Table III.

Baker et al. [29] reported the EMI SE of stainless steel fibers as conductive fillers in a polymer matrix like acetylonitrile-butadiene-styrene (ABS). The distribution of the conducting fibers inside the composite material would make it behave more like a conducting mesh, which could be used for electromagnetic shielding purposes. The SE obtained was around 11 dB in X-band region. They also reported that SE would approximately double by doubling the specimen thickness. The SE of this composite material is influenced by the orientation of the fibers inside the material, incident electric field, opening size and properties of the material. This composite material is used for shielding purposes and for the construction of electromagnetic absorbent walls. A number of other metal fibers such as copper, brass, aluminum and iron have been reported as fillers for EMI shielding composites, but few are used on a commercial basis. The EMI SE value is summarized in Table IV.

Aluminum fibers. Aluminum fibers have the advantage of low specific gravity, while copper fibers offer the highest intrinsic electrical conductivity of any of the metals. Both these materials, however, are subject to surface oxidation under normal environmental conditions. Osawa and Kobayashi[30] prepared polyethylene and various chatter-machined metal fibers (aluminum, copper, steel, and brass) and carbon fiber and examined the effects of the concentration of the fillers and the thermal treatment of the composites at 80°C in air on the SE of EMI. The order of generation of SE was brass > steel > copper ≈ aluminum > carbon. Thermal degradation of SE was scarcely observed in the carbon fiber system and very slightly in the brass and steel system, while remarkable degradation was observed in the copper and aluminum systems. This newly formed oxidized surface increases the contact resistance between fillers to reduce the SE of EMI of the composites.

Of the various flakes and powders that are available as fillers, only aluminum flakes, which have a high aspect ratio and achieved commercial significance in EMI shielding composites. Precious metal powders, silver, gold, platinum are also used but their high cost severely limits the areas of application. The major areas of use of these specialty materials are in conductive elastomers for EMI shielding gaskets and in conductive epoxy adhesives for EMI applications and for mounting electronic components. Normally ABS, Nylon, PC, PET, PPO and PS are used as matrices. The shielding performance of 30–40 dB can be achieved at a 40 wt % loading.

Nickel Coated Graphite Fibers. Nickel coated graphite fibers are used as conductive additives for plastics and combine the advantageous reinforcing properties of carbon/graphite fibers with the conductivity of the

TABLE III
Stainless Steel Fiber Filled Thermoplastics (Adapted from reference 6)

	Resin type-7% stainless steel fiber			
Property	ABS	PA 6.6	PC	PPO
Shielding effectiveness (at 950 MHz)	42	40	37	36
Volume resistivity (W cm)	0.4	0.9	1.1	1.0

TABLE IV
EMI SE Value of Stainless Steel Fibers

Materials	Frequency range	Shielding effectiveness (dB)	References
Acrylonitrile-butadiene-styrene/stainless steel fibers	8-12 GHz	11	28

metal coating. Di Liello et al.[31] reported the polypropylene based composites reinforced with nickel - coated carbon fiber. These composites exhibited high mechanical properties and improved electrical and electromagnetic performance. Huang and Pai[32,33] reported the EMI SE of electroless nickel coated carbon fibers (ENCF) blend with ABS polymer matrix. Adding additives and adopting suitable temperature and loading fiber during the blending process could achieve ideal EMI SE of ENCF/ABS composites. The thermal stability of EMI SE of ENCF/ABS composites was tested by heat-treating composites in a hot air oven at 60°C and SE was measured at an interval of one week to consider the degradation of SE. The best SE of ENCF/ABS composites could be reached was 44 dB at 1 GHz. Chiang and Chiang[34] reported that nickel-coated carbon fiber (NCF) treated with coupling agent (neopentyl (dially) oxy, tri (dioctyl) pyrophosphato titanate) has been used for preparing composites of PC and ABS by melt blending and these composites have been evaluated for EMI SE. The SE of these composites can reach 50 dB at 1 GHz by the coaxial transmission line method. Huang and Wu[35] prepared PC/ABS/nickel-coated carbon fiber (NCF) conductive composites possessing EMI SE by melt blending method. Adding greater amounts of ABS in PC/ABS/NCF composites could markedly improve the processability and fiber mean length of the composites. The EMI shielding effectiveness of these composites is 47 dB at 1 GHz.

Huang and Chiou[36] reported that Ni-coated conductive carbon fiber (NCF) and conductive carbon fiber (CF) were used as conductive filler in ABS matrix. The maximum EMI SE value of ABS/NCF was 47 dB at 1 GHz. The SE values of composites decreased with increasing the number of processing cycles. Therefore, adding NCF to ABS could offer a good EMI SE of composites. The influence of conductive carbon-fiber orientation and weight percentage on the electromagnetic shielding effectiveness in liquid crystal polymer (LCP) composites was investigated experimentally and theoretically.[37] The shielding effectiveness of 20% conductive carbon-fiber-filled LCP composites was measured to be 50 dB at a frequency of 0.3 GHz and 53 dB at 1 GHz. The results are summarized in Table V.

Bigg[38] reported the technique for increasing the electrical conductivity of polymers by electroless plating of metals onto glass fibers, which are then incorporated into the polymer. Other techniques for providing electrical conductivity are the incorporation of short metallic fibers and metal-coated glass fibers into a polymer matrix. Short metallic fibers increase both the thermal and electrical conductivities of polymer composites, while the metal-coated glass fiber-polymer composites are primarily electrically conductive. He reported the EMI shielding data for common steel, nickel-coated glass fiber-polycarbonate, conductive carbon black-polypropylene and unfilled polycarbonate samples in the frequency range of 100 MHz.

Wenderoth et al.[39] described the EMI shielding of metal and ferroelectrics particle filled polymers. The composite containing only metallic fillers (nickel powder) have a SE comparable to conventional products. The addition of a few percent of ferroelectric material (semicarbazide-hydrochloride and triglycine sulfate) to this composite enhances the shielding behavior by several orders of magnitude without increasing its electrical conductivity. In this three component composite system, SE reaches a maximum in the frequency range 1 GHz close to the ferroelectric/para electric transition temperature. The synergetic effect, obtained by the addition of ferroelectric particles, is related to the high dielectric losses of ferroelectric material close to the transition temperature.

Thus, inherently nonconductive plastic materials can be made conductive by the addition of a variety of metal or metallised fillers and reinforcements. However, a number of limitations to this approach have also exposed high materials cost, problems with processing filled composites, less than satisfactory performance compromises, poor surface finishes and appearance. Here uniform conductivity of the composite is a major problem due to the heterogeneity of the system.

Intrinsically conducting polymers

Since the discovery in 1977 of the metallic properties of molecularly doped polyacetylene,[40] there has been

TABLE V
EMI SE Values of Nickel Coated Carbon Fiber Composites

Materials	Frequency range	Shielding effectiveness (dB)	References
Electroless nickel coated carbon fibers/ABS polymer matrix	1 GHz	44	31,32
Nickel coated carbon fiber/PC/ABS treated with coupling agent	1 GHz	50	33
Nickel coated carbon fiber/PC/ABS composites	1 GHz	47	34
Nickel coated conductive carbon fiber/conductive carbon fiber/ABS matrix	1 GHz	47	35

TABLE VI
Shielding Effectiveness of Conductive PAn-Nylon Cloth (Adapted from reference 64)

Frequency (MHz)	SE (dB[a])	Frequency (MHz)	SE (dB)
0.05	37	10.0	7
0.06	36	20.0	3
0.07	35	50.0	2
0.08	35	110.0	3
0.09	36	200.0	1
0.1	36	300.0	1
0.5	31	400.0	2
1.0	29	500.0	1
2.0	23	1000.0	1
5.0	11	–	–

[a] ± 3 dB up to 5 MHz; ± 1 dB at 1000 MHz.

rapid growth in the field of electronically conducting polymers.[41–44] The interest is mainly due to the numerous technological applications of conducting polymers as active electrode materials in energy storage,[45] opto-electronic devices,[46] display devices,[47,48] and their envisaged application for the control of electromagnetic radiation and dissipation of electrostatic charge.[49–58] Hence intrinsically conducting polymers (ICP) are alternative materials for EMI shielding. Conducting polymers are conjugated polymers, which on doping exhibits electronic conductivity and hence are suitable candidates for systems which can be imparted with metallic conductivity. The electronic conduction in conjugated systems occurs via process known as doping either with electron acceptors or donors. This doping process creates the band structure to enhance their conductivity by many orders. For example Shirakawa et al.[40] have shown that when polyacetylene film is exposed to iodine, it attains metallic conductivity. In a similar way all conjugated systems can be imparted with metallic conductivity. Among all conducting polymers, polyaniline (PAn) and polypyrrole (PPY) are mainly used in EMI shielding purposes. One of the inherent problems with intrinsically conductive polymers (ICP) is the inability to process such polymers into useful articles. This is particularly true for PAn, which is known for its environmental stability and has moderate electronic conductivity and is commercially viable material.

Conducting polyaniline

The use of textile materials as substrates and reinforcing materials for many polymers has wide industrial applications and discussed in many papers.[59–65] Trivedi and Dhawan[66–69] described a method to graft conducting PAn onto glass fabric, glass wool and nylon cloth to impart flexibility and mechanical strength to the PAn, which is otherwise powdery and unprocessable. These flexible conductive surfaces can find application as antistatic shields. The effectiveness of the shield is largely as a function of surface conductivity for antistatic applications; the typical resistivity recommended is 10^{2}–10^{6} Ω cm^{-1}. Materials having a surface resistivity below 10 Ω cm^{-1} are suitable as a shield for electromagnetic interference.

The SE depends upon the following factors:

Placement of sample because of difference in directional conductivity of the grafted fabrics.

Thickness of conducting coating.

Time interval given for each measurement in the point-by-point method.

Type and level of doping.

This conducting flexible surfaces are advantageous compared with the presently popular method of preparing conductive composites by the addition of metal powder/flakes or carbon black to conventional polymer, in which uneven mixing reduces the mechanical properties, there is often compatibility between the filler and the polymer matrix, and there is a risk of surface corrosion; whereas conducting PAn grafted surfaces can withstand any level of acidic fumes and high humidity levels without any degradation. The grafted Nylon fabric affords a shielding effectiveness of 37 dB up to 50 KHz and 30 dB up to 1000 KHz, and above this frequency a sudden fall in SE is observed.

TABLE VII
EMI SE Studies on PAn – PTSA/CMC and PAn– CSA/CMC Reinforced conducting E-Glass Fabric

Sample (EMI SE observed in dB)	Conductivity (S/cm)	Frequency in MHz				
		0.1	1	10	100	1000
PAn—PTSA/CMC reinforced conducting E-glass fabric ($t = 0.15$ mm)	0.2	22	17	16	16	21
PAn—PTSA/CMC reinforced conducting E-glass fabric ($t = 1.4$ mm)	0.5	30	31	35	32	38
PAn—PTSA/CMC reinforced conducting E-glass fabric ($t = 3$ mm)	0.8	39	47	46	47	54
PAn—CSA/CMC reinforcedconducting E-glass fabric ($t = 0.15$ mm)	0.04	18	15	10	10	10
PAn—CSA/CMC reinforced conducting E-glass fabric ($t = 1.4$ mm)	0.1	22	17	16	15	14
PAn—CSA/CMC reinforcedconducting E-glass fabric ($t = 3$ mm)	0.3	29	27	26	26	31

t = thickness.

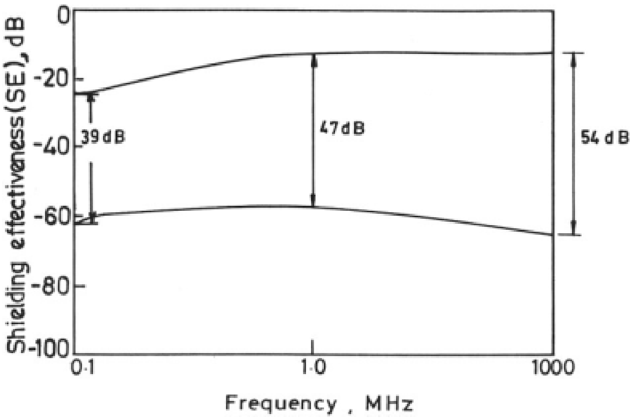

Figure 7 EMI SE curve of PAn-PTSA grafted E-glass fabric coated with PAn–PTSA/chloromethyl phenol complex (Thickness = 3 mm).

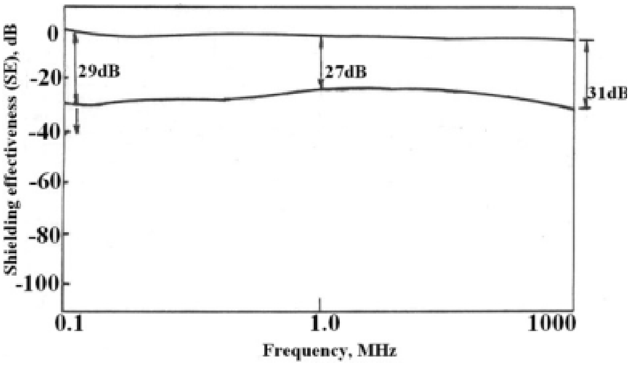

Figure 8 EMI SE curve of PAn-CSA grafted E-glass fabric coated with PAn-CSA/chloromethyl phenol complex (Thickness = 3 mm).

This fall in SE above 1 MHz is due to the porous nature of the substrate material. The extreme values for SE at lower and higher frequencies can be ascribed to stray magnetic fields and low impedance. The SE values are shown in Table VI. This shielding effectiveness study indicates that owing to lower shielding power, these conductive grafted substrates will prove to be good antistatic materials.

Geetha et al.[70] described a method to enhance the electronic conductivity of PAn grafted E-glass fabric using substituted aromatic sulfonic acids as primary dopants. Shielding effectiveness measurements on these PAn-grafted 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. These grafted fabrics can find application as antistatic curtains, carpets and various applications such as armrests. However, Geetha et al.[71,72] prepared PAn reinforced E-glass fabric using *p*-toluene sulfonic acid (PTSA) or camphor-10-sulfonic acid (CSA) as primary dopants and two different type of secondary dopants such as 4-chloro-3-methyl phenol (CMC) and *p*-chlorophenol (PCP). EMI SE studies on PAn- grafted E-glass fabrics coated with doped PAn - chloromethyl phenol complex is shown in Table VII. The pore free conducting fabric reinforced with PAn-PTSA/CMC and PAn-CSA/CMC (Thickness = 3 mm) offered maximum SE of 54 dB and 31dB at 1000 MHz, are shown in Figures 7 and 8. Similarly, EMI SE studies on PAn-grafted E-glass fabrics coated with doped PAn - chlorophenol complex is shown in Table VIII. The pore free conducting fabric reinforced with PAn-PTSA/PCP and PAn-CSA/PCP (Thickness = 3 mm) offered maximum SE of 58 dB and 55 dB at 1000 MHz are shown in Figures 9 and 10.

Polyaniline composites

Conducting polyaniline composites are also mainly used in EMI shielding purposes. Trivedi and Dhawan[73] prepared flexible polyaniline composites with water-soluble polymers like polyvinyl alcohol/carboxymethyl cellulose and their derivatives. Their resistivities lie in the range 60 Ω to 1000 Ω cm and may prove to be useful for dissipation of electrostatic discharge. Kathirgamanathan[74] has described that the

TABLE VIII
EMI SE Studies on PAn—PTSA/PCP and PAn– CSA/PCP reinforced conducting E-glass fabric

Sample (EMI SE observed in dB)	Conductivity (S/cm)	Frequency in MHz				
		0.1	1	10	100	1000
PAn – PTSA/PCP reinforced conducting E-glass fabric (*t* = 0.15 mm)	0.6	30	25	24	26	30
PAn – PTSA/PCP reinforced conducting E-glass fabric (*t* = 1.4 mm)	1	40	35	38	42	48
PAn – PTSA/PCP reinforced Conducting E-glass fabric (*t* = 3 mm)	2	54	48	50	52	58
PAn – CSA/PCP reinforced Conducting E-glass fabric (*t* = 0.15 mm)	1	33	29	28	30	30
PAn – CSA/PCP reinforced Conducting E-glass fabric (*t* = 1.4 mm)	1.5	50	40	40	41	46
PAn – CSA/PCP reinforced Conducting E-glass fabric (*t* = 3 mm)	3	53	50	50	50	55

t = thickness.

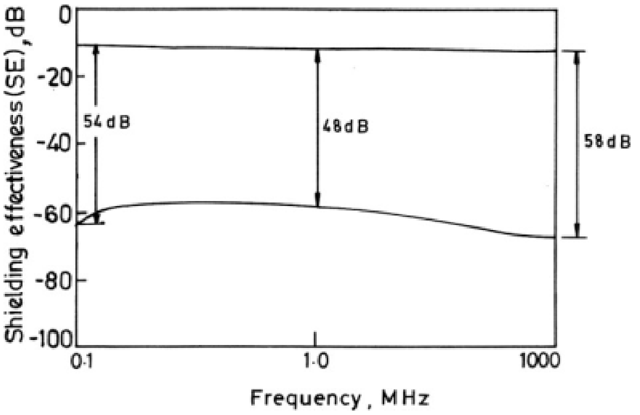

Figure 9 EMI SE curve of PAn-PTSA grafted E-glass fabric coated with PAn-PTSA/chlorophenol complex (Thickness = 3 mm).

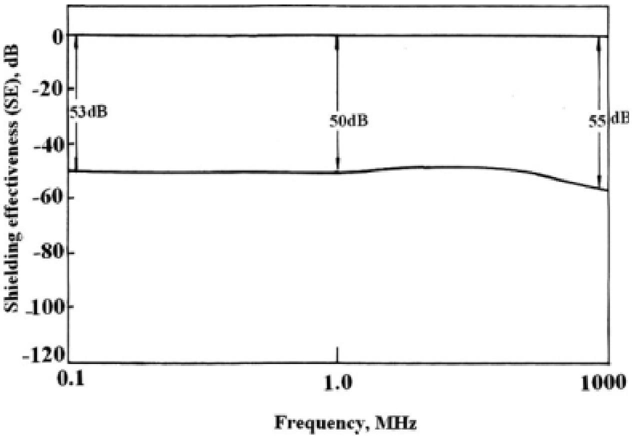

Figure 10 EMI SE curve of PAn-CSA grafted E-glass fabric coated with PAn-CSA/chlorophenol complex (Thickness = 3 mm).

3mm 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.[75] 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 ES without mixing of conductive powder is only ~ 17 dB. They observed that the SE increases with increasing d.c. conductivity and they also observed that the SE against electromagnetic radiation increases through chemical doping and mixing with conducting powder. Wessling[76] reported that by dispersing PAn in a polymer matrix like PVC, PMMA and polyester, conductivity values of around 20 S/cm and in some cases up to 100 S/cm can be achieved. 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 are 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.[77,78]

Park et al.[79] prepared glass fabric/epoxy composites containing conductive multi-walled carbon nanotubes as electrical shielding materials and the electrical properties of the composites were measured using an impedance analyzer in the frequency range 300 MHz to 1 GHz. This composite shielding enclosure had the shielding capacities of more than 90% in the microwave frequency range. Pant et al.[80] synthesized ferrofluid-conducting polyaniline composites of different concentration with a nonconducting polyvinyl alcohol matrix. They found that by

TABLE IX
EMI SE Results of PAn Composites

Materials	Frequency range	Shielding effectiveness (dB)	References
PAn coated nickel spheres/carbon black/co poly(ethylene-propylene) composites	10 KHz–100 MHz	≥20	72
PAn/conducting powders silver, graphite, and carbon black	10 MHz–1GHz		73
ES/graphite		~ 27	
ES/Silver		~ 46	
Mixture of doped PAn/Silver powder/Silver powder		~ 46	
PAn/PVC/PMMA polyester composites	1 GHz	40–75	74
PAn/CSA/m-cresol free standing film	1 GHz	39	75,76
PAn/acrylonitrile-butadiene -styrene/p-toluene sulfonate and dodecyl benzene sulfonate	101 GHz	60	79

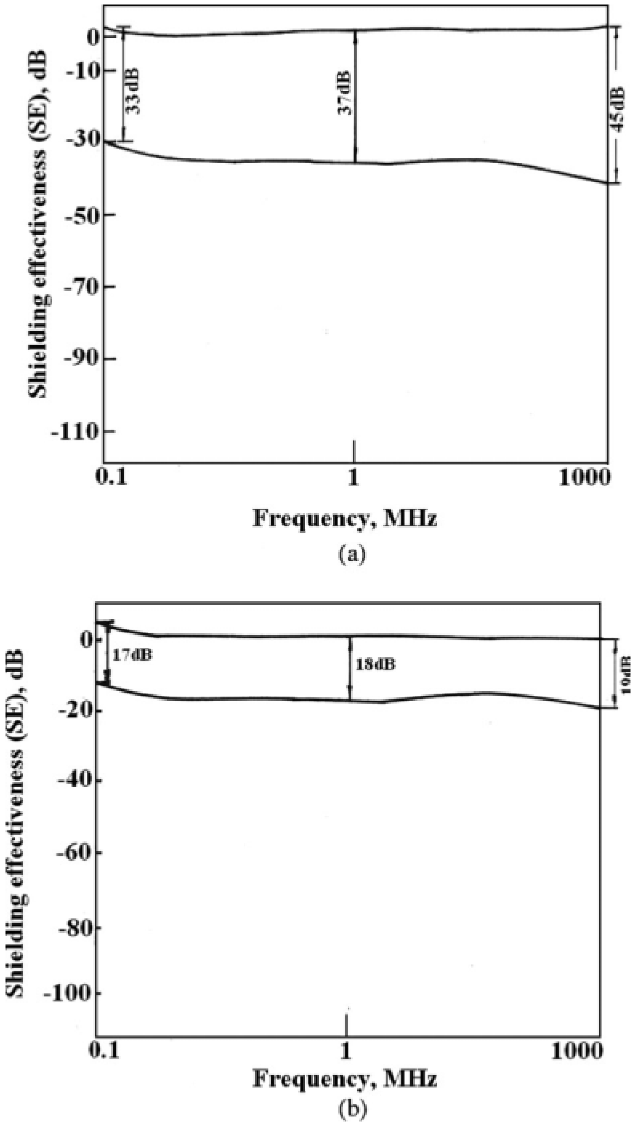

Figure 11 (a) EMI SE curve of free standing conducting PAn–PTSA/chloromethyl phenol complex. (b) EMI SE curve of free standing conducting PAn–CSA/chloromethyl phenol complex.

increasing the ferrofluid concentration the shielding property of the material also increases.

Koul et al.[81] prepared PAn blends with acrylonitrile-butadiene-styrene in presence of mixed organic dopants like *p*-toluene sulfonate and dodecylbenzene sulfonate and studied the EMI/ESD response of conducting composite at 101 GHz. A higher loading levels of PAn in the composite matrix gives a higher shielding effectiveness of 60 dB whereas lower loadings of PAn in the composite (PAn/ABS: 10: 90) shows a shielding effectiveness of ∼ 11 dB. A loading of 5% PAn in ABS gives a shielding effectiveness of the order of ∼ 6 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. Higher loading levels can be used for the shielding of electromagnetic interference at 101 GHz. Gangopadhyay et al.[82] synthesized HCl doped PAn in stable aqueous solution stabilized by PVA and studied the variation of shielding effectiveness of PAn-PVA composites in X-band region (8.2–12 GHz). These composites are found to have appreciable SE depending upon the conductivity as well as thickness of the samples. The EMI SE results are summarized in Table IX.

Satheesh Kumar et al.[83,84] prepared flexible and freestanding conducting polyaniline film of varied thickness using either *p*-toluenesulphonic acid or camphor-10-sulfonic acid as a primary dopant and 4-chloro-3-methyl phenol as a secondary dopant as shown in Figure 11. This flexible and free standing conducting PAn film prepared by this process may find application in the shielding of electromagnetic interference (EMI), conducting wires, as a thin film for batteries, chemical sensor, antistatic agent, zebra connectors for multi-point connections and for making computer cabinet for housing of an electronic assembly to protect it from build up of static charge. The results are shown in Table X.

Light weight and strong EMI shielding and ESD reinforced degradable polymer and monomer material and plastic enclosure materials are provided for electronic devices and EMI shielded rooms.[85] Chandrasekhar and Naishadham[86] reported the first cumulative broadband measurements and computations of all microwave parameters of a conducting polymers relevant for practical application, namely conductivity, absorption, complex permittivity, shielding and reflection. The specific conducting polymers selected is PAn doubly doped to a high doping level with two proprietary sulfonate dopants which otherwise also afford it exceptional environmental durability having a d.c. conductivity at room temperature of 11 S/cm. Measurements have been carried out over a wide

TABLE X
EMI SE Studies on Freestanding Films of Conducting PAn–PTSA/CMC and PAn–CSA/CMC Complex

Sample (EMI SE observed in dB)	Conductivity (S/cm)	Frequency in MHz				
		0.1	1	10	100	1000
PAn-PTSA/chloromethyl phenol complex ($t = 0.6$ mm)	3	33	37	39	37	45
PAn-CSA/chloromethyl phenol complex ($t = 0.6$ mm)	0.1	17	18	18	16	19

TABLE XI
EMI SE of Various PPY/Fabric Complexes at 1 GHz

Sample	Shielding Effectiveness SE (dB)
PPY-AQSA/PET	~ 22
Ag/PE/Ag	~ 55
Ag/PPY-AQSA/Ag Pd/PE/Ag	~ 80

frequency band of 4 to 18 GHz, encompassing the X and K - bands of military radar interest, on bulk PAn using coaxial line techniques.

Polypyrrole composites

Trivedi and Dhawan[87] described a process for the polymerization of pyrrole on insulating surfaces like nylon, terylene and glass fabric and polymer matrix like polyvinyl alcohol (PVA) by vapor phase polymerization. The electrical conductivity of these PVA/PPY composite films is in the range 200 Ω cm to 20 KΩ cm. These conducting polymer coated insulating plastics have valuable applications for the shielding of electromagnetic interference in electronic equipment and for electrostatic charge dissipation and for storing of electronic components. Lee and coworkers[88] synthesized PPY and metal (Ag, Pd) compounds coated on woven polyethylene terephthalate (PET) and nonwoven polyester (PE) fabrics by electrochemical treatment. PPY coated on PET or PE fabrics was electrochemically synthesized by using anthraquinone-2-sulfonic acid (AQSA) as a dopant. Table XI shows the EMI SEs of various PPY/fabric complexes. The results show that both conducting PPY and Ag layers contribute to the increase of EMI SE. The SE of Ag/PPY-AQSA/AgPd/PE/Ag is ~ 80 dB, which implies that this material can be applied to military purpose. Kim et al.[89,90] prepared intrinsically conducting polymer/textile composites by coating polypyrrole or poly (3, 4-ethylenedioxythiopene) PEDOT, on the fabrics through chemical or electrochemical oxidation of pyrrole or EDOT. EMI SE of the composite is about 36 dB in the frequency range of 1.5 GHz.

Pomposa et al.[91] developed intrinsically conducting hot melt adhesives (ICHMAS) based on PPY blends for EMI shielding applications. These new materials retain the advantages of conventional hot melt adhesives (e.g., melt processibility, quick bonding, good adhesion to a wide variety of substrates etc) having a level of electrical conductivity appropriate to be used at room temperature as EMI shields in electronic, computing and telecommunication applications (i.e., form-in-place EMI gaskets, thin film EMI shields, isolation of internal EMI-generating circuits etc.). They reported the theoretical EMI shielding properties at room temperature of the PPY-based ICHMAS. Near field EMI SE values in excess of 80 dB at 1 MHZ are determined for samples containing more than 15% volume fraction of PPY. At 300 MHz, the near field EMI SE values are estimated to remain above 30 dB for the PPY-based ICHMAS. Far field EMI SE values of 22, 27, and 30 dB are determined in the frequency range from 1 to 300 MHz for samples containing 15, 20, and 25% volume fraction of PPY, respectively. A far field EMI SE value of 30 dB corresponding to a signal attenuation of 99.9% is appropriate for many commercial shielding applications.

Kaynak[92] synthesized PPY films of varying electrical conductivities (0.001 S/cm–50 S/cm) using a range of *p*-toluenesulfonate anion dopant concentrations (0.0025–0.1 mol/L) and measured SE as a function of polymer conductivity, frequency and temperature. Highly doped PPY films exhibited SE (40 dB from 300 MHz to 2 GHz. SE of PPY films increased with increase in the dopant concentration and decreased with frequency reaching a plateau at higher frequencies. Highly doped samples were very reflective in the microwave region. Lightly doped films were almost transparent to microwave radiation. Using polypyrrole impregnated conducting polymer composites, Ruckenstein and Park[93] reported far-field EMI shielding effectiveness reaching 26 dB in the frequency range 1–2 GHz. Kathirgamanathan[94] reported far-field EMI SE as high as 40–50 dB in the frequency range 10 KHz to 1GHz for PPY impregnated microporous polyethylene taps. The EMI SE results are summarized in Table XII.

TABLE XII
EMI SE Results of PPY Composites

Materials	Frequency range	Shielding effectiveness (dB)	References
PPY or poly (3,4-ethylene dioxythiopene) PEDOT fabric complexes	1.5 GHz	36	86
PPY based intrinsically hot melt adhesives	300 MHz	30	87
PPY/p-toluenesulfonate complexes	300 MHz–2 GHz	>40	88
PPY impregnated conducting polymer composites	1–2 GHz	26	89
PPY impregnated microporous polyethylene taps	10 KHz–1GHz	40–50	90

CONCLUSIONS

Carbon based shielding materials suffer from limited mechanical flexibility. Metals based shielding materials suffer from heavy weight, corrosion and difficulty in tuning their shielding efficiencies. Therefore synthetic metals like PAn and PPY are the most alternative and attractive candidates for EMI shielding due to their lightweight, noncorrosive nature and commercial viability.

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