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Carbon nanostructure composite for electromagnetic interference shielding

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Abstract. This communication reviews current developments in carbon nanostructure-based composite materials for electromagnetic interference (EMI) shielding. With more and more electronic gadgets being used at different frequencies, there is a need for shielding them from one another to avoid interference. Conventionally, metal-based shielding materials have been used. But due to the requirement of light weight, corrosion resistive materials, lot of work is being done on composite materials. In this research the forerunner is the nanocarbon-based composite material whose different forms add different characteristics to the composite. The article focusses on composites based on graphene, graphene oxide, carbon nanotubes, and several other novel forms of carbon.

Keywords. Electromagnetic shielding; nanocomposites; carbon; polymers.

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1. Introduction

In the past few decades, the modernization in the field of science and technology has created a new kind of pollution, i.e. electromagnetic interference (EMI). EMI is the interference of one electromagnetic signal produced or received by another electronic device. As a consequence one electronic element adversely affects the other's performance. For example, interference of signal of television and sound speakers causes glimmering of picture as well as sound. Similarly, EMI may also affect space explorations, military machineries, scientific equipments, surveillance cameras and so on [1,2]. EMI not only affects electronic gadgets but also affects human health. For example, prolong exposure to EM radiations increases the risk of cancer, heart problems, skin problems, headache and many other diseases [3]. With the rapid development and rejuvenation of gadgets there is a steady increase in the electromagnetic pollution and in order to alleviate these problems, there is an active quest for effective electromagnetic interference materials. IEEE currently provides safety limits on exposure to RF electromagnetic radiations [4].

EMI can be classified either by its mode of travel or characteristic of its frequency. According to the mode of travel, EMI is classified as radiated or conducted interference. Radiated interference is the electromagnetic energy that emanates from an equipment, cable or interconnected wiring. Conducted interference travels through the equipment through external connections. EMI characterized by frequency are categorized as narrow-band or broad-band interference. Broad-band interference is present over a broad frequency range and is further classified as random or impulse noise [5].

Blocking the electromagnetic radiation using barriers made up of conductive or magnetic materials is called EMI shielding. The shielding material helps in absorbing or reflecting the EM radiation thereby acting as a shield by blocking the radiation from penetration into the shielded device. Earlier the most common way of shielding was reflection of radiation using metals. But, with the advancement in the field of science and technology, researchers and scientists were able to find new composites which fulfill the existing requirements, taking into consideration the drawbacks of metal-based shielding material [1,6]. In the present review, we focus on the carbon-based composite materials which can be used for EMI shielding. A prominent thread in the unfolding story of nanotechnology are carbon nanostructures, the discovery and research of which has contributed considerably to the science at the nanoscale. The competences of forming different architectures at nanoscale make carbon a versatile and unique element. The intrinsic properties of carbon have generated enormous interest for its possible implementation in myriad of radio frequency devices, electronic circuits, sensors and so on [6,7]. With the discovery of polymer nanocomposites, a new field of carbon-based polymer composite has been opened [8]. These carbon-based polymer composites are found to be more attractive due to their exceptional properties like low density, good electrical and mechanical properties, ease in processibility and so on [8]. Due to the exciting properties of carbon nanostructures like high tensile strength, high conductivity, low weight, flexibility and high thermal conductivity, they can be used as EMI shielding materials along with other functionalities [7]. The present paper is divided into five sections. Next section describes the theory of shielding and the parameters which affect the EMI shielding properties of the materials. Section 3 deals with materials which are currently being looked at as EMI shielding materials. Section 4 of the article is devoted towards discussing the role of carbon and its composites in shielding. Different nanoarchitectures of carbon-based fillers are discussed. Direct comparison of the performance of materials reported by different researchers is not realistic because the EMI measurements starting from the laboratory to commercial level are performed at different frequencies and methods of processing the materials, thickness and ways of measurement are all different. Further, different frequency ranges have different applications. For example, L band is used by low earth orbit satellites, wireless communication; S band in multimedia applications like mobile, TV, cordless phones, C band finds its applications in long distance radiotelecommunication, Wi-Fi devices, X-band in weather monitoring, air traffic control defence tracking and K_u band is used by very small aperture terminal systems and so on [9]. EMI shielding requirement for each frequency band is different and therefore the materials used for the purpose also vary based on the requirements. However, we have tried to take utmost care to clearly mention the strategies used by different researchers to achieve desirable shielding.

2. Theory and mechanism of EMI shielding

The foremost indicator for measuring shielding effectiveness of a material is attenuation. Shielding efficiency of a shield is the ratio of the magnitude of the incident electric or magnetic field without shielding to the magnitude of electric or magnetic field with shielding. EMI shielding involves two regions, namely, the near-field shielding and far-field shielding. When the distance between the source and the shield is larger than $\lambda/2\pi$, it is called the far-field shielding where electromagnetic plane wave theory is applied. On the other hand, if the distance is smaller than $\lambda/2\pi$, it is called near-field shielding and the theory of electric and magnetic dipoles is used. Thus, profound knowledge of both intrinsic and extrinsic parameters must be taken into consideration before designing a particular shielding material [10]. Figure 1 shows the diagrammatic representation of shielding mechanism. Reflection, absorption and multiple reflections are the three mechanisms of attenuation of EM radiation according to Schelkunoffs theory [5,10]. Shielding effectiveness (SE) is a logarithmic quantity and can be expressed as the sum of SE due to reflection (SE_R), due to absorption (SE_A) and due to multiple reflection (SE_M):

$$SE_T = SE_R + SE_A + SE_M, \quad (1)$$

$$SE_T = 10\log_{10}\frac{P_T}{P_I} = 20\log_{10}\frac{E_T}{E_I} = 20\log_{10}\frac{H_T}{H_I}, \quad (2)$$

where P_I, E_I, H_I are the incident power, electric field and magnetic field intensities respectively, while P_T, E_T, H_T are the transmitted power, electric field and magnetic field intensity respectively.

For materials to show good reflection quality, they should have mobile charge carriers so that they can interact with the EM field in the radiation. Complex scattering parameters are used to correlate reflectance (R) and transmittance (T) which in turn give absorbance (A).

$$T = \frac{|E_T|^2}{|E_I|^2} = |S_{12}|^2 = |S_{21}|^2, \quad (3)$$

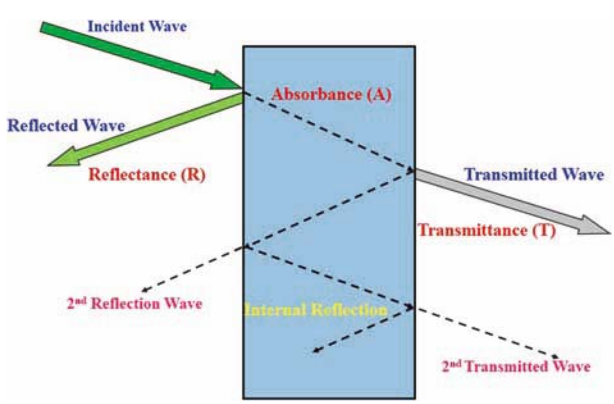

Figure 1. Schematic showing EMI shielding mechanism.

$$R = \frac{|E_\mathrm{R}|^2}{|E_\mathrm{I}|^2} = |S_{11}|^2 = |S_{22}|^2, \tag{4}$$

where S_{11}, S_{22}, S_{12}, S_{21} are the scattering parameters (i.e. S_{11}, S_{22} are the reflection coefficients and S_{21}, S_{12} are the absorption coefficients)

$$A = (1 - R - T). \tag{5}$$

The overall shielding is the sum of the net shielding by reflection, absorption and multiple reflections:

$$\mathrm{SE_T} = \mathrm{SE_R} + \mathrm{SE_A} + \mathrm{SE_M}. \tag{6}$$

The loss due to multiple reflection can be ignored when SE due to material is more than -10 dB. Thus,

$$\mathrm{SE(dB)} \approx \mathrm{SE_R} + \mathrm{SE_A}, \tag{7}$$

where

$$\mathrm{SE_R} = 10\log_{10}(1 - R) = 10\log_{10}(1 - |S_{11}|^2), \tag{8}$$

$$\mathrm{SE_A} = 10\log_{10}(1 - A_\mathrm{eff}) = \log_{10}\left(\frac{T}{(1-R)}\right) = 10\log_{10}\frac{1 - |S_{11}|^2}{|S_{21}|^2}. \tag{9}$$

We can also relate the reflection loss ($\mathrm{SE_R}$) with the relative mismatch between the incident wave and the surface impedance of the shield. It can be expressed as

$$\mathrm{SE_R} = -10\log_{10}\left(\frac{\sigma_\mathrm{T}}{16\omega\epsilon\mu}\right), \tag{10}$$

where t is the shield thickness, μ is the permeability, ϵ is the free space permittivity and σ_T is the total conductivity. Absorption loss is the physical characteristic of the shield and is independent of the type of the source field. The amplitude of the EM wave decreases exponentially when it passes through the medium. Absorption loss occurs due to the ohmic loss by the induced current in the medium and heating of the material where E_t and H_t can be expressed as $E_t = E_i\mathrm{e}^{-t}/\delta$ and $H_t = H_i\mathrm{e}^{-t}/\delta$, where δ is the skin depth and can be defined as the distance required by the wave to attenuate to $1/e$ of its initial value. We know that $\epsilon_r = \epsilon'$

$$\tan\delta = \frac{\epsilon''}{\epsilon'}, \tag{11}$$

$$\sigma_\mathrm{T} = (\sigma_\mathrm{ac} + \sigma_\mathrm{dc})\omega\epsilon_0\epsilon'', \tag{12}$$

$$\tan\delta = \frac{\sigma_\mathrm{T}}{\omega\epsilon_0\epsilon''}, \tag{13}$$

where σ_ac and σ_dc are the microwave frequency-dependent (ac) and independent (dc) components of conductivity and ϵ, μ and ϵ'', μ'' are the complex permittivity and permeability in free space. The generalized equation of $\mathrm{SE_A}$ is

$$\mathrm{SE_A} = 3.34t\sqrt{f\mu_r\sigma_r}, \tag{14}$$

where σ_r and μ_r are conductivity and permeability with respect to copper, $\mu = \mu_0\mu_r$. Further, SE_A can be expressed as

$$SE_A = -8.686\left(\frac{t}{\delta}\right), \tag{15}$$

$$SE_A = -8.686t\left(\sqrt{\frac{\sigma_T\omega\mu}{2}}\right). \tag{16}$$

Absorption loss increases with the increase in frequency. Therefore, high conductivity, high permeability and sufficient thickness are the perquisites to achieve the required skin depth [10–12].

However, high conductivity is not the only criterion for shielding. Rather, it is more important to have good connectivity in the conduction path or percolation in case of composite materials. Metals are therefore good shielding materials, and they mainly work by reflection due to the presence of free electrons. Absorption is the secondary mechanism for shielding. The materials which show shielding due to absorption mainly contain electric and magnetic dipoles which interact with the EM wave [1].

3. Different types of nanocomposites for EMI shielding

As discussed previously, as shielding material, metals have certain drawbacks like heavy weight, corrosion susceptibility, rigidity, uneconomic processing etc. Therefore, the researchers are trying to develop a state-of-the-art and commercially viable nanocomposite which will have all such characteristics to fulfill EMI shielding attributes. EMI shielding of a composite shielding material depends mainly on the aspect ratio, filler's intrinsic conductivity, dielectric constant, magnetic properties and physical geometry [8,11]. According to the EM wave percolation theory, electrical conductivity of the composite is determined by its ease in forming the conductive network [8,12]. There is a certain threshold value when the filler forms an unbroken path through the composite and the conductivity of the composite increases sharply. Percolation threshold is the concentration at which the conductivity path is formed inside the insulating matrix. The intrinsic conductivity of the filler is a major factor which defines the conductivity of the composite beyond this concentration. There are normally two main material constituents of a composite: the matrix phase and the reinforcement phase. There is also a third material constituent called interfacial region between the matrix and the filler. Interfacial region is responsible for the macroscopic properties of the nanocomposite. This is the region, where nanocomposite shows significantly different properties compared to its bulk counterpart [13]. Generally, polymer composites have conductive fillers such as metal nanoparticles, magnetic nanoparticles, carbon-based materials (graphene oxide, CNT, graphene, carbon black, graphite and graphene nanoribbon), fibres, foams, and so on [8,14–17]. The EMI shielding of a composite shielding material depends mainly on the aspect ratio of fillers, filler's intrinsic conductivity, dielectric constant, magnetic properties and physical geometry [8,11]. According to the EM wave percolation theory, electrical conductivity of the composite is determined by its ease in forming the conductive network [8,12]. There is a certain threshold value when the filler forms an unbroken path through the composite and the conductivity of the composite increases sharply. Percolation threshold is the concentration at which the conductivity path is formed inside the insulating matrix. The intrinsic conductivity of the filler is the major factor which defines the conductivity of the composite beyond this concentration.

Researchers are trying to tune the properties of intrinsic conducting polymers or polyconjugate polymers so that they can be used as efficient shielding materials [8]. Conducting polymer possesses shielding effectiveness due to both reflection as well as absorption. The electrical conductivity of the conductive polymers can be regulated by controlling the parameters like oxidation state, doping level, morphology and so on. Some of the examples of polymers which are used for EMI shielding are polyacetylene, polyaniline (PANI), polypyrrole and polythiophene. SE in conducting polymer-based composites depends mainly on absorption, and so these composites may also find application in the field which require absorption of EM radiation such as stealth technology. Mkel *et al* used polyaniline as a shielding material and for making Salisbury structure in the frequency range of 100 kHz to 110 GHz and 0.1 to 1000 MHz [18,19]. Phang *et al* have reported the EMI shielding behaviour of PANI/TiO_2 composite and in another work used Fe_3O_4 and TiO_2 [20,21]. A maximum reflection loss of 31 dB has been achieved by them for this composite [20]. Sani *et al* used PANI/$BaTiO_3$ composite as EMI shielding material for K_u band. For loading 1 : 1 wt% of PANI/TBT, maximum total shielding effectiveness of 71.5 dB was reported [22]. In another work they prepared conducting fabric with PANI incorporated with Fe_3O_4 or $BaTiO_3$ with a maximum shielding of 16.8 and 19.4 dB respectively [23]. The high permittivity value due to the incorporation of $BaTiO_3$ in the PANI-coated fabric results in the enhancement of polarization. Further, the increase in the relaxation effect leads to the enhancement of ϵ'' value which is attributed to the strong dielectric properties of $BaTiO_3$. The overall increase in shielding due to absorption could be due to better mismatching of input impedance, reduction of skin depth as well as addition of dielectric or magnetic losses. Faisal *et al* used polyaniline antimony (PANI/Sb_2O_3) with different weight percent of Sb_2O_3 in PANI to check the shielding property in X- and K_u-bands. Shielding efficiency of 18–21 dB for X-band and 17.5 to 20.5 dB for K_u-band was reported by them [24]. Pomposo *et al* investigated polypyrrole blends for conductivity properties, adhesion characteristic, and far and near field EMI shielding behaviour and also environment stability [25]. In the same line, Jing and his co-workers were successful in making PANI/polyacrylate composite EMI coating [26].

Another class of polymers which are used these days are shape memory polymers (SMP). The composites of SMP have the property to recover easily, have light weight and superior moulding property. Zhang *et al* studied the EMI shielding properties of the shape memory polymer polyurethane with CNT in K-band (18–27 GHz) with a shielding of $\approx$32 dB, in Q-band (33–50 GHz) shielding of $\approx$42 dB and in V-band (40–75 GHz) with a shielding of $\approx$65 dB [27].

Some researchers have also tried to use cement-based composite for achieving high shielding efficiency, as it is slightly conducting. Cao and Chung had used coke powder as an effective admixture in cement for getting decent EMI shielding by reflection. Shielding efficiency of 45 and 49 dB had been attained by them at a frequency of 1.5 GHz using coke powder of 0.51 and 1.02 vol% [28].

4. Carbon-based composites

The last two decades were marked with the discoveries of new allotropic modifications of carbon and related nanostructures. Carbon nanotubes, graphene, fullerene, bucky-ball etc. are a few such forms of carbon which have steered the landscape of advanced materials and have given promises in science and technology; right from biomedical to automobile engineering. This section of the article is further divided into subsections so as to envision the different carbon-based composites and their EMI shielding properties.

4.1 *Graphite*

Luo and Chung [29] for the first time used flexible graphite for shielding applications. Flexible graphite sheet is made up of exfoliated graphite flakes which are compressed without a binder. As a result, it has large surface area and also good electrical conductivity, thereby acting as a good shielding material. They used co-axial cable method to check the shielding effectiveness in the frequency range of 1–2 GHz. Similar work was reported by Gogoi and Bhattacharya [30]. They investigated expanded graphite novolac phenolic resin (EG-NPR) composite for shielding application in X-band (8.2–12.4 GHz). The conduction path in expanded graphite was found to be mainly due to the π-electrons which are free to travel within the flakes. The accumulation of π-electrons at the interface of EG-NPR results in the formation of boundary layer capacitor which generates electric dipolar polarization.

4.2 *Carbon fibre*

Carbon fibres (CF) are interlocked sheets of carbon atoms or graphene with regular hexagonal patterns. Basically, raw material for making turbostratic CF is polyacrylonitrile (or PAN) whereas mesophase pitch are used for making graphitic CF. Nickel-coated CFs have been used to check the EMI shielding [31,32]. Ni was deposited on the carbon fibre by electroplating, to have a better adhesion between carbon and nickel. They achieved very high shielding effectiveness. The excellent results obtained with these fibres were attributed to the high electrical conductivity, ferromagnetic nature, exceptionally small diameter and large aspect ratio. Similar work has been reported by Tzeng and Chang [33]. They compared copper-coated carbon fibre with Ni-coated carbon fibre and showed that Ni had better shielding performance because of its adhesion to carbon fibre. Further, the fibre length distribution in the matrix also plays a crucial role in shielding. As copper tends to oxidize fast, it reduces the length of the fibre, thereby decreasing the shielding performance of the composite compared to Ni-coated fibre.

Chung's group also studied the effect of discontinuous carbon filament (diameter $= 0.1\ \mu$m) on the continuous carbon fibre and observe the shielding effectiveness of 124 dB in the frequency range of 0.3 MHz to 1.5 GHz mainly dominated by reflection [34]. Work has also been done on activation of the surface of carbon fibre using chemical reaction so as to increase the surface area due to the formation of surface pores thereby checking the shielding performance of the composite. These activated carbon fibres in the epoxy matrix show shielding effectiveness of 39 dB in the frequency range of 1–1.5 GHz [35].

In a recent work, Song and his coworkers [36] tried to eliminate the use of insulating polymeric frame. They successfully fabricated carbon nanofibres–graphene–carbon nanofibres (CNF–GN–CNF) heterojunction. The mechanism for the improved shielding in GN/CNF composite network was mainly attributed to the formation of conductive network due to the presence of heterojunction of CNF–GN–CNF. This eliminated poor contact and interfacial conductivity of the polymer matrix. The density of the network was estimated to be $0.08-0.1$ g/cm^3, showing that SE to density ratio was nearly 250 dB/(g/cm^3). In a similar work on CNF, small quantity of CNT was dispersed and was put in polystyrene matrix [37]. This composite is also considered as a promising candidate. CNF has also been used in composite based on polysulphone [38,39].

4.3 *Carbon black*

Carbon black (CB), one of the members of carbon family, has also been used as an additive in polymer matrix so as to achieve desirable EMI shielding. CBs are small particle size carbon pigments which are formed in the gas phase by thermal decomposition of hydrocarbons [40]. Das *et al* [41] have evaluated the EMI shielding performance in two different frequency ranges, i.e. 100–2000 MHz and 8–12 GHz of natural rubber and ethylene vinyl acetate copolymer filled with conductive carbon black and short carbon fibres. They observed that due to the presence of voids in the conductive mesh there is uneven variation in the reflection loss. The voids also have impact on the external reflection. The composite shows good EMI shielding property particularly in the X-band. In another study, researchers have highlighted the impact of the degree of contact between carbon black particle (Conductex and Printex XE2) on conductivity and consequently the EMI shielding property [42]. Composite shows high EMI shielding > 45 dB depending on the filler loading and thickness of the sample. Oh and his coworkers [43] were also successful in designing carbon black-based multilayer radar absorbing structure (RAS) with binder matrix of glass and epoxy. They described the method for optimizing the multilayer of design of RAS so as to achieve good EMI shielding. Carbon black/polypropylene composite has also been investigated as an EMI shielding material in X-band by Al-Saleh and co-workers [44]. They found that the geometry, level of dispersion and distribution of the filler play important roles in showing EMI shielding. Filler structure and the intrinsic conductivity are defining parameters for the type of behaviour shown by the composite, i.e. reflection or absorption. Effect of fluorination of CB on the EMI shielding properties by enhancing the dispersion and adhesion between the CB and CF has also been studied [45]. PAN-based carbon fibre was embedded in fluorinated CB. The carbon nanowebs so produced showed a conductivity of 38 S/cm and a shielding efficiency of 50 dB. The ϵ_r was higher than the ϵ_i as ϵ_i is related to the resistance generated by the change in the surrounding electric field. Similar work was reported by several other researchers [46–52].

4.4 *Carbon nanotubes*

Carbon nanotubes (CNTs) are considered to be the strongest and the stiffest material so far discovered. The Young's modulii of CNTs are estimated to be around 1 to 1.4 TPa. Room-temperature thermal conductivity observed for single-walled carbon nanotubes (SWCNTs) is >3000 W/m·K and electrical conductivity of around 104–106 S/cm has been reported. Due to the presence of high intrinsic conductivity and aspect ratio, CNT-based conductive composite can be prepared with low loading [53]. Intrinsic conductivity and formation of conductive path within the host matrix play very crucial roles in determining the conductivity of the composite, thereby its use as an efficient EMI shielding material. Due to the above-mentioned properties, the percolation threshold of CNT is achieved at very low loading. Thus, CNT without disturbing the properties of the host matrices, helps in enhancing certain aspects of the resultant composite for EMI shielding. There are several reports on CNT-based composites which vary in their studies in the type of CNT, concentration, dispersion, host matrix etc. For example, there are reports of CNT in different matrices with catalyst present along with CNT. Kim *et al* [54] prepared thin and flexible composite films of 60 to 165 μm thickness with different weight fractions of multi-walled carbon nanotubes (MWCNTs) in poly(methylmethacrylate) (PMMA) matrix. The presence of Fe catalyst in MWCNT helped in improving the electrical conductivity and EMI percolation phenomenon. They also observed the presence of Fe-induced charge tunnelling in the composite. The contribution of absorption in the overall EMI shielding (27 dB) was larger than reflection, thereby making the composite an efficient EMI shielding material in RF and microwave frequency ranges. Similarly, MWCNT with nickel impurity in wax and epoxy matrix has been used in the frequency range of 3–18 GHz [55,56]. Liu *et al* made layered composite of Fe_3O_4 and Fe fillers in MWCNT which were dispersed in the epoxy matrix [57]. Absorption was achieved in the frequency range of 3.22–40 GHz in the trilayer composite of both Fe-filled CNT in the epoxy matrix as well as Fe_3O_4 filled CNT. Similarly, core shell nanostrcutures of Fe@Fe_3O_4 were decorated on CNT in the polypropylene grafted maleic anhydride matrix [58].

There are certain reports which highlight the geometric factors involved in the selection of fillers in the composite. In a work done by Wu and coworkers [59], SE of 61–67 dB was achieved for macrofilms with large surface area of CNT and 4 μm thickness. The films made by them consisted of entangled nanotube bundles which formed an interconnected network offering mobile charge carrier channels. Huang and coworkers [60] also checked the influence of geometrical factors in influencing the EMI shielding properties of the composite. They used three different types of SWCNT, which were homogeneously dispersed in the epoxy matrix. The aspect ratio and the wall integrity had effect on the conductivity and the percolation of the composite. Similar studies were also done by others [61,62]. Kotsilkova and coworkers [63] recently used very low weight percent (0.03 to 0.3 wt%) of MWCNT in the epoxy matrix and checked the EMI shielding ability of the composite due to the variation of processing conditions. The alignment of the magnetic nanoparticles in CNT also triggers shielding effectiveness due to geometrical effects. Hong and coworkers [64] synthesized a hybrid structure using carbon fibre reinforced PP in the presence of CNT. Arjmand *et al* [65] checked the EMI shielding properties of different orientations of CNT in the polycarbonate matrix. Effect of fluorination on the EMI shielding properties of MWCNT has also been studied [66–69].

Mohammed H Al-Saleh and Sundararajan [70] tried to explain the shielding phenomenon in polymer composite containing MWCNT. They synthesized PP-based MWCNT composite and studied the shielding behaviour both theoretically and experimentally. They observed that the influence of absorption in the shielding performance of the composite is based on its capability to attenuate power that has not been reflected. The contribution to shielding due to absorption is 62–84% of the overall shielding irrespective of the MWCNT loading and thickness of the plate.

The dispersion of CNT in the polymer matrix is always a major problem faced by researchers. Thomassin and coworkers [71] tried to approach this problem by dispersing CNTs by melt mixing method and coprecipitate method in polypropylene grafted by maleic anhydride matrix. Yu *et al* [72] also developed anisotropic multilayer hybrid structure of CNT-filled polyethylene in polypropylene matrix using high speed thin-walled injection moulding. The anisotropic conductive behaviour of the composite, i.e. conductivity in longitudinal (parallel to the flow) and transverse (perpendicular to the flow) directions was due to polyethylene-filled CNT and insulating behaviour in thickness direction was contributed by polypropylene layer. Thus, it also showed structure-dependent EMI shielding properties.

Park and coworkers in their two different works [73,74] used functionalized CNT in the reactive ethylene terpolymer (RET) for EMI shielding. *In-situ* and *ex-situ* methods for the preparation of MWCNT/PMMA composite has also been explored [75]. In *in-situ* method of preparation of composite, PMMA bonds with MWCNT due to free radical reaction. They concluded that SE depends on the processing method and composite fabrication. They found that 10 layers of stacked MWCNT/PMMA layer of 0.1 mm thickness showed better shielding compared to single 1 mm thick MWCNT/PMMA composite, though the thickness of both the films was the same. Maximum shielding achieved by them was 58.73 dB. In another work done by the same group [76], MWCNT was functionalized via Friedel–Craft acylation with melic anhydride so as to make composite of functionalized MWCNTs with PMMA. Solvent casting is another way which has been used for better dispersion properties of the composite [77,78]. It was found that interfacial polarization of PMMA by CNT resulted in an increase in difference between SE_R and SE_A with increasing CNT concentration. Makeiff *et al* [79] made hybrid composite of PANI-CNT which was dispersed in the PMMA matrix. Surface-functionalized MWCNT in polystyrene/PMMA blend has also been studied on similar lines [80]. Pristine, amine and carboxyl acid functionalized MWCNT were incorporated in the polymer blend. Pristine and NH_2 functionalized MWCNT forms interconnected structure of PMMA in polystyrene matrix upon annealing. Similar work was reported by other researchers [81–83].

Watts *et al* [84] analysed how high permittivity due to the defect in MWCNT helps in using it as an efficient radar absorbing material. Researchers have also prepared composite of CNT with polyurethane [85], polystyrene [86,87], polyacrylate [88], poly vinylalcohol [89], poly(ϵ-caprolactone) [90], silica [91], PANI [92,93], acrylonitrile–butadiene–styrene [94], polytrimethyleneterephthalate) [95], ceramic [96], cement [97] and so on.

4.5 *Graphene (GN)/graphene oxide (GO)*

As graphene shows extraordinary electronic, thermal, mechanical, optical and magnetic properties [98] researchers are trying to tune these properties, so that they can make such nanocomposites that bear all the properties of graphene apart from the properties of host nanostructure. In this section we are trying to focus on graphene and graphene oxide (GO) based nanocomposites that can be used as electromagnetic shielding materials or radar absorbing materials (RAM). Hong *et al* [99] for the first time checked the EMI shielding of monolayer graphene. They used polyethylene terephthalate (PET) film to transfer the monolayer graphene grown using chemical vapour deposition so as to perform the EMI measurements. The experimental findings reveal that 40% of the incident wave was shielded by the monolayer graphene layer. As the number of layers increased, the SE increased linearly from 2.27 dB for monolayer to 4.13 and 6.91 dB for two and three layers. The results also prove that monolayer graphene shows even better results compared to gold film of 10 nm thickness. Plane-wave theory for metal shield is applicable to graphene as well.

Zhang *et al* [100] and Song *et al* [101] fabricated graphene paper (GP) for EMI shielding. Electrical conductivity of graphene paper was in the range of $233-680$ Scm^{-1} and $180-220$ Scm^{-1} respectively. The SE of the GP used by Zhang *et al* having thickness of 50 μm containing 0.9 vol% CH_4 was found to be 40 dB and increased to 60 dB when concentration of CH_4 was increased to 1.1 vol%. The double layer attenuator configuration of GP made by Song *et al* showed SE of 47.7 dB with 0.1 mm thickness due to Fabry–Perot resonance phenomenon. GP proves to be a light weight and flexible material which can be used in aerospace applications.

Yan and coworkers [102] and Chen *et al* [103] used graphene polystyrene composite for EMI shielding. Chen's group prepared two different samples, one containing normal GO and the other containing thermally treated GO apart from Fe_3O_4 nanoparticles. SE of 30 dB was achieved by them.

PANI has been considered as one of the most promising conducting polymers due to its ease in synthesis, environmental stability, low specific mass, relatively high conductivity and economical feasibility. Further, there is chance to tune its properties depending on how we dope PANI. Many researchers are working in the field of making hybrid composites of PANI using graphene and GO. Basavaraja and coworkers [104] synthesized the composite of PANI−gold nanoparticle (GP)–GO composite and checked its EMI shielding in 2–12 GHz frequency range. In another work on PANI–GP–GO composite, PANI was doped using β-naphthalene sulphonic acid [105]. Chen and coworkers [106] used hybrid fillers of CNT and graphene nanosheets (GNS) in PANI. Their experimental results revealed absorption-dominant shielding phenomenon with a shielding of about 27 dB for a loading of 1 wt% of CNT–GNS in PANI. PANI composite filled with graphene decorated with silver (G@Ag) and nickel (G@Ni) nanoparticles has also been studied [107]. Yuan *et al* [108] compared the EMI shielding property of graphene sheets (GS)/PANI with CNT/PANI. In these composites, GS and SWCNT act as electron acceptors whereas PANI acts as an electron donor. GS, when dispersed in PANI, helps in the formation of large contact surface area. There exists strong electrostatic interaction between adjacent GS and PANI which enhances the interface contact thereby helping in the formation of conductive network. As GS gets easily dispersed in PANI compared to CNT, the EMI SE of GS/PANI composite is much higher than CNT/PANI composite. Graphene–Fe_3O_4 (GF) incorporated PANI composite has also been studied [109]. GF hybrid composite structure enables strong polarization due to the formation of solid-state charge transfer complex. The synergistic effect of GF with PANI contributes to higher dielectric and magnetic losses and hence higher SE. High electron mobility in graphene results in high dielectric loss which is related to electron polarization. Skin effect is reduced by the incorporation of GF in PANI matrix. As it is a heterogeneous system, difference in the dielectric constant results in interfacial polarization. As PANI is a conjugated polymer, dipolar polarization contributes to the dielectric permittivity. Due to the presence of large conducting regions, space charge polarization is also developed which again depends on the frequency of the applied field. The composite shows absorption-dominant shielding phenomenon and is considered as a potential candidate for being used as an electromagnetic shielding material.

Kong *et al* [110] used reduced GO sheet modified with γ-Fe_2O_3 colloidal nanoparticle clusters. The interfacial polarization in the magnetic clusters and loss of conductivity in reduced GO contribute in the absorption-dominant shielding mechanism which was explained using resistor capacitor circuit model. Similarly, RGO/γ-Fe_2O_3/carbon fibres have also been studied [111]. In another work [112] researchers used RGO-ferrofluid amalgamated with cement for checking the EMI shielding. The strong polarization and magnetic loss resulted in good shielding behaviour. In one of their recent work [113] γ-Fe_2O_3 decorated, reduced GO–PANI core-shell tubes have been used. The enhancement in the interfacial polarization and hence the effective anisotropic energy in the composite help in increasing the SE to 51 dB. Wang *et al* [114] prepared nanohybrid of graphene Fe_3O_4 due to high surface area, interfacial polarization and separation of magnetic nanoparticles. Defects produced during processing of the hybrid composite show reflection loss of 40.36 dB for 5 mm thick film. Sun and coworkers [115] synthesised laminated magnetic graphene, i.e. graphene–Fe_3O_4 composite using solvothermal route and checked its electromagnetic properties.

Tung *et al* [116] made a hybrid material of Fe_3O_4-decorated RGO with poly(3,4-ethylenedioxythiophene) (PEDOT). They observed superparamagenatic behaviour of the hybrid structure with a loading of only 1 wt% Fe_3O_4 RGO and a shielding of 22 dB. Similarly, researchers have also decorated GO with $BaTiO_3$. There are several such reports of composites of graphene/graphene oxide with epoxy [117], phenolic resins [111], polyurethane [118], wax [119], poly-(ethylene oxide) (PEO) [120], PMMA [121] and so on.

4.6 *Graphene nanoribbon (GNR) and other miscellaneous forms*

Graphene nanoribbon (GNR) is a variant of graphene which has quite different properties compared to its parent structure. The edge-dependent properties shown by GNR make it a potential candidate for a plethora of applications. Work has been done by researchers to make composite of GNR so that it can be used for applications like EMI shielding, high strength, energy storage, transistors etc. In this section we shall throw some light on the use of GNR for EMI shielding. In one of our works, we had used GNR-based composite for EMI application for the first time [11]. A composite of GNR was made with PVA for the purpose. Scanning tunnelling microscopy and spectroscopy study done on GNR showed that they possessed localized density-of-states near the Fermi energy. The local density-of-state present due to the edges of GNR helps the material to behave excellently in the frequency range of 8–12 GHz. For a thickness of 0.6 mm the maximum SE reported by us was 62.67 dB. The percolation threshold was obtained for a very low concentration of GNR in the matrix. Therefore, EMI shielding of 62.67 dB was obtained for films of thickness as low as 0.6 mm and 2.5 wt% of GNR. The thickness-dependent and concentration-dependent results are shown in figure 2. The films were also characterized using atomic force microscope (AFM) to check the distribution of GNR in the matrix. It was found that it formed connected paths in the polymer matrix which had semicrystalline structure. The dangling bonds in GNR at the edges provide additional advantage to it by providing chemically active sites for reaction and thus form a well-dispersed structure in polymer matrix. The AFM images of 2.5 wt% GNR are shown in figure 3. Similarly, we made a composite of GNR–PANI embedded in epoxy matrix [122]. The performance of the composite was found to be around 40 dB and was dominated by absorption-dependent shielding phenomenon. The intention of the work was to obtain a composite which has high strength as well as EMI shielding properties with the possibility of applications in industries such as aerospace. Some workers have also shown EMI shielding in decorated GNR with MnO_2 [123]. Liu *et al* [124] fabricated amorphous carbon matrix composites with self-assembly with interconnected carbon nanoribbon network using rice husk as the source of carbon. SE in the range of 41.8–70.8 dB was achieved in 500 MHz, 1 GHz and 1.5 GHz for different samples.

Apart from the above-mentioned forms of carbon composites, more complex composites have been designed to improve the EMI shielding properties. To mention a few, SiC_f/SiC composites have been made with various thicknesses of pyrolytic carbon interphase [125]. Kumar and coworkers prepared carbon foams by decorating it with MWCNT and by nanosized iron particles derived from organometallic compound [126,127]. They achieved maximum SE of 85 dB and specific shielding effectiveness of

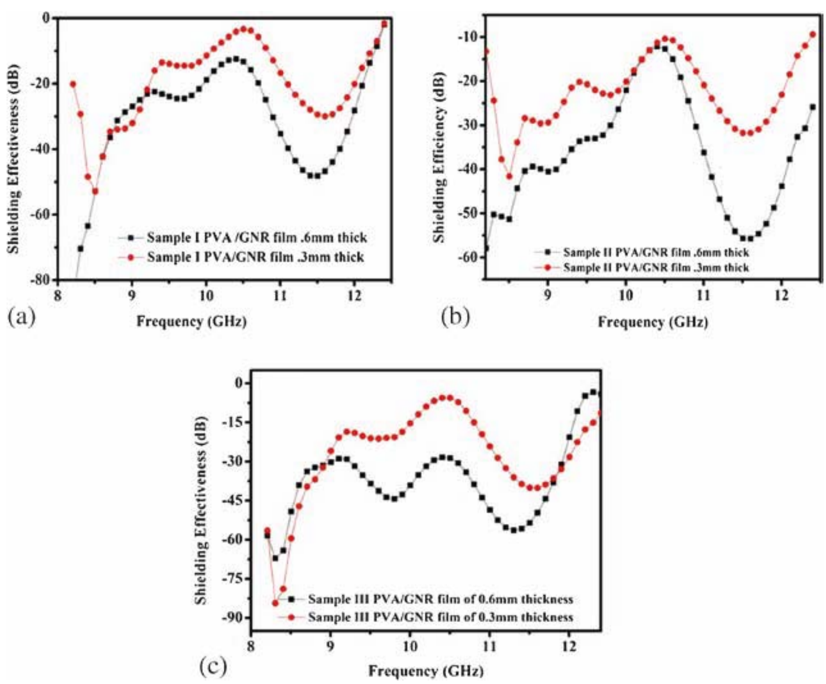

Figure 2. EMI shielding efficiency of the composite with varying thicknesses (0.3 mm and 0.6 mm) for different concentrations of GNR. (**a**) 0.75 wt%, (**b**) 1.5 wt% and (**c**) 2.5 wt%.

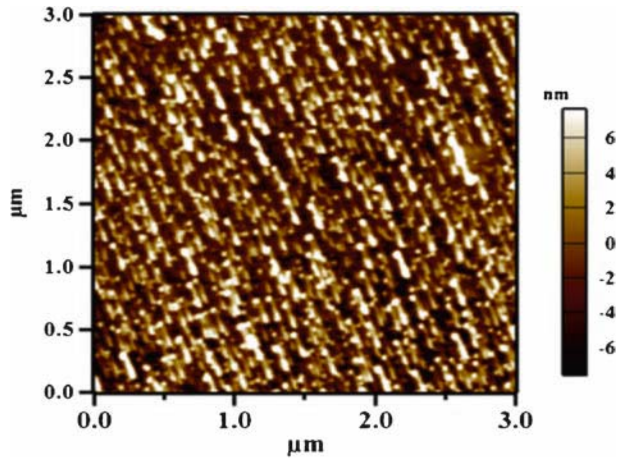

Figure 3. AFM image of 2.5 wt% GNR in PVA matrix.

163 dB cm^3 g^{-1} for MWCNT carbon foam and 130 dB cm^3 g^{-1} for iron nanoparticle carbon foam. Similarly, CNT polystyrene foam [128], CNT buckypaper composite [129], sandwiched structure of carbon fabric/epoxy composite [130], sandwiched structure of CNT polymethacrylimide nanocomposite face and carbon/epoxy composite reflector structures [131], silicone foams filled with carbon nanotubes and functionalized graphene [132], porous carbon wax composite [133], synthesized porous carbon/Co nanostructures [134], polypropylene carbon fibre foam composite [135] are some of the novel structures studied.

5. Conclusions

Although different strategies and considerable amount of work have been done to make different types of nanocomposites for EMI shielding, still many researchers are working in this field to achieve good shielding depending upon its applications. The main issue the researchers are working on, particularly in the composites of carbon nanostructures, is dispersion. Mostly, composites are made at laboratory level and tested. It is important to work on the synthesis mechanism which can be scaled up and can be actually used commercially. Other factors in EMI shielding is the range over which the materials work as shielding materials. Lots of work, reported particularly in low-frequency range, is only for a certain frequency. Efforts are needed to improve the range of shielding for these frequencies. This requires composites with multiple elements blocking radiations at different frequencies. There is also a need for understanding the mechanism of shielding in the case of carbon nanostructures. The factors that decide why a particular material works for a specific frequency range is a question that still has no clear answer. More efforts are needed in simulating these conditions for better understanding.

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