J Mater Sci (2009) 44:3917–3927
DOI 10.1007/s10853-009-3561-1

REVIEW

Polymeric nanocomposites for electromagnetic wave absorption

Jia Huo · Li Wang · Haojie Yu

Received: 10 November 2008 / Accepted: 11 May 2009 / Published online: 2 June 2009

Abstract The need for protecting human or devices from harm and for keeping something from being detected by other instruments is spawning a world of attention in the development of novel electromagnetic (EM) wave absorption materials. An ideal EM wave absorber is necessary to have light weight, thin thickness, high EM wave absorption, broad width, tunable absorption frequency, and multi-functionality. This article introduces the EM wave absorption mechanism and reviews the development of polymer-based nanocomposites for EM wave absorption, in which polymers act as absorbing components or/and matrixes. And we also summarize the approaches to design the ideal absorber, including introduction of nanostructure, and simultaneous action of both dielectric and magnetic materials with special structure by directly mixing, core–shell or multilayer structure.

Introduction

Although electric equipments make our life more convenient, the EM radiation restricted the continuable development of our society because of their pollution to environment, and harm to human beings. Therefore, the need for protecting people or devices from harm and for keeping something from being detected by other instruments is spawning a world of attention in the development of novel EM wave absorption materials [1–16]. As an ideal EM wave absorber, it should possess light weight, high EM wave absorption, broad width, tunable absorption frequency, and multi-functionality [1–3]. To date, considerable efforts have been made to design various materials to reach the ideal targets and various materials have been applied to EM wave absorption.

Traditional inorganic materials, such as ferrites [4–6] and metal powders [9], produced large electric or magnetic loss, but their fatal disadvantages restricted their widespread applications. For example, they have relatively larger densities (e.g., the densities of MnZn ferrite and iron particle are about 5.0 g cm^{-3} and 7.8 g cm^{-3}, respectively); it is relatively difficult to manufacture them for practical use; they often have high electrical conductivity, leading to permeability decreasing rapidly at high frequency caused by the eddy current loss, and their absorption bandwidth is relatively narrow [4–6]. These materials were often used as the low frequency electromagnetic wave absorbers, such as for anechoic chambers.

Polymers, with low densities (e.g., the densities of polyaniline (PANI) and polypyrrole (PPY) are about 1.1 and 1.2 g cm^{-3}, respectively, and even that of foam-like polyacetylene is only 0.04 g cm^{-3}), processibility and even electromagnetic properties, can overcome the problems mentioned above and help to design the ideal EM wave absorber. However, the EM wave absorber with single polymer is not enough to produce larger electric/magnetic loss, which also limits its application in high frequency area. Nanostructure material might be one of the most promising materials to compensate the aforementioned disadvantages and enhance the EM wave absorption ability owing to its higher surface area, more surface atoms, multi-reflection, and thus larger dielectric or/and magnetic loss. Combination of polymers and nanomaterials is able to

---

J. Huo · L. Wang (✉) · H. Yu
State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China
e-mail: opl_wl@dial.zju.edu.cn; hodgeyu@163.com

integrate the large electric/magnetic loss of inorganic materials and the easy tenability of polymer and is possibly an optimal strategy to design excellent EM wave absorption materials.

The objective of this article is to introduce the EM wave absorption mechanism, reviews the development of polymer-based nanocomposites for EM wave absorption, in which polymers act as absorbing components or/and matrixes, and summarizes the approaches to design the ideal absorber to help design an EM wave absorber with light weight, high absorption efficiency, broad absorption bandwidth, tunable absorption frequency, and multi-functionality.

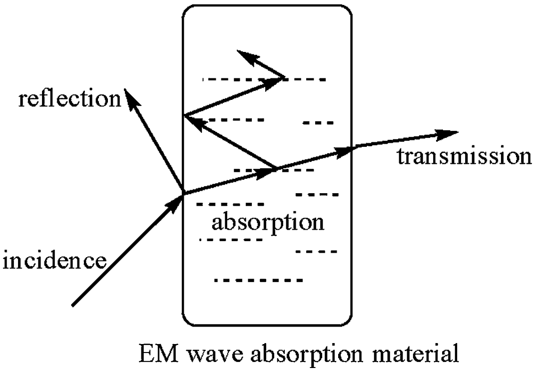
Fundaments of EM wave absorption

EM wave absorption is a process, in which the energy of electromagnetic wave is depleted and then transformed into other energy, such as thermal energy, so that the wave can not be reflected or permeated through the materials [1, 2]. An incident electromagnetic wave through a material undergoes three processes: reflection, absorption and penetration (Scheme 1).

As ideal EM wave absorption materials, they must satisfy two prerequisites: (1) the impedance matching between free space and the material surface to prevent wave being reflected, which need the complex permittivity close to complex permeability; and (2) materials can absorb incident waves as many as possible inside of absorbers, which requires materials exhibit strong magnetic or/and dielectric loss [17]. The EM wave absorption ability was often indicated by the reflection loss (R_L) [1]:

$$R_{\mathrm{L}} = -20\log\left|\frac{Z_{\mathrm{in}}-1}{Z_{\mathrm{in}}+1}\right| \tag{1}$$

wherein



Scheme 1 The general processes of an incident EM wave through an EM absorption material [17]

$$Z_{\mathrm{in}} = \sqrt{\frac{\mu' - j\mu''}{\varepsilon' - j\varepsilon'' - j\sigma/(\omega\varepsilon_0)}} \cdot \mathrm{th}\left(jd\frac{\omega\sqrt{(\mu'-j\mu'')(\varepsilon'-j\varepsilon''-j\sigma/(\omega\varepsilon_0))}}{c}\right),$$

and

$$\omega = 2\pi f$$

where Z_{in}, μ', μ'', ε', ε'', ε_0, σ, f, d, and c represent impedance of incident wave, real part of permeability, image part of permeability, real part of permittivity, image part of permittivity, permittivity of vacuum, conductivity, frequency of EM wave, thickness of material, and light speed, respectively [1].

Value of 10 and 20 dB for R_L represent that 90% and 99% EM waves are absorbed by the materials, respectively [1]. The energy depletion mechanism includes mainly dielectric loss and magnetic loss.

Magnetic loss mechanism

Interacting with electromagnetic wave, magnetic material will produce mainly three energy loss: eddy current loss, magnetic hysteresis loss, and residual loss [18]. The magnetic loss at low frequency and low magnetic flux density can be expressed as Legg's equation [19]:

$$\frac{2\pi tg\delta_{\mathrm{m}}}{\mu} = ef + aB + c \tag{2}$$

where e, a, c, μ, $tg\delta_{\mathrm{m}}$, and B represent eddy current loss coefficient, magnetic hysteresis coefficient, residual loss, permeability, magnetic loss tangent, and magnetic flux density, respectively.

Eddy current loss

If a conducting material was put in an alternating magnetic field, a close induced current would be produced inside the material, which would dissipate the energy, that is, eddy current loss. The eddy current loss at low frequency and low magnetic flux density can be represented by eddy current loss coefficient, e. For a sheet with a thickness of d and electric conductivity of σ, the eddy current loss coefficient can be expressed as [18]:

$$e = \frac{4\pi^2\mu_0 d^2\sigma}{3} \tag{3}$$

According to Eq. 3, in order to increase the eddy current loss, the material must possess large thickness and electric conductivity. However, material with high electric conductivity would make the permeability unstable at high frequency, and then limit its high frequency application

[20]. On the other hand, although Eq. 3 was derived at low frequency, the dependence of d and σ on the eddy current loss was similar to that at high frequency [21], and the eddy current loss was also influenced by other factors, such as orientation, grain size, surface roughness, morphology of material, and so on [18, 22, 23].

Magnetic hysteresis loss

The magnetic hysteresis loss is induced by the irreversible domain movement and magnetic moment rotation of magnetic material. The magnetic hysteresis coefficient at low magnetic flux density is [18]:

$$a = \frac{8b}{3\mu_0\mu^3} \tag{4}$$

where b, μ_0, and μ represent the Rayleigh constant, vacuum permeability, and permeability of material. Equation 4 indicates that the magnetic hysteresis loss depends mainly on the magnetic properties of material, including the Rayleigh constant and permeability of material.

Residual loss

The magnetic loss except eddy current loss and magnetic hysteresis loss is called as residual loss. At low frequency, the residual loss was caused mainly by magnetic after-effect loss, including thermal fluctuation, or the hysteresis of some electrons and ions mowing to equilibrium position relative to the diffusion of applied magnetic field [18]. This kind of loss is determined by the amplitude of alternating magnetic field and relaxation time of material. At high frequency, The residual loss is caused by size resonance, ferromagnetic resonance, natural resonance and/or domain wall resonance [1, 18, 24]. The above mechanisms suggest that the control of particle size, anisotropy of magnetic material, and other magnetic properties can achieve satisfactory magnetic loss.

Dielectric loss

When an EM wave acted on a dielectric material, the material would dissipate electric energy, which then transformed into heat energy, and the energy produced is called as the dielectric loss. The mechanisms of dielectric loss include conductance loss ($tg\delta_{\mathrm{e}}$), dielectric relaxation loss ($tg\delta_{\mathrm{rel}}$), resonance loss ($tg\delta_{\mathrm{res}}$), and other [25, 26].

Conductance loss

Wave absorption material with certain electric conductivity would produce conductance current, when an alternating electric field acted on it, and then the current would dissipate the energy in the form of heat energy. As a result, the conductance loss is determined by the electric conductivity of material, which can be expressed by conductance loss tangent, $tg\delta_{\mathrm{c}}$ [25]:

$$tg\delta_{\mathrm{c}} = 1.8 \times 10^{10}\frac{\sigma}{f\varepsilon_{\mathrm{r}}} \tag{5}$$

Dielectric relaxation loss

Material would be polarized under the electric field, and if the change of polarization is slower than that of electric field, the dielectric relaxation loss would be produced. The polarization mainly contains thermal ion polarization, dipole rotation polarization, electronic displacement polarization, ion polarization, and so on. The time for electronic displacement and ion polarization is very short, about 10^{-15}–10^{-14} s, so these polarizations produce energy loss just at ultra high frequency; however, for thermal ion and dipole rotation polarizations, the time is about 10^{-8}–10^{-2} s [3]. As a result, at high frequency, the thermal ion and dipole rotation polarizations play the greatest role in relaxation loss. The dielectric relaxation loss tangent, $tg\delta_{\mathrm{rel}}$, can be calculated by Debye equation [25]:

$$tg\delta_{\mathrm{rel}} = \frac{\varepsilon''r(\omega)}{\varepsilon'r(\omega)} = \frac{(\varepsilon_{\mathrm{rs}} - \varepsilon_{\mathrm{r}\infty})\omega\tau}{\varepsilon_{\mathrm{rs}} + \varepsilon_{\mathrm{r}\infty}\omega^2\tau^2} \tag{6}$$

where $\varepsilon_{\mathrm{rs}}$, $\varepsilon_{\mathrm{r}\infty}$, and τ represent the permittivity at frequency approaching to zero and infinity, and relaxation time.

Resonance loss and other loss

The resonance loss originates from resonance effect induced by the vibration of atoms, ions, or electrons inside of the wave absorption material, which is produced at the scope of infrared to ultraviolet frequency. There are also other mechanisms to induce the energy loss [25]. For example, Gentner et al. [26] demonstrated that the domain-wall motion also produced dielectric loss in ferroelectric ceramics: the domain-wall motion was ascribed to point detects at low frequency, and the reflection of thermal-lattice wave at high frequency.

Influence factors for electromagnetic wave absorption

According to the above analysis about electromagnetic wave absorption mechanism, the electronic and magnetic properties, size, morphology, and structure of material influence greatly its electromagnetic wave absorption property. In order to achieve better electromagnetic wave absorption property of material, all of parameters must be well designed to reach the impedance matching. Next, we will discuss the main factors affecting the wave absorption property of material.

Basic electromagnetic parameters: complex permittivity and permeability

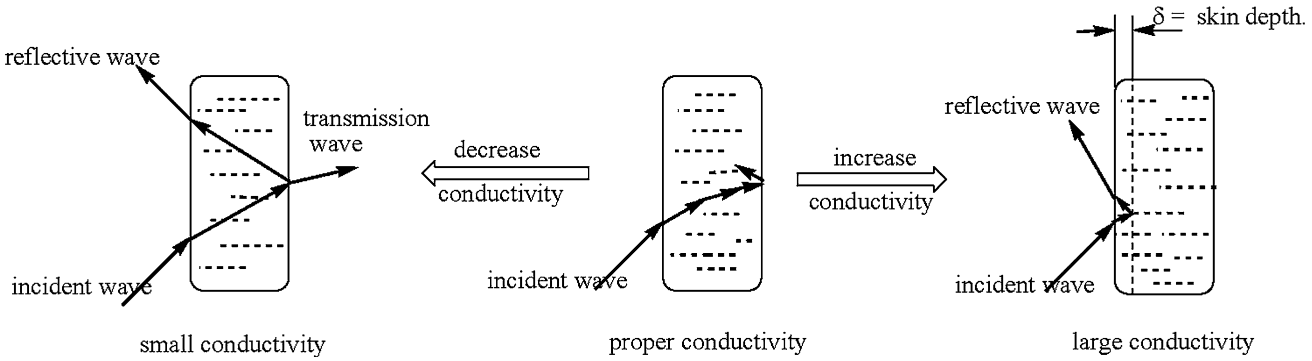
The first electric parameter is the relative complex permittivity of material, one of the basic parameter for material. If the component is used as the wave absorber, it is concluded from the dielectric loss tangent that the bigger the imagine part of complex permittivity, the better the wave absorption effect. As a result, materials with high permittivity are chosen to act as the EM wave absorbers. But, on the other hand, the reflection part of wave is relative large for a material with too high permittivity [27], which suggests we must choose a proper permittivity according to the practical need. If the component is the matrix, such as polymer, the material with low dielectric loss is better for the wave absorption property, which can make more waves transmit into the absorber [28]. Complex permeability is the other basic parameter determining the electromagnetic wave absorption property of material. From the magnetic loss tangent, $tg\delta_m = \mu''/\mu'$, and the magnetic loss mechanism, we also can deduce that the bigger the image part and the smaller the real part of complex permeability, the larger the magnetic loss for wave absorption material. However, according to the principle of impedance match, when the permeability is equal to the permittivity of material, there is no reflection and the electromagnetic wave absorption effect is the best.

Electric conductivity

The discussed wave absorption mechanisms indicate that increasing the conductivity would increase the eddy current loss and conductance loss. However, the impedance of material with high conductivity is very small relative to that of air [29], so that the skin depth is very small and nearly most of electromagnetic wave would be reflected by the materials (Scheme 2). Deng et al. [29] investigated the dependence of electric conductivity on the wave absorption of nanostructural magnetic metallic film by simulation, and it was found that the relaxed FeCoNbZrDy nanocrystalline film exhibited maximum wave absorption (−30 dB) at 10 S/cm, but the wave absorption properties decreased with the increase of conductivity; for resonant FeCoNbZr nanocrystalline film, the wave absorbing intensities increased firstly and decreased then with the increase of conductivity increasing. As a result, a proper electric conductivity of material must be designed to get better wave absorption effect.

Nanoeffect

Material with nanodimension was endowed with excellent electric, magnetic, and optic properties owing to its particular size, surface, and quantum tunnel effect. For example, the density of nanomaterial is relatively lower than that of bulk one; it possesses large specific surface area, and thus there are a large number of active atoms at the material surface, which has large interface dielectric loss caused by interface polarization. On the other hand, the conductivity of metallic magnetic material is too high, which makes the effective permeability decrease at high frequencies due to eddy current loss induced by electromagnetic waves. If the particle size is below the skin depth, the eddy current loss can be induced which can enhance the stability of wave absorption property. Generally, the skin depth of material is about 1 μm at microwave frequencies (10 GHz), and therefore nanoparticle will possess excellent electromagnetic wave absorption property at broad frequencies [30]. Moreover, when the diameter is below a critical size, such as for cylindrical Fe and Ni rods, the critical diameter is 23 nm and 52 nm [31], respectively, magnetic material become monodomain relative to multidomain in the bulk one [18]. For a multidomain magnet, the magnetization process contains two parts: the rotation of magnetic moment and movement of domain wall, in which the latter makes the



Scheme 2 The electromagnetic wave transmission model for materials with different conductivity [29]

magnetic moment rotation more convenient by changing the volume of domain. But for the monodomain, there is no movement of domain wall, which make material have higher coercive force and thus larger magnetic hysteresis loss.

Structure of material

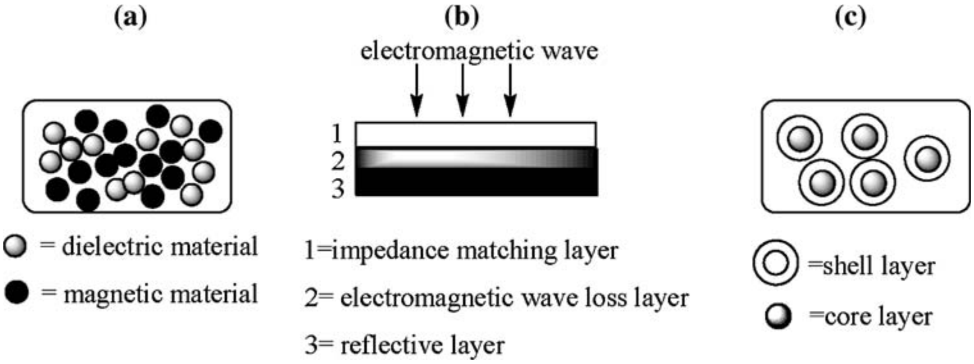
It is well-known now that the single dielectric or magnetic material is difficult to achieve the impedance match and broad frequencies wave absorption, as a result of the Snoek's limit that the permeability value of material is below five at the range of GHz frequency [32]. Hence, it is necessary to design materials with the different structures to get optimal electromagnetic wave absorption properties, including blends with different dielectric and magnetic materials, multilayer structures, core/shell structures and so on. Physical blend is the most convenient method to prepare composites by mixing directly dielectric materials with magnetic particles (Scheme 3a). The multilayer structure is the second method to match the wave impedance, enhance electromagnetic wave absorption ability, and broaden the absorption frequencies of wave absorption material. The basic multilayer includes three layers: impedance matching layer, electromagnetic wave loss layer, and reflective layer, in which the impedance layer can transmit the electromagnetic wave without reflection by adjusting the complex permittivity and permeability of material; the electromagnetic wave is depleted in the electromagnetic wave loss layer composing of high dielectric or magnetic loss materials; the role of the reflective layer is to make a small quantity of transmission wave back to the wave loss layer. Through this specific structure design, the material shows enhanced electromagnetic wave absorption ability and can be used at various frequencies through adjusting the range of impedance match (Scheme 3b). The another approach to the impedance match is combining the two methods above, that is, there is not only the multilayer structure of electric and magnetic materials, but also the nanoparticles dispersing homogenously inside the wave absorption materials (Scheme 3c). As a result, the material with core/shell structure has the potential to exhibit the excellent electromagnetic wave absorption ability.

Polymer-based nanocomposites for EM wave absorption

It is well-known that nanomaterials have low densities and high electric/magnetic loss, which are fit for a thin EM wave absorber, but are difficult to be processed. Polymer-based nanocomposites, combining both the high EM wave loss of nanoparticles, and easy processibility and multifunctionality of polymers, are hopeful to act as ideal EM wave absorber with low density, thin thickness, broad absorption band, high EM wave loss, and even other functionality, such as anti-causticity and intelligentization. Among the polymer-based nanocomposites, polymer not only serves as matrix, such as epoxy resin [33], polyurethane, and rubber, but also improves the EM wave absorption properties, such as PANI.

Epoxy resin as the matrix of nanocomposite

As a matrix, polymer can improve the processibility, avoid the aggregate of nanoparticles, change the electric/magnetic properties of nanoparticles to increase the reflection loss of EM wave, and even improve other chemical or physical properties of materials. Epoxy resins [33], as a kind of popular thermosetting polymer matrixes, are widely used in polymer-based nanocomposites, owing to their excellent mechanical properties, chemical and heat stability, antibacterial properties, low contractibility, and strong adherence. Many nanomaterials, such as single walled carbon nanotube (SWNT), multi walled carbon nanotube (MWNT), carbon nanoparticles, nanoferroelectrics, nanoferrites, etc., have been incorporated into epoxy resins as EM wave absorbers (Table 1). For example, Chen et al. [34] prepared ferroelectric barium titanate ($BaTiO_3$)/epoxy resin nanocomposites by dispersing nano-$BaTiO_3$ with



Scheme 3 The three possible structures for electromagnetic wave absorption materials

Table 1 EM wave absorption properties of epoxy resin-based nanocomposites[a]

	Absorber	D (nm)	d (mm)	ε''	μ''	$tg\delta_\varepsilon$	$tg\delta_\mu$	Δf	$R_{L,\max}$ (f_{im})	Ref
1	8 vol.% $BaTiO_3$	40–60	4	7.5	0	0.5	0	8 (10–18)	19 (12.9)	[34]
2	80 wt% α-Fe/Y_2O_3	30	4	0.6	1.1	0.05	0.55	1.2 (2–3.2)	36 (2.6)	[36]
3	80 wt% α-Fe/Fe_3B/Y_2O_3	20	4	0.6	0.55	0.04	0.44	2.1 (3.5–5.6)	33 (4.5)	[37]
4	51 vol.% Fe_3 N/Y_2O_3	Fe_3N 10 Y_2O_3 30	7.05	2	0.5	0.12	0.28	0.6 (1.5–2.1)	55 (1.8)	[39]
5	80 wt% $Fe_{0.33}Co_{0.67}$/Y_2O_3	$Fe_{0.33}Co_{0.67}$ 20 Y_2O_3 10	4.3	0.5	0.8	0.036	0.47	1.4 (2.5–3.9)	55 (3.2)	[40]
6	75 wt%α-Fe/C(a)	100–1000	2.5	0.4	1	0.033	0.59	3 (4–7)	58 (5.9)	[41]
7	75 wt% Fe_2B/C(a)	100	1.6	0.7	0.6	0.057	0.43	4 (8.4–12.4)	60 (10.7)	[41]
8	75 wt% Y_2Fe_{17}/C(a)	20	1.3	0.6	0.5	0.06	0.5	5 (13–18)	48 (17)	[42]
9	16.7 wt% Fe/MWNT	40	1.2	41	1.9	1.37	0.97	16 (2–18)	25 (11)	[43]
10	44.4 wt% Ni/Ag	7.9	1.8	9	0	0.73	0	2.4 (9.7–12.1)	24 (10.9)	[44]
				0	4	0	0.67	5.3 (28.9–34.2)	27 (31.3)	
11	M[b]: 10 wt α-MnO_2	50–60	2	6	0	0.4	0	9 (9–18)	29 (15.8)	[45]
	A[b]: 30 wt% CB	20–30	3							
12	M[b]: 0.4 wt% MWNT	10–25	1.9	0.6	0	0.11	0	4 (8.2–12.4)	47 (9.8)	[46]
	A[b]: 1.6 wt% MWNT		1.4	5.5	0	0.88				

[a] D, d, Δf, $R_{L\max}$, f_{im}, ε'', μ'', $tg\delta_\varepsilon$ and $tg\delta_\mu$ represent diameter of nanoparticle, sample thickness, bandwidth of reflection loss above 10 dB, maximum reflection loss and frequency of $R_{L\max}$, dielectric loss, magnetic loss, dielectric loss tangent and magnetic loss tangent at f_{im}, respectively

[b] *M* and *A* mean the impedance matching layer and absorption layer, respectively

diameter around 40–60 nm into molten epoxy resins and test their EM wave properties from 8 to 18 GHz. It was found the $R_{L,max}$ increased and shifted to high frequency with the increase of the amount of $BaTiO_3$ and sample thickness; a broad frequency absorption peak ($R_{L,max} =$ 19 dB, $R_L > 10$ dB between 10 and 18 GHz), caused by dielectric loss, was observed at 13 GHz for 8 vol.% $BaTiO_3$/epoxy resin composite.

The absorption intensity of single ferroelectrics is not enough to be used as ideal EM wave absorbers, merely by dielectric loss. Electromagnetic materials such as ferrites and metallic magnetic materials have been widely utilized as EM wave absorbers, thanks to their strong magnetism and dielectric properties. Ferrites, due to the Snoek's limit, are often used as low frequency EM wave absorbers. For example, Chen et al. [35] prepared nano-Zn–Co ferrite, $Zn_{1-x}Co_xFe_2O^4$ ($x = 0$, 0.5, 1), and found that the nanomaterials had a better electromagnetic loss property between 100 and 1800 MHz. By contraries, soft metallic magnetic nanomaterials are able to absorb EM wave at high GHz frequency, since they have both dielectric and magnetic loss, high saturation magnetization, the Snoek's limit appears at high-frequency area, and thus the magnetic loss remains high in a high-frequency range. However, because of high electric conductivity, the metallic particles have to be separated by dielectric materials, such as metal oxides and carbon materials, to induce the eddy current loss.

Liu et al. [36, 37] investigated the EM wave absorbing behaviors of α-Fe/Fe_3B/Y_2O_3 and α-Fe/Y_2O_3/epoxy resin nanocomposites. Different from the previous examples, the EM wave absorbing peaks moved to low frequency with increasing the sample thickness, and peak value firstly increased from 3 mm to 4 mm, but decreased gradually with the increasingly thickness, since the thickness influenced the impedance matching between sample and free space, and the reflection loss might drop instead of increasing when the sample thickness was beyond the matching thickness in a certain frequency range [38]. The reflection loss of 80 wt% α-Fe/Y_2O_3/epoxy resin nanocomposites was greater than 20 dB regardless of thickness between 3 (at 3.5 GHz) and 5 mm (at 2.0 GHz) and $R_{L,max} = 36$ dB was observed at 2.6 GHz for 4.0 mm thick composite. Compared with α-Fe/Y_2O_3 nanocomposite, though the reflection loss was a little smaller, the absorbing peak of 80 wt% α-Fe/Fe_3B/Y_2O_3/epoxy resin nanocomposites moved toward the higher frequency and the bandwidth of R_L over 20 dB increased to 3 GHz (3.5–6.5 GHz) with thickness of 5–3 mm, and the $R_{L,max} = 33$ dB was observed at 4.5 GHz for 4.0 mm thick composite, because of their different complex permeability by the large anisotropy field of Fe_3B. They also replaced α-Fe/Fe_3B with Fe_3N to investigate the effect anisotropy field on EM wave properties of nanocomposites [39]. They found the resonance absorption frequency of Fe_3N/Y_2O_3/epoxy resin nanocomposites shifted to the lower field with increasing thickness, and compared with α-Fe or α-Fe/Fe_3B, the maximum reflection loss had shifted to 1.8 GHz owing to the complicated dependency of permittivity/permeability and EM wave absorption properties. This kind of materials can be used as lower frequency EM wave absorbers. Furthermore, they investigated the effect of Co adding to the α-Fe/Y_2O_3 nanocomposites [40], which possessed large range of saturation magnetization, magnetocrystalline anisotropy and permeability, on the EM wave absorption frequency range. It was concluded that the reflection loss shifted to the lower frequency with the increasingly thickness and the impedance matching thickness was about 4 mm; the position of absorbing peak moved toward higher frequency and absorption bandwidth with $R_L > 20$ dB was broadened (2.2–9.7 GHz with the thickness of 7.4–2.0 mm for 80 wt% $Fe_{0.33}Co_{0.67}$/Y_2O_3/epoxy resin composite) by increasing the amount of Co because of the enhancement of anisotropy field; and maximum absorption intensity with $R_{L,max} = 55$ dB was observed at 3.2 GHz for 4.3 mm thick $Fe_{0.67}Co_{0.33}$/Y_2O_3 nanocomposite. Among these nanocomposites, Y_2O_3 played a very significant role in EM absorbing properties of materials, which acted as the insulator to isolate the ferromagnetic particles to decrease the fast drop of magnetization due to eddy current loss induced by EM wave.

Rare-earth (RE) oxides as separators improved the EM wave absorption performance of nanocomposites, but also brought many problems, such as complicated preparation processes, expensive costs, and high density [41]. To make up these disadvantages, many groups utilized carbon nanomaterials instead of RE oxides, which served as both separators and dielectric loss materials. Liu et al. [41] prepared α-Fe/C (amorphous) and Fe_2B/C (amorphous) nanocomposites by ball-milling the mixture of α-Fe and Fe_2B with amorphous C (C(a)), respectively, then mixed with epoxy resin. Compared with spheric α-Fe nanocomposite, the flake-like α-Fe/C(a) nanocomposite exhibited higher frequency EM wave absorption properties with matching frequency at 5.9 GHz and Fe_2B/C(a) at 10.7 GHz, for their larger anisotropy field. A total of 75 wt% Fe_2B/C(a) exhibited optimum absorption intensity with $R_{L,max} = 60$ dB at 10.7 GHz. It was also found that the C nanocomposites had thinner matching thickness (2.5 mm for α-Fe/C(a) and 1.6 mm for Fe_2B/C(a)) and broad-band absorption ($R_L > 20$ dB from 7 to 15.5 GHz with the thickness of 2.2–1.2 mm). When the Y_2Fe_{17} with larger anisotropy field was used as EM wave absorbing unit [42], the Y_2Fe_{17}/C(a)/epoxy resin nanocomposite had a high and broad frequency magnetic loss (μ'') in the range of 2–18 GHz, and the 75 wt% nanocomposite show a maximum absorption peak ($R_{L,max} = 48$ dB) at 17 GHz with the matching thickness of 1.3 mm.

Metallic magnetic nanoparticle/RE oxide or carbon discussed above were all prepared by direct mixing directly two kinds of materials (Scheme 3a), which, although showed excellent EM wave absorption properties, could not be used repeatedly, as a result of the re-aggregate of nanoparticles. Core/shell structure (Scheme 3b) might overcome this problem and enhance the EM wave absorbing ability of materials, resulting from mutual repulsion of shells, and multi-reflection of layers or/and multi-loss of shell and core materials. Che et al. [43] encapsulated Fe nanoparticles into carbon capsules (C(c)) and multi-walled carbon nanotubes to prepare the Fe/C(c) and Fe/CNT nanocomposites and found they have broad EM wave absorption frequency bandwidth. The reflection loss of 16.7 wt% Fe/C(c) or Fe/CNT/epoxy resin composite with the thickness of 1.2 mm was greater than 10 dB at the frequency of 2–18 GHz, Fe/CNT composite showed larger reflection loss than Fe/C(c) and two absorption peaks at 5 and 11 GHz because of the larger anisotropy field of CNT, and they also found the crystalline of Fe is the key point of EM wave absorption ability of nanocomposites. According to the analysis of complex permittivity and permeability of materials, they proposed the reflection loss was mainly attributed to magnetic loss of crystalline Fe particles caused by the time lag of magnetization. The results above indicated these nanocomposites of metallic magnetic materials separating by carbon nanomaterials could be utilized as excellent thin, broad-band, and high frequency EM wave absorbers. Lee et al. [44] reported the EM wave absorption properties of the epoxy resin composites containing Ni/Ag core-shell nanoparticles and compared with that of Ni or Ag/epoxy resin composites. The 1.8 mm thick nanocomposite with 44.4 wt% Ni/Ag showed a dual-frequency absorption property in 2–18 ($R_{L,max} = 24$ dB at 10.9 GHz) and 18–40 GHz ($R_{L,max} = 27$ dB at 31.3 GHz), although Ni composite exhibited absorption only in 18–40 GHz and no absorption was observed for Ag nanocomposite in the whole frequency range. They proposed that the additional absorption of Ni/Ag nanocomposite in 2–18 GHz might be attributed to the dielectric loss, due to the lags of polarization between the core/shell interfaces.

Employing multilayer absorbing structures is another approach to create broadband and high frequency EM wave absorbers. As described in Scheme 3b, the outermost layer(s) can serve as the impedance matching layer to introduce EM wave into absorbers and the other layers with dielectric or/and magnetic loss materials are able to absorb the incident wave. By controlling the electromagnetic parameters and thickness of matching and absorbing layers, and aiding by the theoretic method, custom-tailored EM wave absorbing materials can be easily designed with required absorbing frequency and efficiency. Duan et al. [45] designed double-layer epoxy-based nanocomposites with low dielectric loss nano α-MnO_2 as the impedance matching layer and high dielectric loss nano-carbon black (CB) as absorbing layer. They found that decreasing the amount of α-MnO_2 would enhance the absorbing ability of nanocomposite because of the improving impedance match between two layers and the nanocomposite, with 2 mm thick and 10 wt% α-MnO_2 and 3 mm thick and 30 wt% CB, showed 8.6 GHz broadband EM wave absorption above 10 dB and maximum reflection loss of 29 dB. Lee et al. [46] used a theoretical method with a genetic algorithm and a theory of the reflection/transmission of EM wave in a multilayer structure to design and optimize the amount of absorber and thickness of each layer for MWNT-filled glass/epoxy plain-weave nanocomposites and fabricated the optimum nanocomposite by the co-curing method and secondary bonding method. The optimized nanocomposite, with 1.9 mm thick and 0.4 wt% MWNT as the matching layer and 1.4 mm thick and 1.6 wt% MWNT as the absorbing layer, could absorb 90% ($R_L = 10$ dB) EM wave between 8.2 and 12.4 GHz and maximum reflection loss of 47 dB at 9.8 GHz, which was in good agreement with theoretical optimized result.

Polyurethanes and other polymers as matrices of nanocomposites

Polyurethanes [47] (PUs) are widely used as matrices of coatings, composites, and so on, because of their excellent mechanical properties, good biocompatibility, designable flexibility, light weight, and low cost. The EM wave absorption data of PU and other polymer-based nanocomposites have been summarized in Table 2. Liu et al. [8] for the first time, investigated the EM wave absorption properties of SWNT/PU nanocomposites prepared by solution-filming method using SWNTs dispersed in PU solutions and found that the EM wave absorption increased from 18.3 to 45.9%, while reflection firstly increased and then decreased from 46.4 to 69.8 to 51.4% with the increase of the SWNT loading from 5 to 20% at the high frequency (such as 12.4 GHz). Then they [7] studied SWNT/PU nanocomposites at various amounts of SWNTs in the range of 2–18 GHz. It was observed that the absorption peak would move toward the lower frequency and absorption intensity would firstly increase and then decrease with increasing SWNT loadings and the impedance matching appeared for 5 wt% SWNT at 8.8 GHz ($R_{L,max} = 21.9$ dB), the mechanism of which was mainly dielectric loss of SWNT. Guo et al. [30] prepared PU nanocomposites filled with the magnetic nanoparticle by surface initiated polymerization of PU on the surface of iron core/iron

Table 2 EM wave absorption properties of other polymer-based nanocomposites

	Absorber	D (nm)	Matrix	d (mm)	ε''max	μ''max	$tg\delta\varepsilon$	$tg\delta\mu$	Δf (GHz)	$R_{L,\max}$ (dB)	Ref
13	5 wt% SWNT	1.2–1.8	PU	2	3.75	0	0.3	0	2.6 (7.5–10.1)	21.9 (8.8)	[7]
14	65 wt% Fe/Fe_2O_3	20	PU	1.7	0	2.4	0	0.11	3 (8–11)	27.5 (10)	[30]
15	7 wt% ZnO	20	PET	1	0.13	0	0.07	0	2 (10–12)	12.28 (10.9)	[48]
16	5% Ni-MWNT	260	PPESK	0.9					4 (9.5–13.5)	27.5 (10.9)	[49]
17	ZnCoBa	65	CSPER	0.5					5.6 (8.4–14)	28.5 (10.4)	[50]
	Iron particle										
18	M:18 wt% NTP and 62 wt% MMP		HNBR	0.65					7.1 (9.2–16.3)	12 (11.2)	[17]
	A:85 wt% MMP			0.55							
19	4 wt% MWNT/PANI-pTsA	20–50	PMMA		100		9			(8.2)	[51]
20	10 wt% γ-Fe_2O_3	70	PANI		2.4	0.66	0.4	0.06	4 (13–17)	25 (16)	[52]
21	75 wt% BF	50–70	PANI		29		2.9		5.6 (12.4–18)	27.5 (18)	[53]
22	A: CNT, etc.		PU	11.6					15 (3–18)	25.5 (6.3)	[54]
	M: PPY fibric										

oxide shell nanoparticles, which showed higher coercive force and maximum reflection loss of 27.5 dB at 10 GHz, and saved the weight 37 and 50% compared with the micron carbonyl iron particle/PU composite and a commercially available microwave absorber, Q-Zorb ginle band absorber.

Polyester is also a kind of common polymer matrix, thanks to its convenient processibility, easy film-forming properties and flexibility. Chen et al. [48] prepared ZnO nanowire/polyester (PET) composites and found the 7 wt% ZnO nanowire/polyester showed maximum reflection loss of 12.28 dB at 10.9 GHz, caused by the interfacial multipoles, the high surface surface-to-volume ratio and the similar shape of the nanowires to antenna. The temperature stability is very important for EM wave absorber applied to military and aerospace fields. Poly(phthalazinone ether sulfone ketone) (PPESK) is a kind of high performance thermoplastic polymer with high glass transition temperature, excellent high-temperature stability, good mechanical properties and radiation stability, and desirable solubility, which enhance the mechanical and processible properties. Feng et al. [49] used PPESK as the matrix to prepare the Ni-MWNT/PPESK nanocomposites by solution processing method and investigated their temperature stability and EM wave absorbing properties. Compared with MWNT/PPESK composite, 5 wt% Ni-MWNT/PPESK exhibited broader frequency absorption of EM wave and higher absorption efficiency because of the synergy interaction of dielectric and magnetic loss, and kept stable up to 500 °C.

Ruan et al. [50] prepared one-layer EM wave absorber with nanocomposites by dispersing nanosized ZnCo-substituted W-type Ba hexaferrite (ZnCoBa) into the chlorosulfonated polyethylene rubber (CSPER) matrix and designed a thin broad-band two-layer absorber integrating nano-ZnCoBa with the commercially iron particle/rubber materials. The reflection loss of nano-ZnCoBa composite was not very high, but it had better impedance matching between materials and free space, and thus could act as the matching layer. The maximum reflection loss of two-layer absorber composing of nano-ZnCoBa composite reached 28.5 dB and the bandwidth above 10 dB was about 5.6 GHz (8.4–14 GHz) compared to only 3.5 GHz for microsized composites. He et al. [17] developed a two-layer EM wave absorber with light weight (3.5 kg m^2), thin thickness (1.2 mm), and broadband and strong absorption aided by computer program. The matching layer was made up of micropowder (MMP), nanotitanium powder (NTP), and hydrogenation acrylonitrile-butadiene rubber (HNBR), which had frequency dispersion with the parameters of permittivity and permeability to match the impedance over a wide frequency range; and the absorbing layer, constructed by MMP and HNBR, possessed a large permeability and magnetic loss. The designed materials showed the maximum reflection loss of 12 dB and the absorption bandwidth above 10 dB of 7.1 GHz (9.2–16.3 GHz).

Conducting polymers as absorbing components of nanocomposites

It has been found that the conducting polymers have many advantages, such as light weight, tunable conductivity, or even magnetic properties, and thus excellent EM wave absorption properties with broad absorbing width and adjustable absorbing frequency. On the other hand, the nanomaterials have shown large electric or/and magnetic loss. The combination of conducting polymers and nanomaterials is probably one of superexcellent approaches to construct the ideal EM wave absorbers (Table 2). Makeiff et al. [51] prepared conductive thermoplastic nanocomposites by mixed pTsA-doping PANI (PANI-pTsA)-coated MWNTs with PMMA. The composites showed stronger EM wave absorption than composites containing only PANI-pTsA or MWNT or even mixture of PANI-pTsA and non-coated MWNT, for the better dispersion of PANI-pTsA-coated MWNTs in the polymer matrix. Wang et al. [52] synthesized γ-Fe_2O_3/protonated PANI nanocomposites with different γ-Fe_2O_3 loadings by in situ polymerization and investigated their EM wave absorbing properties between 7 and 18 GHz. It was found that, because of the simultaneous effect of both dielectric loss and magnetic loss, the nanocomposites with 10 wt% γ-Fe_2O_3 exhibited multi-absorbing peaks at 10.5, 12.2, 13.4, and 16 GHz, with maximum reflection loss of 16, 17, 21, and 27 dB, respectively, and wide absorption band with reflection loss above 10 dB between 13 and 17 GHz. Ohlan et al. [53] studied the EM wave absorption properties of barium ferrite nanoparticle (BF)/PANI composites prepared by emulsion polymerization in 12.4–15 GHz. The composites containing 75 wt% BF showed high absorption efficiency over 20 dB in the test frequency range and maximum absorption intensity of 27.5 dB at 18 GHz. They speculated that the high and broad absorption efficiency was attributed to the dielectric loss induced by strong polarization in PANI and the BF's magnetic loss by magnetocrystalline anisotropy and shape anisotropy, and dielectric loss by the interface polarization and multi scattering. Tellakula et al. [54] prepared multi-layer EM wave absorbers PU composites containing CNTs, carbon fibers and microballoons together with PPY fabrics having different surface resistances as the impedance matching layer. It was concluded that the proper surface resistance for PPY and the order of composite layers were important for the absorption properties of materials, and the 11.6 mm thick sample, constructed with six-layer composites and PPY layer with surface resistance of 15.9 S cm^2, showed a reflection loss above 15 dB from 5.2 to 8 GHz and 20 dB from 8 to 18 GHz.

Conclusions and outlook

We summarize the development of polymer-based nanocomposites for EM wave absorption, in which polymers act as absorbing components or/and matrixes, and introduce approaches to design the ideal absorber, including introduction of nanostructure, and simultaneous action of both dielectric and magnetic materials with disordered structure by direct mixing, core–shell, and multi-layer structure. However, although the current materials have shown strong EM wave absorption intensity at the special frequency and broad EM wave absorption bandwidth of R_L above 10 dB (10% incident wave will be reflected), the bandwidth of R_L above 20 dB (just 1% incident wave will be reflected) is narrower, for example, 16.7 wt% Fe/MWNT show R_L above 10 dB between 2 and 18 GHz, but the R_L above 20 dB was just observed between 4.5 and 5.5 GHz, and between 10 and 11.8 GHz. On the other hand, the application range of current materials is limited owing to their simplex absorption frequency band, and the materials used both in low frequency (MHz) and high frequency (GHz or more). These problems could be solved by reasonable choice of the materials (combination of particles with both magnetic and dielectric loss) and design of the structures (core/shell structure or/and multilayer) of polymer-based nanocomposites. Additionally, multi-functional and intelligent EM absorbers may be the next generation materials, which require more effort to design and prepare these materials. For example, the use of superhydrophobic/superoleophobic polymers would add the self-clean function to composites; the matching frequency can be adjusted automatically according to the environment by addition of intelligent component into nanocomposites and so on.

References

1. Hu CX (2004) Stealth coating technology. Chemical Industry Press, Beijing
2. Liu SH, Liu JM, Dong XL (2006) Electromagnetic wave interference shielding and absorption materials. Chemical Industry Press, Beijing
3. Qiu JX, Wang Y, Gu MY (2007) J Mater Sci 42:166. doi:10.1007/s10853-006-0919-5
4. Yoshida S, Sato M, Sugawara E, Shimada Y (1999) J Appl Phys 85:4636
5. Yoshida S, Ando S, Shimada Y, Suzuki K, Nomura K (2003) J Appl Phys 93:6659
6. Moučka R, Lopatin AV, Kazantseva NE, Vilčáková J, Sáha P (2007) J Mater Sci 42:9480. doi:10.1007/s10853-007-2081-0
7. Liu ZF, Bai G, Huang Y, Li FF, Ma YF, Guo TY, He XB, Lin X, Gao HJ, Chen YS (2007) J Phys Chem C 111:13696
8. Liu ZF, Bai G, Huang Y, Ma YF, Du F, Li FF, Guo TY, Chen YS (2007) Carbon 45:821
9. He YF, Gong RZ, Cao H, Wang X, Zheng Y (2007) Smart Mater Struct 16:1501

10. Phang SW, Daika R, Abdullah MH (2005) Thin Solid Films 477:125
11. Chandrasekhar P, Naishadham K (1999) Synth Met 105:115
12. Håkansson E, Amiet A, Nahavandi S, Kaynak A (2007) Eur Polym J 43:205
13. Phang SW, Hino T, Abdullah MH, Kuramoto N (2007) Mater Chem Phys 104:327
14. Mizobuchi H, Kawai T, Yoshino K (1995) Solid State Commun 96:925
15. Wan MX, Fan JH (1998) J Polym Sci Part A: Polym Chem 36:2749
16. Abbas SM, Dixit AK, Chatterjee R, Goel TC (2005) Mater Sci Eng B 123:167
17. He YF, Gong RZ, Nie Y, He HH, Zhao ZS (2005) J Appl Phys 98:084903
18. Dai DS, Shi FQ, Chen YQ, Chu SL (1976) Ferromagnetics. Science Press, Beijing
19. Ellwood WB, Legg VE (1937) J Appl Phys 8:351
20. Liu JR, Itoh M, Machida K (2006) Appl Phys Lett 88:062503
21. Roshen W (1991) IEEE Trans Magn 27:4407
22. Morgan SP Jr (1949) J Appl Phys 20:352
23. Foster K, Littmann MF (1985) J Appl Phys 57:4203
24. Yamada S, Otsuki E (1997) J Appl Phys 81:4791
25. Li HR (1990) Introduction to dielectric physics. Chengdu University of Technology Press, Chengdu
26. Gentner JO, Gerthsen P, Schmidt NA, Send RE (1978) J Appl Phys 49:4485
27. Zhang XF, Dong XL, Huang H, Lv B, Lei JP, Choi CJ (2007) J Phys D Appl Phys 40:5383
28. Yusoff AN, Abdullah MH, Ahmad SH, Jusoh SF, Mansor AA, Hamid SAA (2007) J Appl Phys 92:876
29. Deng LW, Zhou KS, Jiang JJ, Feng ZQ (2008) J Cent South Univ: Sci Technol 39:59
30. Guo ZH, Park S, Hahn HT, Wei SY, Moldovan M, Karki AB, Young DP (2007) J Appl Phys 101:09M511
31. Xue KH, Bao JC (2006) Nano chemistry: the chemical construction and applications of nanosystems. Chemical Industry Press, Beijing
32. Bregar VB (2004) IEEE Trans Magn 40:1679
33. Njuguna J, Pielichowski K, Alcock JR (2007) Adv Eng Mater 9(10):835
34. Chen XP, Zhuang J, Chi YH, Yang DM, Han GZ, Deng Y (2005) Chin J Inorg Chem 21(3):337
35. Chen X, Wang G, Duan Y, Liu S (2007) J Phys D Appl Phys 40(6):1827
36. Liu JR, Itoh M, Machida K (2003) Appl Phys Lett 83(19):4017
37. Liu JR, Itoh M, Machida K (2003) Chem Lett 32(4):394
38. Naito Y, Suetake K (1971) IEEE Trans Microw Theory Tech 19(1):65
39. Liu JR, Itoh M, Jiang J, Machida K (2004) J Magn Magn Mater 277(3):251
40. Liu JR, Itoh M, Machida K (2005) J Alloy Compd 389(1–2):265
41. Liu JR, Itoh M, Horikawa T, Itakura M, Kuwano N, Machida K (2004) J Phys D Appl Phys 37(19):2737
42. Itoh M, Liu JR, Horikawa T, Machida K (2006) J Alloy Compd 408–412:1400
43. Che RC, Peng LM, Duan XF, Chen Q, Liang XL (2004) Adv Mater 16(5):401
44. Lee CC, Chen DH (2007) Appl Phys Lett 90:193102
45. Duan YP, Yang Y, Ma H, Liu SH, Cui XD, Chen HF (2008) J Phys D Appl Phys 41(12):125403
46. Lee SE, Kang JH, Kim CG (2006) Compos Struct 76(4):397
47. Chattopadhyay DK, Raju KVSN (2007) Prog Polym Sci 32(3): 352
48. Chen YJ, Cao MS, Wang TH, Wan Q (2004) Appl Phys Lett 84(17):3367
49. Feng XB, Liao G, Du JH, Dong LM, Jin KJ, Jian XG (2008) Polym Eng Sci 48(5):1007
50. Ruan S, Xu B, Suo H, Wu F, Xiang S, Zhao M (2000) J Magn Magn Mater 212(1):175
51. Makeiff DA, Huber T (2006) Synth Met 156(7–8):497
52. Wang ZZ, Bi H, Liu J, Sun T, Wu XL (2008) J Magn Magn Mater 320(16):2132
53. Ohlan A, Singh K, Chandra A, Dhawan SK (2008) Appl Phys Lett 93(5):053114
54. Tellakula RA, Varadan VK, Shami TC, Mathur GN (2004) Smart Mater Struct 13(5):1040