Composites Part B 137 (2018) 260–277

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

Graphene-based microwave absorbing composites: A review and prospective

Fanbin Meng[a], Huagao Wang[a], Fei Huang[a], Yifan Guo[a], Zeyong Wang[a], David Hui[b,**], Zuowan Zhou[a,*]

[a] Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu, 610031, PR China
[b] Composite Material Research Laboratory, Department of Mechanical Engineering, University of New Orleans, LA 70148, USA

ARTICLE INFO

Keywords:
Graphene-based composites
Microwave absorbing materials
Reflection loss
Absorption bandwidth
Microwave absorption mechanism

ABSTRACT

With the rapid arising of information technology, microwave absorbing materials (MAMs) are playing an increasingly significant role in electronic reliability, healthcare, and national defense security. Hence, development of high performance MAMs with thin thickness, low density, wide bandwidth, and strong absorption has attracted great interests. Recently, taking graphene as MAMs for high-performance electromagnetic (EM) wave attenuation has grabbed considerable attention, owing to their low density, high specific surface area, strong dielectric loss, and high electronic conductivity. Furthermore, in order to address the interfacial impedance mismatching of the sole graphene materials, incorporation of other lossy materials has been widely studied as the imperative solution to improve its MA performance. In this review, we introduce the theory of microwave absorption and summarize recent advances in the fabrication of graphene-based MAMs, including rational design of the microstructure of pure graphen and tunable chemical integrations with polymers, magnetic metals, ferrites, ceramics, and multicomponents composites. The key point of enhancing MA in graphene-based MAMs is to regulate their EM properties, improve of impedance matching, and create diversified loss mechanisms. Furthermore, the shortcomings, challenges, and prospects of graphene-based MAMs are also put forward, which will be helpful to people working in the related fields.

1. Introduction

Nowadays, the prevalence of digital devices and the rapid development of radar detecting technology can make our life more convenient. However, these also generates a large amount of electromagnetic (EM) waves into the living space of human beings, leading to grim problem of EM interference, which not only causes damage to highly sensitive electronic equipment, but also has a remarkable negative effect on physical health [1–4]. Therefore the protection and shielding of electromagnetic radiation has been widely concerned by the whole society. Recently, development of high performance microwave absorbing materials (MAMs) with thin thickness, low density, wide bandwidth, and strong absorption have attracted great interests to eliminate the electromagnetic pollution [5–7]. Because they can absorb electromagnetic waves effectively and transform electromagnetic energy into heat energy or attenuate electromagnetic waves by interference [8,9].

Generally, most of the MAMs are composed of magnetic loss powders such as ferrites [10,11], magnetic metals [12,13], and dielectric loss materials such as carbon materials (such as carbon fibers [14], carbon black [15], carbon coils [16], carbon nanotubes (CNTs) [17,18] and silicon carbide fibers [19]) and conducting polymers [20]. Among these materials, carbon nanotubes (CNTs) represent one of the most studied systems due to the combined light weight and high specific surface areas and carrier mobility [17,21–23]. Although the microwave absorbing ability of pure CNTs is extremely weak, much effort has been devoted to the fabrication of composites in which the single dielectric loss CNTs are elaborately combined with other magnetic or dielectric loss materials, leading to reach the impedance matching and in turn to achieve an excellent EM absorption due to the synergistic effects on dissipation of the EM wave energy materials, such as ZnO@carbon nanotubes (CNTs) [24], CdS-MWCNTs [25], CNTs@Fe_3O_4 [26] and γ-FeNi/CNT [27]. Recently, as a new kind of carbon material, graphene, a two-dimensional (2D) sheet composed of sp^2-bonded carbon atoms, has drawn significant attention due to its extraordinary electrical, thermal, mechanical properties and high specific surface area [28–31]. These properties make graphene or graphene-based materials very promising in electromagnetic interference shielding, which is designed to absorb

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: DHui@uno.edu (D. Hui), zwzhou@swjtu.edu.cn (Z. Zhou).

https://doi.org/10.1016/j.compositesb.2017.11.023
Received 29 September 2017; Received in revised form 4 November 2017; Accepted 15 November 2017

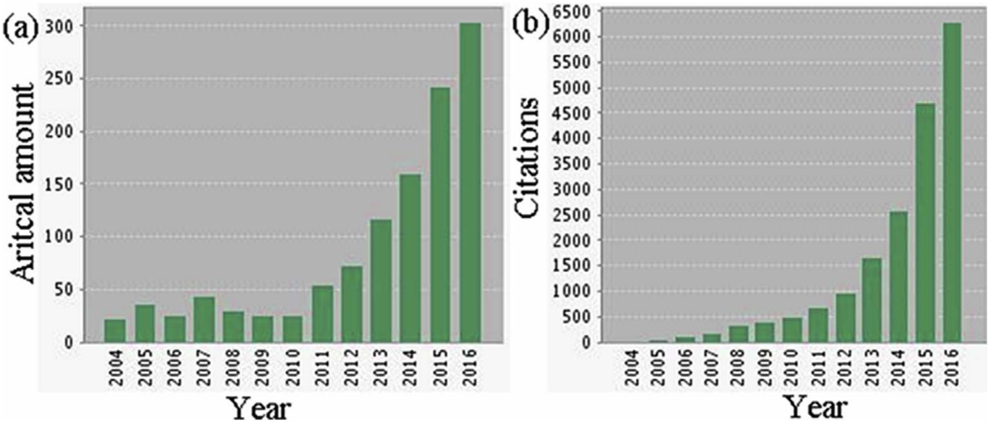

Fig. 1. The artical amount of graphene-based MAMs (a) and the corresponding citations in 2004–2016.

and dissipate incident electromagnetic waves by converting them to thermal energy [32]. Furthermore, graphene's unusual band structure can allows separate the hole and electron, which leads to a new electron conduction phenomenon, and the recent studies indicate the residual defects and groups in the reduced graphene oxide (RGO) can not only improve the impedance match characteristic and prompt energy transition from contiguous states to the Fermi level, but also introduce defects polarization relaxation and groups' electronic dipole relaxation, which are all in favor of electromagnetic wave absorption [33]. Therefore, graphene can be used as a potential dielectric loss MAMs, and could be exhibit stronger MA performance than these of CNTs. Furthermore, development of high-performance graphene-based MAMs to achieve the general goal of “thin, wide, light and strong” MAMs is of great significance to the development of MAMs in military and civil field.

Since the successful fabrication of monolayer graphene by mechanical exfoliation in 2004, the reports and the corresponding citations about graphene-based MAMs increase year by year, as shown the statistical data of Web of Science (Fig. 1). As it is known, sole graphene material suffers from poor dispersion in the matrix [34,35], interfacial impedance mismatching due to improper electrical conductivity [36] and limited loss mechanism [37,38]. Incorporation of other lossy materials has been widely studied as the imperative solution to improve its MA performance [39–41]. Therefore, how to design and prepare good electromagnetic absorbing materials based on graphene is now the research topic. In this review, we discuss the recent progress of graphene-based MAMs, including pure graphene, graphene/polymers, graphene/magnetic metals, graphene/magnetic ferrites, graphene/ceramics and graphene/multicomponent composites. Furthermore, some regular results, shortcomings, challenges, and prospects of graphene-based MAMs are also put forward, which will be helpful to people working in the related fields.

2. Microwave absorption theory

In this section, the fundamental knowledge of microwave absorption will be presented. When the EM wave incidents on a lossy dispersive material, the incident power can be divided into three parts: reflected power (P_r), absorbed power (P_a) and transmitted power (P_t) [42], shown in Fig. 2a and b. The reflection of the EM waves consists of surface reflection and multiple reflection, indicating that the promotion of the multiple reflection will lead to extended transmitted routes of the EM wave, and further enhance the absorbing ability of the EM wave absorbents [43]. Then, the incident microwave energy can create heating within the material through the interactions of the electromagnetic field with the material's molecular and electronic structure, which can transfer the incidence EM wave into thermal energy, leading to an energy dissipation. Therefore, there are two basic methods to promote EM wave absorption, one is by increasing the transmitted routes of the EM wave in the absorbents by regulating their nanostructures, such as pores, multihierarchies, multilayers, etc., and the other is by modifying the electromagnetic parameters to enhance the EM absorption ability. Relative complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and relative complex permeability ($\mu_r = \mu' - j\mu''$) are very important parameters that can determine the MA performance of an absorber. The terms ε' or μ' are associated with energy storage, and ε'' or μ'' stands for the energy dissipation from conduction, dipolar, resonance and relaxation mechanisms [44]. On the basis of relative complex permittivity and relative complex permeability, the refection loss (RL) represents the EM absorption ability is calculated by the transmission line theory, which is summarized as follows [45]:

$$Z_{in} = Z_0\sqrt{\mu_r/\varepsilon_r}\tanh\left[j\left(2\pi fd/c\sqrt{\varepsilon_r/\mu_r}\right)\right] \tag{1}$$

$$R_L = 20\log\left|\frac{(Z_{in} - Z_0)}{(Z_{in} + Z_0)}\right| \tag{2}$$

where ε_r and μ_r are the relative complex permittivity and permeability, respectively, c is the velocity of light, f is the microwave frequency, d is the absorber thickness, Z_{in} is the input impedance of the absorber, and Z_0 is the impedance of free space. So, the closer the values of ε_r and μ_r, the less reflection and the more RL of the EM wave will be achieved [46]. To obtain an effective EM absorption, efficient complementarities between the dielectric and magnetic loss, and its impedance characteristic should be obtained. The dielectric loss ability mainly comes from conductivity loss and polarization loss [47], and the polarization loss can be further divided into ionic polarization, electronic polarization, dipole orientation polarization, and interfacial polarization (space charge polarization) [48]. According to the free electron theory [49], $\varepsilon'' \approx 1/2\pi\rho f\,\varepsilon_o$, where ρ is the resistivity. It can be expected that high electric conductivity (i.e., low resistivity) will enhance the imaginary parts of relative complex permittivity, and thus the conductivity loss plays the main role in the dielectric loss and the polarization loss can be hidden [50]. Ionic polarization and electronic polarization can be easily excluded in microwave absorption because they usually occur at a much higher frequency region (10^3–10^6 GHz). Dipoles-namely, bound charges in dielectric medium, are generally restricted on the defects and residual groups, and cannot move freely like electrons in an external electric field. Under a high-frequency alternating electric field, the dipoles cannot reorient themselves quickly enough to respond to the applied electric field, resulting in dipole orientation polarization, and as a result, ε' and ε'' will start to decrease and produce typical frequency dispersion behaviors [51]. The interfacial polarization and associated relaxation always appears in a heterogeneous system, and the accumulation and uneven distribution of space charges at the interfaces will produce a macroscopic electric moment that can consume the incident EM energy effectively [52]. The relaxation process can be described by a Cole – Cole semicircle, which can be deduced based on the Debye