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Hierarchical electromagnetic absorption in micro-waveguide stuffed with magnetic media for resin-based composites of graphene nanosheets and manganese oxides

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ABSTRACT

Waveguide configurations of hierarchical system are proposed as new microstructures for composites in absorbing enhancement. Supercritical fluid (SCF) one-pot exfoliation of layered graphite and manganese oxide mixing materials is developed to obtain a hierarchical system, containing graphene nanosheets (GNS) and exfoliated manganese oxides (EMO) in different sizes. Composites with GNS–EMO embedded in epoxy resin matrix are produced for a design of dielectric and magnetic loss integrated absorber. Volume fraction of GNS–EMO in composites is given for an optimal quantity of resin epoxy in fixation and formation. The effect of mixing ratios between electric and magnetic components is provided for the design of dielectric and magnetic loss integrated absorbers. Frequency shifting phenomena are revealed in the component adjusting course. Excluding the offsetting sizes, reflection loss of composites is enhanced as thickness increases. Synergistic effect of electric and magnetic coordinated materials demonstrates the superiority of micro-waveguide structures in GNS–EMO composite absorber.

1. Introduction

Nowadays, it is important to make effort to minimize electromagnetic interference (EMI) for protecting electronic devices and avoid electromagnetic (EM) pollution in the electronic age [1–3]. Because of the existence of EMI, the actual performance of electronic devices becomes poor. Microwave absorbing materials are utilized to solve this problem in many cases. Microwave absorbers can be used not only for shielding but also stealth technology. The radar-absorbing material (RAM) has been applied in military defense since many years ago. The demand for a suitable microwave absorber is very high both in commercial and military applications. The development of absorbing materials requires a thin and light microwave absorber having a suitable bandwidth. Microwave absorbers absorb EM energy and then dissipate it into heat energy, via both dielectric and magnetic loss. Therefore, the preparation of composite materials, containing both electric and magnetic components, and their microwave absorbing properties have been extensively investigated for many years [1,4–9]. A suitable absorbing material is the presupposition in engineering design.

As to improve the EMI shielding efficiency, the contribution can result from reflection, absorption, and multiple reflections [1]. However, absorption will play a crucial role for the case requiring little reflection and the application in the dielectric Salisbury screen (DSS). Microwave absorbing can be designed from the aspects of structures and absorbing materials [10]. Numerous works can be attributed to the design of integrating the contribution from electric and magnetic synergistic effect in absorption [1,2,11]. So far, the applied materials in microwave absorbing contain barium titanate [12], cobalt ferrite [13], iron, iron compounds, and other iron/manganese oxides [7,14,15]. The electric conductive components are multi-walled carbon nanotubes [8], carbon black [10], active carbon–carbon fibers [16] and graphene materials [14]. The matrix for the fixation and formation of fillers includes paraffin wax [8], epoxy resin [4,9], rubber [5], polyvinylidene fluoride [14], waterborne polyurethane [15], etc. Single electric application or magnetic application also has been reported in literatures [17–21], as the respective type of dielectric or magnetic loss absorbers. Nevertheless, several works have reported the synergistic effect, such as the case of nanotube and magnetite [8]. It demonstrates that the combination of magnetic and electric type composites can play extraordinary roles in absorbing. Moreover, morphology of fillers is a crucial factor related to wave absorption [20].

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Supercritical fluid (SCF) method is a simple and rapid method to obtain exfoliated products, due to low resistance and high diffusivity of supercritical fluid [22,23]. Layered graphite can be exfoliated into graphene nanosheets (GNS), including multi-layers and single-layer nanosheets [24,25]. Exfoliation of layered manganese oxide can give rise to exfoliated manganese oxides (EMO) in many kinds of morphology with different sizes [23,26]. The hierarchical system can be formed, resulting from a growing course of manganese oxides in supercritical fluid [26]. One-pot exfoliation processing in supercritical N,N-dimethylformamide (DMF) can be developed here to obtain exfoliated mixtures. Thereinto, GNS are one kind of promising materials, with high conductivity and electronic transporting ability [27]. Exfoliated manganese oxides are well-known magnetic materials [23,28], for the particular electron structure of manganese atoms, just as its special position in element table. Moreover, manganese element has a smaller atomic number than iron, cobalt, and nickel elements, which can contribute to lighten the material weight. Nevertheless, the application of manganese oxides in absorbing as a magnetic component is still not many. GNS–EMO composites of these materials are expected to integrate their respective merits, resulting in an excellent absorbing.

In addition, there are already several works involving the application of graphene materials [4,29] and some other carbon material, such as carbon nanofibers [1], in EM absorbing properties. However, few of the works meanwhile verify the effectiveness of thin GNS composites in wave absorbing separately. Magnetic materials also seldom show their single effect. Hence synergistic effect is not given in the way of direct comparison. On the other hand, as to the composites in previous work, much discussion involves thickness and ratio of components [7,9] or parts of these contents [6]. Besides these related contents, direct comparison with component composites of electric and magnetic components is employed in the investigation of resin-based GNS–EMO composites.

Some geometrical sizes are suitable to the absorption of EM wave with special wavelength/frequency, via so called "geometrical effect" [20]. The propagation of EM wave has several modes in media, such as transverse electric wave (TE), transverse magnetic wave (TM), and transverse electro-magnetic waves (TEM), especially in the space with structures forming a waveguide. Waveguide can propagate EM wave and make the incident wave reside in confined space. Therefore, waveguides can confine energy to travel only in specific dimensions according to waveguide types. Nanosheets can realize the multi-reflections in inner layers of multi-layer nanosheets and among nanosheets. Multi-reflection and configurations of waveguide in GNS–EMO composites can give rise to sufficient absorption and conversion in the form of heat [1,30]. On the other hand, magnets among sheets can promote the decay of EM wave. Adequate wave decay and dissipation of confined energy result in enhancement of wave absorbing.

In this work, SCF one-pot method is utilized to process the mixtures of graphite and manganese oxides, as a simplified exfoliation of multi-component precursors, for the fillers of absorbers. The exfoliated products are characterized using X-ray diffraction (XRD), Raman, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), to show the coexistence states of multi-components, morphology and waveguide configuration of multi-reflection in mixtures after exfoliation. Composites are formed by the dispersion of exfoliated products in epoxy resin matrix, to achieve the fixation and formation of fillers. XRD, infrared (IR) spectroscopy, SEM and physical property measurement system (PPMS) provide the information on the dispersion, fixation, combination of exfoliated products in epoxy resin, as well as magnetic properties of composites after fixation and formation. The parameters related to absorbing properties are obtained by network analyzer. Reflection loss (RL) from conversion with programming calculation is taken to estimate absorbing performance, assisted with the evaluation of loss tangent in some places. The volume fraction of fillers in composite materials, the ratio between electric and magnetic parts in mixtures, and the thickness effect of composites are the considered factors for the composite forming scheme. Synergistic effect of electric and magnetic materials is presented from the comparison with respective effect of GNS and EMO.

2. Experimental section

2.1. Reagents

Potassium hydroxide (KOH), manganese oxide (Mn_2O_3), natural graphite and N,N-dimethylformamide were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Epoxy resin 6002, curing agent 5772, and silicon oil are industrial products.

2.2. Preparation and formation of materials

Excepting graphite purchased from commercial products, layered manganese oxides were obtained by a flux grown method in laboratory [23,31]. A stoichiometric mixture of KOH and Mn_2O_3 was calcined at 1073 K for 60 h in flowing O_2. The obtained compound manganese oxide, $K_{0.45}MnO_2$ (5 g), was treated with 1 L of HCl solution (1 mol L^{-1}). In a repeated acid treatment procedure, the acid solution was replaced with a fresh one daily for 10 days, to achieve nearly complete removal of alkali metal ions between layers. The resulting solid, $H_{0.13}MnO_2{\cdot}0.7H_2O$ (HMnO), was washed with copious amounts of water and then air-dried.

SCF processing was completed in a 15 ml sealed stainless-steel reactor. Layered precursors about 70–75 mg were added into a container and dispersed in 10 ml DMF by low-power sonication (40 kHz, maximum output 180 W) for 15 min. The mixtures were injected into the stainless-steel reactor. The reactor was heated to 400 °C in a professionally designed tube furnace. After a moment staying at the preset temperature, the procedure was terminated by an ice cold water bath to finish SC-DMF processing (critical point: 377 °C, 4.4 MPa). The products were collected after repeated washes with fresh solvent. The precursors are graphite, layered manganese oxides, and their mixtures with mass ratios of 1:1, 1:3, 1:5, 3:1, and 5:1 between layered manganese oxides and graphite. So the exfoliated products include GNS, EMO, and the mixtures of GNS–EMO. GNS–EMO sample of ratio 1:1 is utilized in typical characterization of mixture products and its composites.

The epoxy resin was blended uniformly with the exfoliated products in the volume ratio of 1:1 in the investigation on effects of mass ratios of mixture components, the sizes of GNS–EMO absorber, and single GNS/EMO composites. After the addition of curing agent, the mixtures were mixed uniformly again and then cast into hollow cylinder in a short time. Molds for the formation of composites were painted by silicone oil ahead. Molding was carried out under ambient surrounding for one night, to obtain specimens of internal and external diameters equaling to 3.04 and 7 mm, with a thickness of 1–4 mm for reflectivity measurements. The exfoliated products were embedded in solidified resin. As to the investigation on matching volumes between exfoliated products and resin, the adopted volume fractions are 1%, 5%, 10%, 14.3%, and 20%. The mass mixing ratio of fillers adopts unified 1:1 for the investigation of volume allocation.

2.3. Characterization and measurements

X-ray diffraction (XRD) was performed using a D8 Advance X-ray diffraction apparatus (Cu Kα copper radiation of