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Strong and thermostable polymeric graphene/silica textile for lightweight practical microwave absorption composites

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ABSTRACT

Since various criteria including effective absorption intensity, broad absorption bandwidth, sufficient mechanical properties and excellent stability are required to meet the benchmark in practical service, here we propose a novel strategy to fabricate strong and thermostable polymeric graphene/silica textile composites for practical microwave absorption applications. For achieving homogeneous configuration, a unique silica textile coupled with freeze-drying method is employed as the critical factor in the formation of the polymeric composites, allowing reduced graphene oxide (RGO) to in situ form three-dimensional conductive frameworks. With the co-existence of silica textiles and thermoset polymers, such integrated bi-matrices offer the composites with substantial reinforcement in the mechanical properties and thermal stability. As expected, the as-fabricated lightweight composites (~1 g/cm^3) present strong tensile strength of 40 MPa and high thermal stability beyond 225 °C (95% mass retention in air), coupled with a microwave absorption peak at −36 dB and effective absorption in the full X-band at a low filler loading (4.1 wt% RGO). Implication of the results suggests that the excellent overall performance allows such novel polymeric composites for practical microwave absorption applications.

1. Introduction

The materials of electromagnetic absorption and attenuation have attracted increasing attention owing to their significant roles in absorbing and diminishing undesirable electromagnetic irradiations from the electronic devices and communication apparatus [1–7]. For the practical applications such as high-speed aircrafts and shuttles in the aerospace industry, various critical factors are highly concerned in the structural components, including broadband absorption capacity for avoiding signal detection, strong mechanical properties for resisting deformation under stress, sufficient thermal stability for maintaining stable operation under high-speed transport and etc. [4–6,8–12] As a consequence, combination of both functional and structural criteria requires the microwave absorption layers to hold outstanding overall performance, allowing them to reach the benchmark that is capable for practical circumstances.

For the pursuit of broadband absorption, recent advances suggest that carbon-based composites of various morphologies have presented outstanding capability in the microwave absorption, with many advantages including lightweight, low cost, easy processability, excellent corrosion resistance, and etc. [7,13,14] Due to the unique two-dimensional (2D) nanostructures and tunable electrical conductivity, graphene nanosheets of large aspect ratios possess exclusive features in establishing three-dimensional (3D) conductive networks for generating leaking current, enabling to deliver effective electromagnetic energy conversion and attenuation [6,15]. In the past years, explorative efforts have been paid to the development of graphene-based heterofillers, aiming to offering tunable complex permittivity and permeability to meet the impedance matching conditions [16]. For typical examples, Chen et al. have recently prepared reduced graphene oxide (RGO)/Ni heterostructures, and the corresponding wax-based composites

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possessed a maximum reflection loss −17 dB with presence of 60 wt% filler loading [17]. Similarly, Fu et al. have reported that the $NiFe_2O_4$ nanorods/RGO heterofillers exhibited microwave absorption intensity up to −29.2 dB at 60 wt% filler loading [18]. Zhang et al. have synthesized iron oxides/RGO fillers, and their wax-based composites with filler loading of 50 wt% presented a microwave absorption peak around −21 dB in the 2–18 GHz [19]. Likewise, graphene-based hybrid fillers with a variety of hierarchical structures have also been studied [20–22]. However, it is noted that the studies that mainly focus on controllable design of hierarchical fillers generally suffer from some critical issues. As is well known, magnetic nanofillers would primarily contribute to the magnetic loss in the relatively lower frequency regions in GHz. Their contribution in X band (8.2–12.4 GHz) and Ku band (12.4 GHz–18 GHz) is largely on the interfacial control for the dielectric loss in the graphene-based hybrid fillers [13,23]. On the other hand, the presence of the secondary non-conductive heterofillers would usually increase the filler loading in the composites, owing to their impacts on the generation of effective 3D conductive networks for leaking current. Compared to the carbon-based heterofillers, bare carbon fillers are found to be more promising as the effective fillers for microwave absorption composites since they are generally found to deliver highly effective microwave absorption performance at filler loadings below 10 wt% [8,13,16,24–26].

Polymers and ceramics are ideal matrices in designing robust composites of strong mechanical properties. Generally, ceramic-based composites require sintering processes for achieving the dense and strong feature, and thus a portion of carbon-based fillers may not survive at extremely high-temperature treatments. Apparently, polymeric composites of more facile processing appear more practical and thus are attracting extensive explorations in recent studies [27–29]. For instance, Singh et al. fabricated RGO/nitrile butadiene rubber (RGO/NBR) composites by mechanical mixing RGO and NBR in the xylene solution, and the composites with 10 wt% RGO exhibited maximum absorption intensity up to −57 dB and a with a wide effective bandwidth from 7.5 to 12 GHz in the 2–18 GHz investigated region [28]. Wang and coworkers have processed the RGO/$MnFe_2O_4$ hybrids into polyvinylidene fluoride (PVDF) via mechanical mixing with subsequent hot press. Due to the synergetic effect between graphene-based fillers and PVDF matrices, the composites with filler loading of 5 wt% can reach −29.0 dB with effective absorption range from 8.00 to 12.88 GHz [29].

High-temperature service requires the composites to be endowed with thermal stability in the harsh environment, specifically under high-speed transportation [5,30,31]. In the recent attempts made by Cao and coworkers, SiO_2 nanoscale powers have been widely utilized for processing carbon/SiO_2 ceramic composites with the conventional ceramic processing routes [32–35]. Although the as-prepared carbon/SiO_2 composites are able to offer effective microwave absorption at high temperature, the high density (dense ceramic-based composites generally >2 g/cm^3), poor processability and mechanical brittleness of the ceramic composites fabricated from powders are also the concerns in practical applications.

With the consideration of substantial improvements in the filler loading, microwave absorption bandwidth, mechanical properties and thermal stability, here we present a novel strong and thermally stable polymeric graphene/silica textile composite for effective microwave absorption. With the assistance of freeze-drying approach and unique silica textiles, GO nanosheets is allowed to in situ generate homogenous 3D RGO conductive networks in the polymeric composites. More importantly, such silica textiles play significant roles in the considerable enhancement of the overall performance. The lightweight polymeric graphene/silica textile composites (density ~1.0 g/cm^3) at a low filler loading of 4.1 wt% show excellent overall performance, including strong tensile strength (~40 MPa), improved thermal stability (225 °C in air with 95% mass retention) and peak absorption up to −36 dB with effective absorption at full X-band. The exceptional features and advantages coupled with associated opportunities have been discussed.

2. Experimental section

2.1. Graphene oxide

Graphene oxide aqueous solution was prepared according to the modified Hummers method [36]. Briefly, commercial graphite powders (2 g) and $NaNO_3$ (1 g) were added into the concentrated sulphuric acid (120 Ml) in an ice bath, and the mixture was kept at 0 °C for 1 h. Subsequently, $KMnO_4$ (6 g) powders were gently added into the above mixture. (Caution: fast mixing may result in explosion). Until the stirring was applied for 2 h, the mixture was heated and kept at 30 °C for 0.5 h. Then, deionized water (150 mL) was slowly added, and H_2O_2 solution (5%, 50 mL) was subsequently introduced. Upon the completion of the action, the final solution was washed with deionized water and HCl (5%), and the GO aqueous solution was achieved.

2.2. RGO/silica textile

Initially, commercial silica textile (thickness ~0.25 mm, density ~0.7 g/cm^3, where the strength and modulus of a single silica fiber in the textile is 3700 MPa and 91.6 GPa, respectively.) was washed with acetone and water under sonication for 1 h, followed by drying in a vacuum oven. A stripe of the cleansed silica textile was then folded for three times with two ends fixed, with aiming to achieve ~2 mm in thickness. The folded silica textile was immersed in the in the mixture solution of GO and hydroquinone (GO: hydroquinone = 1:5 wt/wt) under sonication for 2 h. It is noted that the height of the GO mixture solution was approximately the same to the thickness of the folded silica textile. Until stable mixture solution was achieved, the mixture was then sealed and heated up to 100 °C for 12 h, allowing GO for in situ self-assembling into RGO networks inside the folded silica textile with the presence of hydroquinone. The as-fabricated samples were then washed with deionized water, followed by freeze-drying overnight.

2.3. RGO/silica textile/PF composites

The as-prepared RGO/silica textile were immersed into the phenol formaldehyde (PF) resin/ethanol (EtOH) solution (PF % = 30 wt%). Until 2 h immersion, the mixture was then transferred into an oven, and was heated to 100 °C for resin curing (~6 h). The dried polymeric samples (RGO/silica textile/PF composite) were cut into different size for further characterizations. Using different initial GO concentrations (5, 7.5 and 10 mg/ml), the corresponding composites of different RGO loadings were obtained. According to the mass track in the entire processing, the final RGO loadings in the three as-prepared RGO/silica textile/PF composites were estimated to be around 1.3, 2.8 and 4.1 wt% (0.5, 1.0, 1.5 vol% as volume fraction), assigned as Composite-1, Composite-2 and Composite-3, respectively. Accordingly, Composite-1, Composite-2 and Composite-3 approximately contained PF of 28.2, 25.9 and 23.2 wt% (14.9, 13.1, 12.1 vol% as volume fraction), with 70.5, 71.3 and 72.7 wt % (84.6, 85.9, 86.4 vol% as volume fraction) in silica textile, respectively. The density of all the samples was estimated around 0.96–1.05 g/cm^3.