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The influence of gradient and sandwich configurations on the electromagnetic interference shielding performance of multilayered thermoplastic polyurethane/graphene composite foams

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ABSTRACT

Multilayered thermoplastic polyurethane/graphene (PUG) composites were fabricated by stacking single-layered PUG foams together. The arrangement of single-layered PUG foams in different orders could realize the gradient concentration of graphene, which was proved to be a facile approach to enhance the microwave-absorbing (MA) property of PUG composites, rather than their electromagnetic interference (EMI) shielding effectiveness (SE). Further sandwiching a wave-transmitting layer between two pieces of PUG foams formed a sandwich structure, by which the SE of the two samples could be significantly improved and the resultant composites still possessed strong MA performance. The SE increment was assigned to the enhanced reflection loss induced by constructive interference, and largely dependent on the thickness of the interlayer d. Particularly, when the values of the d were zero and the quarter of the largest wavelength in the testing frequency range, the minimum and maximum SE could be obtained, respectively. These results are critical to the fabrication of high-performance polymer-based shielding materials with strong MA property.

1. Introduction

The serious electromagnetic (EM) pollution caused by the widespread application of high-frequency electronic devices has concerned the whole society, due to its large threat to human health as well as communication security. Carbon materials including carbon black, carbon fibers, carbon nanotubes and graphene, have good electrical performance, and thereby are frequently blended with polymers to shield or block EM waves, due to their superior properties over traditional metals, such as mechanical flexibility, light weight, corrosion resistance and excellent processability [1–9]. After the introduction of foam structures, such materials can be further made into foams [10–14]. In contrast with the non-foamed or solid shields, foaming materials have three advantages: (1) lower density (to reduce the weight and cost of shielding materials) [15], (2) higher flexibility (to broaden their application in electronic packing) [15–21], and (3) stronger microwave-absorbing (MA) ability (to eliminate the secondary pollution brought by EM reflection) [2,12,15–17,22–26].

In the fabrication of polymer-based shielding composites including solids and foams, a high content of shielding agents (~5–30 wt%) is generally required to achieve a sufficient EM interference (EMI) shielding effectiveness (SE) [10,11,13–15,20,23,24,27–31], which will inevitably increase the viscosity of polymer solutions or melts, resulting in great difficulties in process. A common approach to address this issue is to increase the thickness of shielding materials. Hence, multilayered composites were fabricated by simply stacking several layers of materials randomly together [2,26,32–37], and the results demonstrated that the SE could be significantly improved not only by the increased sample thickness, but also by the enhanced multiple reflections on the internal interfaces.

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Actually, multilayered composites were developed mainly for substituting ordinary monolayer materials in MA application, owing to their more freedom in design, stronger absorbing ability and wider absorption band. As we know, in the fabrication of monolayer MA materials, a homogeneous dispersion of microwave absorbents are generally desired. However, for multilayered MA composites, an inhomogeneous dispersion of microwave absorbents is commonly wanted, in order to improve the matching of wave impedances of adjacent layers and to restrain the reflection loss on each interfaces [12,25,38]. Therefore, multilayered composites with graded dispersion of the fillers [38–40], as well as sandwich structure [34,41], were developed progressively. Nevertheless, there are still some challenges. As multilayered composites are made of single-layered materials, it means that there are numerous ways of permutation and combination for the single-layered components, making the systematic investigation very hard to perform. To date, just a few structure designs have been reported in the gradient structure [39,40,42], as well as the sandwich structure [32,34,41]. Based on these, it is interesting to combine foam structure with gradient and sandwich structures, conduct a systematic investigation on the SE of multilayered composites and provide useful information for the fabrication of lightweight and high-performance EMI shielding materials with strong MA property.

To accomplish this, our group fabricated various EMI shielding foams in previous work, including polymethylmethacrylate (PMMA)/graphene [15], polyurethane (PU)/graphene [21], polyetherimide (PEI)/graphene [23,24,43], polyimide (PI)/graphene [20], carbon and graphene foams [2,26]. In our another research [19], we found that thermoplastic PU/graphene (PUG) foams could be fabricated by means of phase separation even at the high graphene loading of ~17 wt% and the resultant samples possessed similar density, good flexibility and strong self-adhesion, which could help to realize our assumption of designing multilayered composites with foams structure. Inspired by this, we prepared multilayered PUG composites in this contribution by stacking single-layered PUG foams face to face, and systematically studied the effect of the gradient and sandwich structures on their SE performance. The results demonstrated that the gradient structures exerted tremendous impact on the MA property of multilayered composites, instead of their SE. Moreover, there was an optimum design that can endow these materials with the strongest MA property. Compared with the gradient design, sandwich structures were more advantageous in improving the SE of polymer-based composites, and the improvement in SE was highly dependent on the thickness of the wave-transmitting layer.

2. Experimental

2.1. Materials

Polyether-based thermoplastic PU pellets (585A) with a density of 1.12 g/cm^3 and hardness of 85 (Shore A) were provided by Austin Novel Materials Co., Ltd. (China). Graphene was prepared by the thermal exfoliation and reduction of graphite oxide (GO) at 180 °C under air atmosphere, similar to our previous report [44]. To remove the residual oxygen-containing groups in graphene and improve its electrical property, the as-obtained fluffy black power was further annealed at 1500 °C for 1 h in flowing high purity nitrogen at a heating rate of 5 °C/min. *N,N′*-Dimethylformamide (DMF) was supplied by Sinopharm Chemical Reagent (China).

2.2. Preparation of microcellular PUG composite foams

The preparation of microcellular PUG composite foams is schematically illustrated in Fig. 1a. In a typical process, graphene (1.304 g) was dispersed in abundant DMF (500 mL) with the help of ultrasonication for 10 min. The as-obtained graphene suspension was transferred into a round-bottomed flask and PU pellets (15.0 g) were added under vigorous stirring at 60 °C for 5 h. The mixture was then precipitated with aqueous solution, obtaining PUG composite. Afterwards, the composite was dried in vacuum oven at 60 °C for 10 h, and redissolved in DMF (100 mL) to achieve homogeneous PUG solution. After cooling to room temperature, the solution could be either cast on a glass substrate (to fabricate thin samples) or poured into an open Teflon mold (to fabricate much thicker samples), and subsequently exposed to the air with the relative humidity of 80% at room temperature. The resultant sample was then immersed in water to remove residual solvent and dried in a vacuum oven at 60 °C for 24 h. As a result, microcellular PU/8 wt% graphene foam was successfully prepared and noted as PUG8. Similarly, PUG foams with graphene loading of 0, 4, 12, 16 and 20 wt% were successively prepared and denoted as PUG0, PUG4, PUG12, PUG16 and PUG20.

2.3. Characterization

The cell morphology of PUG foams was observed with a Hitachi S-4800 field emission scanning electronic microscopy (SEM) at an accelerating voltage of 8 kV, and the samples needed to be freeze-fractured in liquid nitrogen and coated with gold before the observation. The density of PUG foam was measured via a water displacement method using an electronic density balance (BT224S, SARTORIUS AG). The diffraction behavior of graphene was analyzed at room temperature over the 2θ range of 5–60° using a Bruker AXS X-ray diffractometer (XRD) with Cu Kα radiation at a generator voltage of 40 kV and a current of 40 mA. Additionally, Raman spectra were recorded by a Labram spectrometer (Super LabRam II system) with a laser of 532 nm. X-ray photoelectron spectroscopy (XPS) was conducted with a Kartos multifunctional X-ray photoelectron spectroscope (AXIS ULTRA) using Mg (mono) Kα radiation under 1.2×10^{-9} Torron. The volume electrical conductivity of PUG0 was measured with three-terminal fixture on an EST121 ultrahigh resistance and microcurrent meter (Beijing EST Science & Technology CO. Ltd.). For the rest of the samples, their conductivity was tested with the standard four-probe method.

2.4. EMI shielding performance

The EMI shielding performance was monitored with a R&S ZVA67 vector network analyzer (VNA) using the waveguide method over the frequency range of 12–18 GHz (Ku-band). The corresponding dimension of samples is 15.7×7.8 mm^2, and the thickness of all tested sample is ~2.4 mm, except for that of PUG0 (~1.8 mm). The single-layered samples were measured in a rectangular waveguide immediately, while for the testing procedure of multilayered PUG composites, they were fabricated by simply arranging single-layered PUG foams together without the use of any adhesives, in order to eliminate the adverse effect on their foam structure and eventually EMI SE. During the measurement of EMI shielding, the size of single-layered PUGs was slightly bigger than the chamber of rectangular waveguide so that the samples could be firmly stuck in the chamber. With the assistance of commercial polystyrene (PS) foam, single-layered PUG samples may have a good contact with each other due to their good self-adhesion and remain perpendicular to the incident EM wave simultaneously. Here need to mention, the PS foam should be removed when the measurement was performed, to make sure the accuracy of the results. After the calibration for the VNA, S parameters (S_{11} and S_{21}) were measured, and the coefficients of transmission (T), reflection