Compressible Ni and Reduced Graphene Oxide (Ni-rGO) Coated Polymer Foams for Electromagnetic Interference (EMI) Shielding

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Abstract. Novel high-performance Ni-rGO coated polymer (NiGP) foams for EMI shielding were developed with a dip-coating and reduction method. The obtained NiGP3 foams with a thickness of 10 mm prepared by 3 rounds of dip-coating, exhibited excellent EMI shielding effectiveness (EMI SE) of 24.03−27.71 dB at 30−1500MHz, which can fully meet the requirement of practical application. Furthermore, the NiGP foams maintain the compressibility of the original polymer foams.

1. Introduction
With the rapid development of advanced electronic technology, electromagnetic pollution has been attracting more and more attention of researchers in the field of electronics, aerospace, aviation, information and communication. It is of great value to develop electromagnetic shielding materials to reduce electromagnetic pollution in military and civil fields.

Graphene foam and its composite are promising material for EMI shielding because of low density and good electrical conductivity. Chen et al. developed an ultra-lightweight and highly conductive graphene/polymer foam composite by a one-step process without the use of foaming agents, in which the graphene sheets were fabricated by CVD. It showed a EMI SE of 30 dB over the frequency range of 30−1500MHz and specific shielding effectiveness of 500 dB/(g/cm³), which surpassed the best values of metals and other carbon-based composites. Ling proposed a facile and fast approach to produce scalable lightweight microcellular polyetherimide (PEI)/graphene nanocomposite foams by a phase separation process. It was observed that the strong extensional flow generated during cell growth induced the enrichment and orientation of graphene on cell walls. The foaming process significantly increased the specific EMI SE from 17 to 44 dB/(g/cm³). Liu et al. synthesized ultralight three-dimensional graphene networks by thermal reduction of graphene oxide (GO)/poly (vinyl alcohol) networks. The graphene-based composites possessed the maximum absorption reflection loss reaching 43.5dB at 12.19GHz with a thickness of 3.5 mm. Bin Shen fabricated compressible polyurethane (PU)/graphene (PUG) foams by a simple solution dip-coating of graphene on commercial PU, which possessed low density and comprehensive EMI shielding performance. The PUG foams overcome the problem of brittle mechanical property kinds of graphene foams suffer. However, the PUG foams in Bin Shen’s work also have a drawback, which is that the effective thickness is large.

In order to further improve the EMI SE of the PUG foams, the Ni nanoparticles were introduced to the composite. In the present work, the Ni-rGO coated PU (NiGP) foams were prepared with a simple
solution dip-coating and chemical reduction method. The introduction of Ni nanoparticles enhanced the conductivity of the composite material, resulting in the improvement of EMI SE.

2 Experiment Section

2.1 Fabrication of NiGP Foams

Fig 1. Schematic of process to prepare the NiGP foams

The NiGP foams were prepared using a simple solution dip-coating method followed by reduction with superfluous reductants as shown in Fig1. First, Graphene oxide(GO) synthesized with a modified Hummer’s method and nickel sulfate were dispersed in deionized water with the assistance of ultrasonication, among which the concentration of GO and nickel sulfate are 3 g/L and 0.1 mol/L, respectively. Then the commercial PU foams with a thickness of 10 mm, were immersed in the suspension consisting of GO and nickel sulfate and squeezed repetitively, followed by a drying process in an air-circulating oven at 90°C. Afterward the PU foams coated with GO layer and nickel sulfate were put in a vessel prefilled with superfluous sodium borohydride solution and further reduced at 90°C for 2h. After that, the foams were washed several times and dried at 90°C to get the final NiGP foams. The contents of rGO and Ni nanoparticles in the NiGP foam could be simply tuned by adjusting the number of dips in the GO and nickel sulfate suspension. The resultant foams are noted as NiGP1, NiGP2, and NiGP3 respectively according to the number of dips.

2.2 Characterizations

The morphology and composition of the NiGP foams were observed with a VEGA Ⅱ XMU scanning electron microscope and energy dispersive X-ray spectrometer. The electrical conductivity was measured using a RTS-8 four probe measuring instrument. The Electromagnetic interference shielding effectiveness of specimens was measured by the coaxial cable transmission method in the frequency range of 30-1500 MHz. The samples were cut into disks with a diameter of 115mm to fit the sample holders.

3. Result and discussion

3.1 Morphology and element

As we all know, the graphene oxide films are negatively charged, while the nickel ions are positive in solution, which leads to the inter-attraction between them. The adherence of nickel ions to graphene oxide films makes it easy for nickel ions to coat on the skeletons of the PU foam together with graphene oxide films. The concentration of GO or nickel sulfate cannot be too high. Otherwise the solution will be more viscous, which is not beneficial to the dip-coating. The original PU foams were treated by pray-gold since they are not conductive.
From the appearance point of view, the color of foams was changed remarkably from light white to black. The typical SEM images of the microstructure of the original PU foams and NiGP foams were shown in Fig. 2. Obviously, the surface of the original PU foams was smooth, while that of the NiGP foams was rough. As is shown in Fig. 2D, the surface of the NiGP foams was coated with some particles and plicated sheets, suggesting the successful assembling of rGO sheets and nickel ions on the skeletons of the PU foams. Energy dispersive spectroscopy (EDS) indicates that nickel ions are reduced to nickel particles.

3.2. Electromagnetic interference shielding efficiency

For the sake of comparison, the PU foams only coated with graphene (PUG) were synthetized according the process in section 2.1, just by removing the nickel sulfate in the solution. Fig. 4 gives the results of the EMI SE of PUG foams and NiGP foams. The EMI SE of PUG foam is measured to be 6.04–10.36 dB over the test frequency. However, when the nickel particles were introduced into the composites, the EMI SE of NiGP1 was found to be improved to the range of 14.98 to 19.72 dB. With further increasing the loading of rGO and nickel by increasing the number of dips, the EMI SE value was found to substantially increased up to 21.06–24.88 dB for NiGP2, and to a much higher value.
(24.03–27.71 dB) for NiGP3, which indicates that the EMI shielding properties of those NiGP foams can meet the requirement of commercial applications (20 dB).

Fig. 4. EMI SE of original PUG foams and NiGP foams

Fig. 5. Conductivity and SEaverage of PUG foams and NiGP foams

Electrical conductivity is critical factor for EMI SE, so the electrical conductivity of PUG and NiGP foams were measured, and the relationship between conductivity and average EMI SE was investigated (shown in Fig. 5). The conductivity of the PUG foams was only 0.09 S/m. Compared to the PUG, the NiGP1 possessed a higher electrical conductivity of 0.17 S/m, which suggested that the addition of nickel could enhance the conductivity of composites. The conductivity of NiGP2 and NiGP3 increased to 0.22 S/m and 0.24 S/m, respectively. Obviously, there is a positive association between the average EMI SE and conductivity. The average EMI SE increased with the conductivity of the composites.

4. Conclusion
In summary, we have developed a novel and fast approach for fabrication of compressible Ni-rGO coated polymer foams with excellent EMI shielding performance based on a dip-coating and reduction process. The introduction of Ni significantly improved the conductivity and EMI SE of the composite. The EMI SE of NiGP3 reached 24.03–27.71 dB in the range of 30–1500 MHz, which is fully able to meet the requirement of practical application.

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