Diamond & Related Materials 20 (2011) 1183–1187

Contents lists available at ScienceDirect

Diamond & Related Materials

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

Investigation of the electric conductivity and the electromagnetic interference shielding efficiency of SWCNTs/GNS/PAni nanocomposites☆☆

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ARTICLE INFO

Available online 30 June 2011

Keywords:
SWCNTs
GNS
PAni
Electric conductivity
EMI SE

ABSTRACT

This work demonstrates the fabrications and characterizations of polyaniline (PAni) composites containing single-walled carbon nanotubes (SWCNTs), graphite nanosheets (GNS), or hybrid fillers (SWCNTs/GNS). The characterization of microstructure, examination of fracture surface morphologies, and measurement of electric conductivity and electromagnetic interference shielding efficiency (EMI SE) were performed. It was found that both the electric conductivity and the EMI SE increase with filler loading, and the nanocomposites filled with 1.0 wt.% SWCNTs/GNS possessed the highest electric conductivity of 16.2 S/cm and total EMI SE of 27.0 dB. The experimental results also show that absorption is the primary mechanism of EMI SE for all of the loadings and fillers.

1. Introduction

The rapid development of electronic devices has reduced the space within which high density components must operate. This may increase the electromagnetic interference (EMI) among components, which may cause degradation or malfunction of the device. EMI shielding materials have been used to protect components from EMI radiation. Polymers having conductive fillers or metal coating are the most widely used for EMI shielding. However, metal filler with high loading is usually required for achieving excellent shielding efficiency (SE). Carbon nanotubes (CNTs) with high strength and stiffness, extremely high aspect ratio, and electric conductivity promise efficient EMI shielding at low filling [1–4]. Similar to CNTs, graphite nanosheets (GNS) have also been adopted for fabricating nanocomposites because they possess high surface area, remarkable stiffness, electric conductivity, etc. [5]. Although polymer has the advantages of lightness, versatility, low cost, and easy processability, the low electric conductivity of polymer restricts its application in EMI shielding. Therefore, several efforts have been made to improve the EMI SE by introducing light-conductive fillers such as CNTs and carbon nanofibers into the matrix [1–4,6,7]. Conductive polymer for this purpose has also been developed. Polyaniline (PAni) has become one of the most attractive polymers due to its high electric conductivity, lightness, environmental stability, and ease of synthesis [8,9]. However, the percolation threshold of PAni is high because of low compatibility and low aspect ratio of the conducting polymer [10]. The drawback of low electric conductivity can be solved by adding conducting filler into the PAni polymer.

During the past decade, improvements in EMI SE have been achieved by introducing carbon materials, such as CNTs, graphene, and carbon fibers, into polymer matrices, such as poly(methy methacrylate), epoxy, polypropylene, polyurethane, and liquid crystal polymer [1–9]. Improved EMI SE has been shown to require higher filler loading. For example, EMI SE of 20 dB can be obtained at 15 wt.% filler loading [6]. High EMI SE of multi-walled CNTs (MWCNTs)/PAni composites have been developed, and it was found that absorption dominated total shielding effectiveness [8]. Recently, the electrode properties of the GNS/CNTs composites was explored, and the authors suggested that CNTs were conductive bridges for connecting GNS/PAni particles [11]. Furthermore, it was reported that composites having higher electric conductivity possessed better EMI SE [4]. Therefore, composites with high EMI SE should be obtainable once GNS and CNTs are introduced into the PAni matrix simultaneously. Yet, there has been limited examination of the EMI SE of PAni nanocomposites filled with both SWCNTs and GNS.

The primary objectives of this work are to fabricate nanocomposites that include SWCNTs/PAni, GNS/PAni, or SWCNTs/GNS/PAni and to study the morphologies and microstructure characterizations of the fabricated nanocomposites. Moreover, the EMI SE performance contributed by absorption and reflection is also analyzed.

2. Experimental details

2.1. Syntheses of SWCNTs and GNS

SWCNTs were synthesized using the floating catalyst chemical vapor deposition (FCCVD) method. Xylene (C_8H_{10}), thiophene (C_4H_4S), and

☆☆ Presented at the Diamond 2010, 21st European Conference on Diamond, Diamond- Like Materials, Carbon Nanotubes, and Nitrides, Budapest.

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doi:10.1016/j.diamond.2011.06.007

ferrocene ($Fe(C_5H_5)_2$) were employed as carbon precursor, promoter, and catalyst precursor, respectively. In FCCVD, xylene is mixed with thiophene in a pre-chamber and then reacted with ferrocene under a temperature of 1200 °C in a tube furnace. The details for SWCNT synthesis can be found in our previous work [12]. In the GNS preparation, the first step is immersing the natural graphite flakes in acid solution (20 vol.% HNO_3 and 80 vol.% H_2SO_4), followed by stirring the mixture at room temperature for 16 h. During reaction with acid solution, the graphite layers were intercalated by acid molecules and the bonds between graphite layers became weak. The expandable graphite was filtered using DI water repeatedly until the pH value reached 6 and then subjected to the drying process at 70 °C for several days. For obtaining worm-like expanded graphite (EG), the expandable graphite was heated rapidly using microwave irradiation (JMO23888A, YJEPROUD, 900W) for 30 s. The synthesized EG was subsequently subjected to sonication in alcohol for 16 h following filtration and drying under vacuum at 70 °C for over 48 h.

2.2. Preparation of SWCNTs/GNS/PAni nanocomposites

For synthesizing PAni, 0.2 M sodium dodecyl benzene sulonate (NaDBS) was dissolved in 0.1 M HCl solution. This was stirred for 2 h, after which 0.1 M aniline monomer was slowly added. Afterwards, the ammonium persulfate (0.125 M, $(NH_4)_2S_2O_8$, APS) was added dropwise under stirring. For fabricating nanocomposites, fillers having various loadings were added into the solution before aniline monomer was introduced. Polymerization was performed by stirring the mixture for 16 h at room temperature. Next, the wet composite cake was collected and diluted with DI water until the filtrate became transparent. Finally, the slurry-like product was dried at 70 °C in an oven and was pulverized into powder before use.

2.3. Microstructure characterizations and EMI SE measurements

Superior electric conductivity and EMI SE of nanocomposites rely on the inherent quality of the fillers and the spatial distribution of the fillers in the matrix. Agglomeration of CNTs is the most common problem during processing, but this can be solved by introducing functional groups to the CNT surface or edges. In this work, Fourier transformed infrared spectroscopy (FTIR, Perkin-Elmer Spectrum RXI) and Raman spectrometry (Raman-LabRam HR800) using a He-Ne laser beam having a wavelength of 632.8 nm were employed to characterize the microstructure of the fillers and the nanocomposites. The morphologies and the microstructure of PAni, fillers, and nanocomposites were studied using field emission scanning electron microscopy (FESEM, JEOL 6500F) and transmission electron microscopy (TEM, JEOL JEM-2010).

A four-probe electric measuring instrument (CT5601Y, Chitai Electronic Corp.) was employed for the measurement of electric conductivity. The EMI SE and the permittivity of each specimen were

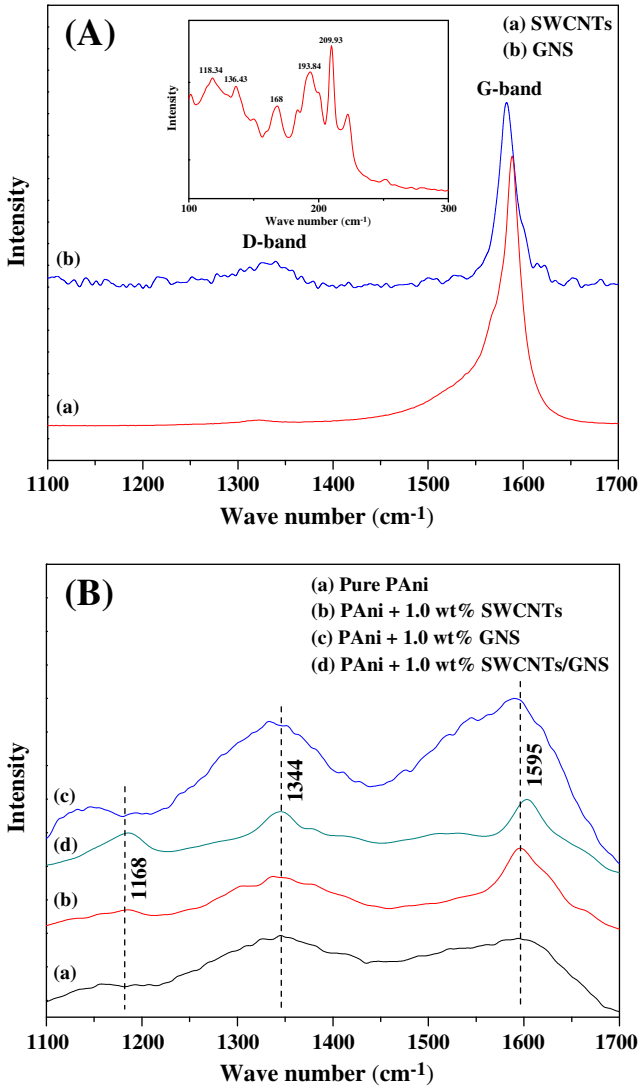

Fig. 1. Raman shifts of (A) (a)SWCNTs (RBM peaks inset) and (b)GNS; (B) (a)pure PANI, (b)Pani + 1.0 wt.% SWCNTs, (c)Pani + 1.0 wt.% GNS and (d)Pani + 1.0 wt.% SWCNTs/GNS.

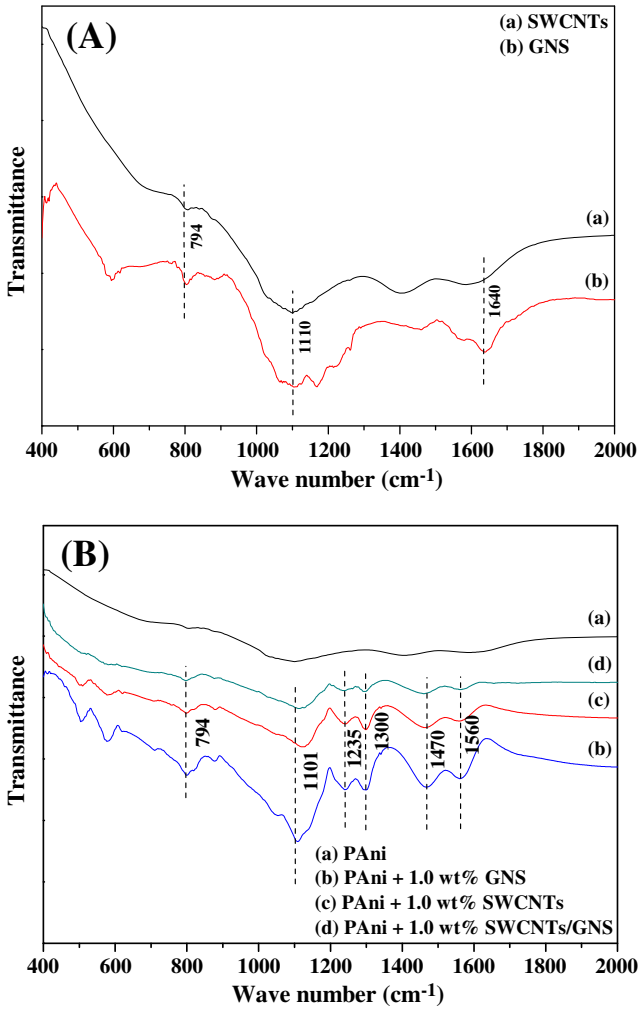

Fig. 2. FTIR spectra of (A) (a)pure SWCNTs and (b)GNS; (B) (a)pure PAni, (b)PAni + 1.0 wt.% SWCNTs, (c)PAni + 1.0 wt.% GNS and (d)PAni + 1.0 wt.% SWCNTs/GNS.