Carbon 132 (2018) 32–41

Contents lists available at ScienceDirect

Carbon

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

Highly flexible and ultra-thin Ni-plated carbon-fabric/polycarbonate film for enhanced electromagnetic interference shielding

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ARTICLE INFO

Article history:

Keywords:
Electromagnetic interference shielding
Electroless Ni plating
Composite film
Sandwiched structure
Carbon fiber
Nonwoven fabric

ABSTRACT

We report in this work a highly flexible, mechanically robust, and ultra-thin Ni-plated nonwoven carbon fabric/polycarbonate (CF/PC/Ni) film that exhibits outstanding electromagnetic interface (EMI) shielding performance. This composite film is fabricated through a four-step process — fabrication of nonwoven carbon fiber/polypropylene/polyethylene (CEF-NF) fabric, catalytic seeding and sensitization, electroless Ni plating, and lamination with polycarbonate. The as-fabricated ultra-thin (0.31 mm) CF/PC/Ni film exhibits superior EMI shielding effectiveness (EMI-SE) of 72.7 dB, which is close to 3× that of an identical film with no Ni plating (25 dB)—demonstrating Ni plating can substantially improve the EMI shielding performance. Compared with similar lightweight EMI-shielding materials, this CF/PC/Ni film shows a superior EMI-SE at lower density and smaller thickness (1376.1 dB cm^2 g^{-1}). 40 min of Ni plating (yielding a Ni thickness of 1.075 μm), followed by 2 MPa of laminating pressure at 190 °C of laminating temperature were found to provide optimal EMI shielding performance. Based on reliability study, the CF/PC/Ni film retains 96.36% of its EMI-SE after 5000 cycles of mechanical bending and 50 h of heating. Therefore, the CF/PC/Ni film exhibits outstanding flexibility, good mechanical strength, and remarkable electrical properties, making it an excellent EMI shielding material.

1. Introduction

The proliferation of electronic systems and devices, such as cellular towers, wireless networks, and personal electronic devices, has been accompanied by the unintended exponential increase in electromagnetic interferences (EMI) [1,2]. Electronic devices with higher power, smaller size, and faster operating speed will emit undesirable electromagnetic waves, which not only interfere with the operations of adjacent equipment or systems, such as aircrafts [3], but also cause potential health risks to human beings [4–6]. Furthermore, the increased prevalence of data theft and hardware security breaches, such as remote wiping or alteration of data on personal devices, necessitate better, consumer-friendly means of electromagnetic shielding to enhance digital privacy [7]. Finally, with the advent of flexible electronics, wearable devices, and implantable biomedical systems, effective and practical EMI shielding solutions have to be ultra-thin, lightweight, and importantly, flexible without being fragile and brittle [8,9].

To achieve effective EMI shielding in day-to-day applications, a minimum EMI shielding effectiveness (EMI-SE) of 20 dB is necessary [10]. Metals and metal alloys are the common EMI shielding materials due to their excellent electric conductivity. However, metals generally do not have the ductility and flexibility required for extensive deformations encountered in consumer devices. Metals are heavy, are subjected to corrosion, and generally require elaborate manufacturing procedures [11], which further restrict their uses in modern-day EMI applications. Therefore, functional materials with high EMI shielding property that are ultra-thin, lightweight, highly flexible, and corrosion-resistant are urgently needed [12]. To address these issues, low-density, non-metallic, porous composite foams have gained tremendous interest as a means to reduce the weights of EMI shielding materials. Zhang et al. [13] fabricated a novel carbon foam by direct carbonization of phthalonitrile (PN)-based polymer foams, achieving an EMI-SE of 51.2 dB at a thickness of 2 mm. Shen et al. [14] proposed a polyetherimide/graphene@Fe_3O_4 composite foam using a water vapor-

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https://doi.org/10.1016/j.carbon.2018.02.001
0008-6223/

induced phase separation method. Their 2.5 mm-thick composite exhibited an EMI-SE of 18.2 dB at 10 wt% graphene@Fe_3O_4 loading. Chen et al. [15] prepared a lightweight and flexible graphene foam composite by a one-step process without using foaming agents, achieving an EMI-SE of 30 dB at 0.8 wt% graphene loading and a thickness of 2.5 mm. The critical shortcoming of the aforementioned porous composite foams is that, to achieve adequate EMI-SE, relatively thick films are needed which may not be suitable for real applications. In addition, high porosity increases the brittleness and hence fragility of these composite foams [15,16]. These disadvantages constrain the EMI shielding applications of such composite foams.

Aside from porous composite foams, nonwoven fabrics or knitted fabrics are ideal EMI shielding materials that can be applied to avionics and flexible electronics owing to their high porosity, being ultra-thin, and excellent flexibility. Bonaldi et al. [17] fabricated a polyester nonwoven fabric coated with carbon nanotubes (CNTs) and found that the inclusion of CNTs effectively enhances the EMI-SE of the polyester fabric. Chaudhary et al. [18] prepared a multi-walled CNT-based mesocarbon-microbead composite, which showed an EMI-SE of 56 dB at a thicknesses of 0.6 mm. However, the EMI shielding performance and the mechanical strength of most available nonwoven fabrics are notably too low for practical application. Thus, there remains a critical need for a high-performance EMI shielding material that is light-weight, flexible, ultra-thin, and mechanically robust.

In our previous work [19], a flexible nonwoven fabric consisted of carbon fibers (CFs) and polypropylene/polyethylene (PP/PE) core/sheath bicomponent fibers—known as CEF-NF composite film—was examined as a potential EMI shielding thin film. It is found that this material possesses good electrical conductivity, electromagnetic shielding performance as well as flexibility. Building on this work, we have successfully fabricated a structurally compact, mechanically robust, ultra-thin, and flexible composite film with excellent EMI-SE (up to 72.7 dB). This film, known as a CF/PC/Ni film, is a sandwiched composite structure consisted of a Ni-plated CEF-NF core laminated between polycarbonate (PC) sheets. This work details the fabrication process of the thin film and characterization of its electrical, electromagnetic shielding, and mechanical properties. In addition, to optimize the EMI-SE performance of the sandwich composite, the influences of laminating parameters and Ni plating time on the EMI shielding properties of the CF/PC/Ni film were investigated in detail through experiments.

2. Materials and methods

2.1. Materials and preparation

Polyacrylonitrile (PAN)-based carbon fibers (CFs) (Torayca® T700SC-12k, Toray Industries, Inc., Japan), polypropylene/polyethylene (PP/PE) core/sheath bicomponent fibers (ESFs) (Qianhai Fiber Technology Company, Hangzhou, China), and 0.125 mm-thick PC films (LEXAN™, SABIC's Specialty Film & Sheet, Saudi Arabia) were used as-purchased without further processing. The complete manufacturing process of a CF/PC/Ni film mainly consists of four major steps, as outlined below illustrated in Fig. 1.

(i) Preparation of CEF-NF thin films: pristine CEF-NFs were prepared by a wet papermaking process followed by a thermal bonding process described in detail in previous work [19,20]. First, chopped CFs and ESFs were weighed and prepared separately according to their specific ratio (CF~40 wt%). Second, the as-prepared chopped CFs and ESFs were dispersed in a 1.2 wt% hydroxyethyl cellulose solution (Hengyu Chemical Company, Guangzhou, China). The mixed solution was stirred at 700 rpm for 4 min followed by 5 min of holding. Then a circular wet preformed CEF-NF was formed through a stainless-steel filter net (#80) mesh and dried at 80 °C for 30 min. Lastly, the dried specimen was heat-pressed using a thermal bonding procedure with a plate curing machine. The heat pressing parameters were optimally set at 6 MPa pressure, 180 °C temperature, and 10 min holding time [19,20]. All CEF-NF specimens used in this work were fabricated with the same parameters: 6 mm-long CFs and ESFs, 40 wt% CF concentration, 40 gsm areal density.

(ii) Process of pretreatment: Before Ni plating process, the as-prepared CEF-NFs were sensitized in 89 mM stannous chloride ($SnCl_2 \cdot 2H_2O$)/485 mM hydrochloric acid (HCl) solution for 10 min and then activated in 1.4 mM palladium chloride ($PdCl_2$)/82 mM HCl solution for 10 min in sequence. Ultrasonic pulse was utilized during the activation and sensitization processes to ensure uniform treatments.

(iii) Electroless Ni plating of CEF-NF thin films: Electroless Ni plating process was conducted at 80 °C for 10, 20, 30, and 40 min, respectively, using nickel sulfate ($NiSO_4 \cdot 6H_2O$) and sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) as the salt and the reducing agent in this system. The solution was adjusted to a pH value of 8.0 by adding $NH_3 \cdot H_2O$. Table 1 lists the bath compositions for the electroless Ni plating process. Next the obtained samples were washed several times with distilled water and dried at room temperature. In addition, it should be mentioned that the thermal bonding strength formed in the first stage can effectively prevent the fibrous porous structure of the preformed CEF-NF from being damaged by the production of hydrogen gas during the electroless Ni plating process.

(iv) Lamination of Ni-plated CEF-NF thin film: A Ni-plated CEF-NF thin film was sandwiched between two 0.125 mm-thick PC films and subsequently laminated together using a thermal bonding procedure, forming an ultra-thin CF/PC/Ni film.

2.2. Characterization

The surface morphologies of CEF-NFs before and after electroless Ni plating were observed by a scanning electron microscopy (SEM, ZEISS Merlin, Jena, Germany). Elemental analysis was performed by an energy dispersive spectroscope (EDS, X-MaxN 50). All specimens used for SEM and EDS were prepared as $10 \times 10\ mm^2$ square pieces. The cross-sections of CF/PC/Ni films were observed via a digital optical microscope (VHX-1000, Keyence Company, Japan). A crystalline structure analysis of the CEF-NFs coated with Ni layer using various plating times was performed using an X-ray diffraction device (XRD, D8 Advance, Bruker AXS, Germany). Diffraction peaks were obtained through 2θ continuous scanning at a speed of 5°/min in the range of 20°–80°.

2.3. Electrical conductivity measurement

The electrical conductivity of as-prepared CF/PC/Ni films were measured by four-point probe method. All electrical measurements were performed at ambient conditions at room temperature (25 °C) to eliminate temperature-induced measurement errors. The reported results are the average value of at least four different specimens. Detailed information was described in previous work [20].

2.4. EMI–SE measurement

The EMI shielding measurement was conducted using a vector