Composites Science and Technology 131 (2016) 77–87

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Carbon nanotube/cellulose papers with high performance in electric heating and electromagnetic interference shielding

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ARTICLE INFO

Article history:
Received 29 February 2016
Received in revised form
9 May 2016
Accepted 9 June 2016
Available online 11 June 2016

Keywords:
Carbon nanotubes
Coating
Functional composites
Electrical properties

ABSTRACT

A series of multi-walled carbon nanotube (MWCNT)-coated cellulose papers were manufactured by a facile dip-coating process, and their performance in electric heating and electromagnetic interference (EMI) shielding materials was investigated by considering the microstructure, thermal stability, and electrical property. With increasing the cycle of the dip-coating process, the apparent thickness of MWCNT/cellulose papers increased on a monotonic basis. It was observed that MWCNTs are coated dominantly on cellulose fibers on the paper surfaces, in addition to their partial coating on the inside of cellulose papers, which is supported by the anisotropic electrical conductivity of the papers in the in-plane or thickness direction. For MWCNT/cellulose paper obtained by single dip-coating cycle, high apparent electrical conductivity in the in-plane direction of 0.02 S/cm was achieved. The electrical conductivity in the in-plane direction increased significantly from 0.02 S/cm to 1.11 S/cm with increasing the dip-coating cycle from 1 to 30. Accordingly, MWCNT/cellulose papers with >1 dip-coating cycle exhibited excellent electric heating performance in terms of temperature responsiveness, steady-state maximum temperature, and electrical energy efficiency at constant applied voltages. In addition, high EMI shielding effectiveness of ~20.3 dB (~99.1% attenuation) was achieved at 1 GHz by MWCNT/cellulose paper with ~1.11 S/cm and ~170 μm only.

1. Introduction

Cellulose, as the main structural constituent of plant cell walls and the most abundant natural polymer on earth, exhibits superior thermal and mechanical properties, in addition to biodegradability, biocompatibility, and cost-effectiveness [1,2]. Thus, owing to the increasing demands caused by the expanding population, rising economy and developing technology, cellulose and its derivatives have been extensively used as renewable polymeric materials for mankind's requirements such as fibers, papers, films, and composite components in aspects of environmental conservation, efficient utilization, and waste reduction [3,4].

Recently, to extend the uses of natural cellulose in advanced application areas including transistor [5], sensor [6], actuator [7], supercapacitor [8], electric heater [9], and electromagnetic interference (EMI) shielding materials [10], one-dimensional carbon nanotubes (CNTs) and their derivatives with high aspect ratio have been chosen as nano-scale functional fillers for cellulose-based composite papers and films, because of their exceptional electrical conductivity, thermal conductivity, mechanical modulus, and thermal stability [11,12]. Generally, a papermaking technique for CNT/cellulose composite papers was known to be efficient and eco-friendly, compared to solution processes for cellulose-based composite films requiring toxic polar or expensive ionic liquid solvents to dissolve hydrogen-bonded cellulose crystals. Fugetsu et al. reported that a cellulose composite paper containing 8.32 wt% CNT manufactured by a conventional papermaking process has a volume electrical conductivity of ~1.87 S/cm as well as EMI shielding effectiveness of >20 dB over the range of 15–40 GHz [13]. Anderson et al. reported that single-walled carbon nanotube (SWCNT)-reinforced cellulose composite papers, which are also prepared by using a papermaking process, possess enhanced electrical conductivity (~0.03 S/cm) and improved flame retardant properties because of the good physical interaction between cellulose and SWCNTs [14]. Imai el al. reported that cellulose-based

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http://dx.doi.org/10.1016/j.compscitech.2016.06.003
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composite papers containing 0.5–16.7 wt% multi-walled carbon nanotube (MWCNT) manufactured by a general papermaking process have a wide range of electrical conductivity of 0.0005–6.71 S/cm and that the composite paper with 4.8 wt% MWCNT attains a high near-field EMI shielding effectiveness of ~50 dB in the range of 5–10 GHz [10]. In addition to the conventional papermaking process, a dip-coating method is considered to be a facile and convenient technique to fabricate cellulose-based composite papers by using commercially-available cellulose papers and CNT aqueous solutions. The dip-coating technique has been proved to be an efficient industrial coating process in terms of short processing time, easy processability, and cost-effectiveness [15,16]. This dip-coating process can be repeated many times, allowing a series of thin films to bulk up to relatively thick final products with desired properties.

In the present study, we have manufactured a series of MWCNT/cellulose papers by using a dip-coating technique for the first time and have investigated their microstructures, thermal and electrical properties as a function of the dip-coating cycle of 1–30. The electrical heating and EMI shielding effectiveness of MWCNT/cellulose papers were analyzed systematically by taking account of the microstructural features and electrical conductivity. Especially, the EMI shielding effectiveness was examined in the frequency range of 0.5–1 GHz, which corresponds to a part of ultra high frequency (UHF) being used widely for the mobile communication of phone, automobile, local area network (LAN), etc.

2. Experimental section

2.1. Materials

Commercially available cellulose paper with average pore size ~22 μm, 150 mm diameter, and ~154 μm thickness was purchased from Whatman Com. (model # 541) and was adopted as a substrate for composite papers. Pristine MWCNT (CM-250, diameter of 10–15 nm and length of ~100 μm) was purchased from Hanwha Chemical Co., Ltd. Sodium dodecyl benzenesulfonate (SDBS, Tech, Aldrich Chemistry Co.) was used as a surfactant to disperse the pristine MWCNT in distillated water.

2.2. Preparation of MWCNT/cellulose paper

A series of MWCNT/cellulose papers were manufactured by a dip-coating process, as shown schematically in Fig. 1. An aqueous MWCNT solution was prepared by dispersing 0.1 wt% pristine MWCNT in distillated water with 1.0 wt% SDBS using a horn-type ultrasonication (VibraCell 505, 500 W, 20 kHz, Sonics and Materials Inc.) for 40 min. Then, a neat cellulose paper was dipped into the 0.1 wt% aqueous MWCNT solution at room temperature and dried at 60 °C for 15 min. This dip-coating process was repeated by 30 cycles to adjust the amount of MWCNT coated on cellulose papers. The final MWCNT-coated cellulose papers were named as M-x, where x denotes the cycle number of dip-coating process.

2.3. Characterization

The apparent thicknesses of MWCNT/cellulose papers manufactured with different dip-coating cycles were measured by using a digital thickness meter. The apparent density and porosity of the papers were evaluated by measured weights and apparent volumes of paper samples with dimensions of 2 cm × 2 cm.

The dispersion state and associated morphology of MWCNTs coated on cellulose papers were characterized by obtaining the surface and cross-section images with aid of a cold-type field emission scanning electron microscope (SEM, S-4800, Hitachi). For the cross-section analysis, the neat cellulose and MWCNT/cellulose papers were cut with a razor blade.

The structural features of pristine MWCNT, neat cellulose paper, and MWCNT/cellulose papers were identified by using a high resolution Raman Spectrometer (LabRAM HR-800 UV–Visible–NIR, Horiba Jobin Yvon).

The electrical properties of MWCNT/cellulose papers were investigated by obtaining current-voltage (I–V) and electric power-voltage (P–V) curves with multiple electrometers (2400, 6517, Keithley Instruments Inc.). For the electrical experiments, the electrode distance of the papers was set to be 10.0 mm. The electric heating behavior of MWCNT/cellulose papers was characterized with an infrared camera (SE/A325, FLIR Systems) and a sourcemeter (2400, Keithley Instruments Inc.).

The EMI shielding effectiveness (SE) of MWCNT/cellulose papers was measured at room temperature in accordance with ASTM D4935-10. S-parameters were measured in the frequency range of 0.5–1.0 GHz by using a coaxial sample holder complying with the test standard and a network analyzer (Agilent E5071C).

3. Results and discussion

3.1. Structural characterization

The structural features of neat cellulose paper and MWCNT/cellulose papers were characterized by using SEM images of Fig. 2. For the neat cellulose paper, the SEM images show a porous structure as well as smooth and clean surface of cellulose fibers in the paper (Fig. 2A–B). In the case of M-10 paper, although the porous structure is entirely similar to that of neat cellulose paper, the cellulose fibers of the paper surface and bulk were found to be homogeneously coated with interconnected MWCNTs (Fig. 2C–D). On the other hand, the density of MWCNTs coated on the cellulose fibers of M-10 paper surface was higher than that of inner parts of the paper, as can be seen in the enlarged SEM images of Fig. 2C–D.

In order to identify the interaction between MWCNTs and cellulose fibers in the papers, Raman spectra of pristine MWCNT, neat cellulose paper, and M-1 paper were obtained, as shown in Fig. 3A. For the neat cellulose fiber, typical vibrational bands at ~1377 cm^{-1}, ~1094 cm^{-1}, and ~898 cm^{-1} were detected, which are assigned to H–C–H/H–C–C/H–C–O/C–O–H mixed bending, glycosidic C–O–C ring breathing, and H–C–C/H–C–O mixed bending modes, respectively [17–19]. The Raman spectrum of neat MWCNT is dominated by two peaks of D- and G-bands. The D band at ~1296 cm^{-1} originates from the structural imperfection of the MWCNT and the G band at ~1581 cm^{-1} stems from the in-plane stretching vibrations of C–C bonds in cylindrical graphene layers. In the case of M-1 paper, the D and G bands of pristine MWCNT were also observed at ~1304 cm^{-1} and ~1605 cm^{-1}, respectively. It is interesting to note that the D and G bands of M-1 paper was detected at higher wavenumbers, compared with the pristine MWCNT [20], which demonstrates the presence of noncovalent π-π interaction between the MWCNT surface and the aromatic ring of SDBS, and hydrophobic interaction between the nanotube surface and the hydrocarbon chain of SDBS [21]. In addition, the specific interaction of anionic surfactant with the hydrophilic groups of cellulose was proven to be present [22,23]. It is thus reasonable to contend that the pristine MWCNTs can be coated tightly on cellulose papers via the multiple specific interactions among MWCNT, SDBS, and cellulose, as represented schematically in Fig. 3B.

The apparent thicknesses of neat cellulose paper and MWCNT/cellulose papers increased monotonically from 154.6 ± 3.9 μm for neat cellulose paper to 170.1 ± 3.9 μm for M-30 paper with the increasing the dip-coating cycle, as summarized in Table 1. Also, the apparent density (d_{paper}) and porosity (P_{paper}) of the neat cellulose