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Carbon composite foams with improved strength and electromagnetic absorption from sucrose and multi-walled carbon nanotube

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HIGHLIGHTS

- Carbon composite foams were prepared from molten sucrose and MWCNT.
- The highest compressive strength of 4.9 MPa is achieved at 0.5 wt% MWCNT.
- EMI shielding effectiveness of 39 dB is achieved at 2.5 wt% MWCNT.
- Local shrinkage of sucrose polymer within the MWCNT agglomerates creates mesopores.
- Mechanism of EMI shielding due to dielectric loss within mesopores is established.

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ABSTRACT

Multi-walled carbon nanotube (MWCNT) reinforced carbon composite foams with interconnected cellular structure were prepared by thermo-foaming of MWCNT dispersions in molten sucrose followed by carbonization. The foaming and foam setting time decreases with an increase in the MWCNT concentration. The carbonization shrinkage, foam density and compressive strength showed a decreasing trend after reaching a maximum at a MWCNT concentration of 0.5 wt% indicating MWCNT agglomeration beyond 0.5 wt%. The maximum compressive strength (4.9 MPa) and specific compressive strength (21 MPa/g/cm^3) obtained at 0.5 wt% MWCNT concentration corresponded to an increase of 189 and 133%, respectively. The cell walls and struts of the carbon composite foams contained micropores produced by an *in situ* activation and large mesopores produced by local shrinkage of sucrose polymer within the MWCNT agglomerates. The carbon composite foam showed the highest EMI shielding effectiveness and specific shielding effectiveness of 39 dB and 166 dB/g/cm^3, respectively, at a MWCNT concentration of 2.5 wt%. The dielectric loss due to the interaction of electromagnetic waves with walls of the mesopores created by the local shrinkage of sucrose polymer within the MWCNT agglomerates contributed to the electromagnetic absorption.

1. Introduction

Carbon foams are macroporous carbonaceous materials having properties like lightweight, fire resistance, tunable thermal and electrical conductivity and relatively good mechanical strength [1–10]. They are widely used in thermal protection, heat sink, heat exchanger, catalyst support, electrode in batteries, host structure for phase change materials, core material in fire resistant composite structures, acoustic absorption and EMI shielding applications [1–10]. Recent researches in the field focus on replacement of fossil fuel based synthetic polymers and pitches with naturally renewable materials as precursors for the preparation of carbon foams. Preparation of carbon foams from naturally renewable materials such as tannin, sucrose, olive stones, birch sawdust and lignin are reported in the literature [11–19]. Compared to the carbon foams derived from synthetic polymers and pitches, the carbon foams prepared from naturally renewable precursors show relatively poor mechanical strength. The reasons for the poor mechanical strength are the presence of large fraction of heteroatoms in the naturally renewable precursors and thus the low carbon yield. Removal of

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this large fraction of heteroatoms during the carbonization creates microcracks and voids which limits the mechanical strength of the carbon foams.

Sucrose is a widely available agricultural product used for the preparation of carbon foams. Thermo-foaming processes based on an aqueous sucrose resin and a molten sucrose are reported for the preparation of carbon foams [14–16,20–24]. Among them, the molten sucrose based process is simple and amenable for the preparation of large foam bodies. Reinforcing additives such as activated carbon powder and milled carbon fiber are studied to improve the carbon yield and mechanical strength of carbon foams prepared from molten sucrose [21–23]. It is well-known that the nano reinforcements are better than the micron sized reinforcements as they produce better improvement in mechanical strength at low concentrations due to their high surface area to volume ratio [25,26]. Carbon nanomaterials such as single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) are widely used as reinforcements in polymer, ceramic and metallic matrix composites [25,27–31]. In addition to the mechanical property improvement, the incorporation of carbon nanotubes increases the functional properties such as electrical conductivity, thermal conductivity, and electromagnetic interference (EMI) shielding properties of the composite materials [32–35]. In many cases, the MWCNT are preferred to SWCNT due to their low cost, easy synthesis and purification [25,26]. Preparation of MWCNT reinforced carbon foams from precursors such as mesophase pitch, coal tar pitch and cyanate ester resin is reported in the literature [36–39]. The incorporation of MWCNT improves not only the compressive strength but also the electrochemical properties and EMI shielding effectiveness of the carbon foams [36,38]. The carbon foam structure provides a low impedance path for the incoming EM radiation which contributes to the EM absorption. Further, the EM radiation may also experiences the ohmic losses from the conducting MWCNT interfaces dispersed in the carbon foam matrix. The present work reports the preparation of MWCNT reinforced carbon composite foams from molten sucrose by thermo-foaming technique. The effect of MWCNT concentration on foaming characteristics of molten sucrose and properties of carbon composite foams is investigated. The EMI shielding effectiveness of the carbon composite foams is also investigated.

2. Experimental

2.1. Preparation of MWCNT reinforced carbon composite foams

The MWCNT procured from Sigma Aldrich, India has the diameter and length in the ranges of 10–25 nm and 5–10 μm, respectively. Analytical reagent grade sucrose and acetone used were procured from Merck, India Ltd., Mumbai. MWCNT and sucrose were mixed by ball milling in acetone medium using a planetary ball (Pulverisette 5, Fritsch, GmbH, Germany) mill for 2 h. The zirconia jar of 500 ml capacity and zirconia balls of 10 mm diameter were used. The milling speed was 200 RPM. The MWCNT concentrations used were in the range of 0–2.5 wt% of sucrose. The sucrose to zirconia ball weight ratio and sucrose to acetone weight ratio used were 1:6 and 1:3, respectively. After ball milling, the slurries were transferred into 1.5 liter glass tray and dried at 70 °C. The dried sucrose-MWCNT mixtures were heated at 170 °C to melt the sucrose. The melt was stirred well with a glass rod to achieve uniform dispersion of MWCNT. The MWCNT dispersions in molten sucrose were cooled to room temperature and then kept in an oven at 140 °C for 72 h for foaming and setting into solid organic foams. The solid organic foams were cut into rectangular pieces of 8 cm × 6 cm × 4 cm and then dehydrated at 200 °C for 3 h using a heating rate of 5 °C/h. The dehydrated foams were subsequently carbonized in an ultra-high pure argon atmosphere at 900 °C for 2 h. The heating rate used was 0.5 °C/min. The density of the carbonized samples was calculated from their weights and dimensions.

2.2. Characterization

The viscosity measurement of the MWCNT dispersions in molten sucrose was carried out at various shear rates in the range of 1–2000 s^{-1} at 140 °C using a rheometer (MCR 102 Modular Compact Rheometer, Anton Paar, USA) with a cone and plate measurement system. The samples were physically inspected during foaming and foam setting at an interval of one hour to determine the approximate foaming and foam setting time. Thermogravimetric analysis (TGA) of the solid organic foam samples was carried out in a nitrogen atmosphere using a thermogravimetric analyzer (Q-50, TA instruments, USA) at a heating rate of 2 °C/min. The microstructure of the MWCNT and carbon composite foams was observed using a Scanning Electron Microscope (SEM, FEI Quanta FEG200). The cell size of the carbon composite foams was measured using ImageJ software from the SEM microstructure. The compressive strength of the carbon composite foams was measured using a universal testing machine (Instron 5050, Instron USA) at a crosshead speed of 0.5 mm/min with 25 mm × 25 mm × 12 mm samples (ASTM standard C365/C365M-05). The maximum stress in the stress-strain graph was noted as the compressive strength. X-Ray diffraction (XRD) measurements of the carbon composite foam samples were carried out in an X-ray diffractometer (X'pert Pro, Philips, USA) using Cu Kα radiations (λ = 1.54056 Å). Powder samples for XRD analysis were prepared by crushing the carbon composite foams using a mortar and pestle. The diffraction patterns were recorded at 2θ values in the range of 10 to 80° with a step size of 0.07° using monochromatic X-rays.

2.2.1. Electrical conductivity

The electrical conductivity of the MWCNT-carbon composite foams was measured using a four probe technique. Fig. 1 shows the digital photographs of the four-probe instrument used to measure the electrical conductivity of the carbon composite foams. The probes used in this measurement are spring-loaded. The probes are carefully placed over the cell walls of the carbon foam by applying minimum pressure to ensure good contact. A constant current was supplied from a programmable source (Keithley 6221) and the voltage drop (V) was measured between two pins separated by a distance of 2 mm using a digital nano-voltmeter. The current and voltage data were used for calculation of bulk electrical resistivity of the carbon foams using the equation (1), where ρ is electrical resistivity and s is the distance between the pins.

$$\rho = 2\pi s\left(\frac{V}{I}\right) \tag{1}$$

2.2.2. EMI shielding

The EMI shielding effectiveness (SE) of the carbon foam samples was measured using a vector network analyzer (E5071C) by fixing the carbon foam in the cavity of a wave guide [40,41]. The rectangular carbon foam samples of dimensions 22.7 mm × 10.2 mm × 5 mm were used for the measurement. The EMI shielding was measured for the X band (8.2–12.4 GHz) in the microwave region using the corresponding waveguides. The X-band frequency region was divided into 201 frequency steps. The digital photograph and schematic of the EMI shielding measurement experimental set up is shown in Fig. 2. The carbon composite