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Characteristics of fluorinated CNTs added carbon foams

Ji-Hyun Kim, Do Young Kim, Euigyung Jeong[1], Young-Seak Lee*

Department of Applied Chemistry and Biological Engineering, Chungnam National University, Daejeon 305-764, Korea

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ABSTRACT

To fabricate carbon foams with high compressive strength and thermal conductivity, carbon foams were prepared by curing and heat treatment of a polymer solution containing CMC, isotropic pitch and fluorinated CNTs. The CNTs were fluorinated at different fluorine gas pressures (F_2:N_2 = 3:7, 5:5, and 7:3). The highly heat-treated carbon foams containing fluorinated CNTs prepared with F_2:N_2 = 5:5 had the highest thermal conductivity of 3.18 ± 0.01 W/mK, and compressive strength of 2.42 ± 0.22 MPa, which were approximately 15% and 133% higher, respectively, than those of the highly heat-treated carbon foams containing un-fluorinated CNTs due to increased crystallinity of CNTs and their adhesion with pitches in highly heat-treated carbon foams through fluorination of CNTs.

1. Introduction

As a porous material, carbon foams have received recent attention for applications in thermal management. Carbon foams are suitable materials for thermal, mechanical and electrical applications, including high temperature isolation, fuel cell electrodes, heat interchangers, brake discs, engine components, and bone surgery materials. The properties of carbon foams include high thermal conductivity, mechanical strength, electrical conductivity, low density, a high thermal expansion coefficient, low cost, and a variety of manufacturing and design options [1–4].

Carbon materials enhance the high thermal conductivity and mechanical strength of carbon foams. Carbon nanotubes (CNTs) were identified as a new type of carbon in 1991. CNTs have been extensively characterized and feature a rolled-up graphite layer structure with a diameter of 1 to 100 nm. The mechanical strength of CNTs is superior to that of existing carbon materials. Single-walled carbon nanotubes (SWNTs) have a thermal conductivity of 3000 W/mK at room temperature. However, aligned SWNTs in bulk and multi-walled carbon nanotubes (MWCNTs) have low thermal conductivities of 250 W/mK and 20 W/mK, respectively. The lower thermal conductivities of aligned SWNTs in bulk and MWCNTs is due to the resistivity of the thermal junctions between nanotubes. Thermal applications of CNTs have been studied extensively, and new composites using CNTs have been prepared due to their excellent thermal conductivity and unique mechanical properties. However, controlled dispersibility of CNTs in a solution or a composite matrix remains challenging due to the strong van der Waals binding energies associated with the CNT aggregates, which result in heterogeneous material and poor properties of CNT-containing composites. Therefore, the high interfacial adhesion of CNTs in a matrix based on pitch and polymer through increased dispersibility of CNTs is essential to enhance the mechanical, thermal and limited properties of the pitch and polymer material [5–9].

There are many fabrication methods for carbon foam. Carbon foams are usually prepared using a carbon precursor solution impregnated in a polymer foam as a template through pressure impregnation and woven graphite fiber structure stacking. However, polymer foams impregnated with a small amount of carbon precursor solution exhibit low compressive strength and thermal conductivity. Therefore, a hydrogel is used as a template to increase the amount of impregnated pitch [10–15].

In this study, highly heat-treated carbon foams were prepared by adding fluorinated CNTs to improve their compressive strength and thermal conductivity. CNTs were treated with fluorine gas mixtures (F_2:N_2 = 3:7, 5:5, and 7:3) before their addition to the polymer solution with pitch. We then investigated the compressive strength and thermal conductivity of the highly heat-treated carbon foams containing the fluorinated CNTs.

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* Corresponding author. Tel.: +82 428217007; fax: +82 428226637.
E-mail address: youngslee@cnu.ac.kr (Y.-S. Lee).

[1] The 4th R&D Institute-4, Agency for Defense Development, Daejeon, 305-600, Korea.

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2. Experimental

2.1. Materials

Pitch (pyrolyzed fuel oil (PFO), GS Caltex Refinery Company, softening point (SP) 250 °C) was used as the carbon precursor for the carbon foams. Multi-walled carbon nanotubes (CNTs, Hanhwa, CM-350) were used as the filler in the carbon foams. Carboxymethyl cellulose (CMC, H-1496A, DAI-ICHI KOGYO SEIYAKU CO., LTD.) was used as the binder between the CNTs and pitch. Polyvinyl alcohol (PVA, 98–99%, MW 30,000–50,000, Aldrich, USA) and acrylic acid (AAc, 99%, Aldrich, USA) were used as the hydrophilic polymer and organic compound, respectively, to prepare the hydrogel. Glutaraldehyde (GA, 25 wt% dissolved in water, Kanto Chemical CO., Inc.) and ethylene glycol dimethacrylate (EGDMA, 98%, Aldrich, USA) were used as cross-linking agents, and potassium persulfate (KPS, 99%, Aldrich, USA) was prepared as the radical initiator.

2.2. Fluorination of CNTs

The CNTs were fluorinated to increase the dispersibility of the CNTs in the polymer solution with pitch and the crystallinity. The CNTs were dried at 100 °C for 1 h to improve their reactivity with fluorine gas. The CNTs (0.25 g) were loaded onto a nickel boat in the reactor and degassed with a high-vacuum pump twice using nitrogen gas (purity 99.999%) at room temperature to remove impurities. The fluorination was conducted at 1 bar for 10 min with different partial pressures of fluorine:nitrogen = 3:7, 5:5, and 7:3, denoted FN37C, FN55C and FN73C, respectively.

2.3. Fabrication of carbon foams containing fluorinated CNTs

PVA (6 g) was dissolved in 1 M NaOH solution (52 mL) at 140 °C for 10 min. After cooling the solution, AAc (15 mL) and CMC (0.6 g) were added to the PVA solution and stirred for 10 min. GA (1 mL), EGDMA (1.5 mL) and KPS (2 wt% dissolved in water) (1 mL) were added to the solution and stirred for 3 min. The pitch (32 g) and CNTs or fluorinated CNTs (0.01 g) were added to the prepared polymer solution. The CNTs were added to the carbon foams at approximately 0.03 w/w% by weight (polymers:pitch:CNT = 21.77:32.00:0.01 g) and stirred for 1 h to mix the pitch. The CNTs were completely dispersed in the polymer solution. The hydrogel containing pitch and CNTs was cured for 9 h at 60 °C. The prepared gel was dried at 140 °C for 13 h in an air atmosphere, and the dried gel was heat-treated at 600 °C at a heating rate of 5 °C/min for 1 h, followed by 1000 °C at a heating rate of 5 °C/min for 1 h in a nitrogen atmosphere. The resulting samples were denoted pitch and pitch-CNTs (Pi and Pi-C). The fabricated carbon foam was highly heat-treated at 2800 °C at a heating rate of 5 °C/min for 1 h in an argon atmosphere. The highly heat-treated carbon foams were denoted highly heat-treated pitch-CNTs, highly heat-treated pitch-FN37CNTs, highly heat-treated pitch-FN55CNTs, and highly heat-treated pitch-FN73CNTs (HTPi-C, HTPi-FN37C, HTPi-FN55C, and HTPi-FN73C).

2.4. Thermal conductivity

The thermal conductivity, κ, of the carbon foams containing CNTs was analyzed using a Xenon flash diffusivity technique in the axial direction. The thermal diffusivity α was measured on samples with dimensions of 12.5 × 12.5 × 3 mm^3 (ASTM E 1461) at 25, 100, 200, 300 °C using a Netzsch-Geraetebau LFA447 Nanoflash. The thermal conductivity of at least three specimens was determined. The sample density ρ and specific heat capacity C_ρ (assumed to be 1.0 J/gK) were used to calculate the thermal conductivity using Eq. (1):

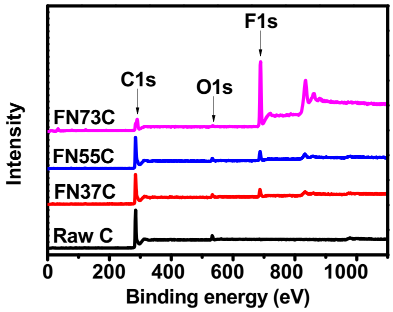

Fig. 1. XPS data for the un-fluorinated and fluorinated CNTs.

Table 1
Elemental surface analysis of the un-fluorinated and fluorinated CNTs.

Samples	Elemental content (at.%)			O/C (%)	F/C (%)
	C1s	O1s	F1s		
Raw C	95.14	4.86	–	5.11	–
FN37C	90.99	3.17	5.83	3.48	6.41
FN55C	89.64	3.65	6.71	4.07	7.49
FN73C	49.98	1.53	48.49	3.06	97.02

$$\kappa = \alpha \cdot \rho \cdot C_\rho \qquad (1)$$

2.5. Characterization of the CNT-containing carbon foams

X-ray photoelectron spectra (XPS) were obtained using a MultiLab 2000 spectrometer (Thermo Electron Corporation, UK) and were used to identify the elements present in the fluorinated CNTs. The morphologies and bubble diameter of the prepared CNT-containing carbon foams was analyzed by field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4700). The crystallinity of the CNTs and the fluorinated CNTs in carbon foams as a function of the different partial fluorine gas pressures and heat treatments were analyzed by Raman spectroscopy analysis (RM 1000-InVia, Renishaw) at 514 nm with 10 mV excitation power and X-ray diffraction (XRD, D/MAX-2200 Ultima/PC, Rigaku International, Japan). The thermal stability of the samples was analyzed by thermogravimetric analysis (TGA, Shimadzu, TGA-50H) under a nitrogen atmosphere. The porosities of the samples were characterized by determining the true densities under He using an automatic gas pycnometer (Quantachrome/Ultrapycnometer 1200e). The compressive strengths of the CNT-containing carbon foams were determined using a Micro Material Teste (INSTRON, INSTRON 5848, 500 N) with a sample size of 3 × 3 × 3 mm^3. The compressive strengths of at least five specimens were determined.

3. Results and discussion

3.1. XPS analysis of fluorinated CNTs

The CNTs were fluorinated to remove impurities and improve their dispersibility in polymer solution with pitch [16–18]. The fluorinated CNTs were analyzed by XPS to analyze the C-, O-, and F-peaks at 284.5, 533.1, and 687.0 eV, as shown in Fig. 1. As a reference material, the C- and O- peaks of Raw C represented 93.14% and 4.86%, respectively, whereas the F-peak was not detected (Table 1). The fluorine functional groups of FN37C, FN55C, and FN73C increased from 5.83% to 48.49% with increasing fluorine partial pressure, and C- and O- were reduced from 95.14% to 49.98% and from 4.86% to 1.53%, respectively. The carbon and oxygen related