

Thermal Behavior of Polyacrylonitrile/Acid-Functionalized Multi-Walled Carbon Nanotubes

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Introduction

Polyacrylonitrile (PAN) is used as one of carbon fiber precursors due to the high tensile strength in resulting carbon fiber. Carbon nanotubes (CNTs) are considered to be ideal materials to enhance not only tensile strength and modulus of carbon fiber [1, 2]. However, the main limitations of MWCNTs for reinforcement of carbon fiber are their poor dispersion in a polymer matrix and poor interfacial interaction with the matrix. Several approaches have been examined to disperse individual MWCNTs efficiently in a polymer. The surface treatment of MWCNTs with acids, oxidizing agents and surfactants introduces functional groups such as carboxylic and hydroxyl groups, which improve the dispersibility and interaction properties of MWNTs with polymer matrix [3,4]. The carboxylic group of functionalized CNTs is also considered to be used as an external initiating agent for the nitrile cyclization in PAN homopolymer [5-6].

In this study, the effect of surface acidity on the solubility and thermal behavior of MWCNTs/PAN composites was reported. The isophthalic acid group was covalently functionalized on the surface of MWCNT by solvent-free functionalization method and then characterized.

Experimental

Materials

MWCNTs were purchased from Nanocyl(Nanocyl 3100), Belgium. 5-Amino isophthalic acid and polyacrylonitrile (PAN) were obtained from Sigma-Aldrich, USA. Sodium nitrite was purchased from Tokyo chemical Industries Ltd, Japan. Sulfuric acid (H_2SO_4) and Nitric acid (HNO_3) (60%) were purchased from PFP Matunoen chemicals Ltd, Japan. *N,N'*-Dimethylformamide (DMF) was obtained Samchun chemical, Korea. Ethanol was purchased Wako pure chemicals industries Ltd, Japan.

Preparation of Acid Treated MWCNTs (O-MWCNTs)

The surface treatment of the MWCNTs was carried out in a flask. The flask was mounted on a preheated oil bath at a constant temperature for a specific period. 0.5 g of MWCNTs was immersed in a 1:3 mixture of concentrated HNO_3 and H_2SO_4 (200 mL) at room temperature and sonicated for 30 min. The mixture was then poured into a flask. The oxidation process was carried out at 110°C for 1h. The oxidized MWCNTs (O-MWCNTs) were washed with excess deionized

(DI) water until the pH was approximately 7 and finally washed with ethanol.

Preparation of Isophthalic Acid Treated MWCNTs (IPA-O-MWCNTs) (Fig. 1.)

O-MWCNTs (0.3 g) was immersed in a 100 mL H_2SO_4 solution at room temperature and sonicated for 30 min. The mixture was then poured into a flask. After that, 5-amino isophthalic acid (1.8 g) and sodium nitrite (0.69 g) was quickly added via syringe. The mixture suspension was vigorously stirred at 60°C for 1h. After cooling to room temperature, the suspension was diluted and then washed with ethanol to remove remaining DMF. The product was dried at 60°C for 24h in a vacuum oven.

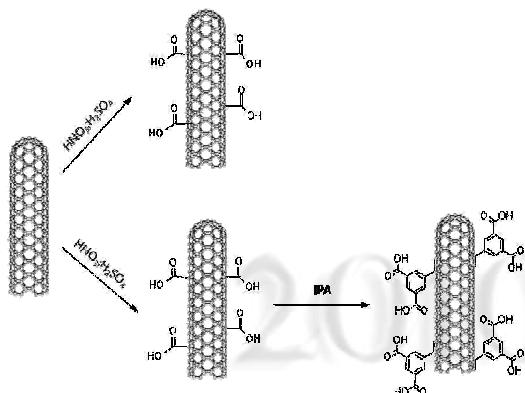


Fig. 1. Synthetic scheme of O-MWCNTs and IPA-O-MWCNTs.

Preparation of CNT/PAN Composites

CNTs (0.01 g) was immersed in a DMF (40 mL) solution and sonicated for 30 min. After that, PAN (1 g) was added and stirred for 3h. The mixture was poured in a petri dish and dried at 80°C.

Characterization

The surface functional groups generated were investigated by Raman (633 nm excitation, Horiba Ltd, Japan) and XPS (X-ray photoelectron microscopy, AXIS-NOVA, Kratos Inc, USA). TGA analysis was performed in a N_2 atmosphere with a rate of 10°C/min using a TGA Q50(TA instrument, USA). The thermal behavior of CNT reinforced PAN composites was examined by DSC (TA Q50, USA) at a heating rate of 5°C/min under air atmosphere.

Results and Discussion

The acid-functionalization of CNTs was carried out by following the solvent-free technique [7]. The functionalized MWCNTs were characterized by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA). Raman spectra of pristine MWCNTs and surface treated MWCNTs show that the disorder (1320 cm^{-1}) mode of acid-functionalized MWCNTs is enhanced compared to the pristine MWCNT, indicating covalent functionalization of isophthalic acid (IPA) unit on the MWCNT. X-ray photoelectron spectroscopy (XPS) of MWCNT functionalized

with IPA showed the presence of oxygen (O1s) at 531.6 eV and 533.6 eV. The spectra of Raman and XPS clearly confirm the presence of IPA unit on the MWCNT. TGA was also used to measure degree of functionalization. While the observed percent weight loss of pristine CNT from TGA (10 °C/min to 500 °C in N₂) is 0%, percent weight loss of IPA-O-MWCNT is 13%. The solubility of IPA-O-CNT was 0.1 mg/mL in DMF while O-CNT showed 0.01 mg/mL in DMF.

The thermal behavior of PAN/f-MWCNT composites was studied by DSC (5 °C/min to 350°C in air). Fig. 3 showed the cyclization temperature of pure PAN and O-MWCNT/PAN composite film is a single peak at around 292°C and 285°C, respectively. It is believed that acid functional group of MWCNT can act as external initiator for the nitrile cyclization in PAN [2]. Compared to the O-MWCNT/PAN composite, cyclization temperature of IPA-O-MWCNT/PAN composite film is around 292°C, which is similar to that of pure PAN film. However, the heat capacity of IPA-O-MWCNT/PAN film is much lower than those of O-MWCNTs and pure PAN.

Conclusions

Acid (IPA) functionalized MWCNTs were prepared by solvent-free functionalization method. Raman, XPS, and TGA clearly show that MWCNTs are covalently functionalized on the surface of MWCNTs. It is considered that the IPA group of MWCNTs provides not only high solubility of MWCNT in DMF but also lowers heat capacity of resulting MWCNT/PAN composites.

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References

- [1] Chae HG, Choi YH, Minus ML, Kumar S. Carbon nanotube reinforced small diameter polyacrylonitrile based carbon fiber. Compos. Sci. Technol., 2009;69, 406-413.
- [2] Sreekumar TV, Chandra L, Srivastava A, Kumar S. Oxidative stabilization of polyacrylonitrile in the presence of functionalized carbon nanotubes. Carbon 2007;45:1114-1116.
- [3] Peng X, Wong SS. Functional covalent chemistry of carbon nanotube surfaces. Adv. Mater. 2009; 21:625-642.
- [4] Spitalsky z, Tasis D, Paragelis K, Galiotis. Carbon nanotube-polymer composites: Chemistry , Processing, Mechanical and electrical properties. Prog. Polym. Sci. 2010;35:357-401.
- [5] Bajaj P, Sreekumar TV, Sen K. Thermal behavior of acrylonitrile copolymers having methacrylic and itaconic acid copolymers. Polymer 2001;42:1707-1718.
- [6] Ouyang Q, Cheng L, Wang H, Li K. Mechanism and kinetics of the stabilizations of itaconic acid modified polyacrylonitrile. Polym. Degrad. Stab. 2008;93:1415-1421.
- [7] Dyke AC, Tour JM, Solvent-free functionalization of carbon nanotubes. J. Am. Chem. Soc. 2003;126,1156-1157.

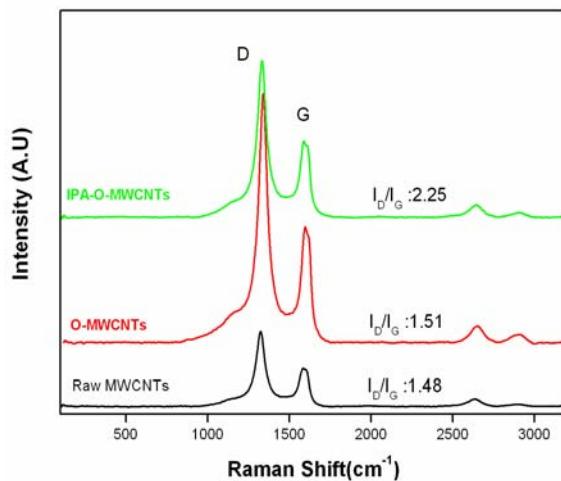


Fig. 2. Raman curves of Raw MWCNTs and surface functionalized MWCNTs.

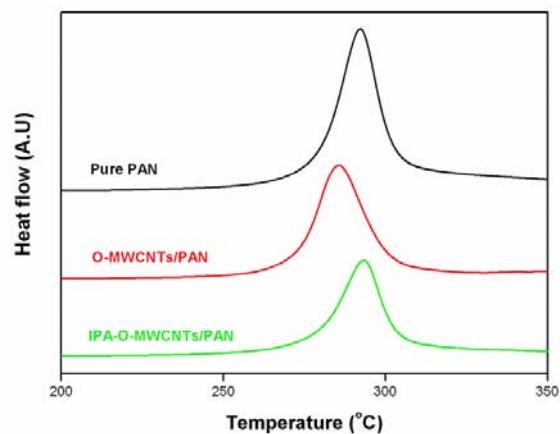


Fig. 3. DCS thermogram of pure PAN and surface functionalized MWCNT/PAN composites.