



Encapsulation of multi-walled carbon nanotubes by poly(4-vinylpyridine) and its dispersion stability in various solvent media

Sanghyun Hong^a, Myunghun Kim^a, Chang Kook Hong^b, Dongsoo Jung^c, Sang Eun Shim^{a,*}

^a Department of Chemical Engineering, Inha University, 253 Yonghyundong, Namgu, Incheon 402-751, South Korea

^b School of Applied Chemical Engineering, Chonnam National University, 300 Yongbong-dong, Puk-gu, Gwangju 500-757, South Korea

^c Department of Mechanical Engineering, Inha University, 253 Yonghyundong, Namgu, Incheon 402-751, South Korea

ARTICLE INFO

Article history:

Received 28 January 2008

Received in revised form 15 June 2008

Accepted 18 June 2008

Keywords:

Carbon nanotubes
Phase transfer catalysis
Microencapsulation
Modification
Dispersion stability

ABSTRACT

MWNTs were effectively functionalized with KMnO_4 in the presence of a phase transfer catalyst at room temperature. The hydroxyl functionalized MWNTs were reacted with a vinyl group-carrying silane-coupling agent and the terminal vinyl groups were used to fabricate poly(4-vinylpyridine) brushes by solution polymerization. Finally, P4VP-encapsulated MWNTs were obtained. The resulting materials were analyzed using TEM, TGA and their dispersion stability in various solvents was characterized by Turbiscan. It was found that the dispersion stability of P4VP-encapsulated MWNTs is dramatically improved in alcoholic medium due to the chemical affinity of P4VP with alcohol. This functionalization technique would provide a facile route to prepare various polymer brushes on the surface of MWNTs in order to improve the dispersion of MWNTs for potential applications.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Carbon nanotubes (CNTs) have brought considerable attention to a wide range of science and technology since their discovery in 1991 [1–4]. Due to their superior mechanical, thermal, electrical, and optical properties, it is expected that CNTs are expected to substitute a variety of classical materials in near future [5]. However, it is crucial to find an economic and effective method to increase dispersibility in liquids or solid matrices against self-agglomeration. In order to overcome the problem, chemical modification on the CNTs' surface is thought to be an effective way to improve their wettability and adhesion with host matrix materials [6]. Primary chemical covalent functionalization of CNTs such as hydroxyl group or carboxyl group is a promising practice to solve the problem. On the other hand, wrapping CNTs with polymer molecules using the interfacial activity of CNTs is the method to treat the surface of CNTs with minimizing damage of CNTs. But their adhesive energy is not high enough to transfer the stress between materials [7]. Therefore, grafting polymer molecules using surface-initiated polymerization in which growing polymer chains are covalently coupled onto the surface of CNTs has become the most adaptable pathway to improve dispersion stability and wettability of CNTs in polymer nanocom-

posites [8]. The CNTs uniformly dispersed in solvents can be utilized in direct conductive coating, further sol–gel process, and nanocomposite manufacturing.

Recently, a novel chemical oxidation process using KMnO_4 in the presence of a phase transfer catalyst (PTC) has been explored. There exist a few publications in which PTCs are employed for the surface modification of fullerene or CNTs consisting of a planar wall and a hemispherical cap [9–11]. It has been found that PTC methodology possesses several advantages over conventional oxidation methods using strong acids: (1) efficiency of oxidation drastically increases, (2) product selectivity between carboxylic acid and hydroxyl group is improved, (3) reaction condition is very mild, and (4) damage of CNTs is minimized [9]. Their tendency of locating at the interface of two phases (liquid–liquid or solid–liquid) introduces continuity between the two different phases [12]. In this experiment PTC assists to extract permanganate from the water phase to organic liquid phase. Permanganate is a powerful oxidizing agent in organic reaction [13,14]. Hydroxyl group with high selectivity is generated by contact of CNTs in methylene chloride, KMnO_4 , acetic acid employing tetrapropyl ammonium bromide (TPABr) as a PTC dissolved in water.

In our previous report, we devised a new method to synthesize the surface-initiated polymer brush in which polymerizable terminal vinyl groups were covalently attached on the surface of CNTs, named CNT-mer. The CNT-mer was used as a reactive monomer in the subsequent *in situ* solution polymerization [15]. In

* Corresponding author. Tel.: +82 32 860 7475; fax: +82 32 872 0959.
E-mail address: seshim@inha.ac.kr (S.E. Shim).