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Influence of dry and wet ball milling on dispersion characteristics of the multi-walled carbon nanotubes in aqueous solution with and without surfactant

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ABSTRACT

The current paper presents a new approach of attaining the optimum grinding condition of a planetary ball mill and simple method for purifying multi-walled carbon nanotubes (MWCNTs) to investigate the dispersion characteristics of MWCNTs. This work was conducted under dry and wet grinding conditions at various rotation speeds (200 rpm–500 rpm), and the dispersion characteristics of MWCNTs in aqueous solutions with and without surfactant were studied. The results were examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), particle-size analysis (PSA), UV-spectrophotometry and zeta potential (ζ) measurements. The purification results show that the structures of amorphous carbon and carbon particles of MWCNTs were completely eliminated and the tips of nanotubes opened. Moreover, both dry and wet grinding caused the lengths of the MWCNTs to be shortened with increasing rotation speed. The maximum absorbance of nanofluid was revealed to be 2.485 abs at wavelength of 253 nm for the best dispersion. The best dispersion characteristics were observed for wet grinding at a rotation speed of 500 rpm assisted by the ultrasonication dispersion of CNTs in aqueous solutions with surfactant.

1. Introduction

Nanofluids are suspensions of solid nanoparticles with typical sizes of 1–100 nm in base fluids such as water, anhydrous ethanol and organic liquids [1,2]. Nanoparticles are made of chemically stable metals, metal oxides or carbon in various forms [3]. The size of the nanoparticles imparts some unique characteristics to these fluids, including greatly enhanced heat and mass transfer, wetting and spreading and antibacterial activities. The possible areas of application of nanofluids are in advanced cooling systems and micro/nano-electromechanical devices as well as in various thermal management systems, viz. heat exchangers, evaporators and industrial cooling applications [4–6].

Since their discovery in 1991 [7], carbon nanotubes (CNTs) have been promising reinforcements for nanofluids due to their exceptional mechanical and physical properties, i.e., extraordinary high strength-to-weight ratio and superior flexibility. The applications of CNTs have been reported in previous published literatures [8–11]. However, there are two main issues facing their applications in structural materials. First, the entanglement of CNTs occurs due to their long and winding shapes, as well as due to the van der Waals forces between them. Second, weak interfacial interactions between CNTs and their surrounding matrix occur due to the hydrophobic surfaces of the CNTs. These phenomena degrade the material properties of CNT-reinforced composites.

To overcome the aforementioned issues, several research have been conducted using various dispersion methods, such as ultrasonication [12,13], chemical functionalization [14] and mechanical grinding [15,16]. Ultrasonication is generally used to disperse CNTs. For example, the amorphous, crystalline carbon impurities and metal particles removed from SWCNT samples with the assistance of ultrasonication were studied in Shelimov et al. [17]. They found that the damaged CNT walls are caused by ultrasonically assisted filtrations. Furthermore, raw CNTs contain a large amount of impurities, such as catalyst particles, amorphous carbon, and multishell carbon nanocapsules [18,19]. These impurities are serious impediment to the extensive characterization of the properties of CNTs and the further exploration of the applications of CNTs. A large variety of purifying methods, such as physical separation [20], gas-phase oxidation [21], liquid-phase oxidation [22] and combinatorial purification [23], have emerged to purify CNTs. Physical separation is only useful for the preparation of small amounts of purified samples. Gas-phase oxidation is only slightly efficient for the removal of graphitic impurities and catalyst particles. Liquid-phase oxidation is generally carried out with acid solutions such as HNO_3 or mixtures of H_2SO_4/HNO_3 or $H_2SO_4/KMnO_4$. In addition, Yen et al. [24] compared the dispersibility of raw and acid oxidized MWCNTs in base fluid. The better dispersibility of nanofluid for acid oxidized MWCNTs in base fluid was clearly observed.

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Dispersion using surfactants diminishes the agglomerations because they can be removed easily by washing. To date, a wide variety of surfactants have been investigated for the dispersion of carbon nanotubes, such as sodium dodecyl benzene sulfonate (SDBS) [25], dodecyl trimethyl ammonium bromide (DTAB) [26], hexa decyl trimethyl ammonium bromide (CTAB) [27], octyl phenol ethoxylate (Triton X-100) [28], and sodium dodecyl sulfate (SDS). In view of the large number of surfactants available for dispersion, it is imperative to conduct a systematic study of different parameters, such as concentration, nature, and stability, to choose the right surfactants for certain application. Sodium dodecyl sulfate (SDS) has been studied in Alias et al. [29] due to their excellent ability to stabilize and resulted in the SDS surfactant complementing the based fluid of water to steadily disperse the CNT particles and reduce agglomeration for long periods of time. It is suggested that the SDS is the right surfactant for dispersion of CNTs particle in base fluid.

Grinding is also used to disperse agglomerated CNTs [30,31]. Pierard et al. [32] applied grinding to CNTs and showed a decrease in aggregation and complete disruption of the CNT structure. Kukovecz et al. [33] reported that extended grinding had a low impact on the CNTs. The resulting CNTs appeared clean and well separated. In addition, an improvement in the specific surface area with increasing grinding time was observed. A similar study by Kim et al. [34] showed that the grinding of CNTs resulted in shortened and densely packed CNTs with increased grinding time due to increased cleavage. In addition, Kano et al. [35] reported that the high rotation speed of both the pot and disk causes the balls to strongly and violently move inside a pot, hence the particles and balls impact with high energy, which improves the grinding performance.

In an earlier work, Li et al. [36] studied CNTs treated by high-energy grinding for different grinding times. It was reported that broken nanotubes and many onion-like carbon particles were obtained in a sample ground for 15 min. When the grinding time was increased to 60 min, the CNTs turned into amorphous carbon. In a more recent work, Jiang et al. [37] reported that an SDS surfactant containing a single, long, straight-chain hydrophobic segment and a terminal hydrophilic segment proved to be a suitable CNT dispersant. In a recent work, Yu et al. [38] demonstrated the dispersion mechanism of MWCNTs in an aqueous surfactant solution and reported the factors that influence the efficiency of the dispersion. It was noted that the time-dependent sonication experiments revealed that the maximum achievable dispersion of MWCNTs corresponds to the maximum UV–visible absorbance of the solution. In a more recent work, Tang et al. [39] conducted the wet ground MWCNTs ultrasonically dispersed in chitosan solution and results were characterized by UV-spectroscopy. It was found that wet-grinding could improve the water wettability of MWCNTs and eliminate the barrier of air layer around MWCNTs to ultrasonic waves. Recently, Krause et al. [40] investigated the as-grown and ball milled CNTs with regard to their morphology, nanotube length distribution, and dispersion stability. They found that the increasing ball milling time with significantly decreased agglomerate size and length shortened.

Although less attention has been paid to the systematic investigation of the parameters governing the dispersion behavior of MWCNTs, such as grinding speed as a function of time under both dry and wet conditions, purifying CNTs using surfactant and ultrasonication energy has not yet been incorporated into relevant studies. The purpose of our study was to compare the dry and wet types of grinding at rotation speeds of 200 rpm, 300 rpm, 400 rpm and 500 rpm assisted by the ultrasonication dispersion of MWCNTs in aqueous solutions with surfactant and without surfactant. A simple method for purifying MWCNTs using nitric acid and sulfuric acid was employed.

2. Experimental procedures

2.1. Materials

The MWCNTs with approximately 20 nm in diameter and 5 μm in length, with greater than 95% purity, and less than 3% amorphous carbon used in this work were synthesized by chemical vapor deposition (CVD) (Carbon Nanomaterial Technology Co., Ltd, South Korea). SEM micrograph of the as-received MWCNT is shown in Fig. 1.

2.2. Grinding in a planetary ball mill

A planetary ball mill made by Haji Engineering, Korea was used to grind samples in this study. The collision medium was monosized (3.00 mm) spherical zirconia (ZrO_2) balls (purchased from Haji Engineering, Korea). Grinding was performed as follows: MWCNTs and zirconia balls were mixed and placed into cylindrical stainless pot (40 mm in inner diameter and 45 mm in height) lined by ZrO_2; a 56-cm^3-volume pot was filled with 80 vol.% of particles and balls. For grinding in the dry condition, 0.5 g MWCNTs and 105.0 g zirconia balls were added to each pot. In the wet grinding condition of the experiment, 20 ml distilled water was added to each pot. The direction of the pot rotation was set counter to that of the disk revolution. The configuration of the planetary ball mill is shown in Fig. 2. Moreover, Mio et al. [41] reported that a significant grinding rate is obtained when the mill pot is rotated near the critical speed ratio counter-directionally to the disk revolution, which is also rotated at a speed near the critical speed ratio. To compare the effective processing parameters, the MWCNTs were ground at various speeds under dry and wet conditions. Specifically, the agitator-applied grinding speeds were 200 rpm, 300 rpm, 400 rpm and 500 rpm, and grinding time was adjusted to 1 h. Changes in the particle shapes and sizes of the ground powder with increasing grinding speed were analyzed using a high-magnification scanning electron microscope (SEM, JSM-5610, JEOL) and particle-size analyzer (PSA, Mastersizer2000, Malvern Instruments Ltd., UK), respectively. The Mastersizer2000 particle-size analyzer is designed to measure the sizes of emulsion, suspension and dry-powder particles ranging from 0.01 μm to 2000 μm in size. This method is widely used in the field of powder technology, particularly for measuring CNT powder particles.

2.3. MWCNT-purifying process

A simple method for purifying MWCNTs by using nitric acid (HNO_3) and sulfuric acid (H_2SO_4) was employed as follows. Raw MWCNTs were mixed with nitric acid and sulfuric acid (purchased Matsunoen Chemicals Co., Ltd, Japan) with concentrations of 63%

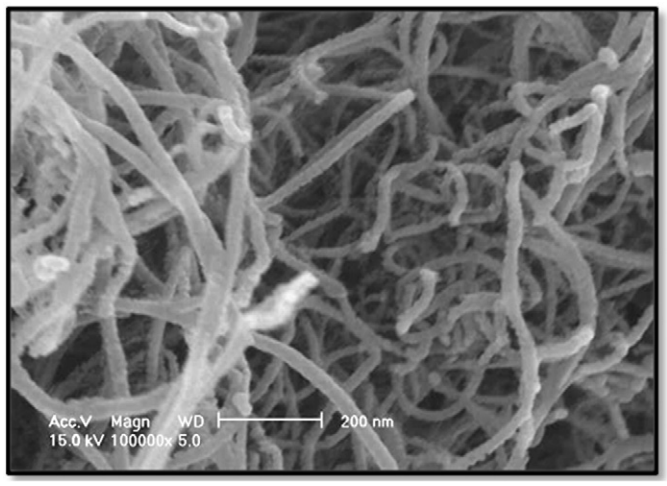

Fig. 1. SEM micrograph of the MWCNTs employed in the current study.