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Milling and dispersion of multi-walled carbon nanotubes in texanol

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Abstract

Rheological results were used to determine the optimum type of dispersant and its concentration for six commercial dispersants for the dispersion of multi-walled carbon nanotube (MWCNT) agglomerates in texanol. An unsaturated polycarboxylic acid copolymer (BYK P-104) exhibited the optimum performance with the lowest MWCNT slurry viscosity in texanol. The cutting and dispersion efficiencies of MWCNTs with 20 wt.% of BYK P-104 dispersant were compared using conventional ball milling and high energy milling, whereby the latter was found to be more effective. High energy milling for 2 h produced a large portion of MWCNT agglomerates smaller than 150 nm, showing a drastic increase in slurry viscosity due to the dispersion into individual CNTs. On the other hand, 120 h ball milling was required to achieve the agglomerate size of 300 nm with less viscosity increase upon milling. Decrease in the degree of MWCNT crystallinity was observed by both milling, even though 2 h high energy milling showed slightly less damage than 120 h ball milling based on XRD and Raman spectroscopy results.

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Keywords: Carbon nanotubes; High energy milling; Dispersion; Raman spectra

1. Introduction

Carbon nanotubes (CNTs), with their excellent electronic, mechanical and structural characteristics, have promising potential for a wide range of applications to new functional materials and devices such as field emission displays (FED) [1], super-capacitors [2], storage for hydrogen [3], catalytic supports [4] and many more. These applications all benefit from the nano-sized structure, large surface area and high electrical conductivity with low loading rate of CNTs. However, the dispersion of CNTs has been a consistent issue because of their strong tendency to form aggregates due to the high van der Waals interactions.

Therefore, recent efforts have focused on enhancing the dispersion of CNTs by surface treatments or cutting. Many kinds of surface treatment using plasma [5] or UV/ozone [6], and functionalization techniques with polymeric agents have been introduced [7–9]. Various physical or chemical CNT cutting methods include the utilization of ultrasound [10], ball mill [11], vibration mill [12] or two-roller mill [13], oxidation in acidic condition [14], fluorination and pyrolysis [15] and gamma radiation [16]. For example, ball milling for CNT cutting has been demonstrated even though it generally takes more than 100 h to get an average CNT agglomerate size of 200–300 nm [14,17]. Compared to the conventional ball mills which require a long time, modern high energy mills equipped with a high speed rotor rotating up to several thousands times per minute are known to be very effective for milling or cutting. Their high energy input and use of small grinding media with a diameter of 0.02–0.8 mm allow the achievement of a very small particle size in a very short processing time, especially in ceramic fields [18]. The efficient CNT cutting is prerequisite for the application as a field emitter, while maintaining the CNT loading rate as small as possible due to the rheological issue. Since electrons are emitted from the CNT tips, the high surface-exposed CNT density is very important to get a high electron emission density. However, no studies have investigated the efficiency of high energy mill in CNT cutting.

From these overall perspectives, we tried to cut and disperse CNTs using a high energy mill for the first time and systematically compared the efficiency of this method with that of conventional ball milling after adding a commercial dispersant into CNT slurry. Since CNTs are known to be

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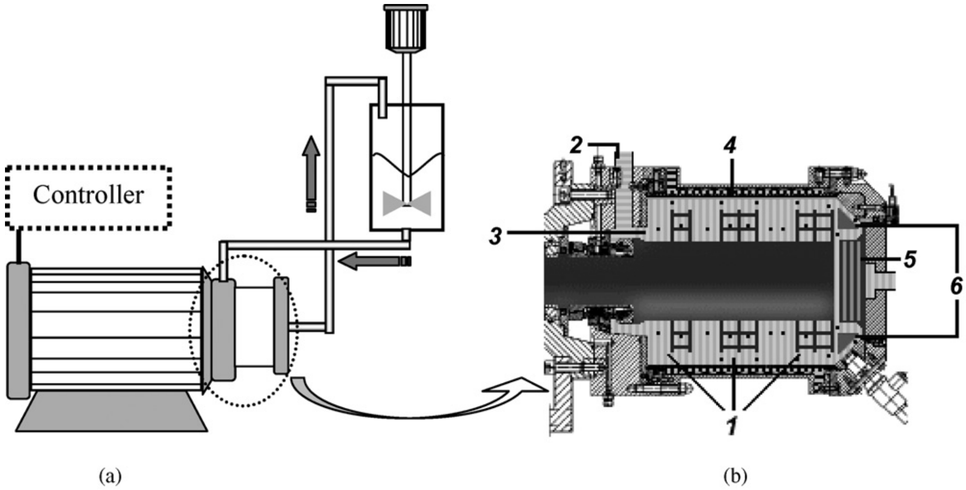

Fig. 1. Schematic of (a) high-energy mill and (b) the milling chamber of the high energy mill [20]. 1: Rotor with discs, 2: inlet, 3: milling media, 4: cooling jacket, 5 and 6: separation system.

damaged by milling process [12], the degree of damage associated with two different milling methods was characterized using high resolution transmission electron microscopy (HRTEM), Raman spectroscopy and X-ray diffraction (XRD).

2. Experimental

2.1. Determination of the best dispersant and the optimum concentration

Multi-walled carbon nanotubes (MWCNTs) grown by catalytic CVD method (CMP-310F, Iljin Nanotech, Korea) according to the supplier's data with a mean diameter of 3–5 nm, a length of 10–20 μm and a specific surface area of 797 m^2/g were used for this experiment. In order to compare the dispersion efficiency of commercial dispersants, six types of dispersant were chosen according to vendors' suggestion, as shown in Table 1. After 10 min of ultrasonication (HD 2070, Bandelin using 20 kHz and 40 W, Germany) for the slurries containing 2 wt.% of MWCNTs in texanol ($C_{12}H_{24}O_3$: 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate), the rheological behavior of slurries with different dispersants was investigated at 20 °C using a computer-controlled cone-type viscometer (LVDV-II+, Brookfield, MA, USA) with CPE-52 spindle at various shear rates. Each dispersant was added at a ratio of 20 wt.% with respect to the CNT content. Texanol was used as a solvent because it is widely used in the synthesis of CNT paste for FED application [19]. Since BYK P-104 gave the most favorable results among the six types of dispersant, the optimum amount of this dispersant in MWCNT slurry was further decided by varying the addition amount to 20, 50 and 100 wt.% with respect to MWCNTs.

2.2. Ball milling and high energy milling process

In order to compare the milling efficiency between ball milling and high energy milling, the following experiment was performed. For ball milling, slurry was prepared by adding 1.4 g of BYK P-104 and 7 g of MWCNTs (i.e., 20 wt.% of dispersant with respect to the MWCNT content) into 350 g of texanol to form a slurry of 2 wt.% MWCNTs with respect to the solvent content. This slurry was ball-milled in a 500 cc polypropylene bottle for 120 h with 2 mm spherical ZrO_2 balls. Fig. 1 presents a schematic of (a) high energy mill system (MiniCer, Netzsch, Germany) and (b) the grinding chamber of this mill. This mill had a ZrO_2 lining with an 180 cc of milling chamber which was filled with 80 vol.% of 0.8 mm ZrO_2 balls. High energy milling was performed at 2000 rpm for the same composition of MWCNT slurry for 2 h by adopting a continuous circulation method, where a small amount of sample was taken at a planned time for the characterization.

2.3. Characterization of the MWCNTs

The following characterization was performed for the samples collected occasionally during this experiment. Optical

Table 1
Details of the six dispersants used in this study

Dispersant	Abbreviation	Supplier	Suppliers' description on the functional group of dispersant
Rhodafac RE-610	RE-610	Rhodia	Nonylphenol ethoxylate based phosphate esters
Disperbyk-2001	BYK-2001	BYK	Modified acrylate block copolymer
Disperbyk-111	BYK-111	BYK	Copolymer with acidic groups
Disperbyk-103	BYK-103	BYK	Copolymer with pigment affinic groups
BYK-9076	BYK-9076	BYK	Alkylammonium salt of a high molecular weight copolymer
BYK P-104	BYK P-104	BYK	Low molecular weight unsaturated polycarboxylic acid copolymer