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Correlation between electrokinetic potential, dispersibility, surface chemistry and energy of carbon nanotubes

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ABSTRACT

This paper proposes the correlation between the electrokinetic potential, dispersibility in solvents, surface energy and oxygen content of carbon nanotubes (CNTs) affected by functionalization. Colloidal systems consisting of CNTs with varying degrees of dispersion are prepared and characterized to evaluate CNT dispersibility and suspension stability in solvents with different polarities. The results show that an absolute value of zeta potential at about 25 mV is closely related to the micro- and macroscopic dispersion of CNTs, whereas a high absolute value of 40 mV is regarded as an indication of high quality CNT dispersion with much enhanced suspension stability in solvents. The absolute zeta potential value increases consistently with increasing degree of CNT functionality, the increase being most pronounced in a hydrophilic liquid such as water. A linear correlation is established between the surface energy of a CNT film and the oxygen to carbon ratio of CNT surface. The CNT dispersibility in a liquid is determined not only by their physical states, but also by the hydrophilicity and surface functionality of CNTs, all of which are reflected by zeta potential.

1. Introduction

With unique structural and transporting properties, such as excellent strength, modulus, electrical and thermal conductivities along with a low density, carbon nanotubes (CNTs) have attracted much interest as the reinforcement for polymer matrix composites [1–3]. The CNT/polymer composites hold the promise of delivering exceptional mechanical performance and multi-functional characteristics. The potential of employing CNTs as reinforcements has, however, been severely limited because of difficulties associated with dispersion of inherently entangled CNTs and poor wetting of inert CNTs with most polymers. To maximize the reinforcement effect of CNTs for composites, proper dispersion and good interfacial interactions between the CNTs and polymer matrix have to be guaranteed [3–5].

A number of techniques [3], including mechanical dispersion of various nature, acid treatment, ultraviolet/ozone (UV/O_3) and plasma treatments, wrapping of CNTs with polymer molecules and surfactants, chemo-mechanical method and silane treatment, have been applied to address the above issues with varying degrees of success. For the fabrication of CNT/polymer composites, a method based on the pre-dispersion of CNTs in a solvent and following mixing with a monomer or a polymer has been proven to be an effective method to obtain satisfactory CNT dispersion in polymer matrix [1–6]. However, the evaluation of CNT dispersion quality in a liquid is still a challenge because of the lack of standards and/or proper tools to rate the dispersion quality. The concentration of CNTs dispersed in a solvent for composite fabrication is usually above 0.1 mg/ml, resulting in a non-transparent and completely dark solution if the CNT dispersion remains stable. Very dilute CNT dispersions are transparent, and their dispersion qualities can be characterized using the ultraviolet-visible-near infrared (UV–Vis–NIR) or photoluminescence spectra [7,8], and these techniques are known to be useful for characterizing single-walled CNTs. The most frequently used technique for qualitative evaluation of multi-walled CNTs so far is to observe with naked eyes or using a digital photograph to compare whether the previously dispersed CNTs are precipitated after a certain period of time [9], or to monitor the sedimentation of dispersed CNTs using UV–Vis spectroscopy [10–12] or centrifugal forces [13]. Although these methods give information on the amount of nanotubes dispersed, they are lack of providing information on the dispersion quality of CNTs. There is no systematic quantitative evaluation technique reported on CNT dispersibility in liquids.

It is well known that the dispersion and stabilization of colloidal particles in a solvent are dependent on the electrostatic repulsion resulting from the surface charge on the particles. The charge can be measured in terms of zeta potential, the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particles. It represents the degree of repulsion between adjacent, similarly charged particles in dispersion

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[14]. When the particles are small enough, a high zeta potential means stability, i.e., the solution or dispersion resists aggregation of particles. When the potential is low, attraction among colloid particles exceeds the repulsion and the dispersion will break and flocculate. In other words, particles with a high zeta potential are electrokinetically stabilized while those with a low zeta potential tend to coagulate. A value of 25 mV (positive or negative) is taken as the arbitrary value that separates low-charged particle surfaces from highly-charged ones [14]. This concept has recently been applied to evaluate the dispersion of CNTs affected by various surfactant treatments [9,15–17]. However, there was little information concerning the reliability of this process and the role played by different types of solvent (polar or non-polar) used for CNT dispersion. Nor have studies so far been reported on the effects of surface functionality and surface energies on the electrokinetic potential of CNT dispersion.

This paper is part of a large project on the development of CNT functionalization techniques for improved dispersion and interfacial interactions with polymer resins. In the present work, a method for quantitative evaluation of CNT suspension stability in liquids was developed by measuring the zeta potential of several different colloidal systems consisting of CNTs with different dispersibility, whose correlation was established with the surface functionality and surface energy of CNTs. All these results are further confirmed by macroscopic observation and electronic microscopy.

2. Experimental

2.1. Materials and functionalization of CNTs

Vapor grown multi-walled CNTs were used in this study. Table 1 summarizes the physical properties of these CNTs. The dispersion behavior of CNTs with two distinct dispersion features in dry state, i.e., one in the form of large bundles (CNT-A and CNT-B) and the other with well dispersed individual CNTs (CNT-C), were studied here. Typical SEM morphologies of these CNTs taken at two different magnifications are presented in Fig. 1. To the authors' knowledge, CNT-B was produced by treating CNT-C in ethanol to a compacted form. For the functionalization, CNTs were exposed to ultraviolet light in an ozone chamber (Jelight 144AX-220 UV/O_3 Cleaning System) for varying durations of 5, 10, 30, 60 and 90 min. The UV/O_3 treatment is known to be a convenient, dry method to produce oxygenated surface functionalities on carbon materials [18–20].

2.2. Characterization

The zeta potential values of different CNT/solvent suspensions were measured using an analyzer (Zeta Plus, BIC) at 10 cycles per run. Suspensions were prepared using three different solvents, namely distilled water, ethanol and hexane, with a fixed CNT concentration of 0.02 mg/ml, equivalent to 1.1×10^{-3} vol% (assuming CNT density is 1.8 g/cm^3 [1]). CNTs were dispersed using a sonicator (Branson 2510, Bransonic) in a water bath for 30 s. The physical state, dispersion behavior and particle size distribution of CNTs were examined by scanning electronic microscopy (SEM, JSM-6700F, JEOL), transmission electronic microscopy (TEM, 2010F, JEOL) and particle size analyzer (Beckmann Coulter LS230), respectively. The suspension stability of CNTs in solvents was also evaluated by macroscopic observation after 30 min of dispersion.

The elemental composition of CNTs before and after UV/O_3 treatment was evaluated by X-ray photoelectron spectroscopy (XPS, surface analysis PHI5600, Physical Electronics Inc.). A monochromatic Al K_α X-ray was used at an electron voltage of 14 kV. The XPS curve fitting of C 1s was carried out using MultiPak V6.0 A (Physical Electronics Inc.). The relationship between zeta potential and surface functionality of CNTs was also studied. The surface energies of CNTs before and after functionalization were assessed by measuring the contact angles of CNT films. For sample preparation, CNT/ethanol solutions at a concentration of 0.2 mg/ml were prepared and the CNTs were dispersed using a sonicator (Branson 2510, Bransonic) in a water bath for 10 min. CNT films were obtained by vacuum filtration of dispersed CNTs through a cellulose filter with pore size of 0.2 μm [6]. Contact angles of the CNT films were measured on a goniometer (Digidrop, BGX Scientific Instruments) at room temperature. At least five measurements were made within 10 s of droplet formation for each sample, and the average values were used to calculate the surface energy of CNT films. The relationship between the surface energy of CNT, γ_S, and the contact angle, θ, can be expressed by the Young's equation:

$$\gamma_{LS} = \gamma_S - \gamma_L \cos(\theta) \tag{1}$$

where γ_S, γ_L and γ_{LS} are the surface energies of solid, liquid and solid–liquid interface, respectively. The surface energy consists of two components, namely the polar, γ^p, and dispersive, γ^d, components. These components can be determined based on the harmonic mean method as expressed by [6,21–23]:

$$\gamma_{LS} = \gamma_L + \gamma_S - 4\left(\frac{\gamma_L^p \times \gamma_S^p}{\gamma_L^p + \gamma_S^p} + \frac{\gamma_L^d \times \gamma_S^d}{\gamma_L^d + \gamma_S^d}\right) \tag{2}$$

If two liquids with known components of surface energies were used in the contact angle measurements, the corresponding solid and solid–liquid surface energies, i.e., γ_S and γ_{LS}, can be determined. Water and formamide were employed as probe liquids, and the two surface energy components used for calculation are 50.7 and 22.1 mJ/m^2 for water, and 19.0 and 39.0 mJ/m^2 for formamide, respectively [22].

3. Results and discussion

3.1. Zeta potential and dispersibility of CNTs

The solvents used for CNT dispersion in the study were representative of different molecular structures, i.e., solvents containing polar (distilled water), semi-polar (ethanol) and non-polar groups (hexane). Table 2 summarizes the zeta potentials of CNTs in these solvents along with their dielectric constants. It is interesting to note that for CNT-A, the zeta potentials were negative, and these values were independent on the type of solvents used. The possible reason was that some functional groups, mainly in the form of hydroxyl and carboxylic groups, were introduced on the CNT-A surface during the purification of raw materials [18], and these groups were ionized in solvents thus resulting in the adsorption of negative charges on CNT surface. For CNT-B and CNT-C, however, the values were positive in water and hexane, but they were negative in ethanol. It appears that the different signs of zeta potentials were associated with the polarities of solvents used for CNT dispersion. It is reported that the dielectric constant of a solvent, a reflection of solvent polarity, can affect the zeta potential of particles (without ionic species) dispersed in an organic medium

Table 1
Properties of CNTs used in this study.

	Diameter (nm)	Length (μm)	Physical state	Supplier
CNT-A	10–20	10–50	Solid powder	Iljin Nanotech, Korea
CNT-B	40–60	10–40	Solid powder	Nano-Karbon, Korea
CNT-C	40–60	10–40	Fluffy powder	Nano-Karbon, Korea