Plasma Coating and Enhanced Dispersion of Carbon Nanotubes

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ABSTRACT

Ultrathin polymer films have been deposited on both multi-wall and aligned carbon nanotubes using a plasma polymerization treatment. TEM experimental results showed that a thin film of polystyrene layer (several nanometers) was uniformly deposited on the surfaces of the nanotubes including inner wall surfaces of the multi-wall nanotubes. The coated multi-wall nanotubes were mixed in polymer solutions for studying the effects of plasma coating on dispersion. It was found that the dispersion of multi-wall carbon nanotubes in polystyrene composite was significantly improved. The deposition mechanisms and the effects of plasma treatment parameters are discussed.

INTRODUCTION

Recently, it has been shown in laboratory scale tests that the physical properties and performance of composite materials can be significantly improved by the addition of small percentages (~2%) of carbon nanotube particles [1-5]. However, there have not been many successful large-scale tests using a wide variety of soft phase materials that show the advantage of using nanotubes as fillers over traditional carbon fibers. The main problem is in dispersing the nanotubes and creating a strong interface between the nanaotube and the polymer matrix. This strong interface between the nanaotube and the polymer matrix is essential to transfer the load from the matrix to the nanotubes and thereby to enhance the mechanical properties of the composite. A crucial reason for these difficulties is that the nanotubes are atomically smooth and have nearly the same diameters and aspect ratios as polymer chains. In addition, the as-produced nanotubes usually form as aggregates that behave differently in response to a load as compared to individual nanotubes. To maximize the advantage of nanotubes as reinforcing particles in high strength composites, the aggregates need to be broken up and dispersed or cross-linked to prevent slippage.

In our previous works we developed new nano structures by a unique plasma treatment for the synthesis of polymer composites [6-10]. The unique properties required in these composites have been shown to be best achieved by our plasma method. The goal of the research is to enhance nanotube dispersion in the polymer and the interfacial bonding between the carbon nanotubes and matrix by depositing ultrathin films on the surfaces of the nanotubes, and to study the fundamental interfacial structures related to the bonding mechanisms. In this report, we will show some recent experimental results on coating of various types of carbon nanotubes and their modified dispersion properties.

EXPERIMENTAL DETAILS

In this experiment, we used Pyrograf III PR-24-HT [11] carbon nanotubes and aligned carbon nanotubes as substrates for plasma deposition of polymer thin films. The multi-wall carbon nanotubes (MWCNT's) were purchased from Pyrograf Products Inc. The aligned carbon nanotubes (ACNT's) were synthesized on silicon substrates by plasma-enhanced chemical vapor deposition (PECVD). The substrates were first coated with a layer of Ni (5 - 40 nm thick) as catalyst by magnetron sputtering at temperatures of 150 - 300 degrees C. During growth, a pressure of 1 - 20 Torr was maintained with gas flows of NH_3 at 80 SCCM and C_2H_2 at 20 SCCM. The substrates were heated at 500 - 700 degrees C resistively. The growth time was about 5 - 10 minutes to obtain the desired length [12-15].

The plasma reactor for thin film deposition of nanotubes is shown in Fig. 1. The vacuum chamber of the plasma reactor consists of a Pyrex glass column about 80 cm in height and 6 cm in internal diameter. The carbon nanotubes are vigorously stirred at the bottom of the tube and thus the surfaces of nanotubes can be continuously rotated and exposed to the plasma for thin film deposition during the plasma polymerization process. A magnetic bar was used to stir the powders. The gases and monomers were introduced from the gas inlet during the plasma cleaning treatment or plasma polymerization. The system pressure was measured by a thermocouple pressure gauge. A RF power generator operating at 13.56 MHz was used for the plasma film deposition [16-18].

***Figure 1**. The plasma reactor for thin polymer film coating of the nanotubes.*

Before the plasma treatment, the chamber pressure was pumped down to less than 5 Pa at which time the monomer vapors were introduced into the reactor chamber. The operating pressure was adjusted by the mass flow controller. Styrene was used as the monomer for plasma polymerization. To be able to distinguish the deposited polymer thin film and the surface of carbon nanotubes, we introduced a small fraction of C_6F_{14} to copolymerize with the styrene monomer. In this way, we were able to characterize the deposited thin film in the TOFSIMS experiments. During the plasma polymerization process, the RF power was 15 W and the system pressure was 30 Pa. The plasma treatment time was 30 minutes per batch of 0.3 grams of powder. Compare with MWCNT, processing of ACNT is much easier. The ACNT chip is simply put at the center of plasma chamber. Other parameters used for ACNT processing is the same as MWCNT processing.

After the plasma treatment, the carbon nanotubes were examined using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The high-resolution TEM experiments were performed using a JEOL JEM 2010F electron microscope with a field emission source. The accelerating voltage was 200 kV. The SEM experiments were performed on a Philips XL30 FEG SEM.

The Pyrograf III carbon nanotubes have similar size features with a hollow channel with outside diameters averaging about 70 nm. Some nanotubes become curved during their growth with the open ends. An HRTEM image (Fig. 2A) of the original Pyrograf III PR-24-HT carbon nanotubes shows the graphite structure with the interlayer spacing d_{002}=0.34 nm. Based on the bright-field TEM and HREM images, the wall thickness of the nanotubes can be estimated to be about 20~30 nm for both the Pyrograf III PR-24-HT carbon nanotubes. The edge dislocations can be seen due to the disorder of the graphite layers (002). It is noticed that both the outer and inner surfaces terminate at the graphite (002) layer without the addition of a surface layer, for the originally uncoated nanotubes (Fig. 2A). The bright field and high-resolution TEM images of these nanotubes after plasma treatment are shown in Fig. 2B. An ultrathin film amorphous layer can be clearly seen covering both the inner and outer surfaces of carbon nanotubes (Fig 2B). The thin film is uniform on both surfaces, however, with a larger thickness on the outer wall (7 nm) than on the inner wall (1~3 nm) surface (Fig. 2B). The thickness of ultrathin film is approximately 2~7 nm all the way surrounding the nanotube surfaces. The film is also thicker and more uniform than the roughness (<1 nm) on the outer surface of the carbon nanotubes (Fig. 2A). The lattice image of graphite can be clearly seen with an extremely thin layer of polymer film on its surface.

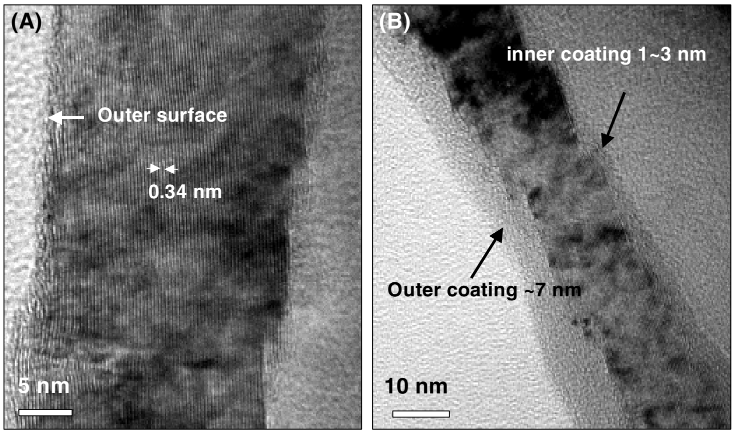

Figure 2. *HRTEM images of Pyrograf III PR-24-HT nanotube: (A) The fragments of the wall with inclined planes (002) showing lattice space on the outer and inner surfaces of uncoated Pyrograf III PR-24-HT nanotubes with slight roughness (<1 nm) on the surface; (B) An ultrathin film of pyrrole can be observed on both outer and inner surfaces of coated Pyrograf III PR-24-HT nanotubes.*

Fig. 3A is the SEM image of the coated ACNT's. Compare to uncoated ACNT's (Fig. 3B), one can see that the surface morphology exhibits smooth and around curvatures indicating coated polymer films. Fig. 4A is the TEM image of the uncoated ACNT's. In this figure, the silicon substrate, aligned CNT's and the nickel catalyst used in the CNT growth can be well identified. Fig. 4B shows the coating layer clearly on the surfaces of the aligned CNT's. The coating thickness is estimated about 30 nm.

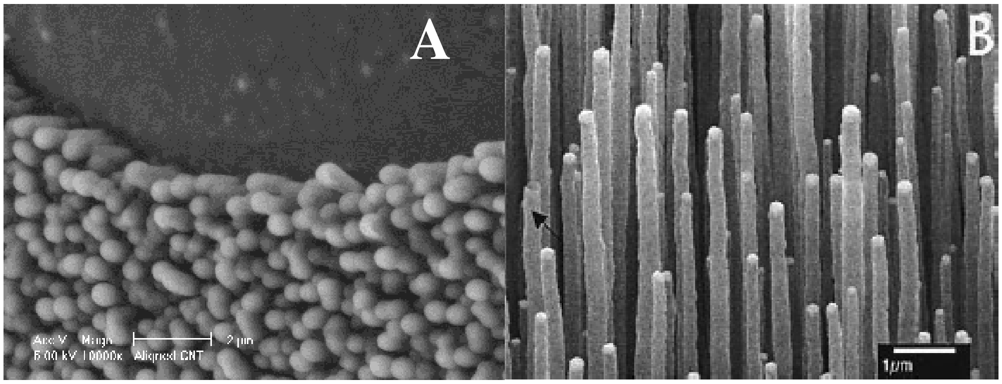

Figure 3. *HRTEM images of aligned carbon nanotubes: (A) coated with polystyrene; (B) uncoated*

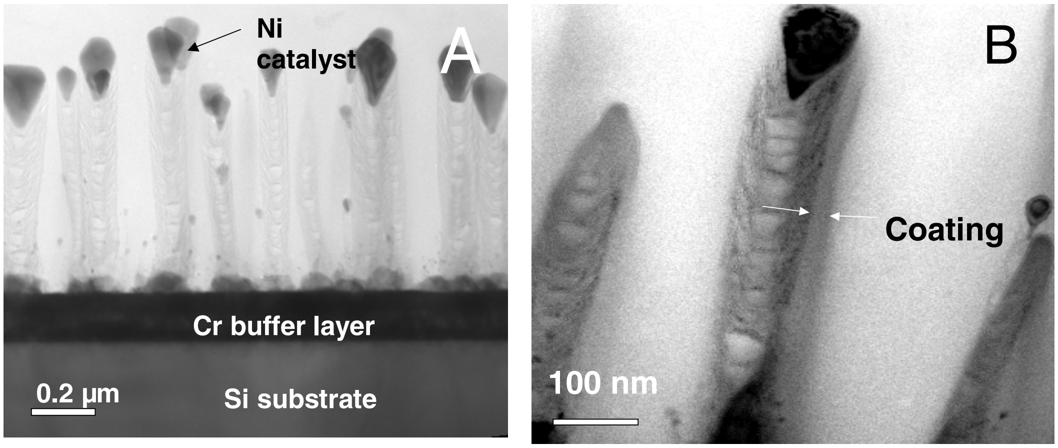

***Figure 4**. TEM images of (A) uncoated ACNT and (B) coated ACNT.*

After the surfaces of MWCNT's were modified by the plasma coating, they were mixed into polymer solutions for synthesizing the composites. Although these coated MWCNT's could be used in various polymers for the optimum properties, the most common polystyrene was used in the initial experiments. As a simple procedure, 2 grams of polystyrene powder were weighed and then mixed with coated or uncoated MWCNT's in appropriate proportions, i.e. 0 wt. %, 1wt. %, 3wt. %, and 5 wt. %. A solvent (50 ml toluene) was then added to the pre-mixed powers and the powder was thoroughly dispersed ultrasonically. The solution was evaporated until its volume reduced to ~20 ml (the ultrasonic vibration is kept on during this process) and then poured into an 80mm x 60mm x 6.5mm aluminum mold. The mold and the solution were kept at room temperature and dried for seven days.

The first observation took place in the solution stage. After ultrasonic mixing, the solutions with coated and uncoated MWCNT's were stored in small jars as shown in Figure 5. A stunning difference at this stage was that, as shown in this figure, the solution of uncoated MWCNT's quickly separated within 24 hours (Fig. 5, right, MWCNT's are precipitated from the solvent and concentrated at the bottom of the jar), while the solution with coated MWCNT's remained homogenously suspended as shown in Fig. 5 (left) for as long as several months. This phenomenon clearly indicates the significantly modified surface behaviors due to plasma coating.

Fig. 6 shows the fracture surface of the 3 wt. % coated and uncoated samples. For uncoated MWCNT's, they are highly clustered in the matrix with approximately a ~10 μm diameter (Fig. 6A), as indicated by the arrows. These clusters appear to be densely distributed with a small spacing of ~25 μm. Another important characteristic of the uncoated CNT composite is the rather flat fracture surface indicating the nature of brittle fracture. At these fracture surfaces severe pullouts of MWCNTs were also observed. In sharp contrast, the dispersion is greatly improved in the coated MWCNT composite. Figure 6B shows the fracture surfaces of the 3 wt. % coated MWCNT composite. The coated MWCNT's are well dispersed in the matrix with a wavy type of fracture surface morphology.

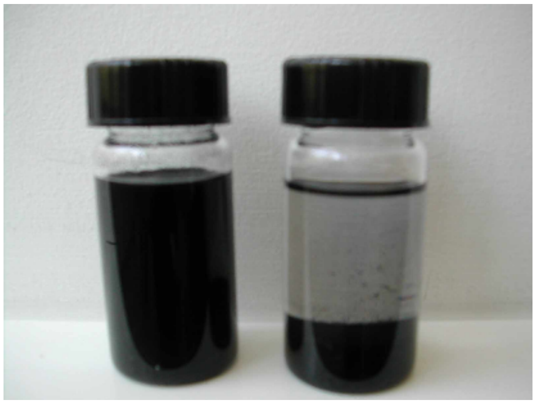

Figure 5. *Solutions with coated (left) and uncoated (right) WMCNT's.*

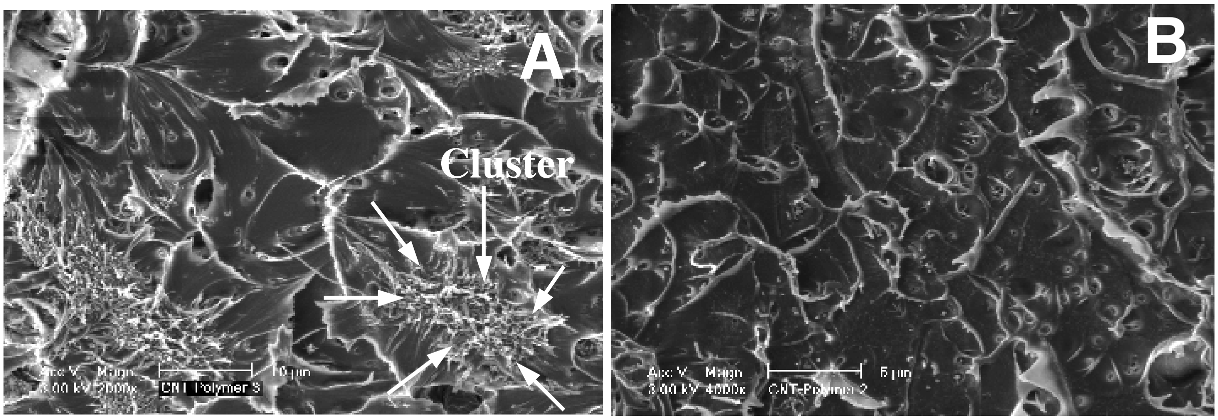

Figure 6 *Fracture surface of (A) uncoated WMCNT's and (B) the coated MWCNT's.*

Generally, nanoparticles are difficult to disperse in the plasma polymerization coating process due to aggregation and large surface area per unit mass of the nanoparticles. In the plasma thin film coating process, it is necessary to expose the surface of the nanoparticles to the plasma. The unexposed regions of the powder particles are hardly modified. The fluidized bed reactor is an ideal tool for gas-particle reactions due to the intensive mass and heat transfer between the two phases, short reaction time, and flat temperature profile [15-17]. Therefore, the combination of plasma polymerization and the fluidized bed process represents an innovative approach for low temperature surface modification of nanoparticles.

Both multi-wall carbon nanotubes (MWCNT's) and aligned carbon nanotubes (ACNTs) have been surface-modified by plasma polymerization in this study. The monomers with which we have extensive experience include pyrrole, hexamethyldisiloxane, perfluorinated hexane, acrylic acid and acetylene. The results presented in this paper focused on polystyrene coating. By varying their deposition conditions between high power/low pressures to low pressure/high power, we have been able to vary the mechanical properties from high modulus/high crosslink density to low modulus/low crosslink density. The plasma film structures are dependent on reactor size and geometry. An important factor, that is directly related to the size of nanotubes, is that the surface energy of these particles can be so high, i.e., several hundreds of mJ/m^2, that the organic monomer is very strongly and uniformly adsorbed on them. It was observed, for instance, in our preliminary work with nanosize Al_2O_3 and ZnO particles [6-9]. The film structure is then mainly determined by ion and radiation impact of adsorbed monomer and much less by the radicals formed in the plasma. The current research deals with coating nanotubes with the monomers HMDS and pyrrole, which have a large difference in radical lifetime in plasma polymerization. Films of the monomers will be deposited under different deposition conditions and their structure and properties will be determined using Langmuir probe and spectroscopy measurements.

In summary, we have deposited a thin polymer film on the surfaces of multi-wall and aligned carbon nanotubes by means of a plasma polymerization treatment. The polymer layer is not only uniform on both inner and outer surfaces of the MWCNT's, but it is also deposited in an extremely thin layer of 2~7 nm. By controlling the plasma coating conditions, the deposition rate can be closely controlled so that the film thickness on both the inner and outer wall surfaces is uniform and nearly identical. Due to surface modifications, the dispersion of these nanotubes is found to be significantly improved.

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