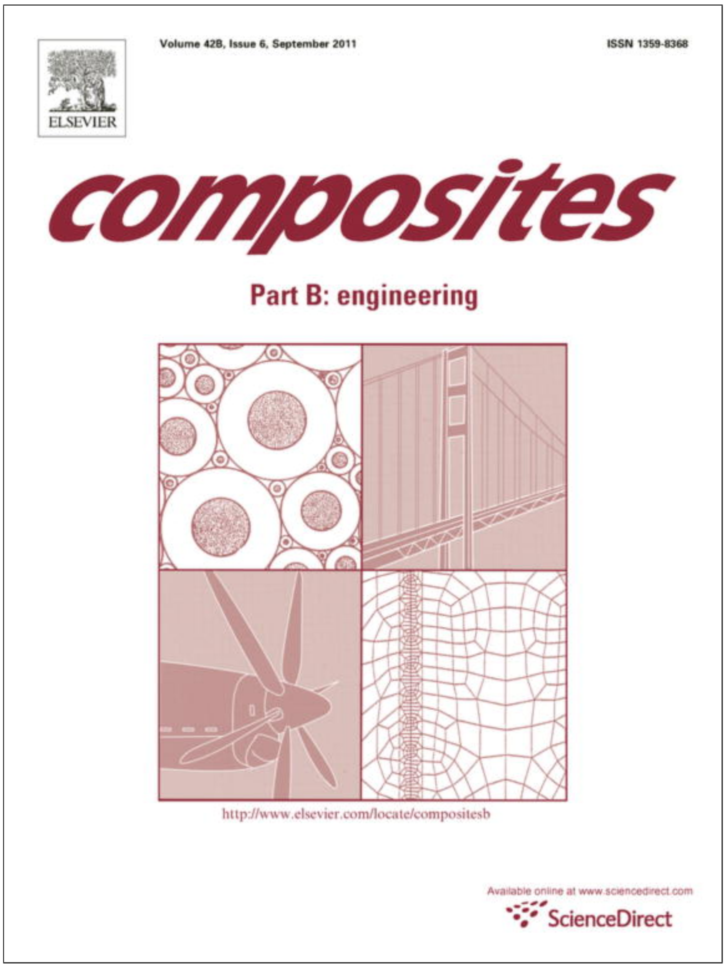
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Magnetic alignment of Ni/Co-coated carbon nanotubes in polystyrene composites

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ABSTRACT

Multiwall carbon nanotubes (MWCNT) are coated with ferromagnetic nickel and cobalt by a solution method. It results in a coating on the carbon nanotube surfaces in form of Ni/CoO nanoparticles. As a result of nano-scale Ni/CoO coating, MWCNT–polystyrene composites exhibit superparamagnetism at room temperature. As 3 wt.% of Ni/CoO coated MWCNT is dispersed in polystyrene matrix, a viscous liquid with solvent is developed for magnetic alignment. It is found that the Ni/CoO coated MWCNT respond to magnetic field susceptibly in the viscous liquid and arrange themselves in the direction of the applied field up to 5 T. Upon drying with magnetic field on, MWCNT are found to be well aligned in the direction of the field in the polystyrene matrices, as evidenced in the SEM and TEM experiments. As a result, strong anisotropy in tensile strength has been observed in the MWCNT–polystyrene composites. Magnetic alignment mechanism, surface coating microstructure of MWCNT, and related mechanical behaviors are discussed.

1. Introduction

Recent research has shown that the physical and mechanical properties of composite materials can be significantly improved by a small addition of carbon nanotubes (CNT) [1–10]. 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. An important aspect in the enhancement of composite properties involves the orientations of CNT. Control and manipulation of the CNT orientations in the polymer matrix can effectively change both physical and mechanical behaviors including electrical and thermal conductivities, mechanical strength, and anisotropy. On the other hand, for fundamental studies, it is also desirable to have nanotubes well aligned along certain specified directions. In this way, one may be able to study the anisotropic behaviors of the composites in terms of transport properties. Some previous attempts mainly focused on single wall carbon nanotubes (SWCNT) due to their considerable magnetic susceptibility from the catalyst elements such as nickel and cobalt [11–14]. For multi wall carbon nanotubes (MWCNT), however, only a few studies have been reported on magnetic alignment as a result of the weakly diamagnetic nature of these materials. The previous CNT alignment techniques replied mostly on mechanical straining [15], resulting in only partial alignment on the samples surfaces. For both the study of basic properties and engineering applications, it is highly preferred to have the CNT oriented uniformly through out the bulk of the materials. It is to be noted that the previous works on CNT alignment by using mechanical shear employed a high volume fraction of nanotubes, reaching a maximum of 50 wt.%. For a small concentration of CNT, the anisotropic behavior may be minimum or unobservable by the mechanical shear approach. In most recent reports on CNT–polymer composites, the CNT concentration is only between 1 and 5 wt.% [9,10]. Therefore, the magnetic alignment of a small fraction of MWCNT in polymer composites presents a great interest and challenge.

Another important aspect deals with dispersing the CNT and creating a strong interface between the nanotubes and the polymer matrix. The strong interface between the CNT 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. The as-produced nanotubes usually form as aggregates that behave differently in response to a load as compared to individual nanotubes. To maximize the

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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 previous research [16], we reported magnetic alignment of WMCNT in the polystyrene composites. In this research, we further studied the magnetic behaviors of the magnetically aligned MWCNT and found that the nanoparticles of Ni/CoO exhibited superparamagnetism, an essential property for magnetic alignment. For comparison, the uncoated MWCNT were also incorporated into the polystyrene composites and aligned at high magnetic field of 3 T. The experimental results indicated clear differences that only those with coated Ni/CoO nanoparticles resulted in significant alignment. We present experimental results on MWCNT surface microstructure, alignment, magnetization, and mechanical properties of the polymer composites reinforced with aligned and surface modified MWCNT.

2. Experimental details

Commercial Pyrograf III carbon nanotubes [17] were used in this study. These MWCNT dimensions are 70–200 nm in diameter, 50–100 μm long. A plasma method was used to surface-treat the MWCNT for the enhancement of dispersion. The plasma polymerization parameters have been reported previously [18–21]. The MWCNT was stirred magnetically in a vacuum chamber of the plasma reactor consisted of a Pyrex glass column, 80 cm in height and 6 cm in internal diameter. The monomers were introduced from the gas inlet during plasma polymerization. The plasma zone was created by a RF power generator operating at 13.56 MHz.

MWCNT was first coated with nickel and cobalt oxides by a solution method. A solution was developed by dissolving 5 g of $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ (2.5 g each) in 100 ml water. Ultrasonic method was used to mix 1 g of MWCNT with the solution for 2 h. The mixed solution was dried at 100 °C first, and then heat treated at 300 °C for 3 h. $Ni(NO_3)_2$ and $Co(NO_3)_2$ were entirely decomposed into NiO and CoO after the heat treatment. The NiO/CoO-coated nanotubes were plasma treated, as the last step, by surface deposition of a polystyrene thin film for enhanced dispersion.

For all composite samples used in the magnetic alignment experiments, the concentration of MWCNT used was 3 wt.%. A solution was produced by dissolving 2 g of polystyrene in 30 ml toluene. Ni/CoO coated MWCNT was dispersed into 30 ml toluene by ultrasonic method for 2 h. The two solutions were ultrasonically mixed together for another 2 h. The mixed solution was poured into a Teflon mold for magnetic alignment.

An Oxford Instruments Superconducting Magnet was used for MWCNT alignment in the polymer matrix. A split pair coil mounted in a cryostat is specially designed for creating a horizontal center field up to 5 T. Two 120 mm bores are available for room temperature access to the field, one horizontal aligned on the field

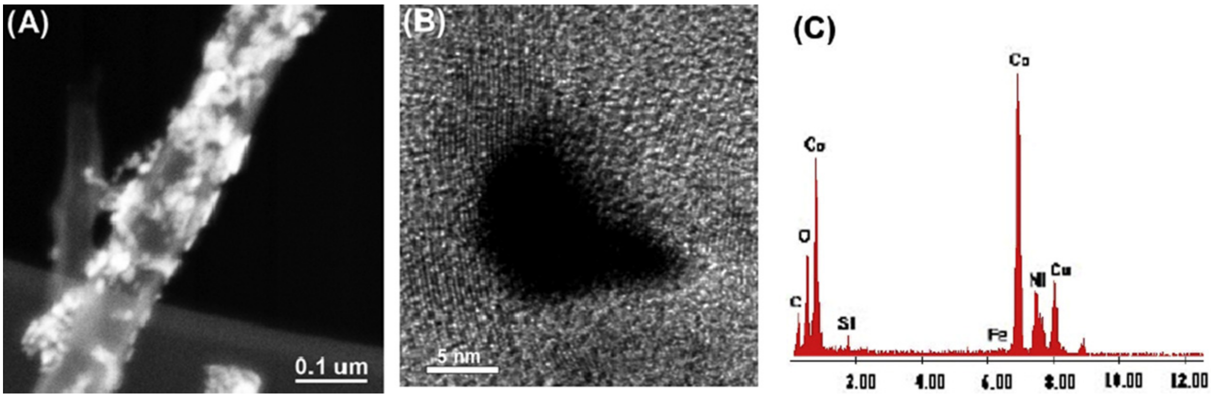

Fig. 1. (A) Bright-field TEM image showing the surface coated Ni/CoO nanoparticles. (B) HRTEM image showing a magnetic nanoparticle on the surface of carbon nanotube. (C) EDS spectrum of Ni/CoO magnetic particles on the carbon nanotube surface.

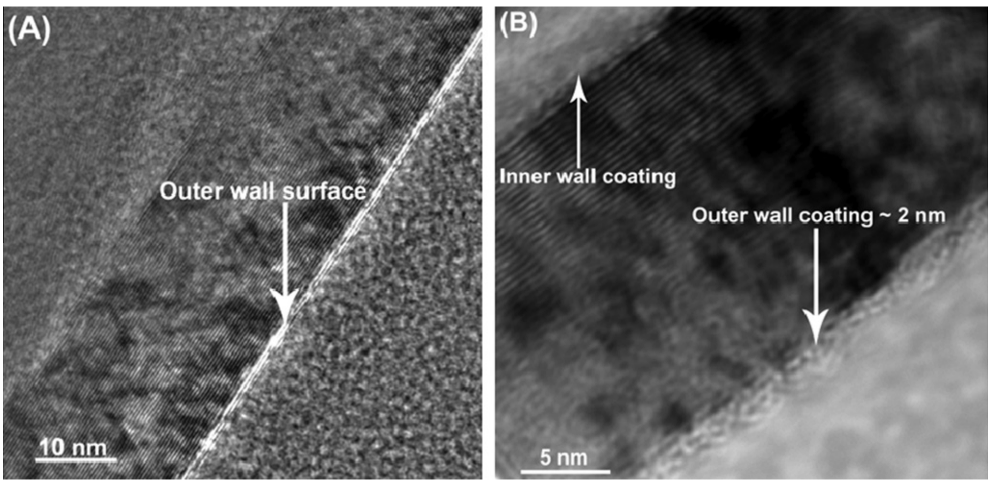

Fig. 2. (A) HRTEM image showing the original, uncoated MWCNT surface. (B) HRTEM imaging showing the plasma-coated MWCNT. Both inner and outer walls are coated uniformly with a 2 nm-thick thin film of polystyrene.

axis and one vertical through the magnet split. A horizontal magnetic field up to 5 T can be generated by the NbTi coil cooled in a liquid helium bath at 4.2 K. The homogeneity of the field is one part in 10^3 over a 10 mm diameter spherical volume.

The procedure for magnetic alignment of MWCNT in polymer matrix is described as follows [16]. The magnetic field is gradually ramped up and stabilized at a desired value, for instance at 1 T. The liquid mixture of MWCNT and polystyrene in a mold is placed at the center region of uniform magnetic field. As a result of surface coated magnetic NiO and CoO particles, each MWCNT acts as a magnetic dipole and is oriented horizontally in the applied magnetic field. Since the field is applied horizontally, most of the MWCNT would be aligned parallel to the surface of the liquid. The magnetic field is kept on until all the solvent slowly evaporated through the vertical bore of the magnet. It took an average of 24 h for a complete consolidation of the polymer composite. After the sample was dried entirely, it was removed from the mold for microstructure and property characterization.

Scanning electron microscopy (SEM) observation was carried out to investigate the microstructure using a Philips XL30 FEG SEM. A JEOL 2010F high-resolution transmission electron microscopy (HRTEM) was employed to study the interface structures that are responsible for the improved properties. TEM samples were prepared by dispersing MWCNT directly on carbon films supported with Cu grids. The composite samples were thinned by ultramicrotomy with a cutting thickness of 60 nm. A Model 2525-818 Instron mechanical testing machine was used for mechanical property evaluation, with a 1 mm/min cross head speed.

The polymer composites with NiO/CoO coated MWCNT were characterized by using the Quantum Design MPMS-5 SQUID magnetometer. To eliminate demagnetization factor, the samples were cut in the shape of squares with the edges parallel and perpendicular to the alignment field direction. Both temperature and field dependences of the composite samples were studied up to 300 K and 5 T, respectively.

3. Results and discussion

As described in the experimental procedure, the MWCNT were first liquid-coated with Ni/CoO. Fig. 1A shows the TEM Z-contrast image of Ni/CoO coated WMCNT. The white spots are the Ni/CoO nanoparticles on the nanotube surface. Fig. 1B is a HRTEM image showing a magnetic particle on the surface of carbon nanotube. Fig. 1C is the EDS spectrum of Ni/CoO magnetic particles on the carbon nanotube surfaces. As can be seen in this spectrum both No and Co are present indicating the magnetic components on the surfaces of MWCNT. This is an essential property required in the magnetic alignment experiments.

As has been shown in our previous experiments, plasma treatment can result in significant improvement in CNT dispersion. Extensive studies on this topic have been previously reported [17–21]. Fig. 2A shows the HRTEM image of the typical uncoated MWCNT surface. It shows the clear carbon lattice image with a smooth surface without any deposits. After plasma deposition, as shown in Fig. 2B, a thin layer of polystyrene can be seen on both inner and outer MWCNT surfaces. The film thickness is around 2 nm. More detailed information on plasma deposition and surface characterization can be found in Refs. [17,18].

After magnetic alignment, the composite samples were examined by SEM. Fig. 3 shows the natural surfaces of the samples aligned at different magnetic field. Fig. 3A shows the SEM image of the composite sample surface before magnetic alignment. As can be seen, the surface is quite smooth with MWCNT randomly oriented. Note that, even at low magnification, MWCNT can be seen as well dispersed irregular short white lines. As the samples

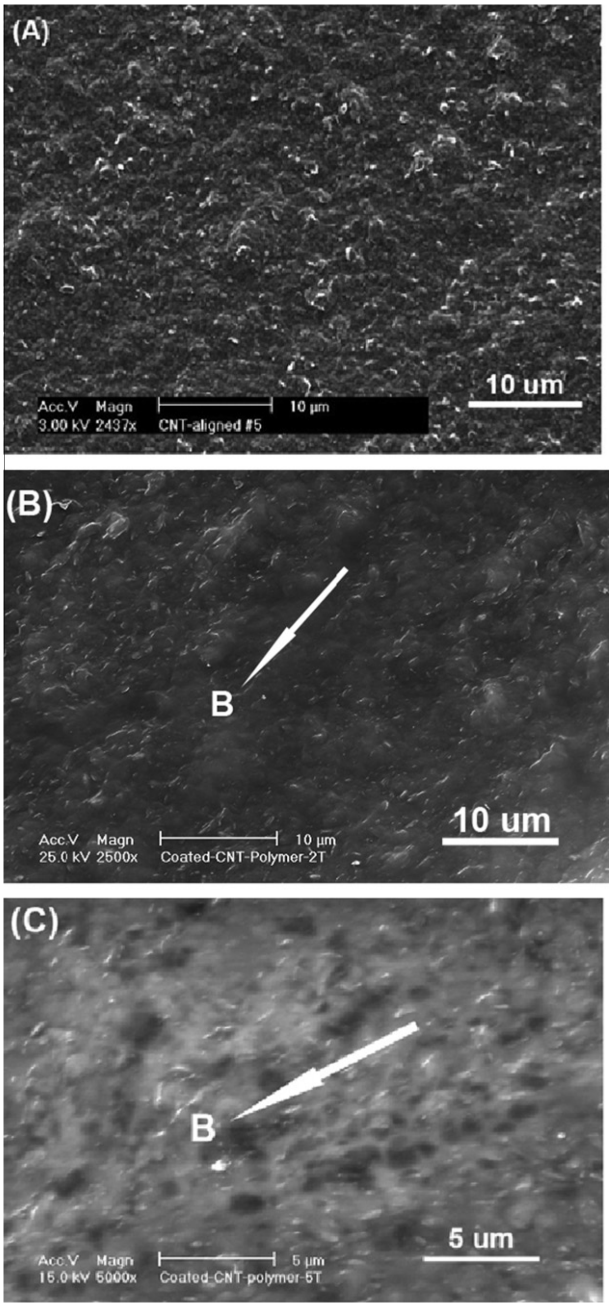

Fig. 3. (A) SEM micrograph showing the randomly oriented MWCNT in polystyrene matrix without magnetic alignment; (B) SEM micrograph showing magnetically aligned MWCNT under the applied field of 2 T, and (C) SEM micrograph showing magnetically aligned MWCNT under the applied field of 3 T. Note that the direction of the field is indicated by the arrows in the figure.

are magnetically aligned at 2 T (Fig. 3B) and 5 T (Fig. 3C), the MWCNT appear to be well ordered as can be seen in Fig. 3B and C, respectively. The WMCNT are aligned in the field directions as indicated by the arrows in Fig. 3B and C. An interesting feature to be noted here is that WMCNT in the sample before alignment seem deformed and curved, shaped like vermiform while they are more straightened in the magnetic aligned samples.

In order to study the MWCNT inside the sample, part of the sample was peeled off from the surfaces and their microstructures can be seen in Fig. 4. Fig. 4A is the SEM image showing the randomly oriented WMCNT just below the top surface. No orientation is observed for the sample aligned at 1 T as shown in Fig. 4B. As the magnetic field increases to 3 T (Fig. 4C) and 5 T (Fig. 4D), the

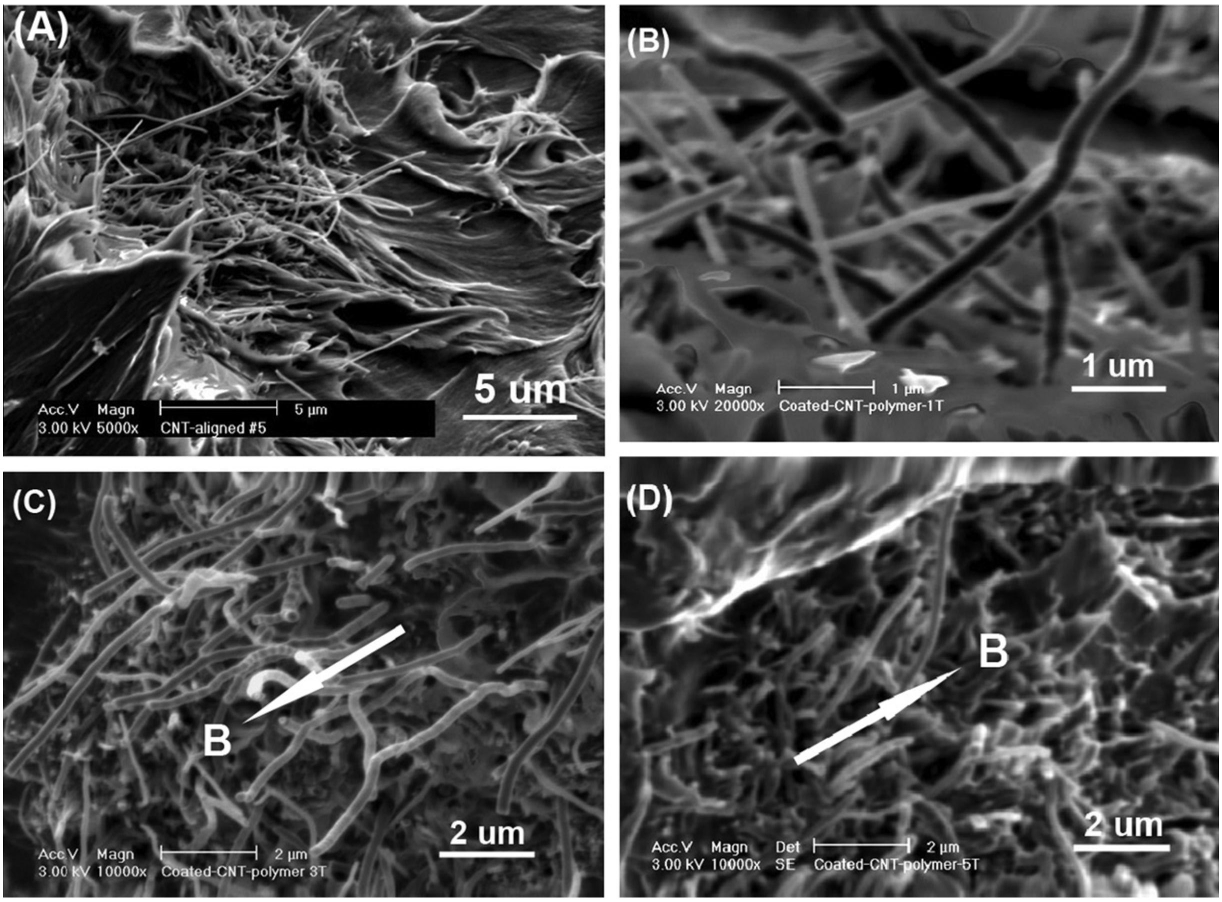

Fig. 4. (A) SEM micrographs showing randomly oriented MWCNT on the polystyrene composite sample surface without magnetic alignment; (B) randomly oriented MWCNT on the polystyrene composite sample surface magnetically aligned at 1 T; (C) considerably aligned MWCNT on the polystyrene composite sample surface magnetically aligned at 3 T, and (D) more aligned MWCNT on the polystyrene composite sample surface magnetically aligned at 5 T.

MWCNT can be seen to exhibit considerable alignment. Most of MWCNT point upward in a parallel fashion, particularly at the lower portions of the WMCNT.

To further study the microstructures, some SEM micrographs at higher magnifications are obtained and shown in Fig. 5. In this figure, two samples aligned at 1 T and 3 T, respectively, are shown. Fig. 5A and B are the SEM micrographs taken at two different magnifications for the sample aligned at 3 T. As can be seen, most of the MWCNT are aligned in the field direction, however, with some of them curved off. In sharp contrast, as shown in Fig. 5C and D, the MWCNT are not well aligned and randomly oriented in the 1T sample. As part of sample surface was peeled off for exposing the carbon nanotubes; the corresponding microstructures can be seen in Fig. 6. Consistently, there appears significant MWCNT alignment in the 3 T sample (particularly seen at the lower portions of the nanotubes as the top parts are elastically curved as shown in Fig. 6B, while the majority of the MWCNT exhibits randomness on the surface in the 1 T sample (Fig. 6A).

Figs. 3–6 are clear indications of MWCNT alignment in the applied magnetic field. The magnetic alignment is a result of Ni and Co component that is coated on the surface of MWCNT as the original nanotubes are only weakly diamagnetic on the order of 10^{-6} emu/g at 300 K [13], that is not capable of providing sufficient torque in a viscous liquid under applied magnetic field. To verify the magnetic properties of Ni/CoO coated MWCNT, magnetization experiments were carried out by using Quantum Design SQUID. 5×5 mm square sample was sectioned with each axis parallel and normal to the direction of the alignment. Fig. 7 shows the magnetization curves of the samples at 1 T, 2 T, and 3 T, respectively. The measurements were taken in two configurations: field in measurements parallel to the direction of the field used to align the MWCNT (M1Tp for 1 T as shown in Fig. 7A), and field in measurements perpendicular to the direction of the field of alignment (M1Tpp for 1 T as shown in Fig. 7A). The samples aligned at 1 T, 2 T, and 3 T exhibit reversible magnetization, indicating the superparamagnetic behavior.

Elements such as Ni and Co are known to be ferromagnetic in nature. The superparamagnetism is likely due to the nano-scale NiO and CoO particles shown in Fig. 1. As the particle size decreases, it becomes the single domain and magnetizes to its saturation. However, the magnetization can be thermally flipped by thermal noise, characterized by the so-called Neél relaxation time. In zero-field, if the measuring time is longer than the relaxation time, magnetization cannot be established, which is said to be in the superparamagnetic state. Magnetization in applied field exhibits its reversible behavior, which is fundamentally different from the irreversible ferromagnetism. Thus, it is consistent that the strong superparamagnetic property of the MWCNT found in this study is provided by the surface coated Ni/CoO nanoparticles. From both TEM and magnetization data, we show that the Ni-and Co-coated MWCNT used in this experiment are highly superparamagnetic [22–26].

Due to superparamagnetism, it is possible to align MWCNT in applied magnetic filed even for a large bulk volume. This approach is different from surface mechanical shear of conventional alignment method. The advantages include alignment of small fraction of nanotubes in a large volume of materials. Assuming each nanotube is uniformly magnetic with a high aspect ratio, then the moment of

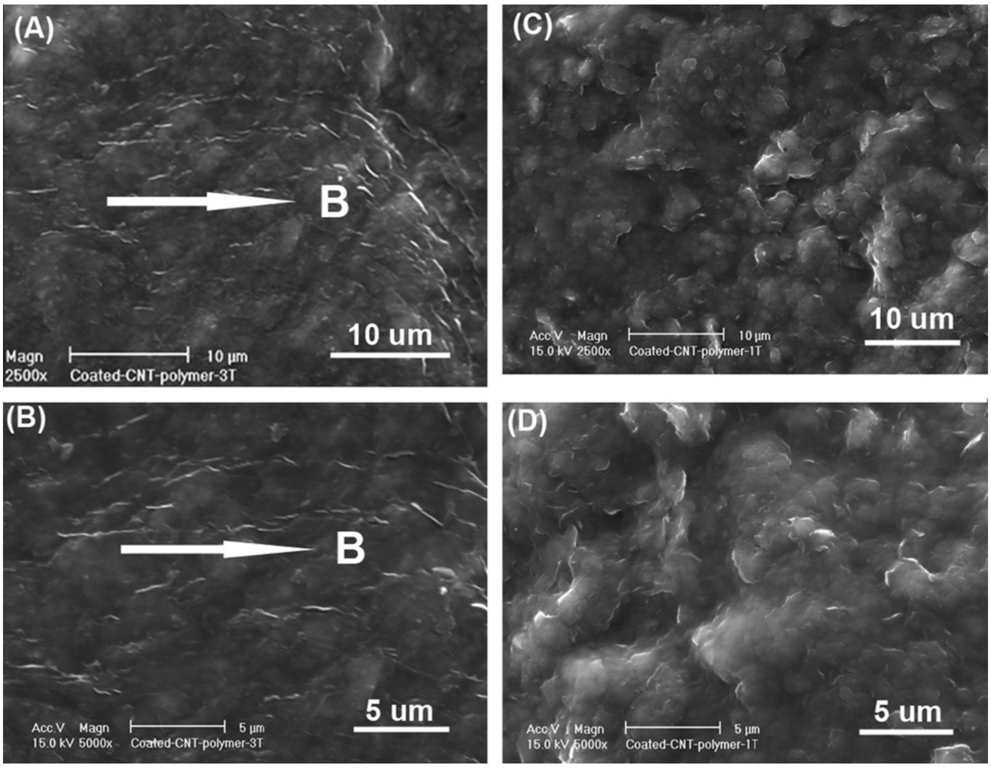

Fig. 5. (A and C) SEM micrographs showing the aligned MWCNT in the polystyrene composite sample magnetically aligned at 3 T, and (B and D) randomly oriented MWCNT in the polystyrene composite sample magnetically aligned at 1 T.

these nanotubes has a mean value : $\langle M \rangle = N \langle \mu \rangle$, where N is the number of nanotubes and $\langle M \rangle$ is along the long axis of the nanotube. The aspect ratio ρ is estimated to be 0.05 for an average of 2 μm long, and 100 nm diameter nanotube. This aspect ratio should result in efficient alignment under significant applied field. The Torque can be expressed as

$$T = -C\langle M \rangle B_{ext} sin\,\theta$$

where C is proportional to the number of nanotubes to be aligned and θ is the angle between applied field, B_{ext} and $\langle M \rangle$. In a viscous liquid, the torque induced by the applied field on each nanotube can be calculated based on the magnetic moment induced from the Ni/CoO coating. An average value of individual moment $\langle \mu \rangle$ maybe estimated if the coating geometry is known. The nanotube alignment mechanism can be established based on the parameters such as the nanotube aspect ratio, coating thickness and uniformity, and the strength of the applied field. The current research is focused on studying the effects of these factors on magnetic alignment of carbon nanotubes in viscous liquid.

To study the effects of aligned MWCNT on the mechanical properties of polymer composites, tensile tests were carried out. A magnetically aligned and dried sample was sectioned into several

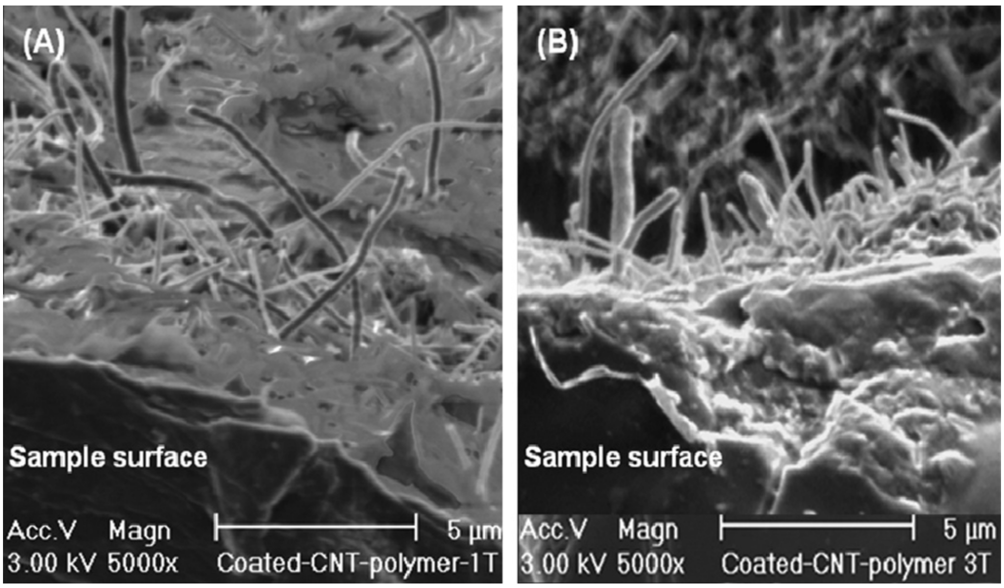

Fig. 6. (A) SEM micrographs showing randomly oriented MWCNT on the polystyrene composite sample surface magnetically aligned at 1 T, and (B) aligned MWCNT on the polystyrene composite sample surface magnetically aligned at 3 T.

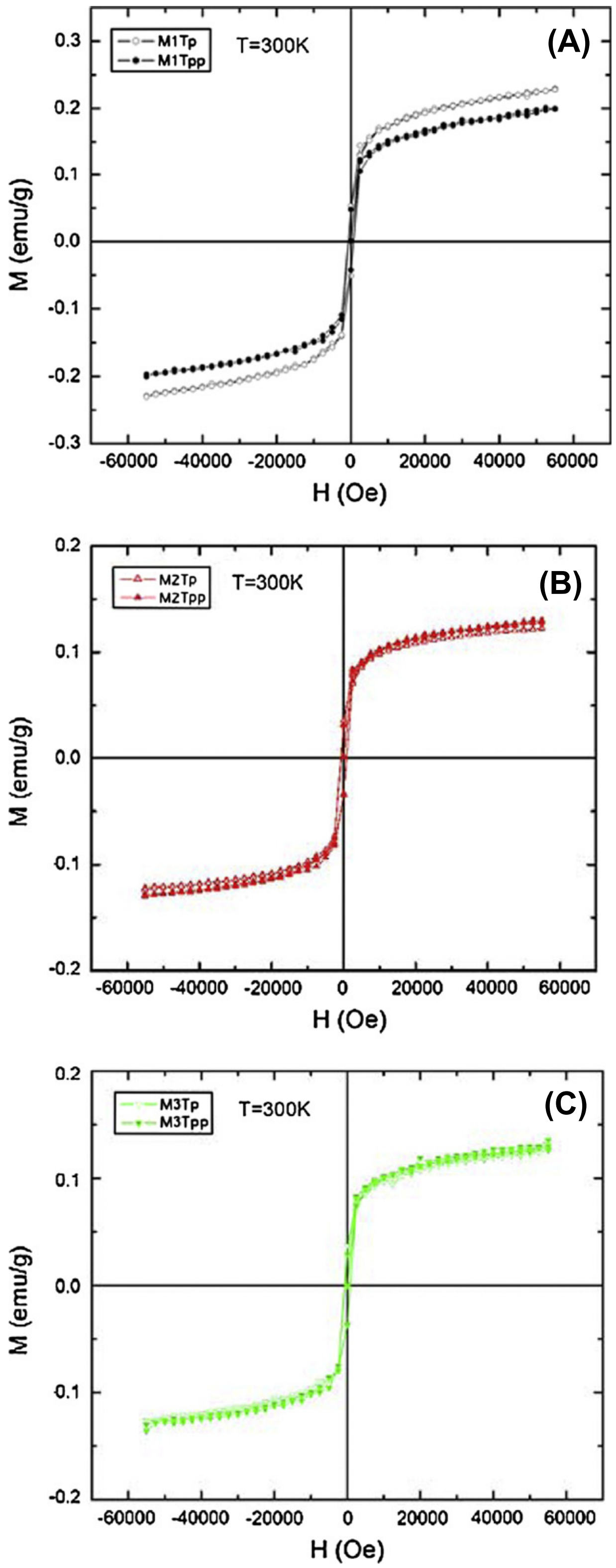

Fig. 7. Magnetization vs. applied field for samples aligned at (A) 1 T, (B) 2 T, and (C) 3 T. Note that M1Tp is the curve for field in measurements parallel to the direction of the field used to align WMCNT at 1 T and M1Tpp is the curve for field in measurements perpendicular to the direction of the field of alignment at 1 T. The similar labeling of the curves is used for the 2 T and 3 T samples (for instance of the 3 T sample: M3Tp and M3Tpp), respectively.

pieces of $40 \times 6 \times 0.4\ mm^3$ dimensions. The tensile tests were conducted in the fashion that the stress was applied in two directions: one parallel and one perpendicular to the direction of the applied field, or MWCNT alignment. Fig. 8A shows the tensile strength as a function of the applied magnetic field for both directions. At low field of 1 T, the MWCNT are still randomly oriented as shown in Fig. 4B. Therefore the tensile strengths in both directions are not of great differences indicating a more homogeneous microstructure. However, one can see a more pronounced anisotropy as the applied field increases, reaching a maximum at 2 T. For instance, this difference has increased from 9.45 MPa to 14.68 MPa at 2 T resulting in a ratio of 1.55. At 3 T, the tensile strength has increased from 14.51 MPa to 21.86 MPa, a significant increase in mechanical strength. But the anisotropy ratio is somewhat lower (1.51). At 5 T, this ratio is even smaller at 1.32. The anisotropy ratio as a function of applied magnetic field is shown in Fig. 8B.

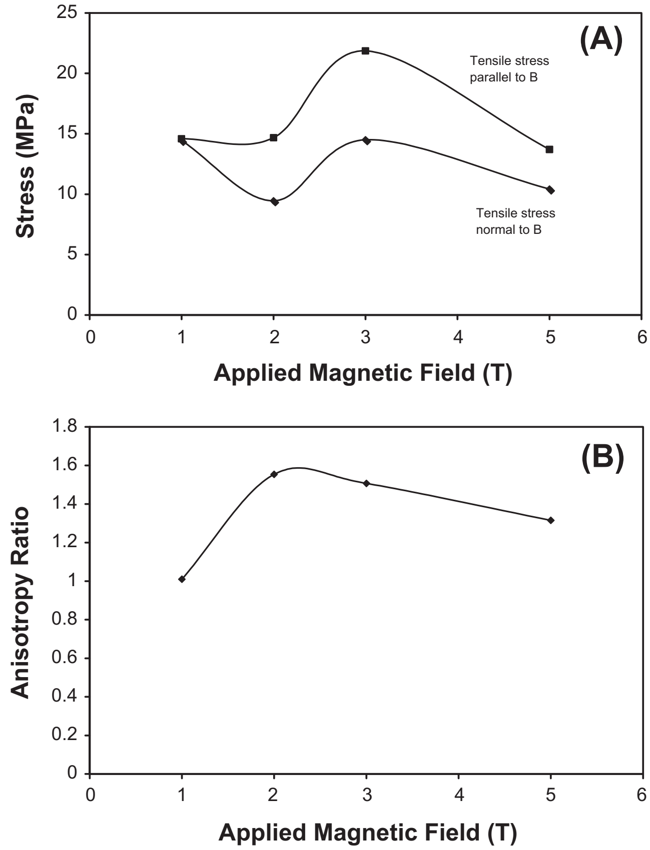

Fig. 8. (A) Tensile strength vs. applied magnetic field for both stress directions, and (B) anisotropy ratio vs. applied field.

Note that the same MWCNT alignment experiments were also carried out at various fields for those original nanotubes without surface Ni/CoO coating. This implies that the MWCNT may not orient themselves in the field direction as a result of their weakly diamagnetic behaviors. An original nanotube composite sample without Ni/CoO coating was magnetically aligned at 3 T. The tensile tests result in a horizontal strength of 14.58 MPa and a vertical strength of 14.59 MPa, respectively. At 5 T, the horizontal strength is 14.03 MPa and the vertical strength is 14.86 MPa, indicating randomness of MWCNT in the composite. These data clearly indicate that there is no MWCNT alignment in the original samples without Ni/CoO coating. Thus, it is clearly evident that coating of MWCNT with magnetic species would be essential in the magnetic alignment experiments.

4. Summary

In this study, MWCNT have been coated with ferromagnetic NiO and CoO for the purpose of magnetic alignment in the polystyrene matrix. By controlling the orientation of MWCNT, the mechanical properties of the composite can be effectively enhanced. Both TEM and SEM investigations have shown quite uniform coating of NiO and CoO on the MWCNT surfaces. The coated NiO and CoO assume nanoparticles on the nanotube surfaces, resulting in a superparamagnetic behavior, which is essential for magnetic alignment. By subjecting the viscous liquid of the MWCNT/polystyrene mixture in the magnetic field up to 5 T, the nanotubes have been found to respond to the external field by arranging themselves in the field direction. This has been verified by both SEM and TEM experiments. Furthermore, the mechanical tensile tests of the nanocomposites have shown pronounced anisotropy in tensile strength, particularly at high field, that is consistent with the microscopic observations. In sharp contrast, no anisotropy has been found in the composite sample without Ni/CoO coating, even under a high field of 3 T. These results have shown strong evidence that MWCNT can be effectively magnetically aligned in polymer composites in a bulk fashion. This unique approach presents great advantages over the conventional mechanical shear method, and potential practical applications.

Acknowledgments

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