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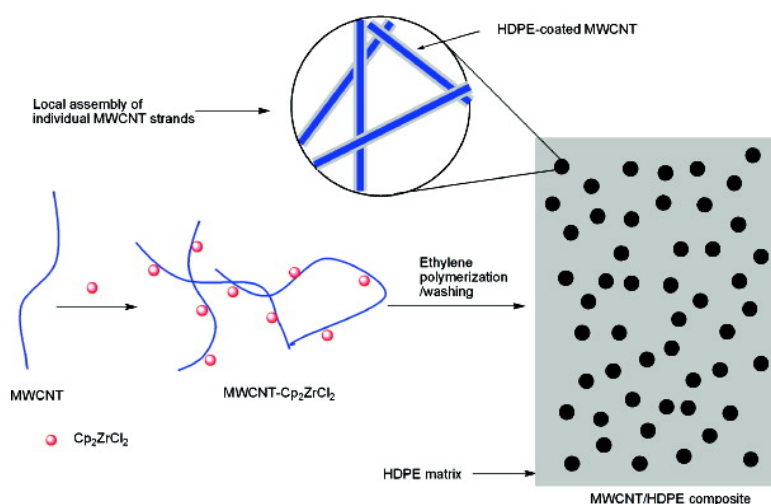
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Pristine Multiwalled Carbon Nanotube/Polyethylene Nanocomposites by Immobilized Catalysts

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In this work, we achieved the production of pristine multiwalled carbon nanotube (MWCNT)/polyethylene (PE) composites composed of uniformly dispersed, PE-coated MWCNT strands, by the in situ polymerization of ethylene with Cp_2ZrCl_2 immobilized onto the sidewalls of pristine MWCNTs as a catalyst. The prepared composites showed a highly increased Young's modulus (359%) as compared to homopolyethylene, due to well-dispersed pristine MWCNTs in the PE matrices. Electronic interactions and binding modes between zirconocenes and CNTs were investigated by theoretical and experimental methods, and both methods indicated that the sidewalls of CNTs could form a coordination bond with the positively charged active species and act as a ligand with strong electron donation.

Introduction

Pristine carbon nanotubes (CNTs), without any physical or chemical treatments, show excellent mechanical, thermal, and electrical properties.^{1–12} These unique properties of CNTs are generally not maintained in many applications including CNT-based composites because CNTs easily aggregate into bundles due to multiple van der Waals forces and π – π interactions. The aggregation causes a decrease or loss of the unique properties of individual CNT strands. In this respect, various methods for dispersing individual CNT strands in matrices intensively have been investigated in the area of CNT-based composites. Generally, shortened or covalently functionalized CNTs are well-dispersed in various solutions and polymer matrices and show reasonable me-

chanical, thermal, and electrical properties.^{13–19} However, modified CNTs are deformed structures, and consequently, the unique properties of pristine CNTs would be deteriorated. Other methods have been proposed, including ultrasonication, solution mixing of a suspension of CNTs in dissolved polymers, mechanical blending of CNTs and melted polymers, and in situ polymerization of monomers with CNTs.^{20–23} Although blending and in situ polymerization methods could maintain the unique structure of CNTs, these methods usually yield a less uniform dispersion of individual CNT strands in the polymer matrices than the methods with modified CNTs. Therefore, it is a formidable challenge to maintain the unique properties of pristine CNTs and to achieve uniform dispersion of individual CNT strands simultaneously. In this paper, we report a simple preparation of pristine multiwalled CNT (MWCNT)/polyethylene (PE) composites with greatly enhanced mechanical properties by using a Cp_2ZrCl_2 catalyst immobilized onto pristine MWCNTs: for example, the enhancements of Young's modulus were 359

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- (1) Iijima, S. *Nature (London, U.K.)* **1991**, *354*, 56.
- (2) Ajayan, P. M.; Stephan, O.; Colliex, C.; Trauth, D. *Science (Washington, DC, U.S.)* **1994**, *265*, 1212.
- (3) Yu, M.-F.; Lourie, O.; Dyer, M. J.; Moloni, K.; Kelly, T. F.; Ruoff, R. S. *Science (Washington, DC, U.S.)* **2000**, *287*, 640.
- (4) Ajayan, P. M. *Chem. Rev.* **1999**, *99*, 1787.
- (5) Thostenson, E. T.; Ren, Z.; Chou, T.-W. *Compos. Sci. Technol.* **2001**, *61*, 1899.
- (6) Dai, H. *Acc. Chem. Res.* **2002**, *35*, 1035.
- (7) Ouyang, M.; Huang, J. L.; Lieber, C. M. *Acc. Chem. Res.* **2002**, *35*, 1018.
- (8) Harris, P. *Int. Mater. Rev.* **2004**, *49*, 31.
- (9) Shimizu, T.; Masuda, M.; Minamikawa, H. *Chem. Rev.* **2005**, *105*, 1401.
- (10) Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. *Chem. Rev.* **2006**, *106*, 1105.
- (11) Moniruzzaman, M.; Winey, K. I. *Macromolecules* **2006**, *39*, 5194.
- (12) Coleman, J. N.; Khan, U.; Gun'ko, Y. K. *Adv. Mater.* **2006**, *18*, 689.

- (13) Shaffer, M. S. P.; Windle, A. H. *Adv. Mater.* **1999**, *11*, 937.
- (14) Geng, H. Z.; Rosen, R.; Zheng, B.; Shimoda, H.; Fleming, L.; Liu, J.; Zhou, O. *Adv. Mater.* **2002**, *14*, 1387.
- (15) Blake, R.; Gun'ko, Y. K.; Coleman, J.; Cadek, M.; Fonseca, A.; Nagy, J. B.; Blau, W. J. *J. Am. Chem. Soc.* **2004**, *126*, 10226.
- (16) Gao, J.; Zhao, B.; Itkis, M. E.; Bekyarova, E.; Hu, H.; Kranak, V.; Yu, A.; Haddon, R. C. *J. Am. Chem. Soc.* **2006**, *128*, 7492.
- (17) Shofner, M. L.; Khabashesku, V. N.; Barrera, E. V. *Chem. Mater.* **2006**, *18*, 906.
- (18) Zhang, Q.; Lippits, D. R.; Rastogi, S. *Macromolecules* **2006**, *39*, 658.
- (19) Bredeau, S.; Boggioni, L.; Bertini, F.; Tritto, I.; Monteverde, F.; Alexandre, M.; Dubois, P. *Macromol. Rapid Commun.* **2007**, *28*, 822.
- (20) Haggenueller, R.; Gommans, H. H.; Rinzler, A. G.; Fischer, J. E.; Winey, K. I. *Chem. Phys. Lett.* **2000**, *330*, 219.
- (21) Tang, W.; Santare, M. H.; Advani, S. G. *Carbon* **2003**, *41*, 2779.
- (22) Zou, Y.; Feng, Y.; Wang, L.; Liu, X. *Carbon* **2004**, *42*, 271.
- (23) McNally, T.; Potschke, P.; Halley, P.; Murphy, M.; Martin, D.; Bell, S. E. J.; Brennan, G. P.; Bein, D.; Lemoine, P.; Quinn, J. P. *Polymer* **2005**, *46*, 8222.

and 281% with respect to the reference PE and mechanically blended MWCNT/PE composite, respectively. The binding mode and electronic interactions between Cp_2ZrCl_2 and MWCNT were investigated by theoretical and experimental methods.

Experimental Procedures

Preparation of MWCNT/HDPE Composites by Using an Immobilized Catalyst. Ethylene polymerization was carried out at 50 °C in a 2 L stainless steel reactor equipped with a mechanical stirrer at 7 atm of ethylene pressure. In all polymerization experiments, 1 L of *n*-hexane, primitive MAO (EURECEN AL 5100-10-Toluol from Crompton GmbH), and MWCNT- $\text{Cp}_2\text{ZrCl}_2^{35/}$ hexane slurry were added to the reactor in sequence. After 5 min of stirring for preactivation, the reactor was charged by ethylene with a program to calculate total ethylene consumption by the determination of accumulated ethylene flow. When the amount of total ethylene consumption reached the predetermined ratios of polymers and MWCNTs (10–15 nm diameter, from ILJIN Nanotech), polymerization was terminated by removing ethylene gas from the reaction mixture and quenching with a small volume of acidified ethanol. After quenching of polymerization, the reaction vessel was washed throughout, and the composite powders were collected. The precipitated MWCNT/HDPE composites were collected by filtration, washed with ethanol, and dried in a vacuum oven at 70 °C for 12 h. The exact amounts of the composites were determined by weighing the dried composites. The resulting composite powders weighed 90–100 g, and the amount of the residual powders that were not washed out and remained in the reaction vessel was very small, typically less than several tens of milligrams.

Preparation of MWCNT/HDPE Composites by Mixing HDPE and MWCNTs. We calculated the amounts of HDPE and pristine MWCNTs required for the formation of mechanically blended composites that had the same wt % MWCNTs and same weight scale as those of composites formed by using the immobilized catalysts and carefully weighed HDPE and MWCNTs. HDPE and pristine MWCNTs in *n*-hexane with predetermined ratios of HDPE and pristine MWCNTs were mixed by mechanical stirring for 2 h in a 2 L stainless steel reactor. After mixing, the precipitated polymers were collected by filtration, washed with ethanol, and dried in a vacuum oven at 70 °C for 12 h.

Measurement of Mechanical Properties. The samples were produced by melting at 210 °C and 6 atm for 10 min and pressing at 140 atm for 5 min. The resulting samples were then punched by the molds, followed by annealing for 1 day at 23 °C and 50% humidity. The samples were prepared and investigated as standard tests [American Society for Testing and Materials D792 (density), D638 (tensile test), and D790 (flexural test) and Japanese Industrial Standard K 7110 (IZOD impact test)]. Five pieces of the samples were used for the tensile and flexural tests and three pieces of the samples for the IZOD impact test. The measured values were averaged. Young's modulus was automatically determined as the maximum slope of stress vs strain at the elastic region. The value of ultimate strength, which was the maximum value of stress in the tensile test, was the same as the value of yield strength that was determined as the value of stress at the yield point. The tensile strength was measured as the stress at the fracture point.

Theoretical Calculations. The SIMOMM (surface integrated molecular orbital/molecular mechanics) method²⁴ was used for the

theoretical calculations of (8,0) SWCNT with zirconocenes. Two different SIMOMM models were designed: one composed of $\text{C}_{24}\text{H}_{12}$ embedded in a $\text{C}_{128}\text{H}_{16}$ cluster of (8,0) SWCNT with zirconocenes within a quantum region and the other composed of $\text{C}_{54}\text{H}_{18}$ embedded in a $\text{C}_{128}\text{H}_{16}$ cluster of (8,0) SWCNT with zirconocenes within a quantum region. MM3²⁵ parameters were used for the molecular mechanics optimization portion of the computations. Geometry optimizations were performed by using a restricted Hartree–Fock (RHF) level of theory with the 3-21G standard basis set.²⁶ To improve the energetics of the optimized structures and fulfill the Mulliken population analysis, single-point calculations were carried out via density functional theory (DFT), employing Becke's three-parameter hybrid exchange functional combined with the Lee, Yang, and Parr correlation functional (B3LYP),²⁷ in conjunction with mixed basis sets, which consisted of the SBKJC effective core potential (ECP) and its valence basis set²⁸ for only Zr and the all-electron 6-31G(d) standard basis set²⁹ for all other atoms. All calculations were achieved with the general atomic and molecular electronic structure system (GAMESS) electronic structure program.³⁰

CNT Field-Effect Transistor (CNTFET) Experiment. CNT-FET was fabricated on a 500 nm thick SiO_2 dielectric layer over a degenerately p-doped silicon substrate. SWCNTs synthesized by the HiPCO process were dispersed in 1,2-dichloroethane by ultrasonication. The SWCNT solution was spun on the SiO_2 substrate, and individual SWCNTs were located using atomic force microscopy (AFM). The 12 nm thick Pd source/drain electrodes were defined over a SWCNT ($d \sim 1.5$ nm) by e-beam lithography. The channel length of the CNTFET was 1.2 μm . Measurements were performed in air with a bias voltage V_{DS} of 0.2 V. The first measurement was obtained after immersion in the Cp_2ZrCl_2 solution for 10 min and washing with toluene. After the first measurement, the substrate was immersed in the Cp_2ZrCl_2 solution for 1 h, and the second measurement was performed without washing.

Instruments. Melting points of PE were characterized using a differential scanning calorimeter (TADSC2910, PerkinElmer). Molecular weights of PE extracted by trichlorobenzene were determined by gel permeation chromatography (PL-GPC220, Polymer Laboratories). The field emission scanning electron microscopy (FE-SEM) images were obtained by Sirion 400 (FEI Co). The mechanical properties were measured by Instron 4466 for tensile tests, Instron 6022 for flexural tests, Mirage SD-120L for density tests, and Toyoseiki CAT No. 612 for IZOD impact strength.

Results and Discussion

Preparation of MWCNT/PE Composites. We prepared the composites by adsorbing a metallocene catalyst, Cp_2ZrCl_2 , onto pristine MWCNTs and polymerizing a

(24) Shoemaker, J. R.; Burgraff, L. W.; Gordon, M. S. *J. Phys. Chem. A* **1999**, *103*, 3245.

- (25) (a) Allinger, N. L.; Yuh, Y. H.; Lii, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 8551. (b) Lii, J. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8566. (c) Lii, J. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8576.
- (26) (a) Binkley, S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1983**, *104*, 2797.
- (27) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (28) (a) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026. (b) Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, *98*, 5555.
- (29) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
- (30) Schmidt, M. W.; Balbridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comput. Chem.* **1993**, *14*, 1347–1363.

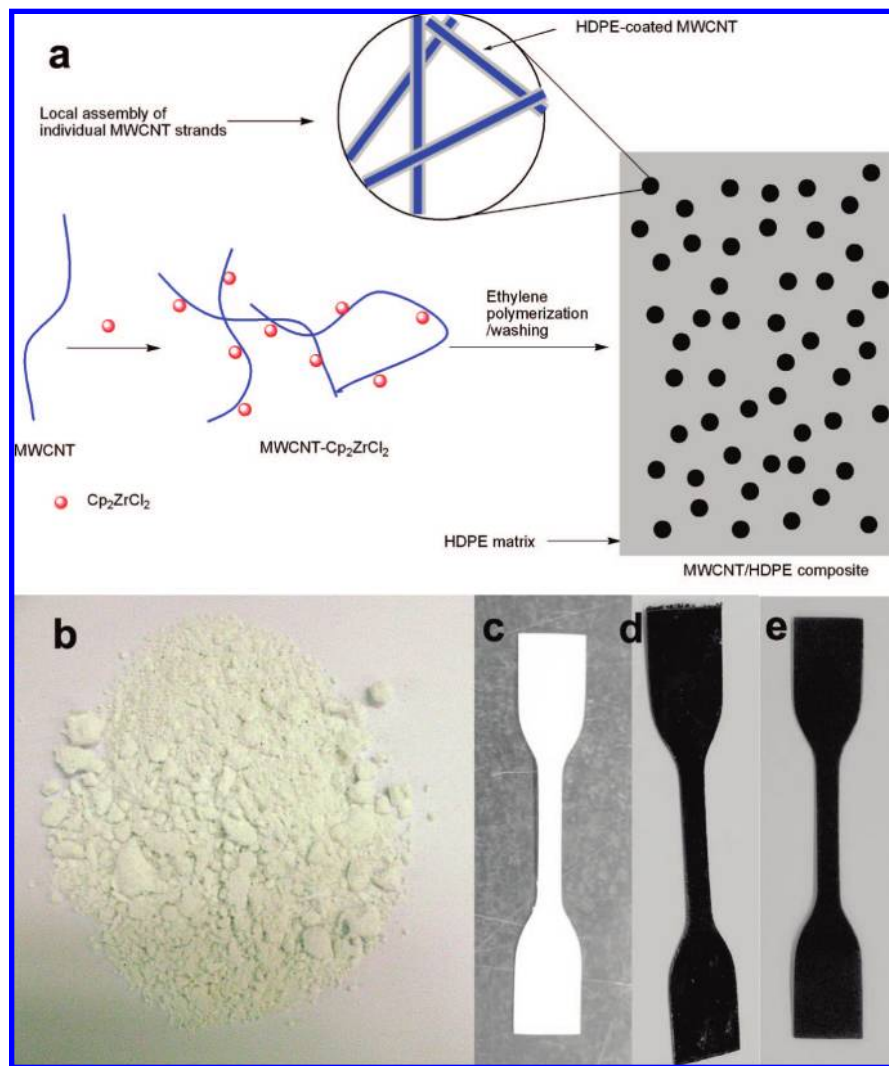


Figure 1. Synthetic procedure for the formation of pristine MWCNT/HDPE composites and images of composite and reference samples. (a) Pristine MWCNT/HDPE composites were obtained by ethylene polymerization using Cp_2ZrCl_2 immobilized onto the sidewalls of MWCNTs as a catalyst. The resulting composites were composed of well-dispersed local assemblies of individual MWCNT strands that were slightly interlocked. (b) Dried powder sample of the composite. (c) Specimen of **ref** for tensile test. (d) Specimen of **comp-1** for tensile test. (e) Specimen of **m-comp-1** for tensile test.

monomer, ethylene (Figure 1a). Physisorption of chemical species onto the graphitic surface of CNTs by π - π stacking or van der Waals interactions is a useful method for the noncovalent functionalization of CNTs,^{31–34} and we recently reported that inorganic complexes containing the cyclopentadienyl (Cp) group also could be adsorbed onto the sidewalls of pristine MWCNTs via the Cp group.³⁵ To produce CNT/polyolefin composites, we chose Cp_2ZrCl_2 , having two Cp groups, as an inorganic catalyst in this work because Cp_2ZrCl_2 was widely used as a catalyst for olefin polymerization.^{36,37} Among polyolefins, PE was chosen as a model polymer for this work; PE is one of the most important and

commercially valuable polymer materials with worldwide markets because of its high impact strength, excellent chemical resistance, good durability, and abrasive wear resistance.³⁸ However, the aggregation tendency of CNTs makes it practically difficult to obtain the uniform dispersion of individual CNTs in hydrophobic and nonpolar PE matrices.

We obtained ~ 100 g of pristine MWCNT/PE composites as grayish white powders (Figure 1b) by simply stirring a mixture of Cp_2ZrCl_2 and pristine MWCNTs—to form a complex of Cp_2ZrCl_2 and MWCNTs ($\text{MWCNT-Cp}_2\text{ZrCl}_2$)—and subsequently employing the standard conditions for ethylene polymerization. Three composite samples with different CNT contents were prepared: **comp-1** (1.25 wt %), **comp-2** (2.22 wt %), and **comp-3** (4.11 wt %). The molecular weights were 538 000, 341 000, and 542 000, and the melting temperatures (T_m) were 135.6, 134.1, and 132.7

(31) Sun, Y. P.; Fu, K.; Lin, Y.; Huang, W. *Acc. Chem. Res.* **2002**, *35*, 1096.

(32) Zhang, J.; Lee, J. K.; Wu, Y.; Murray, R. W. *Nano Lett.* **2003**, *3*, 403.

(33) Mickelson, E. T.; Chiang, I. W.; Zimmerman, J. L.; Boul, P. J.; Lozano, J.; Liu, J.; Smalley, R. E.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem. B* **1999**, *103*, 4318.

(34) Chen, R. J.; Zhang, Y.; Wang, D.; Dai, H. *J. Am. Chem. Soc.* **2001**, *123*, 3838.

(35) Park, S.; Yoon, S. W.; Lee, K.-B.; Kim, D. J.; Jung, Y. H.; Do, Y.; Paik, H.-j.; Choi, I. S. *Macromol. Rapid Commun.* **2006**, *27*, 47.

(36) Alt, H. G.; Koppl, A. *J. Am. Chem. Soc.* **2000**, *100*, 1205.

(37) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *J. Am. Chem. Soc.* **2000**, *100*, 1253.

(38) Vasile, C. *Handbook of Polyolefins*. Marcel Dekker, Inc.: New York, 2000.

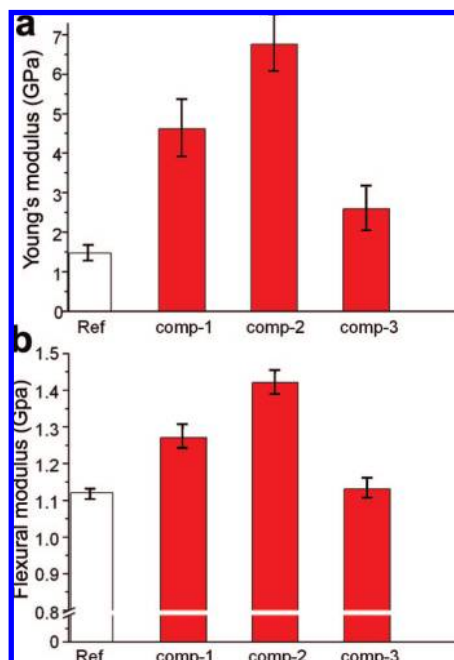


Figure 2. (a) Graph of Young's modulus and (b) graph of flexural modulus.

Table 1. Mechanical Properties of Composite and Reference Samples

| properties | comp-1 | comp-2 | comp-3 | ref |
|-----------------------------------|-------------|-------------|-------------|-------------|
| wt % MWCNT | 1.25 | 2.22 | 4.11 | |
| Young's modulus (GPa) | 4.61 ± 1.44 | 6.75 ± 1.51 | 2.58 ± 1.16 | 1.47 ± 0.31 |
| yield strength (MPa) ^a | 23.3 ± 0.4 | 24.6 ± 0.3 | 23.3 ± 0.4 | 22.3 ± 0.2 |
| elongation (%) | 320 ± 39 | 77 ± 31 | 44 ± 22 | 709 ± 45 |
| flexural modulus (GPa) | 1.27 ± 0.06 | 1.42 ± 0.07 | 1.13 ± 0.05 | 1.12 ± 0.01 |
| density (g/mL) | 0.962 | 0.977 | 0.987 | 0.943 |

^a Yield strength: stress at the yield point.

°C, respectively. The T_m range of 132–135 °C indicated that the prepared PEs were HDPE.

Mechanical Properties of MWCNT/PE Composites. For measurements of mechanical properties, the black composite specimens and white specimens of a homo-HDPE sample (**ref**: $M_w = 456\,000$ and $T_m = 134.7$ °C) were fabricated by melting at 210 °C and pressing at 140 atm (Figure 1c–e). Young's modulus, one of the most important mechanical properties concerning the hardness of materials, was found to be greatly enhanced by the formation of the composites. For example, Young's modulus of **comp-2** was measured to be 6.75 GPa (Figure 2a), which was a 359% enhanced value as compared to that of **ref** (1.47 GPa) (Table 1). As a comparison, we also fabricated other composite samples (**m-comp-1**, **-2**, and **-3**) with the same wt % MWCNTs as **comp-1**, **-2**, and **-3**, by mechanical blending of HDPE and pristine MWCNTs (Table 2). Young's modulus of **m-comp-2**, having 2.22 wt % MWCNTs, was 1.77 GPa (20% enhancement as compared to that of **ref**). The enhancement of **comp-2** was, therefore, 18 times higher than that of **m-comp-2**.

We observed the effect of wt % MWCNTs on mechanical properties. Young's modulus of the **comp** samples was much higher than those of the **ref** and **m-comp** samples for all the three **comp** samples prepared. Young's modulus of the **comp**

Table 2. Properties of m-comp Samples

| properties | m-comp-1 | m-comp-2 | m-comp-3 |
|------------------------|-------------|-------------|-------------|
| wt % MWCNT | 1.25 | 2.22 | 4.11 |
| Young's modulus (GPa) | 1.74 ± 0.50 | 1.77 ± 0.35 | 2.10 ± 1.42 |
| yield strength (MPa) | 23.1 ± 0.2 | 22.2 ± 0.1 | 22.7 ± 0.3 |
| elongation (%) | 79 ± 20 | 77 ± 22 | 51 ± 7 |
| flexural modulus (GPa) | 0.97 ± 0.03 | 1.03 ± 0.03 | 0.90 ± 0.01 |
| density (g/mL) | 0.946 | 0.949 | 0.942 |

samples was higher than that of **ref** by over 3.14 GPa (for **comp-1**), 5.28 GPa (for **comp-2**), and 1.11 GPa (for **comp-3**); the 2.22 wt % incorporation of MWCNTs into the PE matrix gave the highest enhancement in our system. On the other hand, Young's modulus of the **m-comp** samples was slightly higher (0.27–0.63 GPa) than that of the **ref** sample for all wt % MWCNTs. The yield strength of the **comp** and **m-comp** samples was comparable to that of **ref** (Tables 1 and 2).

The flexural modulus was determined at a load of 0.11 kg. All the samples were not broken, indicating no significant change of flexibility after incorporation of MWCNTs as a filler. The flexural modulus of the **comp** samples also was higher than those of the **ref** and **m-comp** samples for all wt % MWCNTs. For example, the flexural modulus of **comp-2** (1.42 GPa) was higher than that of **ref** by 0.3 GPa. In contrast, the flexural modulus of the **m-comp** samples was lower than that of **ref** (by 0.09–0.22 GPa). The 5 mm thick samples of **ref**, **comp-1**, and **comp-2** were not broken by tests of IZOD impact strength at 23 °C. The **ref** sample showed a flexible behavior of typical PE samples, and the incorporation of MWCNTs as a filler into HDPE did not change the brittleness of the samples.

FE-SEM Images. To reveal the reasons for the high enhancement in the mechanical properties of the **comp** samples, we first investigated dispersion characteristics of pristine MWCNTs in HDPE matrices. We scanned the 1 mm thick composite samples of **comp-1** and **m-comp-1** (Figure 3a,b). The scanned image of the **comp-1** sample showed a uniform black color, indicating well-dispersed MWCNTs in the HDPE matrices. In contrast, the scanned image of the **m-comp-1** sample, containing the same wt % MWCNTs as **comp-1**, showed scattered black spots presumably induced by the aggregation of MWCNTs in addition to the white areas of HDPE. To obtain more detailed information on the dispersion of MWCNTs and the local structure of the composites, we used FE-SEM. Two **comp-2** samples were

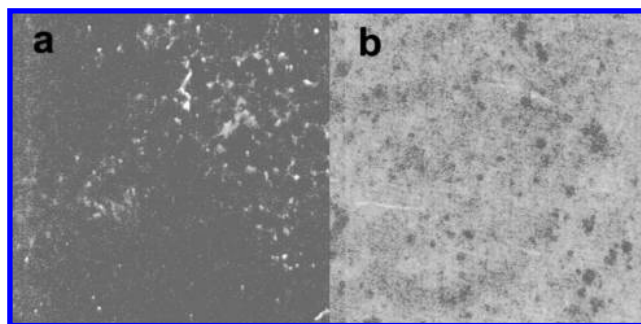


Figure 3. Scanned images of composite samples (thickness: 1 mm). (a) Scanned image of **comp-1** (50 mm × 50 mm) and (b) scanned image of **m-comp-1** (50 mm × 50 mm).

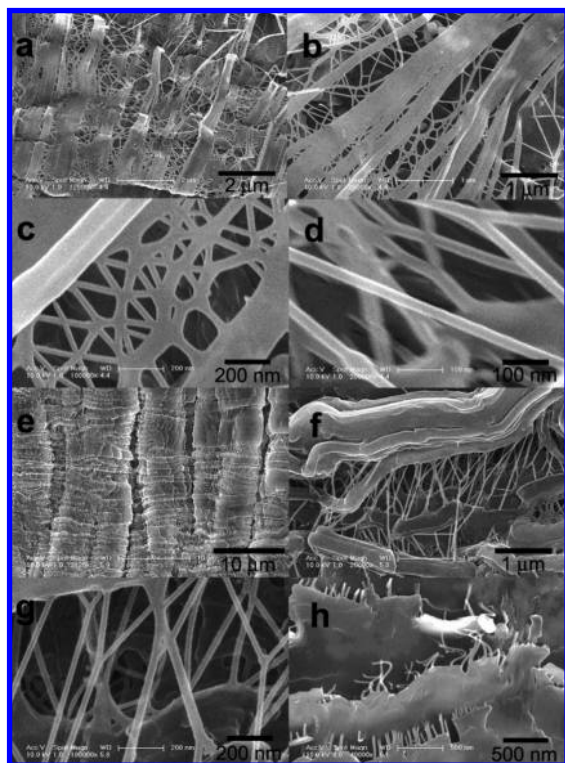


Figure 4. FE-SEM images of **comp-2**. (a–d) Images of cross-sections of broken samples at different magnifications. (e–g) Images of cross-sections of samples elongated and fractured by tensile tests at different magnifications. (h) Image of the surface of samples elongated and fractured by tensile tests.

used for the FE-SEM characterizations of the surfaces and cross-sections of the composites: the **comp-2** sample broken at a low temperatures and the **comp-2** sample elongated and fractured by tensile tests (Figure 4). The FE-SEM images showed well-dispersed local assemblies (not bundles) of MWCNTs in the HDPE matrices. The local assemblies of MWCNTs were composed of individual MWCNT strands that slightly interlocked with one another (Figure 4b,c). The diameter of the MWCNT strands was ~ 25 – 30 nm (the diameter of the used pristine MWCNTs was 10 – 15 nm), indicating the presence of individual MWCNT strands that were coated with HDPE (Figure 4d). As a comparison, the FE-SEM images of the cross-section of **m-comp-2**, possessing slightly enhanced moduli, showed aggregated MWCNT bundles (Figure 5b–d).

In our polymerization system, a vacant site of Zr, for monomer insertion and chain growth of PE, was generated by the reaction of Cl groups with methylalumoxane (MAO). The bonds between Zr and Cp groups, therefore, remained intact during polymerization, and PE was continuously grown from the Zr center immobilized onto the sidewalls of individual MWCNT strands.^{35–37} The grown PE would make gaps between the MWCNT strands in aggregated MWCNT bundles. As the PE chains were longer, the gaps would be bigger. At the same time, the grown PE would wrap the individual MWCNTs, on which the active centers were located, due to spatial proximity between a grown PE chain from the active center and a MWCNT strand containing the active site. The resulting PE-coated MWCNT strands finally lost the aggregation property of MWCNTs because the

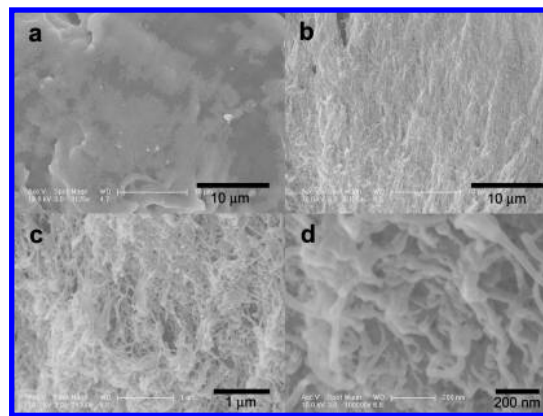


Figure 5. Cross-sectional FE-SEM images. (a) Image of **ref** and (b–d) images of **m-comp-2** at different magnifications.

sidewalls of MWCNTs were covered by PE, resulting in well-dispersed individual PE-coated MWCNT strands in the HDPE matrices and an increased contact area between polymer matrices and MWCNTs. One of the load transfer mechanisms^{39,40} for the CNT-based polymer composites is load transfer through interfacial shear stress between polymers and sidewalls of CNTs. Therefore, we believe that the increased interfacial surface areas in our system could be an important factor in the observed enhancement of the mechanical properties.

The FE-SEM images of the cross-section of the **comp-2** sample broken at low temperatures (Figure 4a–d) showed the local assemblies of randomly oriented MWCNT strands and HDPE matrices cross-linked by MWCNTs. After tensile loading, the MWCNT strands were perpendicularly aligned to the cracking direction of HDPE and cross-linked between the HDPE matrices to transfer the applied force (Figure 4h). The twisted and interlocked MWCNT strands in the local assemblies were broken down to individual MWCNT strands, producing a reinforcing effect of mechanical properties (Figures 4e–h). This breaking-down phenomenon from the aggregated bundles of MWCNTs to the individual MWCNT strands is known to be one of the reinforcing mechanisms in the tensile test.^{39,40} Taken together, the presence of local assemblies of individual MWCNT strands, which were slightly interlocked, and the well-dispersed local assemblies in the HDPE matrices were important factors in the reinforcement of mechanical properties.

The density of **ref** was 0.943 , which is a typical value of HDPE (0.941 – 0.967).³⁸ The density of the **m-comp** samples was similar to that of **ref** (0.942 – 0.949) (Table 2). In contrast, the densities of **comp-1**, **-2**, and **-3** were 0.962 , 0.977 , and 0.987 , respectively (Table 1). These values are higher than those of **ref** and **m-comp** and increased with the wt % dispersed MWCNTs. Although high-density MWCNTs (1 – 2 g/cm³)⁴ were added to the HDPE matrices, the density of **m-comp** was not changed presumably because of the presence of empty spaces near self-aggregated MWCNT bundles. In contrast, MWCNTs in the **comp**

(39) Schädler, L. S.; Giannaris, S. C.; Ajayan, P. M. *Appl. Phys. Lett.* **1998**, *73*, 3842.

(40) Ajayan, P. M.; Schädler, L. S.; Giannaris, S. C.; Rubio, A. *Adv. Mater.* **2000**, *12*, 750.

Table 3. Calculation Results for Distances, Binding Energies, and Variation of Mulliken Charges of Zirconocenes and (8,0) SWCNTs

| | distance (Å) ^a | | | | | binding energy (kcal/mol) ^b | | variation of Mulliken charges (e) ^c | |
|---------------|-----------------------------------|-------|------------------------------------|-------|-------|--|------------------------------------|--|------------------------------------|
| | Cp ₂ ZrCl ₂ | | Cp ₂ Zr ⁺ Me | | | Cp ₂ ZrCl ₂ | Cp ₂ Zr ⁺ Me | Cp ₂ ZrCl ₂ | Cp ₂ Zr ⁺ Me |
| | to C | to H | to C | to H | to Zr | | | | |
| small QM size | 3.947 | 3.080 | 3.311 | 2.697 | 2.839 | 4.000 | 31.026 | −0.049 | −0.354 |
| large QM size | 3.979 | 3.065 | 3.318 | 2.638 | 2.849 | 3.385 | 31.752 | −0.042 | −0.363 |

^a Distance between (8,0) SWCNT and an atom in zirconocenes. ^b Binding energy of zirconocenes on (8,0) SWCNT. ^c Calculated by using B3LYP/6-31G*, SBKJC with respect to the separated zirconocenes and (8,0) SWCNT.

samples were uniformly dispersed as individual strands, resulting in the elimination of empty spaces in the aggregated bundles. These results also indicated well-dispersed local assemblies of MWCNTs.

Theoretical Calculations for Interactions between Zirconocenes and CNTs. We used (8,0) SWCNTs as a model for the theoretical calculations. Because the active species of Cp₂ZrCl₂-based ethylene polymerization is Cp₂Zr⁺Me, which is generated from the reaction of Cp₂ZrCl₂ (catalytic precursor) with MAO,^{41,42} binding configurations of both Cp₂ZrCl₂ and Cp₂Zr⁺Me onto the sidewalls of the CNTs were investigated by minimum energy calculations. After exhaustive attempts, only one binding configuration for each Cp₂ZrCl₂ and Cp₂Zr⁺Me was found. The shortest distance between Cp₂ZrCl₂ and sidewall of (8,0) SWCNT was ~4.0 Å, and the binding energy was ~3.4–4.0 kcal/mol (Table 3). Cp₂ZrCl₂ was adsorbed onto the sidewall of (8,0) SWCNT at the side of Cp rings by van der Waals interactions (Figure 6a). In contrast, Cp₂Zr⁺Me was calculated to interact with the sidewall of (8,0) SWCNT much more strongly: the distance from the sidewall of (8,0) SWCNT to the Zr atom of Cp₂Zr⁺Me was ~2.8 Å, and the binding energy was ~31.0–31.8 kcal/mol. From these results, it was deduced that the C=C double bonds of (8,0) SWCNT could form a coordination bond with the positively charged Zr atom in Cp₂Zr⁺Me, strongly indicating that (8,0) SWCNT could act as a ligand. In short, the binding configuration was changed from the side of the Cp ring to Zr by the strong affinity of positively charged Zr to electron-rich CNTs (Figure 6b). The degrees of charge transfer also were estimated by theoretical calculations. The Mulliken charge of the Cp₂ZrCl₂/(8,0) SWCNT hybrid system was compared to that of Cp₂ZrCl₂ separated from (8,0) SWCNT. The total Mulliken charges of Cp₂ZrCl₂ on (8,0) SWCNT were −0.042 to −0.049 *e* with respect to separated Cp₂ZrCl₂. In the case of the Cp₂Zr⁺Me/(8,0) SWCNT hybrid system, the direction of the total Mulliken charge transfer was the same, but the net amount was much larger (−0.354 to −0.363 *e* with respect to separated Cp₂Zr⁺Me). Therefore, the theoretical calculations indicated that CNTs strongly donate electrons to the active species, Cp₂Zr⁺Me. The theoretical results were in agreement with the experimental results: we reported the increase in the molecular weight of polyethylene when we used Cp₂ZrCl₂ adsorbed onto MWCNTs as a catalyst for ethylene polymerization.³⁵ The molecular weight was increased from 300 000 (in the free

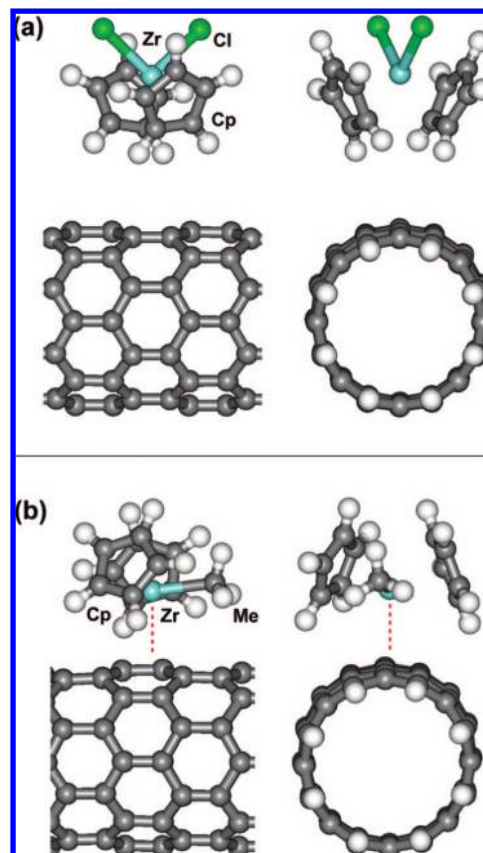


Figure 6. (a) Binding modes between Cp₂ZrCl₂ and sidewall of CNTs. (b) Binding modes between Cp₂Zr⁺Me and sidewall of CNTs.

Cp₂ZrCl₂ system) to 1 000 000 (in the Cp₂ZrCl₂/MWCNT hybrid system). Generally, the molecular weight is increased by the presence of sterically bulky ligands and/or electron donating ligands around the active species.^{43,44} Therefore, we believe that the increased molecular weight of PE from the Cp₂ZrCl₂/MWCNT hybrid system was induced by a strong electron donating effect and/or steric bulkiness of CNTs to Cp₂Zr⁺Me.

CNTFET Experiment for Electronic Interactions between Zirconocenes and CNTs. We also experimentally examined the electronic interactions between Cp₂ZrCl₂ and CNTs by using the CNTFET device. The device showed typical p-type behavior of Pd-contacted CNTFETs, where

(43) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205.

(44) (a) Piccolirovazzi, N.; Pino, P.; Consiglio, G.; Sironi, A.; Moret, M. *Organometallics* **1990**, *9*, 3098. (b) Nekhaeva, L. A.; Bondarenko, G. N.; Rykov, S. V.; Nekhaev, A. I.; Krentsel, B. A. *J. Organomet. Chem.* **1991**, *406*, 139. (c) Lee, I.-M.; Gauthier, W. J.; Bell, J. M.; Iyengar, B.; Collins, S. *Organometallics* **1992**, *11*, 2115. (d) Takayama, C.; Yamaguchi, Y.; Mise, T.; Suzuki, N. *J. Chem. Soc., Dalton Trans.* **2001**, 948.

(41) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed.* **1995**, *34*, 1143.

(42) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

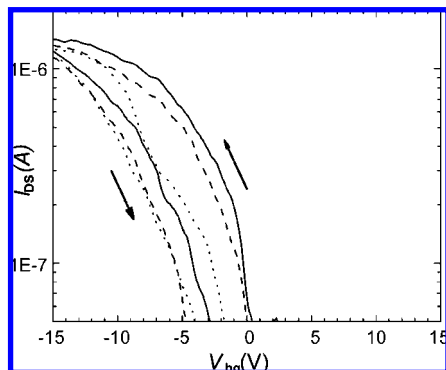


Figure 7. I_{DS} – V_{bg} curves with a bias voltage V_{DS} of 0.2 V after immersion in pure toluene (dotted curves) and in the Cp_2ZrCl_2 solution for 10 min (dashed curves) and for 1 h (solid curves). The curves are averaged results from three V_{bg} sweeps for each sample treatment stage. The arrows indicate a V_{bg} sweep.

the device was turned on at gate voltages below a certain threshold value V_{th} .⁴⁵ The drain current modulations by backgate voltage sweeps are given in Figure 7. The gate voltage responses of the device exhibited advancing hysteresis caused by charge trap sites on SWCNT.⁴⁶ After the sample was immersed in the Cp_2ZrCl_2 solution, the hysteresis increased. Averaging the results from V_{bg} sweeps in both positive and negative directions gave a V_{th} shift of ca. +1 V at this stage. After the sample was immersed in the Cp_2ZrCl_2

solution for a longer time, an additional +1 V increase of V_{th} was observed. We thought that these positive shifts of V_{th} resulted from hole-doping to the semiconducting SWCNT, which was caused by partial negative charge transfer from SWCNT to Cp_2ZrCl_2 . Therefore, the CNTFET experiment also indicated that SWCNT operated as an electron donor to the Zr species in our system.

Conclusion

We developed a simple but versatile method for producing pristine MWCNT/polyolefin composites with highly enhanced mechanical properties. As an example, we prepared MWCNT/HDPE composites, where HDPE-coated pristine MWCNT strands were well-dispersed in HDPE matrices. Both theoretical and experimental results suggested charge transfer from CNTs to Cp_2ZrCl_2 (and Cp_2Zr^+Me), and the theoretical calculations proposed that the sidewalls of CNTs could form a coordination bond with the positively charged Zr of Cp_2Zr^+Me and act as a ligand. The methods demonstrated herein can be readily adapted and incorporated into existing industrial processes, where immobilized catalysts are currently used for PE polymerization. We also believe that our bottom-up process, based on the design of catalysts at the molecular level, could be used for fabrications of other composite materials.

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(45) Javey, A.; Guo, J.; Wang, Q.; Lundstrom, M.; Dai, H. *Nature (London, U.K.)* **2003**, *424*, 654.

(46) (a) Bradley, K.; Cumings, J.; Star, A.; Gabriel, J.-C. P.; Gruner, G. *Nano Lett.* **2003**, *3*, 639. (b) Kim, W.; Javey, A.; Vermesh, O.; Wang, Q.; Li, Y.; Dai, H. *Nano Lett.* **2003**, *3*, 193.