

Surface Modification of Single-Walled Carbon Nanotubes with Polyethylene via *In Situ* Ziegler–Natta Polymerization

Xin Tong,¹ Chang Liu,¹ Hui-Ming Cheng,¹ Haichao Zhao,² Feng Yang,² Xuequan Zhang²

¹Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

²Polymer Engineering Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun 130022, China

Received 16 June 2003; accepted 5 December 2003

ABSTRACT: Single-walled carbon nanotubes (SWNTs) were modified with polyethylene (PE) prepared by *in situ* Ziegler–Natta polymerization. Because of the catalyst pretreated on the surface of the SWNTs, the ethylene was expected to polymerize there. Scanning electron microscopy images and solubility measurements showed that the surface of the SWNTs was covered with a PE layer, and a crosslink may have formed between the SWNTs and PE. When the SWNTs covered with a PE layer were mixed with commercialized PE by melt blending, the resulting compos-

ite had better mechanical properties than the composite from the SWNTs without a PE layer. The yield strength, the tensile strength and modulus, the strain at break, and the fracture energy of the modified-SWNT/PE composites were improved by 25, 15.2, 25.4, 21, and 38% in comparison with those of the raw-SWNT/PE composites. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3697–3700, 2004

Key words: Ziegler–Natta polymerization; interfaces; composites

INTRODUCTION

It is well known that polymer composites containing carbon materials, such as carbon fibers, are widely used in many fields. As a new member of the carbon group, carbon nanotubes (CNTs) have attracted more and more attention in their applications in polymer composites.^{1–3} Because CNTs have not only unique electrical properties but also excellent mechanical properties, they have great potential for the preparation of functionalized structural composites. Direct mixing and *in situ* polymerization are two major techniques used for the preparation of CNT/polymer composites. In comparison with direct mixing, *in situ* polymerization is a better way of obtaining a homogeneous dispersion and a strong interface between CNTs and a polymer matrix. Jia et al.⁴ initially reported the fabrication of CNT/poly(methyl methacrylate) (PMMA) composites by *in situ* polymerization. The results showed that a strong binding interface was formed between the CNTs and PMMA because the CNTs could be initiated by azobisisobutyronitrile to open their π bonds and participate in the PMMA polymerization.

The emergence of coordinative catalytic polymerization has led to not only a new generation of catalysts supported on organic or inorganic fillers but also a new method of producing polymerization-filled polyethylene (PE) composites. The first experiments with a $\text{TiCl}_4/\text{AlR}_3$ catalyst for ethylene polymerization onto cellulose fibers⁵ and carbon black particles⁶ were carried out in 1964 and 1965. Now the technique is widely used in PE/clay nanocomposites. Usually, PE/clay nanocomposites are prepared in one step: the ethylene is polymerized by a coordination catalyst anchored on the surface of mineral particles. This provides the clay with a PE coating and finally results in homogeneous composites with high interfacial strength. Yang et al.⁷ used montmorillonite (MMT)/ $\text{MgCl}_2/\text{TiCl}_4$ activated by $\text{Al}(\text{Et})_3$ as the catalyst for the preparation of PE/MMT nanocomposites by *in situ* coordination polymerization. The tensile strength was significantly improved because of the confinement of the nanodispersed MMT layers to the PE molecular chain and the strong interaction between the nanoscale MMT layers and PE matrix. To obtain a strong interfacial interaction between single-walled carbon nanotubes (SWNTs) and PE, we prepared SWNTs covered with PE by the same method.

Correspondence to: H.-M. Cheng (cheng@imr.ac.cn).
Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50025204 and 59920035.
Contract grant sponsor: Chinese Academy of Sciences.

EXPERIMENTAL

Materials

The SWNTs were synthesized by the hydrogen arc-discharge method with multiwalled CNTs as the start-

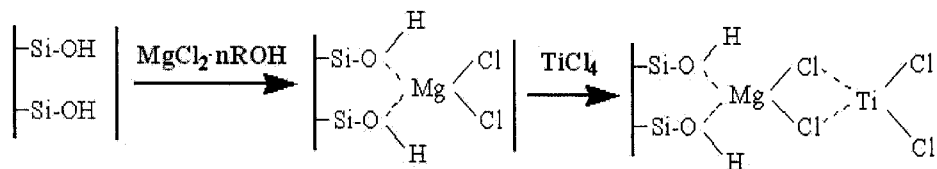


Figure 1 Scheme of the supported catalyst for the polymerization of PE.

ing material. The process is described in detail in ref. 8. The as-prepared SWNTs contained some catalyst impurities and small amounts of other carbon species. For purification, the as-prepared SWNTs were refluxed in 3M HNO_3 for 16 h. Thermogravimetric analysis and scanning electron microscopy (SEM) observations showed that most of the metal catalyst impurities were removed, although carbonaceous impurities could still be found. Hexane, used as a solvent, was refluxed and distilled over a sodium/potassium alloy before it was used. *n*-Butanol was dried over molecular sieves and distilled before it was used. The other raw materials were used as received without further purification.

Preparation of the SWNT/ MgCl_2 / TiCl_4 catalyst

A certain amount of the purified SWNTs was added to an MgCl_2 /*n*-butanol homogeneous solution under a nitrogen atmosphere at 60°C. After vigorous stirring for 2 h, excess *n*-butanol was removed by evacuation. The solid was treated with excess TiCl_4 at 60°C for 2 h, and then the suspension was filtered. The precipitate was washed with hexane 5 times, and this was followed by vacuum drying. The catalyst covering the surface of the SWNTs was thus obtained. The titanium content was analyzed with inductively coupled plasma/atomic emission spectroscopy to be 1.0 wt %.

Polymerization of ethylene

Ethylene polymerization was carried out in a glass reactor equipped with a mechanical stirrer. After alternating heating and evacuation for about 1 h, the reactor was filled with ethylene up to a pressure of 0.01 MPa. A certain amount of hexane, triisobutylaluminum, and a catalyst ($[\text{Al}]/[\text{Ti}] = 70:1$ mol/mol) were introduced into the reactor in succession. The polymerization was controlled at 50°C and at an ethylene pressure of 0.01 MPa for 1 h, and then it was terminated with acidified ethanol. The polymerization product was washed with ethanol several times and then dried *in vacuo* at 60°C for 24 h.

Preparation of the SWNT/PE composites by melt blending

To investigate the influence of the surface modification of SWNTs on the mechanical properties of

SWNT/PE composites, we prepared two kinds of SWNT/PE composites by melt blending SWNTs with and without a PE layer. The PE used for the melt blend (1055P HDPE) was supplied by Liaoyang Petrochemical Co. (China). The composite preparation process was as follows. First, the PE powder and the SWNTs were mixed via grinding in a mortar. Then, the mixture was melt-blended at 180°C in a torque rheometer at a mixer speed of 30 rpm and for a mixing time of 10 min after a stable torque was reached; all the samples were compression-molded at 180°C. The content of the SWNTs was 0.5 wt % in all composites. For the SWNTs with a PE layer, only the net weight of the SWNTs was taken into account.

Characterization

A Philip XL-30 SEM instrument (The Netherlands) was used to observe the microstructures of the samples. The thermal behavior of the samples was measured on a PerkinElmer DSC-7 differential scanning calorimeter (USA) at a scanning rate of 10°C/min in nitrogen. Tensile tests were performed at room temperature with dumbbell-shaped specimens on an Instron 1121 electronic testing machine (UK) at a cross-head speed of 50 mm/min. The average value of five specimens was taken.

RESULTS AND DISCUSSION

The key point to polymerization-filled PE composites is that the active catalyst can be anchored on the surface of the filler. Generally, the filler surface contains some OH groups, which can react with active catalysts. For example, Yang et al.⁷ reported that MMT may form a complex catalyst with MgCl_2 / TiCl_4 according to the scheme shown in Figure 1. For the purified SWNTs, their surface often contains some hydroxyl and carboxylic groups.^{9–11} Therefore, it is possible to attach the MgCl_2 / TiCl_4 catalyst to SWNTs. We used the method proposed by Yang et al. to anchor the catalyst onto the surface of the SWNTs; it was then used to polymerize the ethylene, although at this stage the reactive mechanism is not very clear. SEM images of the SWNTs before and after polymerization are shown in Figure 2. The surface of the SWNTs was covered with a PE layer after polymerization. To investigate the nature of the interaction between the

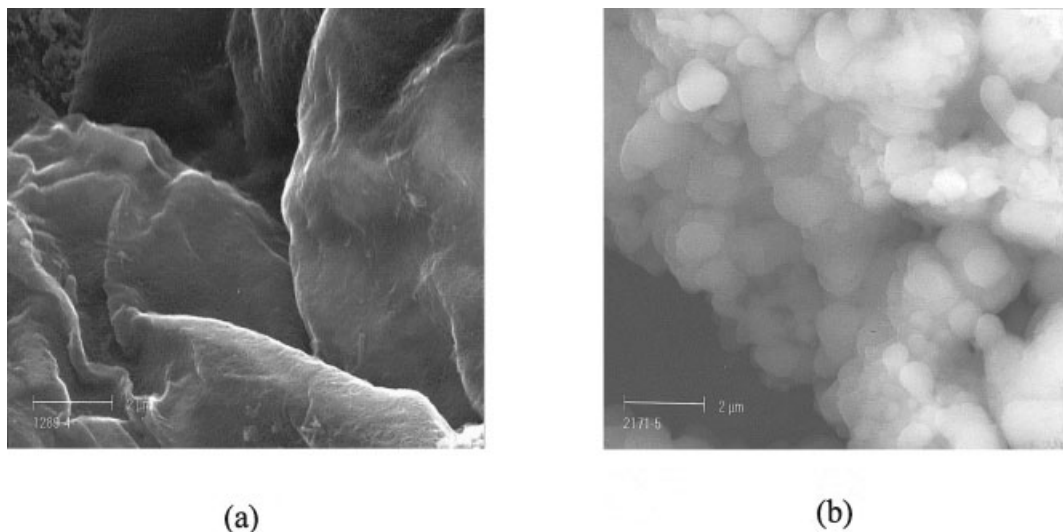


Figure 2 SEM images of SWNTs (a) before and (b) after the *in situ* polymerization of PE.

SWNTs and PE, we took solubility measurements of the SWNTs with a PE layer. After they were washed with decalin, a good solvent for PE, in an extractor for 48 h, all the soluble species were removed. If the PE was crosslinked on the surface of the SWNTs, it could not be extracted. The results showed that the weight loss of the sample was 14% after extraction. Because the content of SWNTs in the PE-covered SWNTs was only 6 wt %, most of the PE could not be extracted and remained. This showed that a strong interaction existed between the SWNTs and PE.

To investigate the influence of the surface modification of SWNTs on the mechanical properties of SWNT/PE composites, we prepared two kinds of SWNT/PE composites by melt blending SWNTs with and without a PE layer. For clarity, the composites from SWNTs without modification are called raw-SWNT/PE composites, and the composites from SWNTs with a PE layer are called modified-SWNT/PE composites. The mechanical properties of the composites are shown in Table I. All the mechanical properties of the raw-SWNT/PE composites decreased greatly in comparison with those of pure PE. This could be attributed to the agglomeration of the SWNTs and the weak interaction between the SWNTs

and the matrix. It is well known that SWNTs are difficult to disperse in any matrix because a strong van der Waals force exists among SWNT bundles. In addition, for the purified SWNTs, the surfaces were hydrophilic because of the existence of some hydroxyl and carboxylic groups, whereas the PE chain was hydrophobic; therefore, the interaction was weak between the SWNTs and PE. After the surface of the SWNTs was modified by an *in situ* polymerized PE layer, their dispersion was better than before on a macroscopic scale, although it was still not homogeneous. Meanwhile, because of the strong interaction between the *in situ* polymerized PE and SWNTs in the modified-SWNT/PE composites, the mechanical properties of the modified-SWNT/PE composites were obviously better than those of the raw-SWNT/PE composites, which were close to those of pure PE. In comparison with the raw-SWNT/PE composites, the yield strength, tensile strength, and modulus of the modified-SWNT/PE composites were improved by 25.0, 15.2, and 25.4%, respectively. Accordingly, its strain at break and fractured energy were improved by 21 and 38%, respectively. All these results showed that the modification of the SWNTs was very important to the preparation of the SWNT/PE composites. According

TABLE I
Mechanical Properties of the SWNT/PE Composites and Pure PE

Sample	Yield strength (MPa)	Strain at break (%)	Tensile strength (MPa)	Tensile modulus (MPa)	UK $\times 10^{-6}$ (J/m ²)
PE	27.0 \pm 0.5	801.4 \pm 107.3	34.1 \pm 4.9	807.5 \pm 52.5	3.77 \pm 0.96
Raw-SWNT/PE composite	22.0 \pm 1.2	769.5 \pm 68.5	28.9 \pm 2.1	638 \pm 76	3.15 \pm 0.35
Modified-SWNT/PE composite	27.5 \pm 0.6	931.3 \pm 90.5	33.3 \pm 2.5	800 \pm 38.5	4.35 \pm 0.58

UK = fracture strain energy.

to these results, the tensile strength and modulus of the modified-SWNT/PE composites were not improved over those of pure PE, although they were improved over those of the raw-SWNT/PE composites. This was due to the imperfect dispersion and relatively low content of SWNTs. In this stage, the dispersion of SWNTs in an alcohol solution was not good enough. Improving it would be helpful for evenly anchoring the catalyst on the surface of SWNTs, and this would lead to an even polymerization of PE on the surface of SWNTs and, consequently, an even dispersion of SWNTs in SWNT/PE composites. With an improvement in the interfacial interaction and dispersion and an increase in the content of SWNTs, the mechanical properties of SWNT/PE composites would be improved. Therefore, future work will be focused on the dispersion of SWNTs in alcohol solutions.

CONCLUSIONS

On the basis of the principle of polymerization-filled composites, SWNTs covered with a PE layer were prepared by *in situ* Ziegler–Natta polymerization. The solubility measurements showed that most of the PE remained on the surface of the SWNTs after they were washed with a good solvent for PE. Therefore, a

strong interaction existed between the SWNTs and the *in situ* polymerized PE. Additionally, when the SWNTs modified by the *in situ* polymerization of PE were mixed with a commercialized PE by melt blending, the mechanical properties of the resulting composites were better than those of SWNTs without modification. It was concluded that the *in situ* polymerized PE layer played an important role as an interfacial modifier.

References

1. Ajayan, P. M.; Stephan, O.; Colliex, C.; Tauth, D. *Science* 1994, 265, 1212.
2. Calvert, P. *Nature* 1999, 399, 210.
3. Ajayan, P. M.; Schadler, L. S.; Giannaris, C.; Rubio, A. *Adv Mater* 2000, 12, 750.
4. Jia, Z.; Wang, Z.; Xu, C.; Liang, J.; Wei, B.; Wu, D.; Zhu, S. *Mater Sci Eng A* 1999, 271, 395.
5. Orsino, J. A.; Herman, D. F.; Brancato, J. U.S. Pat. 3,121,698 (1964).
6. Herman, D. F.; Kurse, U.; Brancato, J. J. *J Polym Sci* 1965, 11, 75.
7. Yang, F.; Zhang, X. H.; Zhao, H. C.; Chen, B.; Huang, B. T.; Feng, Z. L. *J Appl Polym Sci* 2003, 89, 3680.
8. Zhong, R.; Cong, H.; Liu, C. *Carbon* 2002, 40, 2961.
9. Hiura, H.; Ebbesen, T. W.; Tanigaki, K. *Adv Mater* 1995, 7, 275.
10. Kuznetsova, A.; Mawhineey, D. B.; Naumenko, V.; Yates, J. T.; Liu, J.; Smalley, R. E. *Chem Phys Lett* 2000, 321, 292.
11. Mawhineey, D. B.; Naumenko, V. J.; Yates, T.; Liu, J.; Smalley, R. E. *Chem Phys Lett* 2000, 324, 213.