Preparation of a HDPE/Carbon Nanotube Composite
Sheng-Haur Yu*, Jen-Taut Yeh**, Bo-Chi Huang* and Kuo-Shien Huang*
*Department of Polymer Materials, Kun Shan University, Yung Kang, Tainan, Taiwan
**Graduate School of Polymer Engineering, National Taiwan University of Technology, Taipei, Taiwan

Online publication date: 06 December 2010

To cite this Article Yu, Sheng-Haur, Yeh, Jen-Taut, Huang, Bo-Chi and Huang, Kuo-Shien (2010) ‘Preparation of a HDPE/Carbon Nanotube Composite’, Polymer-Plastics Technology and Engineering, 49: 15, 1534 — 1539

To link to this Article: DOI: 10.1080/03602559.2010.512332
URL: http://dx.doi.org/10.1080/03602559.2010.512332

PLEASE SCROLL DOWN FOR ARTICLE
Preparation of a HDPE/Carbon Nanotube Composite

Sheng-Haur Yu1, Jen-Taut Yeh2, Bo-Chi Huang1, and Kuo-Shien Huang1
1Department of Polymer Materials, Kun Shan University, Yung Kang, Tainan, Taiwan
2Graduate School of Polymer Engineering, National Taiwan University of Technology, Taipei, Taiwan

This experiment adopted mixed acid (H2SO4:HNO3 = 3:1) to purify multi-walled carbon nanotubes, and used a silane coupling agent n-octyltriethoxysilane (OTES) to modify carbon nanotubes, respectively. Then we mixed OTES-modified carbon nanotubes (CNTs) with high-density polyethylene (HDPE) resin to make a composite. TGA analysis results revealed that as the CNTs' content increased, the Td 10 tended to rise. The amount of composite residual at 500°C also increased, as well as the composite electrical conductivity. When a concentration of 5% OTES was used to modify the CNT, the resultant composite exhibited better electrical conductivity.

Keywords Carbon nanotubes; Composite; Electrical conductivity; Silane coupling agent; Thermal stability

INTRODUCTION

Nanocomposites are presently an area of new growth in the field of composite materials. They are fabricated by dispersing prepared nanoparticles into matrix material. A nanocomposite is defined as a composite compounded by two or more nanoscale-sized solid phases that are 1–100 nm in at least one dimension[1]. The small size and quantum effects can be combined to produce excellent polymer characteristics, such as low density, corrosion resistance and processibility, revealing distinctive characteristics.

In a nanocomposite system, the addition of a small amount of nanofiller (2–10%) can greatly improve the system performance. The introduction of nanoparticles not only improves the polymer strength, rigidity, and flexibility, but also facilitates the improvement of the polymer light transmission, barrier property, thermal resistance, electrical conductivity, germicide and fungicide properties, microwave absorption, and UV resistance[2–8].

Carbon nanotubes (CNTs) have a unique electrical conductivity that can be as high as 1000–2000 S/cm, enabling the passage of excessive current density at 10⁶A/cm². When combined with a polymer, they can greatly improve the electrical conductivity of the resulting polymer composite. It has been demonstrated that CNT conductivity depends on temperature[9,10]. Thus, CNTs have many potential applications in electromagnetic shielding, overcurrent protection, electrostatic protection, electromagnetic absorption, and transducers[11–15]. In recent years, polymer/CNT composites have become a new emphasis in research[16].

Recently, many investigations have taken advantage of the superior properties of CNTs to reinforce polyolefin resin. Tong et al.[17] used an in situ synthesis method to prepare a carbon nanotube/polyethylene (CNT/PE) composite. Many researchers have also used a simple melting mix method to reinforce PE with CNT[18–24].

However, the simple mixing method of multi-wall carbon nanotubes (MWCNTs) and polymer molecules has the disadvantage that the dispersion of CNTs in the composites is a weak static equilibrium: once the material temperature rises, molecular heat movement intensifies, and CNT dispersion status is destroyed, leading to recoagulation. The resultant improvement in mechanical strength and thermal stability is therefore limited. A chemical modification to CNTs so that their surfaces carry an electrostatic charge or form functional groups to participate in a reaction (e.g., –OH or –COOH) and polymerize with monomers to change the surface structure and status, would allow them to be mixed homogenously with a substrate, thus improving the physical properties of the substrate[25].

In the present study, we mixed octyltriethoxysilane (OTES)-modified CNTs with high-density polyethylene resin (HDPE) to produce a composite and examined the resulting thermal resistance and electrical conductivity under various mixing conditions to characterize its properties and apply it to supplement other composites.

EXPERIMENTAL

Materials

Multi-walled carbon nanotubes (95%, MW carbon nanotube) with an average particle diameter of 10–40 nm were supplied by Desunnano Co., Ltd., Taiwan. Sulfuric acid, nitric acid, ammonium, and isopropanol and Dioctyl...
Methods

**Purification of Carbon Nanotube.** The SWCNTs were purified using the following method. The SWCNT (2 mg) was Soxhlet extracted with 50 ml of toluene for 6 h. After Soxhlet extraction, the nanotubes were rinsed with acetone and finally dried in the air oven at 100°C. Mixed acid (20% HNO3 and 20% H2SO4 in 1:3 V/V) was first prepared. The carbon nanotube was added to the mixed acid until full submergence, and then heated to 100°C and stirred for 40 min, respectively. The specimens were filtered and rinsed with distilled water until reaching a neutral pH, and baked at 100°C. The carbon nanotubes were labeled as C40.

**Preparation of OTES-Modified Carbon Nanotubes.** The purified carbon nanotube (C40) 1 g and 2.5 ml isopropanol, 2.5 ml 2% sulfuric acid and 2.5 ml distilled water, were mixed with various volumes (2.5, 5, 10 and 20 ml) of OTES in a 4-mouth flask, which was fastened and mounted with a stirring motor and condenser. The specimen was heated to 70°C and stirred under reflux for 120 min. The treated SWCNTs were vacuum filtered using an ultrafiltration membrane and washed repeatedly with deionized water until the washings showed no acidity. The filtered solid was dried under vacuum for 24 h at 40°C. The modified carbon nanotube was labeled as MOCn (where n = 2.5, 5, 10 or 20).

**Preparation of MOC5/HDPE Composite.** DOA (1 ml) was added to 50 g HDPE, and various concentrations (0.25, 0.5, 0.75, 1.0, or 1.5%) of MOC5 were mixed until homogeneous. The mixture was placed in a twin-screw mill to be mixed at a heater temperature range of 130–180°C to produce the MOC5/HDPE composite. The composite was placed into a hot press to press-form at 160°C. The resultant MOC5/HDPE composite was denoted as CHn, where n = 0.25, 0.5, 0.75, 1 or 1.5.

Results and Discussion

**Purification of Carbon Nanotubes**

Different CNT synthesis methods are known to yield CNTs with different types and amounts of impurities, (e.g., amorphous carbon and catalyst particles). Several strategies have already been developed over the past decade to purify CNTs without significantly damaging the structure of nanotubes. The optimum conditions reported in the literature were used. The SWCNTs were then treated with acid solution for removal of amorphous carbon.

This treatment removes the carbonaceous particles that are shelled off from the SWCNTs. The reflux treatment with sulfuric acid and functional reagents has been reported for oxidative functionalization of SWCNTs. However, such severe treatment conditions are also reported to damage the structure of nanotube walls and reduce their aspect ratio.

**SEM of Purified Carbon Nanotube.** Figure 1 shows the SEM images of carbon nanotube before and after purification.
purification. The original carbon nanotube image in Figure 1a shows that, the primary original product is carbon nanotube, but it contains excessive impurities, and carbon nanotube is encapsulated by foreign substances. The SEM images of purified carbon nanotube (C₄₀) in Figure 1b show that, acid treatment removes metal catalyst particles, amorphous carbons, and graphite fragment from carbon nanotube. Moreover, as seen in Figure 1b, carbon nanotube has a typical hollow structure, with tube diameter of dozens of nm and length of dozens of μm, entangled with each other.

**FTIR and Number of Carboxyl Groups of Purified Carbon Nanotubes.** The formation of carbon nanotube surface functional groups is due to the oxidization of foreign substances of carbon nanotube by strong acid. The erosion of carbon nanotube wall also destroys the carbon nanotube wall structure so that the carbon nanotube is broken or fractured, thus resulting in hydroxyl (-OH) and carbonyl (-COOH) groups.

Figure 2 shows the FTIR spectra of carbon nanotube after various treatment times. As seen, purified carbon tube (C₄₀) hydroxyl(-OH) peak at 3429 cm⁻¹ was improved significantly, while distinct carboxyl (-COOH) absorption peak appeared at 1730 cm⁻¹, and C-C structure peak at 1588 cm⁻¹ showed no change. The peak at 1730 cm⁻¹ is clearly assigned to the C=O stretching vibration in acid-treated SWCNT. The broad peak at ~3429 cm⁻¹ is assigned to the O-H stretching vibration while the peak in the frequency range of 1380–1430 cm⁻¹ may be due to the bending vibrations of O-H groups[27].

These observations are direct evidence for the introduction of a carboxylic acid group on the nanotubes. The degree of functionalization (a measure of the number of carboxyl groups present on the surface of the carbon nanotubes) depends on the oxidative treatment time and temperature. This indicated that treatment of H₂SO₄+HNO₃ mixed acid could make carbon nanotube surface have rich surface functional groups, and increase carbon nanotube surface activity, which is very favorable to carbon nanotube surface modification.

**FTIR of Modified Carbon Nanotube**

Figure 3 shows the FTIR spectra of purified carbon nanotube (C₄₀) after modified by OTES in various ratios. As shown in Figure 3, for OTES modified carbon nanotube, as OTES ratio increased, 2925 cm⁻¹ (C-H, >CH₂, -CH₃) absorption became stronger, and 3435 cm⁻¹ and 1553 cm⁻¹ hydroxyl(-OH) absorption intensities weakened. This is because the hydroxyl (-OH) group in purified carbon nanotube (C₄₀) reacted with OTES, which could be proved by the increasingly strong carbon tube absorption at 1107 cm⁻¹ (Si-O-C). The analysis results showed that carbon nanotube (C₄₀) was successfully modified by OTES.

**Analysis and Measurement of Composites**

**FT-IR.** The composite had a distinct absorption peak at 3430 cm⁻¹, as shown in Figure 4, because the CNTs were oxidized by strong acid to produce hydroxyl groups (-OH). Hence, a (Si-O-Si) absorption peak appeared at 1115 cm⁻¹, indicating that OTES was grated to CNTs and evenly dispersed in the HDPE.

**SEM.** Figure 5 shows an SEM micrograph of the composite. After the MWCNT was grafted with OTES coupling agent, the CNT hydrophobicity improved greatly so as to improve its affinity to HDPE. This was because OTES is hydrophobic. Thus, the MWCNT was dispersed.
easily and homogenously in organic material, and enhanced the interface bondability with HDPE substrate greatly, improving the interface repellence so that the MWCNT could be dispersed homogenously.

Electrical Conductivity. The HDPE surface resistance was greater than $1 \times 10^{17} \Omega$. However, as shown in Table 1, the addition of trace MOCn reduced the resistivity significantly due to the excellent electrical conductivity of the CNT since its amorphous structure conferred the electrical conductivity or semiconductor property, and its electrical conductivity can be 10,000 times that of copper.

Thus, the addition of 0.75% MOC5 could meet the anti-static material standard (surface resistance of $10^{12} - 10^{10} \Omega$). At 1% MOC5, it was electrostatic discharge (ESD) material (surface resistance of $10^{9} - 10^{5} \Omega$). MOC2.5 and MOC20 surface resistances were not as ideal as MOC5, probably because MOC2.5 contained less OTES so that the modified CNT could not be affined to HDPE; as a result, CNT dispersion in HDPE was worse than in MOC5 and the composite surface resistance increased. Therefore, excessive OTES-based composite, i.e., MOC20, covered the CNTs fully to lower the affinity between the CNTs and HDPE, resulting in unsatisfactory composite electrical conductivity.

TGA. Figure 6 and Table 2 show the MOC5/HDPE nanocomposite TGA graph and thermal property data, respectively. The maximal decomposition temperatures of all other composites were higher than that of HDPE, indicating an improvement in the nanocomposite thermal resistance. This was because the CNT had excellent thermal conductivity and, as shown in the FTIR spectra, the MOC5 contained Si after modification with OTES so that the CNTs were evenly mixed in HDPE.

When HDPE was mixed with various concentrations of modified CNTs (0, 0.25, 0.5, 0.75, 1 or 1.5%) to make a nanocomposite, the Td10 of composites (CHn) were 384.05, 443.09, 452.70, 454.51, 467.17, and 470.09°C, respectively, while composite residuals at 500°C were

<table>
<thead>
<tr>
<th>Sample</th>
<th>MOC2.5</th>
<th>MOC5</th>
<th>MOC20</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH0.25</td>
<td>$3.65 \times 10^{14}$</td>
<td>$6.73 \times 10^{14}$</td>
<td>$3.41 \times 10^{14}$</td>
</tr>
<tr>
<td>CH0.5</td>
<td>$3.26 \times 10^{13}$</td>
<td>$1.18 \times 10^{13}$</td>
<td>$1.17 \times 10^{14}$</td>
</tr>
<tr>
<td>CH0.75</td>
<td>$5.25 \times 10^{12}$</td>
<td>$1.61 \times 10^{11}$</td>
<td>$2.64 \times 10^{13}$</td>
</tr>
<tr>
<td>CH1.0</td>
<td>$1.39 \times 10^{12}$</td>
<td>$2.86 \times 10^{8}$</td>
<td>$5.02 \times 10^{13}$</td>
</tr>
<tr>
<td>CH1.5</td>
<td>$2.47 \times 10^{11}$</td>
<td>$9.24 \times 10^{6}$</td>
<td>$5.25 \times 10^{10}$</td>
</tr>
</tbody>
</table>

Note: HDPE surface resistivity is greater than $1 \times 10^{17} \Omega$.
increased the composite Td10, significantly improving activity also increased. When the concentration of OTES used to modify the CNTs was 5%, the composite exhibited better electrical conductivity.

CONCLUSIONS

This work used a silane coupling agent (OTES) to modify CNTs mixed with HDPE to produce composite materials. The experimental results showed that as the CNT content increased, the composite Td10 tended to rise, and the amount of composite residuals increased at 500°C. In terms of the composite electrical conductivity, as the CNT content increased, the composite electrical conductivity also increased. When the concentration of OTES used to modify the CNTs was 5%, the composite exhibited better electrical conductivity.

TABLE 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Td10 (°C)</th>
<th>Degradation rate (%/°C)</th>
<th>Residual (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>384.05</td>
<td>1.338</td>
<td>2.465</td>
</tr>
<tr>
<td>CH0.25</td>
<td>443.09</td>
<td>2.024</td>
<td>6.284</td>
</tr>
<tr>
<td>CH0.5</td>
<td>452.70</td>
<td>2.395</td>
<td>8.401</td>
</tr>
<tr>
<td>CH0.75</td>
<td>454.51</td>
<td>2.406</td>
<td>13.191</td>
</tr>
<tr>
<td>CH1</td>
<td>467.17</td>
<td>2.452</td>
<td>32.415</td>
</tr>
<tr>
<td>CH1.5</td>
<td>470.09</td>
<td>2.439</td>
<td>42.422</td>
</tr>
</tbody>
</table>

Residual at 500°C.

2.465, 6.284, 8.401, 13.191, 32.415, and 42.422%, respectively, indicating that the addition of modified CNT increased the composite Td10, significantly improving composite thermal stability.

REFERENCES


