Effects of Carbon Nanotubes on Processing Stability of Polyoxymethylene in Melt—Mixing Process

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Carbon nanotubes (CNTs) filled polyoxymethylene (POM) composites were fabricated in order to form conducting pathways at a low CNT loading. It was found that addition of CNTs would lead to a drastic degradation of POM in the melt—mixing process. The effects of CNTs on the processing stability of POM were investigated by differential scanning calorimetry and thermogravimetric analysis. The results obtained show that the degradation behavior of POM is closely related to the surface chemical properties of CNTs. The presence of carboxylic acid groups on CNT surfaces catalyzes and accelerates the degradation of POM through acidolysis and hydrolysis, and results in a significant decrease in the processing stability of POM. However, graphitized CNT—POM mixtures show high processing stability due to the effective removal of functional groups on CNT surfaces during the graphitization process. Graphitized CNT/POM composites possess good electrical properties and a low percolation threshold of ca. 0.5 wt %, so they have a large potential to be applied as electronic components, self-controlled heaters, overcurrent protectors, and other functional devices.

1. Introduction

Carbon nanotubes (CNTs) exhibit extraordinary physical and mechanical properties due to their unique hollow structures consisting of concentric graphene cylinders, and they have potential applications in mechanical reinforcement, electron transport, energy storage, and so on. As far as the practical applications of CNTs are concerned, it has been proved that the combination of CNTs and polymeric matrix is an effective method for taking full advantage of both CNTs and polymers. The CNT/polymer composites show excellent electrical conductivity, electromagnetic interference shielding, optical limiting behavior, photovoltaic conversion, positive temperature coefficient, etc.

For functional CNT-based composites, the design and construction of conducting pathways throughout matrix are so essential and interesting that they have attracted intense efforts from both academia and industry. Various CNTs (multiwalled, single-walled, and double-walled CNTs) and polymers [e.g., high-density polyethylene (HDPE), polypropylene (PP), polycarbonate, polyamide (PA), epoxy, etc.] have been chosen as functional fillers and matrix, and those CNT/polymer composites and their electrical properties have been studied in a wide range. Meanwhile, several models, for example, percolation theory, effective medium theory, and connectivity model, have been developed to describe conducting mechanisms. For the CNT-filled semicrystalline polymer composites, there is a widely accepted viewpoint that CNTs can be exclusive from the crystalline regions of matrix and be prone to aggregate in the amorphous regions; such a selective localization of CNTs is helpful for forming conducting pathways throughout polymer matrix at a low CNT loading.

Polyoxymethylene (POM) is a highly crystalline linear thermoplastic with excellent properties, such as exceptional dimension stability, high strength, good heat resistance, and so on. It is notable that POM has a high degree of crystallinity above 70% due to its significant main-chain flexibility, and such a highly crystalline structure of POM will be helpful for fabricating the conducting CNT/POM composites at a low CNT loading due to the selective localization of CNTs in amorphous regions. Moreover, the CNT/POM composites may exhibit good heat resistance attributed to the high melting point of POM above 170 °C. So far, the CNT/POM composites and their electrical properties have not yet been reported in detail.

In our experiments, the CNT/POM composites were prepared by the conventional melt—mixing technique. However, we found that when CNTs were added into the molten POM, a drastic degradation of POM occurred and the toxic formaldehyde gas was emitted, which consequently led to a failure in processing. Obviously, such a sharp decrease in processing stability of POM is associated closely with the presence of CNTs. What is the main influencing factor in determining the thermal stability of CNT—POM mixtures: impurities in CNTs, or chemical properties of CNTs, or something else? How can the processing stability of CNT—POM mixtures be improved? What about the electrical conductivity of CNT/POM composites?

The aim of this work mainly focuses on answering the above questions, that is, on understanding the effects of CNTs on processing stability of POM in the melt—mixing process. Three types of CNTs, pristine, chemically purified, and graphitized, were chosen as the conducting fillers, and their microstructures and surface chemical properties were systematically character-
ized; the processing stability of CNT–POM mixtures in the melt–mixing process was studied by thermal analysis. The results obtained show that the drastic degradation of CNT–POM mixtures in the melt–mixing process is related closely to the surface chemical properties of CNTs; the graphitization treatment can effectively remove the functional groups from the CNT surfaces and consequently improve the processing stability of the CNT–POM mixtures. Finally, graphitized CNT/POM composites were fabricated and their electrical properties were investigated.

2. Experimental Section

2.1. Raw Materials. The matrix used in this study is POM homopolymer (Delrin 390PM, supplied from DuPont) with a melting point of 178 °C and a melt index of 9 g/min. The multiwalled CNTs were produced by the chemical vapor deposition (CVD) method and were supplied from Shenyang Gina New Material Co. Ltd. In order to remove residual catalysts in pristine CNTs, chemical purification and high-temperature graphitization treatment were carried out separately. Chemically purified CNTs were prepared as follows: pristine CNTs were sunk into a nitric acid solution of 2 M, heated up to boiling and refluxed for 12 h, and then cooled down to room temperature and washed repeatedly in distilled water until the washings show no acidity. Graphitized CNTs were prepared as follows: pristine CNTs were heated in a high-purity argon atmosphere to 2600 °C and kept for 45 min, then cooled down slowly to room temperature.

2.2. Characterization of CNTs. Morphologies and microstructures of CNTs were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. Structural parameters of CNTs, such as interlayer spacing, degree of graphitization, and average crystalline size, were characterized by X-ray diffraction (XRD) and Raman spectroscopy. Thermogravimetric analysis (TGA) technique was utilized to measure the thermal stability of CNTs at a heating rate of 10 °C/min, and the purity of CNTs was calculated on the basis of mass change during the heating process. The pH value of CNTs was measured by a digital pH meter with reference to the test method of boiling slurry for carbon black–pH value (ASTM D1512-05): the aqueous solution of the weighted CNTs was heated up to the boiling point and kept for several minutes, then cooled down to room temperature; the electrode of a digital pH meter was inserted into the CNT sludge, and the pH value of CNTs was obtained. X-ray photoelectron spectroscopy (XPS) was performed to examine the elemental composition of CNT surfaces.

2.3. Processing Stability of POM in the Presence of CNTs. Effects of CNTs on the processing stability of POM were investigated by TGA and differential scanning calorimetry (DSC). The CNTs and POM pellets were weighed accurately and mixed well in advance; the mixtures were put into the thermal analyzer and heated at a rate of 10 °C/min in air; the change in heat flow and in mass was recorded during the heating process. In addition, the melt–mixing process can be considered as an isothermal process, so the degradation behavior of CNT–POM mixtures at a constant temperature of 220 °C was also investigated by TGA.

2.4. Fabrication of CNT/POM Composites. The CNT/POM composites were prepared by a conventional melt–mixing technique. POM pellets were weighed and put into an internal two-roller mixer that was preheated up to 190 °C. After those

TABLE 1: Structural Parameters of the CNTs Used

<table>
<thead>
<tr>
<th>CNTs</th>
<th>2θ, a deg</th>
<th>interlayer spacing of (002) planes (d_{002}), nm</th>
<th>graphitization degree (P), b %</th>
<th>crystalline size (L_c), nm</th>
<th>R value (I_D/I_G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine</td>
<td>25.52</td>
<td>0.349</td>
<td>amorphous</td>
<td>2.4</td>
<td>1.07</td>
</tr>
<tr>
<td>chemically purified</td>
<td>25.76</td>
<td>0.346</td>
<td>amorphous</td>
<td>2.7</td>
<td>1.01</td>
</tr>
<tr>
<td>graphitized</td>
<td>26.20</td>
<td>0.340</td>
<td>crystalline</td>
<td>44</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.29</td>
</tr>
</tbody>
</table>

a Measured by XRD. b Based on the formula \( P = \left[ \frac{(0.344 - d_{002})}{(0.344 - 0.335)} \right] \times 100\% \), where 0.344 and 0.335 are the interlayer spacings of amorphous carbon and graphite, respectively. c R value is the ratio of intensity of D-band (I_D) to that of G-band (I_G), measured by Raman spectroscopy.
and then the CNTs were added into the molten POM matrix, pellets were completely molten at a rotation speed of 30 rpm, and the weighed CNTs were added into the molten POM matrix, and then the CNT–POM mixtures were mixed further for 10 min at 190 °C at 90 rpm; such a high rotation speed and long mixing time was proved necessary to obtain a homogeneous dispersion of CNTs throughout the matrix; subsequently the CNT/POM blends were heated up to 190 °C, molded into a sheet of 1 mm thickness under a pressure of 10 MPa, then cooled down slowly to room temperature, and thus the CNT/POM composites were obtained.

2.5. Electrical Properties of the CNT/POM Composites. The sheet of CNT/POM composites was tailored into square specimens of 30 mm × 30 mm. Both the upper and lower surfaces of the specimens were coated with conductive silver paint to ensure an intimate contact between specimen surfaces and electrodes. Electrical resistance ($R_v$) of the composites was measured with a digital multimeter for $R_v < 10^5 \Omega$ or a high-resistance meter for $R_v > 10^5 \Omega$ alternatively, and the volume resistivity ($\rho_v$) of the composites was calculated according to the following formula: $\rho_v = R_v A / t$, where $A$ is the effective area of the measuring electrode and $t$ is the thickness of the specimen.

### 3. Results and Discussion

3.1. Microstructures of CNTs. Figure 1 shows the microscopical morphologies of CNTs observed by SEM (panel a) and TEM (panel b). The CNTs have diameters in the range 50–100 nm and a large aspect ratio (length to diameter ratio) of ca. 500. Such a unique structure is helpful for long-range electron transfer and formation of conducting network at a low CNT loading.

HRTEM images of pristine, chemically purified, and graphitized CNTs are shown in Figure 1c–e. Both pristine and chemically purified CNTs exhibit clearly the turbostratic structure, whereas graphitized CNTs show an ordered microstructure and few defects attributed to the rearrangement of disordered layers during the graphitization process at 2600 °C. Table 1 summarizes the CNT structural parameters measured by XRD and Raman spectroscopy. There is no significant difference in structural parameters between pristine and chemically purified CNTs, but graphitized CNTs exhibit distinctive structural characteristics, having the smallest interlayer spacing of 0.340 nm, the highest graphitization degree of 44%, and the largest average crystalline size of 8.9 nm among all the CNTs used; furthermore, a decrease of $R_v$ value from 1.07 to 0.29 in Raman spectra also confirms the structural transformation from disordered to highly ordered CNTs upon graphitization.

Consequently, graphitized CNTs exhibit much better electrical and thermal transport properties due to their integrated microstructures and few defects.

#### Table 2: pH Values of Different CNTs

<table>
<thead>
<tr>
<th>CNTs</th>
<th>pH value*</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine</td>
<td>5.0–5.1</td>
</tr>
<tr>
<td>chemically purified</td>
<td>2.7–2.8</td>
</tr>
<tr>
<td>graphitized</td>
<td>6.6–6.8</td>
</tr>
</tbody>
</table>

*p Measured by use of a digital pH meter with reference to ASTM D1512-05.

3.2. Effects of CNTs on Processing Stability of POM. When the CNTs were added into the molten POM matrix in the melt–mixing process of fabricating the CNT/POM composites, it was observed that drastic POM degradation occurred, accompanied by the release of toxic formaldehyde gas, which led to a failure in processing. Such poor processing stability of POM in the presence of CNTs might be associated with impurities in CNTs and the CNT–POM interactions.

For those pristine CNTs produced by CVD, some impurities of metal catalysts left in CNTs can influence the physical and chemical properties of CNT-based composites to some extent; therefore, purification is necessary to eliminate the effects of impurities in CNTs. Figure 2 shows the TGA curves of CNTs at a heating rate of 10 °C/min in air. Obviously, chemically purified and graphitized CNTs exhibit high purity due to effective removal of impurities during the chemical and graphitization treatments, and only 1 wt % residues are left at 1200 °C in comparison to 8.7 wt % for pristine CNTs. However, chemically purified CNTs show poor thermal stability attributed to the acid etching of CNT sidewalls during chemical purifica-
influence the thermal degradation mechanism of POM. For neat POM, the thermal degradation in air is autoxidation degradation accompanied by an exothermic effect, and the degradation mechanism is as follows:30,31

Such an exothermic effect is evidence of oxygen attack leading to carbonyl and hydroperoxide formation.32 However, for POM in the presence of CNTs, its thermal degradation is an endothermic process (see Figure 3a). The carboxylic groups on CNT surfaces can catalyze and accelerate the POM degradation according to the following mechanism:31

\[
\begin{align*}
\text{ROCH}_2\text{OCH}_2\text{OCH}_2\text{OR} + \text{H}_2\text{O} &\rightarrow \text{ROCH}_2\text{OCH}_2\text{OCH}_2\text{H}^+ + \text{HOCH}_2\text{OR} \\
\text{ROCH}_2\text{OCH}_2\text{OCH}_2\text{OR} + \text{O}_2 &\rightarrow \text{ROCH}_2\text{OCH}_2\text{OCH}_2\text{O}^+ \\
\text{ROCH}_2\text{OCH}_2\text{OCH}_2\text{O}^+ + \text{H}_2\text{O} &\rightarrow \text{ROCH}_2\text{OCH}_2\text{OCH}_2\text{OH}^+ + \text{HOCH}_2\text{O} \\
\text{ROCH}_2\text{OCH}_2\text{OCH}_2\text{OR} + \text{OH} &\rightarrow \text{ROCH}_2\text{OCH}_2\text{OCH}_2\text{OH} + \text{O}^+ \\
\text{ROCH}_2\text{OCH}_2\text{OCH}_2\text{OR} + \text{H} &\rightarrow \text{ROCH}_2\text{OCH}_2\text{OCH}_2\text{H} + \text{O}^+ \\
\end{align*}
\]

POM degradation consists of acidolysis and hydrolysis reactions accompanied by a strong endothermic effect.31 Because hydrogen ion plays a role as accelerator for POM degradation, there is a lower activation energy of ca. 80 kJ/mol for the cationic depolymerization of POM than that of ca. 110 kJ/mol for the thermal degradation.30 Therefore, the CNT–POM mixture exhibits lower thermal stability than neat POM in Figure 3 due to the existence of carboxylic acid groups on CNT surfaces. Furthermore, the thermal stability of CNT–POM mixtures is associated closely with the concentration of oxygen-containing functional groups on CNT surfaces: the lower the carboxylic group concentration on CNT surfaces, the higher the onset temperature of POM degradation and the better the thermal stability of CNT–POM mixtures. Graphitized CNTs show a rather low oxygen concentration due to the effective removal of functional groups on CNT surfaces during the high-temperature treatment, and thus the graphitized CNT–POM mixture shows good thermal stability as shown in Figure 3. As a result, graphitized CNT/POM composites can be fabricated successfully by the conventional melt–mixing process.

It is notable that the presence of carboxylic groups on CNT surfaces also has significant influences on the processing properties of other CNT-filled polymer composites, for example, shortening the curing time for CNT/epoxy system,33 lowering the vulcanization rate for CNT/NR composites,34 etc. The effects of surface functional groups of CNTs on the processability of polymer matrix should be paid much attention in fabricating CNT-filled polymer composites.

3.3. Microstructures and Electrical Properties of CNT/POM Composites. Figure 5 shows typical SEM images of graphitized CNT/POM composites. A spherulite structure of POM, which consists of aggregates of lamellar crystals, is observed clearly in Figure 5a, and there is a uniform distribution of CNTs in the POM matrix due to the effective dispersion of CNTs in the high-shear mixing process.35 It is notable that lamellar crystals of POM with thickness 10–50 nm have a similar nanometer size to the CNTs, and the presence of CNTs does not affect significantly the spherulite growth.36 As shown in Figure 5b, the CNTs are located between the lamellar crystals, and POM exhibits a highly crystalline structure; such a high crystallinity of polymeric matrix is helpful for fabricating a conducting composite at low CNT loading.

Figure 6 plots the volume electrical resistivity of graphitized CNT/POM composites against CNT loading. It can be seen that low CNT loading can have a remarkable impact upon the electrical properties of the composites. Neat POM has electrical resistivity as high as 1014 Ω·cm, whereas graphitized CNT/POM composites at 0.5 wt % CNT loading show low resistivity of ca. 108 Ω·cm, indicating that graphitized CNT/POM composite has a percolation threshold as low as 0.5 wt %. Moreover, increasing the CNT loading can further result in a progressive improvement in electrical conduction, and the electrical resistiv-
ity of graphitized CNT/POM composites at 3 wt % CNT loading can fall down to ca. 50 Ω cm at room temperature.

For graphitized CNT/POM composites, their electrical properties are associated with the electrical conductivity of CNTs and the crystallinity of POM matrix. On one hand, graphitized CNTs have a large aspect ratio, graphitic structures, and few defects, and hence there is low contact resistance between CNTs, which is beneficial to formation of conducting pathways in composites at a rather low CNT loading. On the other hand, there is a tendency for CNTs to aggregate in the amorphous regions of POM matrix,\textsuperscript{18} the higher the crystallinity degree of the polymer, the smaller the amorphous regions, the higher the contact probability between CNTs, and the lower the electrical resistivity of the composites. Owing to the high crystallinity degree of POM and the excellent conductivity of CNTs, graphitized CNT/POM composites exhibit good electrical properties.

4. Conclusions

The surface chemical properties of CNTs have strong influences on the processing stability of POM in the melt−mixing process. Although acid purification is an effective method for removing the impurities from CNTs, the CNT surfaces are acid-oxidized severely and show strong acidity. Those carboxylic acid functional groups on CNT surfaces can result in drastic degradation of POM through acidolysis and hydrolysis. The higher the carboxylic acid concentration on CNT surfaces, the lower the onset temperature of POM degradation and the worse the thermal stability of CNT−POM mixtures. On the contrary, graphitization treatment can not only purify CNTs and improve their structural integrity but also remove effectively the functional groups from CNT surfaces, and thus considerably improve the processing stability of CNT−POM mixtures. Moreover, graphitized CNT/POM composites show good electrical properties and their percolation threshold is as low as 0.5 wt %, attributed to the excellent electrical conductivity and large aspect ratio of graphitized CNTs and the high crystallinity of POM. Such CNT/POM composites may have great potential applications in electronic components, self-controlled heaters, overcurrent protectors, and other functional devices.

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Supporting Information Available: X-ray diffraction and Raman patterns for the CNTs (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


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