INVESTIGATION OF THE MECHANICAL AND THERMAL PROPERTIES OF FUNCTIONALIZED CNTS/POLYPROPYLENE COMPOSITES

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ABSTRACT

The poor dispersion and interfacial interactions of multi-walled carbon nanotubes (MWCNTs) remain two critical obstacles in limiting the application of MWCNTs-based composites. Covalent and noncovalent functionalization have been successfully applied to enhance the dispersion and interfacial interactions of MWCNTs in polymer. Accordingly, the present work incorporated covalent and noncovalent functionalized CNTs (pristine MWCNTs, MWCNTs-COOH, TritonX-100/MWCNTs, polyvinylpyrrolidone (PVP)/MWCNTs and polyaniline (PANI)/MWCNTs) into polypropylene (PP) to improve its properties by melt blending. By comparing the properties of MWCNTs/PP composites, the effects of different functionalization methods of MWCNTs on the dispersion, mechanical and thermal properties of MWCNTs/PP composites were reported. The photomicrograph showed that except for PVP/MWCNTs, the interfacial interactions between MWCNTs and PP become better after functionalization of MWCNTs, especially, MWCNTs-COOH. Due to the better good dispersion and interfacial interactions between MWCNTs-COOH and PP, MWCNTs-COOH/PP has better mechanical (elastic modulus and yield strength) and dynamic thermo-mechanical properties than that of noncovalent functionalized MWCNTs.

1 INTRODUCTION

Owing to its excellent mechanical properties, high specific strength and modulus, as well as the good thermo-physical properties, carbon nanotubes (CNTs) have been widely used as desired reinforcer to improve the properties of polymers. Recently, the CNTs reinforced polymers were often applied in electronic industry, aerospace, automobile, and biomedical science fields[1-3].

Among all important thermoplastic polymers, polypropylene (PP) has been widely applied in furniture, household appliances, automobile and pipes fields, due to its easy modeling, low cost and good comprehensive properties[4]. However, the applications of PP are largely limited by its disadvantages such as low strength and poor thermal properties[5]. In order to improve its mechanical and thermal properties, many researchers devoted themselves to adding CNTs into PP due to excellent properties of CNTs[6-9].

However, strong van der Waals force and π-π stacking between the tubes result in its agglomerations or entanglements. It is well-known that the chemical inert and smooth surface of CNTs resulted from carbonization and graphitization process will cause poor compatibility and weak adhesion between CNTs and polymer matrix, which limit the practice application of mechanical and thermal properties of CNTs/PP nanocomposites[10-12]. At present, covalent and noncovalent functionalization are two effective methods to improve the disperse and compatibility of CNTs[13-16]. Among them, covalent functionalization method could securely connect the hydrophilic group (NH₂-, COOH-) with CNTs by covalent bonding. But this method damages sp² hybridization of carbon atoms and π-electron conjugated system, resulting in its low properties [13, 17-20]. The most common covalent functionalized CNTs are CNTs-COOH. In addition, noncovalent method can also connect the hydrophilic group with CNTs by strong van der Waals force and π-π stacking between CNTs and amphiphatic molecules, which preserve the original structure of CNTs. But the binding force between CNTs and dispersants is weaker than that of covalent method [21-24]. In general, noncovalent
functionalization has been implemented with surfactants\[25, 26\] and polymers\[27, 28\], etc. Experimental results demonstrate that nonionic surfactant (TritonX-100) can disperse better than ionic surfactant \[21, 29, 30\]. As a nonionic polymer, polyvinylpyrrolidone (PVP) has good compatibility with PP because of their similar structure \[31-34\]. Therefore, PVP functionalized CNTs not only can disperse well CNTs, but also can improve the interfacial interactions between CNTs and PP. Besides polyaniline (PANI) \[35\] have also good compatibility with PP. Rong et al\[34\] found that noncovalent functionalized CNTs by sulfonated poly(ether ether ketone) can improve the mechanical properties of poly(ether ether ketone) better than CNTs-COOH. However, for PP, most of researches studied the effect of filler size and content on the mechanical and thermal properties of PP composites filled with the CNTs. Liang et al\[5\] study the thermal properties and thermal stability of PP/MWCNTs composites and found MWCNTs could improve the thermal stability. Afterwards, they added different filler size and content MWCNTs into PP and found crystallization temperature, crystallization peak temperature went up with increasing MWCNTs weight fraction and with decreasing filler average diameter. Krause et al\[36\] used different content and types of single walled carbon nanotube(SWCNTs) to prepare PP composites and found Tuball\textsuperscript{TM} SWCNTs seems to be very promising for conductivity enhancement. But the study on the influence of functionalization method of CNTs on the properties of PP was rare. Therefore, it’s worth studying the impact of functionalization methods on the mechanical and thermal properties of PP composites filled with functionalized CNTs.

This paper adopts several common dispersants to functionalize CNTs, such as pristine multi-walled carbon nanotubes (MWCNTs), nitric acid treated MWCNTs, TritonX-100, PVP and PANI noncovalently functionalized MWCNTs. The five CNTs were used to prepare composites with polypropylene by melt mixing using a single screw injection molding machine. In order to study the influence of functionalization method of CNTs on the dispersion, mechanical and thermal properties of CNTs/PP composites, The dispersion of MWCNTs in PP matrix, mechanical and thermal properties of PP composites were characterized by photomicrograph, tensile testing and dynamic mechanical analysis (DMA), respectively.

2 MATERIALS AND METHOD

2.1 Materials

The pristine MWCNTs and carboxyl-functionalized MWCNTs with diameter of 10~20 nm and length of 10~30 μm were purchased from XFNANO (Nanjing, China) and used without further purification. Polyethylene glycol octylphenol ether (TritonX-100), polyvinylpyrrolidone (PVP) and Polyaniline (PANI) were purchased from Deng Feng, Reagent and Kuer chemical technology Co., Ltd, respectively. They were used to noncovalently functionalize MWCNTs, which were also used as reinforcements to compare with pristine MWCNTs. The polypropylene (PP) used as the composite matrix was supplied from SINOPEC Maoming Co., Ltd.

2.2 Functionalization of MWCNTs

Firstly, the equal amount of MWCNTs and dispersants (TritonX-100, PVP, PANI) were dissolved in deionized water (10 ml) and sonicated (SONICS VCX800) for 30 min. Finally, the obtained powders were dried at 60 °C for 24 h.

2.3 Preparation of PP Composites

PP composites containing 0.2 wt% CNTs were fabricated by melt mixing using a single screw injection molding machine (TY-7003, Jiangsu Tianyuan). Injection molding was carried out at 170~260 °C, holding at 0.5 MPa for 5 s to mold the dog bone specimens.

3 EXPERIMENTAL
3.1 Functionalization of MWCNTs

The scanning electron microscopy (SEM) images of the pristine MWCNTs and functionalized MWCNTs were obtained using a MIRA3LMH. To further characterize the functionalization of MWCNTs, Fourier transform infrared spectrometer (FTIR, VERTEX70, Germany Bruker Co., Ltd) and Raman spectrometer (Renishaw Invia) were employed.

3.2 Dispersion of MWCNTs in PP Matrix

Microscopy (OLYMPUS, CX41) was employed to observe the dispersion of MWCNTs in PP matrix. All the composites were ground to a thickness of 0.4 mm-0.5 mm.

3.3 Mechanical and Thermal Testing

Mechanical properties of the PP composites were measured at room temperature using a tensile tester (Instron 5966, America) at a displacement rate of 5 mm/min. Three specimens were tested for each PP samples.

The dynamic mechanical properties of composites were studied a dynamic mechanical analyzer (DMA, NETZSCH-242E). The samples were analyzed with three-point bending mode, from -50 °C to 150 °C under a heating rate of 2 °C/min and at a frequency of 1 Hz.

4 RESULTS AND DISCUSSION

4.1 Microtopography and Functionalization of MWCNTs

Figure 1(a) shows the SEM image of the pristine MWCNTs, where large aggregations of MWCNTs could be observed. Figure 1(b-d) shows the SEM of noncovalent functionalized MWCNTs, where the large aggregation disappeared. Therefore, noncovalent functionalization of MWCNTs could avoid shortening of CNTs and its diameter enlarged to some degree. In Figure 1(b, c), compared with the pristine MWCNTs, the diameters of TritonX-100/MWCNTs and PVP/MWCNTs turned out to be large. In Figure 1(d), there are some white floc in PANI/MWCNTs between the tubes and tubes. These results indicated that MWCNTs was functionalized successfully with dispersants by physical absorption without structural destruction of MWCNTs.

![Figure 1: Microtopography and Functionalization of MWCNTs](image-url)
The functionalization of MWCNTs was further investigated by FTIR spectrometry. As shown in Figure 2, the strongest O-H stretch (3426 cm\(^{-1}\)) is the characteristic hydroxy peak introduced by the water molecules in the air. The relatively strong peak at ~1620 cm\(^{-1}\) can be assigned to the stretching vibration of C=C in aromatic ring of MWCNTs, it upshifted to higher wavenumber when dispersants adsorbed on the MWCNTs surface. It was attributed to the strong interaction between dispersant and MWCNTs. Bending vibration of C-H of alkyl chain and C-O-R (ether groups) in TritonX-100 was observed at 1511 cm\(^{-1}\) and 1114 cm\(^{-1}\) in the FTIR spectra of TritonX-100/MWCNTs, respectively [11, 29, 37]. It indicated that TritonX-100 successfully adsorbed on the surface of MWCNTs. A new peak at 1200 cm\(^{-1}\) corresponded to the stretching vibrations of C-N in PVP was observed in PVP/MWCNTs spectrum. Likely, there is also a new C-N peak of PANI in PANI/MWCNTs spectrum [38]. It indicates that MWCNTs were successfully functionalized.

![FTIR spectra of pristine and functionalized MWCNTs](image)

Figure 2 FTIR spectra of pristine and functionalized MWCNTs

The Raman spectroscopy is well known as a very valuable method for the characterization of carbon-based nanostructures. CNTs have usually exhibit two characteristic bands: the D band (~1350 cm\(^{-1}\)) and G band (~1580 cm\(^{-1}\)). Intensity ratio \(I_D/I_G\) of the D band and G band is often used to evaluate the defect density of CNTs. Figure 3 presents Raman spectra of pristine and functionalized MWCNTs. The ID/IG values decreased compared to that of pristine MWCNTs. The results indicate that noncovalent functionalization of MWCNTs can avoid the destruction of its chemical structure.
Figure 3 Raman spectra of pristine and functionalized MWCNTs

4.2 Mechanical properties of PP composites

Figure 4 shows the dispersion of MWCNTs and functionalized MWCNTs in PP matrix. Black spots represent the agglomeration of CNTs. Many small black spots were evenly distributed in Figure 4(a,b), which suggest that pristine MWCNTs and MWCNTs-COOH have good dispersion in PP matrix. Compared to MWCNTs/PP and MWCNTs-COOH/PP, larger and less black spots were observed in Figure 4(c), (d) and (e), which demonstrates that noncovalent functionalized MWCNTs
(TritonX-100/MWCNTs, PVP/MWCNTs and PANI/MWCNTs) presented poor dispersion, especially TritonX-100/MWCNTs in PP. But the interface between CNTs and PP is unclear after functionalization of MWCNTs in Figure 4(b,c,e). It indicates the good interfacial adhesion between CNTs and PP. In addition, some wirelike MWCNTs-COOH were observed in Figure 4(b), which could because MWCNTs-COOH/PP have better interfacial adhesion between MWCNTs-COOH and PP than that of noncovalent functionalized MWCNTs.

4.3 Mechanical properties of PP composites

The mechanical properties of PP composites were test for PP containing CNTs nanofillers in Table 1. Figure 5 shows the bar graph of elastic modulus and yield strength vs. different CNTs. It was also found that the elastic modulus and yield strength of the samples followed the sequence: MWCNTs-COOH/PP > MWCNTs/PP > PANI/MWCNTs/PP > PVP/MWCNTs/PP > TritonX-100/MWCNTs/PP. The elastic modulus and yield strength of MWCNTs-COOH/PP was higher than that of noncovalent functionalized MWCNTs/PP. This is because the carboxyl covalent functionalized MWCNTs has stronger interfacial interaction between MWCNTs-COOH and PP than that of noncovalent functionalization of MWCNTs, the result is consistent with the dispersion of CNTs in PP (Figure 4 b). TritonX-100/MWCNTs/PP has the smallest elastic modulus and yield strength. It is because the TritonX-100/MWCNTs has poor dispersion in PP matrix (Figure 4 c).

![Figure 5: The mechanical properties (a) Elastic Modulus and (b) Yield Strength of PP composites.](image)

1 is MWCNTs/PP; 2 is MWCNTs-COOH/PP; 3 is TritonX-100/MWCNTs/PP; 4 is PVP/MWCNTs; 5 is PANI/MWCNTs

<table>
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<th>Number</th>
<th>Samples</th>
<th>Elastic Modulus (GPa)</th>
<th>Yield Strength (MPa)</th>
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<tr>
<td>1</td>
<td>MWCNTs/PP</td>
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<td>37.8±1.4</td>
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<tr>
<td>2</td>
<td>MWCNTs-COOH/PP</td>
<td>1.03±0.17</td>
<td>39.1±6.5</td>
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<tr>
<td>3</td>
<td>TritonX-100/MWCNTs/PP</td>
<td>0.84±0.09</td>
<td>34.4±2.0</td>
</tr>
<tr>
<td>4</td>
<td>PVP/MWCNTs/PP</td>
<td>0.87±0.03</td>
<td>33.7±1.2</td>
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<tr>
<td>5</td>
<td>PANI/MWCNTs/PP</td>
<td>0.88±0.01</td>
<td>36.2±0.2</td>
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</table>

Table 1: The mechanical properties of PP composites

4.4 Dynamic Thermo-mechanical analyses of PP composites

Besides quasi-static mechanical testing, dynamic mechanical analysis (DMA) is an effective way to
assess the interface interaction of CNTs reinforced composites. The thermomechanical properties of PP nanocomposites were studied by the variation of shear storage modulus (E’), loss modulus (E’’) and damping value (tan δ) as a function of temperature (Figure 5). DMA results of the PP composites were shown in Table 2.

![Graphs showing DMA results](image_url)

**Figure 6** The DMA curves of PP composites: (a) storage modulus E’ (b) loss modulus E’’ and (c) loss factor tan δ

<table>
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<tr>
<th>Samples</th>
<th>E’ (-25℃) (MPa)</th>
<th>E’ (25℃) (MPa)</th>
<th>E’’ (-25℃) (MPa)</th>
<th>E’’ (25℃) (MPa)</th>
<th>Tan δ-max</th>
<th>Tg (℃)</th>
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<td>222.3</td>
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<td>TritonX-100/MWCNTs/PP</td>
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<td>PVP/MWCNTs/PP</td>
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<td>2042</td>
<td>260.5</td>
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<tr>
<td>PANI/MWCNTs/PP</td>
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<td>1946</td>
<td>274.7</td>
<td>200.4</td>
<td>0.11</td>
<td>14.3</td>
</tr>
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</table>

Table 2 DMA results of PP composites

In Figure 6(a), the storage modulus (E’) is the energy storage in the nanocomposites during the test, and it represent the elastic and stiffness behavior [39]. According to Table 2, the storage modulus at -25 ℃ and 25 ℃ of the samples followed this sequence: MWCNTs/PP > MWCNTs-COOH/PP > PVP/MWCNTs/PP > TritonX-100/MWCNTs/PP ≥ PANI/MWCNTs/PP. The E’ of PP composites decreased with the functionalization of MWCNTs. This is because induction of dispersants leads to an enlarged free volume between interface of the CNTs and PP, which can enhance the mobility of the PP chains and cause a reduction of moduli. Moreover, it was also found that covalent functionalization
have stronger interfacial adhesion between PP and fibers than noncovalent functionalization. The results are consistent with the results obtained in the Figure 4.

As shown in Figure 6 (b), the loss modulus $E''$ is proportional to the amount of dissipated energy and it usually indicates the material’s viscosity [40]. According to Table 2, the $E''$ at -25 °C and 25 °C of the samples followed this sequence: MWCNTs-COOH/PP > MWCNTs/PP > PANI/MWCNTs/PP ≥ PVP/MWCNTs/PP > TritonX-100/MWCNTs/PP. Similarly, covalent functionalized MWCNTs have better viscosity than noncovalent functionalized MWCNTs. Compared to noncovalent functionalized MWCNTs, excellent interfacial adhesion of MWCNTs-COOH/PP restricted the movement of PP molecular, which leading to an increased $E''$ and a higher viscosity of system[40].

Figure 6 (c) shows the mechanical loss factor spectra (tan δ) of the CNTs/PP composites. The tan δ is the ratio of the $E''$ to the $E'$, and the peak of tan δ is often used to determine the glass transition temperature (Tg), which was shown in Table 2. According to Table 2, the Tg of the samples followed this sequence: MWCNTs/PP > PVP/MWCNTs/PP > TritonX-100/MWCNTs/PP > PANI/MWCNTs/PP > MWCNTs-COOH/PP. It was found that the Tg of PP composites decreased with functionalization of MWCNTs. Meanwhile, covalent functionalized MWCNTs/PP has lower Tg than noncovalent functionalized MWCNTs/PP. It is attributed to the enlarged free volume between the CNTs and PP matrix. These results are consistent with the results obtained in the Figure 6 (a) and (b). In addition, according to Table 2, all composites have higher tan δ_max values than the MWCNTs/ PP due to the strengthening effect of functionalized CNTs,

Therefore, it was found that MWCNTs-COOH has better properties than noncovalent functionalization between CNTs and PP, such as strong interfacial adhesion between CNTs and PP, good viscosity, and low Tg.

9 CONCLUSIONS

In this work, multi-walled carbon nanotubes (MWCNTs) were noncovalently functionalized by TritonX-100, polyvinylpyrrolidone (PVP) and polyaniline (PANI). To study the influence of different functionalization of MWCNTs on the dispersion, mechanical and dynamic thermo-mechanical properties of MWCNTs/PP composites, we fabricated PP nanocomposites with four MWCNTs (pristine MWCNTs, MWCNTs-COOH, TritonX-100/MWCNTs, PVP/MWCNTs, PANI/MWCNTs) by melt blending. It was found that MWCNTs-COOH have better dispersion, mechanical (elastic modulus and yield strength) and dynamic thermo-mechanical properties than noncovalent functionalized MWCNTs due to its strong interfacial interactions.

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