**Fabrication and Characterization of Soluble Multi-Walled Carbon Nanotubes Reinforced P(MMA-co-EMA) Composites**

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**Introduction**

Owing to the good elasticity and extremely high Young’s modulus, 1,2 as well as their high aspect ratios, carbon nanotubes (CNTs) are expected to be used as effective reinforcing additives in composite materials. Till now, many studies have been carried on the CNTs/polymer composites. 3–12 These studies show that three main factors greatly influence the reinforcement of the CNTs/polymer composite: (1) a good dispersion of the CNTs in polymer matrix, 3–6 (2) a strong interfacial bonding between CNTs and polymer, 5,7,8 (3) good alignment of the CNTs in polymer matrix. 9–12 Because of the weak interaction between polymer matrix and CNTs and the strong van der Waals forces between CNTs themselves, CNTs tend to agglomerate in composites and the composite strength may not be effectively enhanced. It has been suggested that sufficient dispersion is one of the key factors to realize the nanoreinforcement of the composite. In order to improve the dispersion of multi-walled carbon nanotubes (MWNTs) in polymer matrix, various approaches have been taken: Gong et al. 13 used nonionic surfactants to aid the dispersion of CNTs in epoxy, which resulted a higher Tg and elastic modulus; Jin et al. 14 used PVDF to assist the melt-blending of MWNTs in PMMA, which led to a significant improvement in the storage moduli of the MWNTs/PMMA composite at low temperatures.

Recently, chemical functionalization of CNTs has been realized and full solubility of CNTs in some solvents can be obtained. 13–15 This is very important for CNTs’
application as additives for reinforcement of polymer materials, because the functionalization of CNTs not only simplifies the fabrication process of CNTs/polymer composites, but also improves the interfacial bonding between the polymer matrix and the CNTs.

To our knowledge, there are few reports on the enhancement of mechanical properties of polymer composites using soluble CNTs.\[16–18\] In this paper, we prepared a series of polymer composites of octadecylamine functionalized MWNTs (s-MWNTs) with copolymer of methyl and ethyl methacrylate (P(MMA-co-EMA)). The Young’s modulus and tensile strength of the MWNTs/P(MMA-co-EMA) composite were greatly improved over the native P(MMA-co-EMA).

**Experimental Part**

**Materials**

MWNTs produced by chemical vapor deposition (CVD) were bought from Sun Nanotech Co. Ltd (Nanchang, China). The pristine MWNTs were purified according to ref. [19] and the product was named p-MWNTs. P(MMA-co-EMA) (\(M_n = 15\,000\), polydispersity: 1.6) was synthesized via a dispersion polymerization in our laboratory.

**Synthesis of Octadecylamine-Functionalized MWNTs**

The octadecylamine-functionalized MWNTs (s-MWNTs) were prepared by Guo et al., which have been characterized in detail and is published elsewhere.\[20\] The MWNTs content in s-MWNTs is about 70 wt.-%. The synthesis procedure can be briefly described as follows: the p-MWNTs were stirred in freshly distilled thionyl chloride at 70 °C for 24 h to convert the surface-bound carboxylic acid groups into acyl chloride groups. A mixture of the resulting solid and octadecylamine (ODA) was stirred under N\(_2\) atmosphere at 80 °C for 96 h. After cooling to room temperature, the resulting solid mixture was placed in a Soxhlet extractor and ethanol was employed as extraction solvent to remove the excess amine. After 24 h, the ethanol solution was discarded, and chloroform was used as extraction solvent to obtain the s-MWNTs. The product was dried at 50 °C in vacuum overnight before use.

**Fabrication of Polymer Composites**

The MWNTs/P(MMA-co-EMA) composites were fabricated using a solution-mixing method. Typically, to a 150 ml round bottom flask, 15 g of P(MMA-co-EMA) polymer was dissolved in 100 ml dichloromethane. In another flask, 20 ml of dichloromethane and a certain amount of p-MWNTs or s-MWNTs were added and sonicated for 20 min. The carbon nanotubes’ dispersion was added to the polymer solution dropwise under sonication. The solution mixture was then kept sonicated for 1 h. After that, the solution was homogenized by a Fluko FA-25 high-shear dispersing emulsifier at 22 000 rpm for 1 h. The resulting dispersion was decanted into a glass dish and allowed to stand at room temperature for 2 d. The black composite was further vacuum-dried at 70 °C for 3 d to remove the residual solvents. These composites were then mixed in a Laboratory Mixing Molder (Atlas, USA) at 230 °C for 5 min at a speed of 120 rpm. The mixtures were then extruded into an ASTMD-1708 mould to form a dumb-bell like strip.

**Characterization**

The tensile properties of the polymer composites were determined on an autograph tensile tester Instron 5567. The stretching rate was kept at 5 mm·min\(^{-1}\). The data of tensile strength and Young’s modulus reported here were the average values of five tests under the same conditions. The dynamical mechanical properties were measured by a dynamic mechanical analyzer Netzsch DMA-242. The specimens were 4.70 mm wide and 1.60 mm thick. The mode of force loading was three-point bending. The samples were heated from room temperature to 150 °C at a heating rate of 3 K·min\(^{-1}\) and a frequency of 1 Hz.

Thermogravimetric analysis (TGA) measurements were performed on Perkin-Elmer Pyris 1 under a nitrogen atmosphere from room temperature to 600 °C. SEM images were measured on a Philips XL 30 scanning electron microscope at an accelerating voltage of 25 kV. The samples were fractured in liquid nitrogen and the cross-section surface was observed by SEM.

**Results and Discussion**

**Mechanical Properties**

The stress-strain curves of both the s-MWNTs/P(MMA-co-EMA) and p-MWNTs/P(MMA-co-EMA) composites with different MWNTs weight fractions are shown in Figure 1. It can be observed that both Young’s modulus and tensile strength of the composites are increased when s-MWNTs or p-MWNTs are added. With the increase of the MWNTs content in the composites, the tensile strength increases...
gradually, but the elongation decreases in parallel. In comparison with \( p \)-MWNTs/P(MMA-co-EMA) composite, the \( s \)-MWNTs reinforced composite possesses clearly higher tensile strength and larger elongation. This indicates that surface modification of the MWNTs can improve the miscibility of MWNTs and polymer matrix, the improved interfacial bonding can realize the load transfer from matrix to MWNTs.

Figure 2 and 3 show the influence of the MWNTs content on the Young’s modulus and tensile strength of the composites. With the increasing concentrations of \( p \)-MWNTs or \( s \)-MWNTs in composites, both the Young’s modulus and tensile strength increase. The stiffening effect is more evident in \( s \)-MWNTs/P(MMA-co-EMA) composites. The \( s \)-MWNTs/P(MMA-co-EMA) composite with 10 wt.-% \( s \)-MWNTs has a Young’s modulus of 2325 MPa and a tensile strength of 73.4 MPa, showing, respectively, a 135% and 49% increase over the pure P(MMA-co-EMA), and a 9.2% increase in Young’s modulus and a 12.8% increase in tensile strength over that of 10 wt.-% \( p \)-MWNTs composite. The enhanced performance of the \( s \)-MWNTs composite may be attributed to the alkyl chains on the surface of \( s \)-MWNTs. This improves \( s \)-MWNTs dispersion in polymer matrix and the interfacial bonding between the CNTs and polymer, and allows an effective load transfer from the polymer to the MWNTs. The function of grafting chains was similar to the surfactant in CNTs/epoxy composite.\(^{[3]}\)

**Dynamic Mechanical Analysis**

Figure 4 is the plot of the storage modulus of the \( s \)-MWNTs/P(MMA-co-EMA) composites as a function of temperature. From the data of Figure 4, we can see that the stiffening effect is significant, especially for the higher content of \( s \)-MWNTs. The strengthening of storage modulus is more evident at high temperature, especially between 80 and 100 °C. Similar results were also obtained by Jin et al.\(^{[21]}\)

Figure 5 shows the tan \( \delta \) peaks of the composites. The maximum of the tan \( \delta \) peak is generally considered as the glass transition temperature (\( T_g \)) of the composite. From this Figure, it can be observed that the \( T_g \) of the composite is raised by the addition of MWNTs and increases by MWNTs content (Table 1). From Table 1, we also can find that the \( T_g \) of the \( s \)-MWNTs composite is slightly lower than that of the \( p \)-MWNTs composite at the same concentration. This should be explained by the fact that the content of pure MWNTs in \( s \)-MWNTs is lower than that in \( p \)-MWNTs. The lower pure MWNTs amount in the composite will reduce the hindrance of the segmental motion of the P(MMA-co-EMA) chains, thus lowering the \( T_g \) of the composites.

**Thermal Stability**

Figure 6 shows the TGA curves of P(MMA-co-EMA) with various content of \( s \)-MWNTs. Pure P(MMA-co-EMA) starts to degrade in nitrogen atmosphere at about 160 °C.
and is completely degraded at 430 °C. The TGA curve of P(MMA-co-EMA) obviously shows two stages of composition. When s-MWNTs were added in P(MMA-co-EMA), it can be observed that the thermal degradation of the composites was retarded and the onset of the degradation increased with the increasing s-MWNTs content. The composite containing over 5 wt.% s-MWNTs starts to decompose at about 270 °C, which is 110 K higher than the pure P(MMA-co-EMA). The weight of the composite remains constant at the temperature beyond 430 °C, indicating that the P(MMA-co-EMA) matrix has decomposed completely, the residual weight was the MWNTs content in the composites. From the residual weights, the original feed of the composites can be checked.

Morphological Study of CNTs Composites

Figure 7 shows the morphologies of the fracture surface of the 10 wt.% p-MWNTs in P(MMA-co-EMA) composite and 10 wt.% s-MWNTs in P(MMA-co-EMA) composite.

Table 1. Glass transition temperatures of the MWNT/P(MMA-co-EMA) composites.

<table>
<thead>
<tr>
<th>Samplea)</th>
<th>$T_g$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(MMA-co-EMA)</td>
<td>89</td>
</tr>
<tr>
<td>1 wt.% p-MWNT</td>
<td>101</td>
</tr>
<tr>
<td>1 wt.% s-MWNT</td>
<td>90</td>
</tr>
<tr>
<td>5 wt.% p-MWNT</td>
<td>103</td>
</tr>
<tr>
<td>5 wt.% s-MWNT</td>
<td>100</td>
</tr>
<tr>
<td>10 wt.% p-MWNT</td>
<td>107</td>
</tr>
<tr>
<td>10 wt.% s-MWNT</td>
<td>106</td>
</tr>
</tbody>
</table>

a) ‘p-MWNT’ and ‘s-MWNT’ denote the purified and soluble MWNT, respectively.

From Figure 7(a) we can find that most MWNT’s rich domains disperse in the polymer matrix. Magnifying the MWNT’s rich domain (Figure 7(b)), we can see that many MWNTs bundle together. This means that p-MWNTs can not well disperse in P(MMA-co-EMA) matrix. While in Figure 7(c), the s-MWNTs within the fracture surface are evenly dispersed, no obvious MWNT’s rich domains exist in the polymer matrix. Magnifying the fracture surface (Figure 7(d)), we can find that s-MWNTs dispersion in the polymer matrix is better than that of p-MWNTs. The difference structures of p-MWNTs/P(MMA-co-EMA) and s-MWNTs/P(MMA-co-EMA) composite indicate that the interactions between MWNTs and polymer matrix are stronger in (c, d) than that in (a, b). This results further explain why the s-MWNTs/P(MMA-co-EMA) composite possesses better mechanical properties.

Conclusion

In this paper, a solution-mixing method was used to fabricate the ODA-functionalized MWNTs/P(MMA-co-EMA) composites. Mechanical characterization and TGA were performed on the s-MWNTs reinforced composites as well as the p-MWNTs reinforced composites. Results show that the Young’s modulus and tensile strength of the composite with 10 wt.% s-MWNTs have, respectively, 135% and 49% improvements over the pure P(MMA-co-EMA), and a 9.2% increase in Young’s modulus and 12.8% increase in tensile strength over of 10 wt.% p-MWNTs reinforced P(MMA-co-EMA). Glass transition temperature increases from 89 to 106 °C with the addition of 10 wt.% in the s-MWNTs composite. The improved performance of the s-MWNTs/P(MMA-co-EMA) composites was due to better interactions between the polymer matrix and the CNTs interface.
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Figure 7. SEM images of (a), (b) 10 wt.-% p-MWNT in P(MMA-co-EMA) composite and (c), (d) 10 wt.-% wt s-MWNTs in P(MMA-co-EMA) composite.