

# Comparison of Polyimide/Multiwalled Carbon Nanotube (MWNT) Nanocomposites by *In Situ* Polymerization and Blending

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**ABSTRACT:** In this research, multiwalled carbon nanotube (MWNT) was oxidized and then modified to form carboxylic groups ( $-\text{COOH}$ ) on the surface and the end of the tube. After that, the MWNT was added to polyimide matrix to enhance its mechanical and electrical properties by *in situ* polymerization and blending. The PI/MWNT composites were obtained by spin coating and multistep thermal curing process. The comparison of *in situ* polymerization and blending as well as the effect of unmodified and modified MWNT were discussed in this study. The results indicate that *in situ* polymerization is able to make a perfect dispersion by adding modified

MWNT into polyimide matrix. Thermal and mechanical properties of the composites can be improved by hydrogen bonding interaction between the modified MWNT and polyimide matrix. Electrical resistance of the composites can be decreased to meet the criterion of electrostatic charge (ESC) mitigation as the surface resistance is reduced into the range of  $10^6$ – $10^{10}$   $\Omega/\text{cm}^2$  by adding modified MWNT. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3111–3117, 2010

**Key words:** polyimide; multiwalled carbon nanotube; surface modification; nanocomposite; electrostatic charge

## INTRODUCTION

Recently, organic–inorganic hybrid materials combining the advantages of the inorganic material (likes thermal stability and rigidity) and the organic polymer (likes flexibility, dielectric and processability) have been widely studied.<sup>1–6</sup> In preparation of the hybrid composites, it is very important to prevent phase separation. The size of the inorganic segment in the composites could be governed by the combination of synthesis and processing methods.

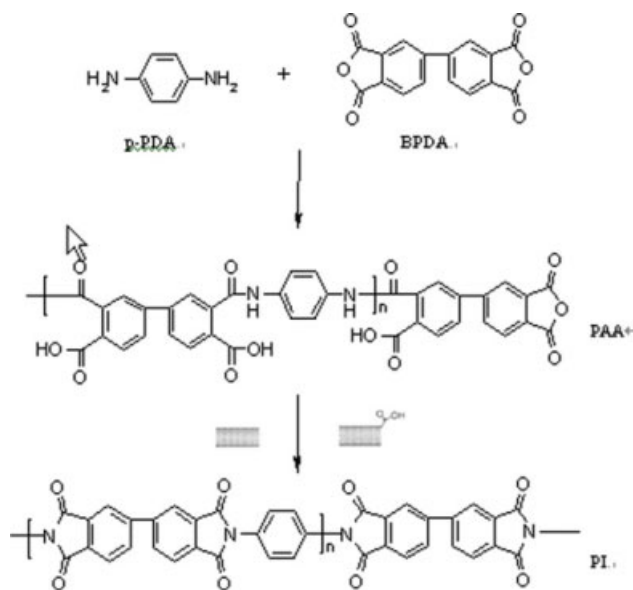
Carbon nanotube (CNT) has attracted much attention from worldwide, because it has superior physical and electrical potentials to be applied to hydrogen storage,<sup>7</sup> chemical sensor,<sup>8,9</sup> nanoelectronic devices,<sup>10,11</sup> flat-panel field-emission displays<sup>12</sup> and nano-reinforcement applications for composites. Because of the intrinsic high aspect ratio structure, CNT has extraordinarily high strength and moderate electrostatic charge (ESC) mitigation with low weight loading. However, the application of CNT in composites has been a challenge for its poor dispersion in organic polymer matrix. In other words, the difficulty is primarily due to the nonreactive surface

of CNT and weak interfacial bonding between CNT and polymer.<sup>13</sup> The intrinsic van der Waals attraction among CNTs with their high surface area and high aspect ratio often leads to significant agglomeration. To get a complete dispersion of CNT in polymer matrix, most studies have been directed toward chemical modification on the surface of CNT to form the functional group.<sup>14–17</sup>

Polyimide is a high-performance polymer, particularly attractive for their excellent mechanical properties, thermal stability, low color, and processibility.<sup>18–21</sup> Based on the excellent chemical, thermal and mechanical characteristics, polyimide has been widely used in the fabrication of aircraft structure, microelectronic devices, insulator, semiconductor, mechanical component, and so on. However, due to its insulating nature as well as radiation resistance, electrostatic charge may accumulate on the surface of polyimide. This causes local heating and consequently thermal degradation of material. To mitigate the build-up of electrostatic charge, the surface resistance can be reduced into the range of  $10^6$ – $10^{10}$   $\Omega/\text{cm}^2$  by adding single wall carbon nanotube (SWCNT) in polyimide composites.<sup>22,23</sup>

Recently, melt mixing compounding,<sup>24–26</sup> *in situ* polymerization<sup>27–29</sup> and coagulation method<sup>30,31</sup> are usually used to prepare polymer/CNT composites. In this study, we propose *in situ* polymerization process of polyimide with MWNT for fabricating

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**Figure 1** Reaction scheme for preparing PI/MWNT composites by blending.

composite films to investigate the electrical properties, mechanical and thermal properties. To pursue more perfect dispersion of MWNT in polyimide matrix, we put MWNT in a solvent under the ultra-sonication to form a loose network structure for the further *in situ* polymerization. Moreover, we prepare polyimide/MWNT composite by blending for the purpose of comparison.

## EXPERIMENTAL

### Materials

Pristine MWNT with diameter 10–30 nm and length 5–15  $\mu\text{m}$  were manufactured by CVD process and the purification was up to 95%. 1-methyl-2-pyrrolidinone (NMP, Acros, 99%), sulfuric acid ( $\text{H}_2\text{SO}_4$ , Acros, 95–98%), nitric acid ( $\text{HNO}_3$ , Acros, 65%), 3,3',4,4'-Biphenyl tetracarboxylic dianhydride (BPDA, CHRISKEV, 98%) and *p*-phenylenediamine (*p*-PDA, Acros, 99%) were used as received without further purification.

### Preparation of functionalized MWNT

Pristine MWNT was purified by air oxidation at 550°C in air for 45 min to remove amorphous carbon and residual metal catalysts to obtain the unmodified MWNT. It was mixed with sulfuric and nitric acids (3 : 1 by weight) by ultra-sonication for dispersion for 4 h to obtain acid-treated MWNT, after washing and filtering the mixture with distilled water and methanol.

### Preparation of poly(amic acid) (PAA)

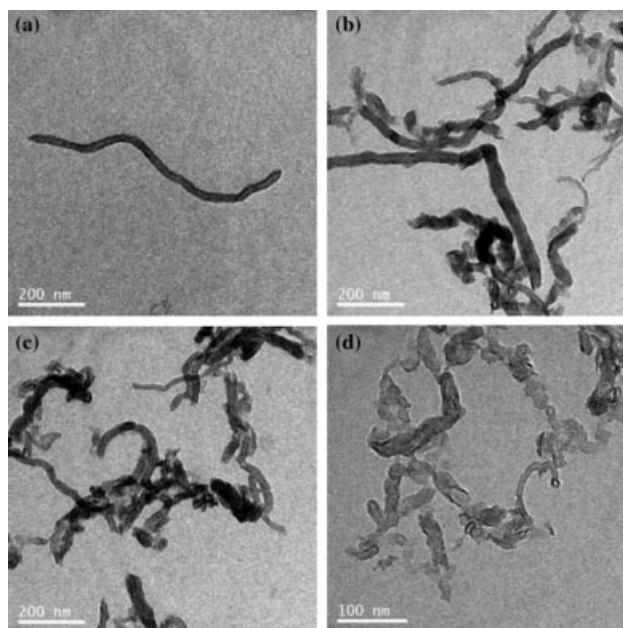
For the preparation of poly(amic acid) (PAA), the precursor of polyimide (PI), diamine *p*-PDA was added into a flask and dissolved in NMP with vigorous stirring. After 30 min, dianhydride BPDA was added and reacted at room temperature under nitrogen purged for 4 h. The PAA solution was obtained, and the solid content of PAA is 13 wt %. To control the molecular weight, the molar ratio of dianhydride and diamine was kept on 1.02 : 1. From the GPC test, the number averaged molecular weight and polydispersion index ( $M_n$ , PDI) of the prepared PAA is (798856, 1.59).

### Preparation of PAA/MWNT composites by blending

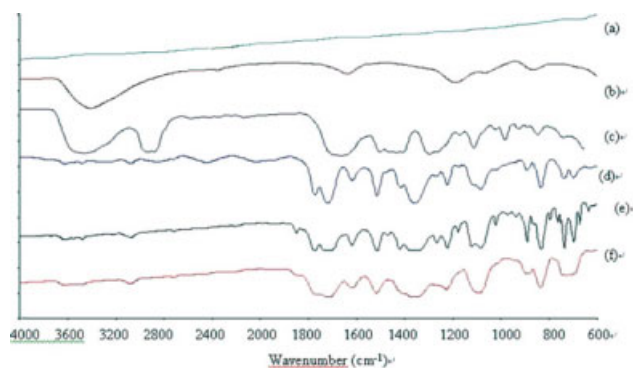
Unmodified and modified MWNT were added to NMP and ultrasonicated for 6 h to obtain uniformly dispersed MWNT suspension, and then the solution was mixed with the above prepared precursor of PAA. The mixture was stirred at room temperature under nitrogen purged for 12 h to obtain the PAA-MWNT composites by blending. The reaction scheme for preparing PI/MWNT composites was shown in Figure 1.

### Preparation of PAA/MWNT composites by *in situ* polymerization

Unmodified and modified MWNT were pretreated with NMP under ultra-sonication for half an hour



**Figure 2** TEM image of MWNT: (a) Pristine MWNT; (b) after acid treatment for 2 hrs at 500°C; (c) after acid treatment for 4 hrs at 500°C; (d) after acid treatment for 6 hrs at 500°C.



**Figure 3** FTIR spectra of polyimide and polyimide/MWNT composites: (a) unmodified MWNT; (b) modified MWNT; (c) PAA; (d) PI; (e) PI/MWNT by *in situ* polymerization; (f) PI/MWNT by blending. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

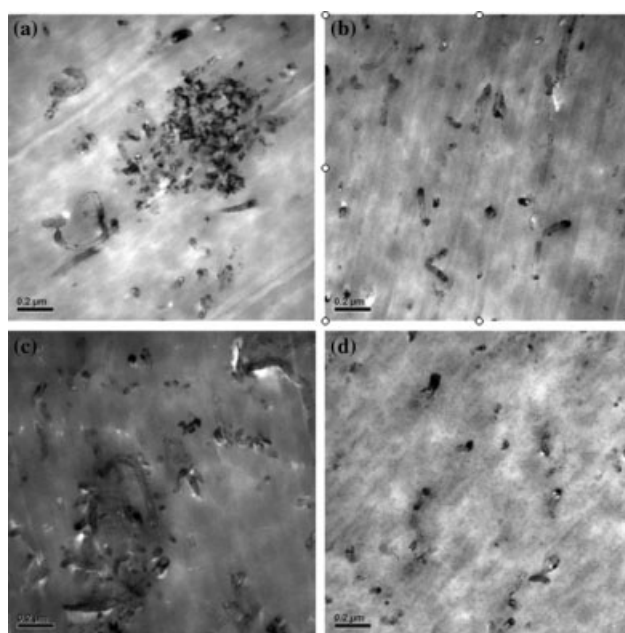
and to form loose network of MWNT suspension to achieve better dispersion in the composites. Diamine *p*-PDA was then added into it for 30 min stirring, and dianhydride BPDA was added to react under nitrogen purged with vigorous stirring for 12 h at room temperature. The precursor of the PAA-MWNT composites solution by *in situ* polymerization was then obtained.

### Synthesis of PI/MWNT hybrid films

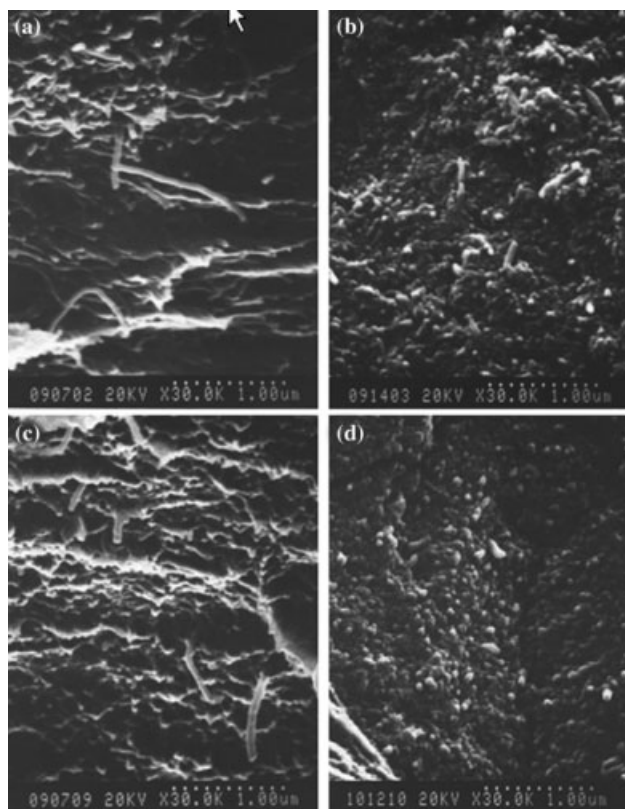
After the preparation of the precursor PAA solution, the films were prepared by casting PAA solution onto glass plates for multistep thermal curing processes (80°C for 1 h, 100°C for 1 h, 150°C for 1 h, 200°C for 1 h, 250°C for 1 h, 300°C for 1 h, and finally at 400°C for 1 h). The PI-MWNT films were then obtained.

### Characterization

The molecular weight distribution of prepared polymer was determined by a GPC equipped with PLgel 5  $\mu\text{m}$  MIXED-C and D columns in the elution solvent of DMF at 1 mL/min. FTIR analysis was performed with a Perkin-Elmer FTIR System. TEM was performed by employing a JEOL-JEM-1230 transmission electron microscope. SEM was performed by employing a JEOL-5610 scanning electron microscope. Thermal analysis was performed by a TA TGA 2950 under nitrogen with a heating rate of 20°C/min from 40 to 800°C. Tensile test was measured with an Instron 4466 tester, and the tensile rate is 5 mm/min at room temperature. The electrical properties were measured with an ULTRA Mesoh-meter SM-8200, and the test was



**Figure 4** TEM image of the hybrid films: (a) PI with 3% unmodified MWNT by blending; (b) PI with 3% modified MWNT by blending; (c) PI with 3% unmodified MWNT by *in situ* polymerization; (d) PI with 3% modified MWNT by *in situ* polymerization.



**Figure 5** Cross section SEM image of the hybrid films by *in situ* polymerization: (a) 6% unmodified MWNT; (b) 6% modified MWNT; (c) 12% unmodified MWNT; (d) 12% modified MWNT.



**TABLE I**  
**Thermal Properties of Polyimide and Polyimide/MWNT Composites**

Sample	Unmodified (wt%) MWNT	Modified (wt%) MWNT	$T_d$ (°C)		Remark	
			<i>In situ</i>	Blending	<i>In situ</i>	Blending
PI	0	–		562	T	T
P1	3	–	564	563	T	T
P2	6	–	567	575	O	O
P3	9	–	568	569	O	O
P4	12	–	567	564	O	O
P5	–	3	572	568	T	T
P6	–	6	573	571	O	O
P7	–	9	575	564	O	O
P8	–	12	574	568	O	O

$T_d$  10% decomposition temperature; T, transparent; O, opaque.

conducted at room temperature with the same voltage of 100 V.

## RESULTS AND DISCUSSION

TEM image shown in Figure 2 presents the influence of MWNT with the acid treatment for various times at 50°C. The length of MWNT decreases with the increase of acid treatment time as shown in TEM spectra. Before the acid treatment, the length of MWNT is about 1.5  $\mu\text{m}$ . After the acid treatment for 2hrs, 4hrs and 6hrs, the length of MWNT is about 800 nm, 400 nm, and 200 nm, respectively. To reduce electrical resistance, chemical modification of MWNT would be necessary to get a well dispersed composite. Tube-to-tube distance of MWNT must be short and close enough to form a conductive path to transfer electron, acid treatment for 4 hrs would be therefore chosen in this study. We can find the surfaces of modified MWNT have carboxyl acid and hydroxyl groups, which form at defect sites along the surface of MWNT or at the end of MWNT dur-

ing the acid treatment process. Absorption peaks at 3400  $\text{cm}^{-1}$  for  $-\text{OH}$  group, 1720  $\text{cm}^{-1}$  for  $\text{C}=\text{O}$  group and 1210  $\text{cm}^{-1}$  for  $\text{C}-\text{O}$  group can be observed in Figure 3 of the FTIR spectra.

For the preparation of PI/MWNT composites by *in situ* polymerization, MWNT was first pretreated in NMP solvent under ultrasonic to form loose network structure to make a uniform dispersion of MWNT in PI. The viscosity of the solution containing MWNT became higher than pure solvent, which indicated that a large amount of solvent was percolated into MWNT network. Figure 3 compares the FTIR spectra of PAA, PI and PI/MWNT hybrid materials. It is found that the PAA/MWNT contains characteristic absorptions around 2860–3200  $\text{cm}^{-1}$  and 3400  $\text{cm}^{-1}$  (N–H and carbonyl acid O–H), 1537  $\text{cm}^{-1}$  and 1710  $\text{cm}^{-1}$  (amic acid (C–NH) and carbonyl acid C=O). The conversion of PAA to PI can be elucidated by the decrease of the carbonyl acid absorption at 1672  $\text{cm}^{-1}$ , and by the characteristic absorption bands of imide group observed at 1773  $\text{cm}^{-1}$  (C=O asymmetric stretching), 1703  $\text{cm}^{-1}$

**TABLE II**  
**Mechanical Properties of Polyimide and Polyimide/MWNT Composites**

Sample	Unmodified MWNT (wt %)	Modified MWNT (wt %)	Strength (MPa)		Elongation (%)	
			<i>In situ</i>	Blending	<i>In situ</i>	Blending
PI	0	–	83.7 $\pm$ 3.5		8.26 $\pm$ 0.12	
P1	3	–	96.9 $\pm$ 3.6	95.4 $\pm$ 4.7	7.17 $\pm$ 0.13	7.65 $\pm$ 0.26
P2	6	–	102.2 $\pm$ 3.8	115.2 $\pm$ 4.6	6.73 $\pm$ 0.14	5.82 $\pm$ 0.22
P3	9	–	110.8 $\pm$ 3.0	91.5 $\pm$ 3.9	5.92 $\pm$ 0.13	4.24 $\pm$ 0.34
P4	12	–	119.5 $\pm$ 4.2	70.0 $\pm$ 5.6	5.25 $\pm$ 0.15	2.85 $\pm$ 0.37
P5	–	3	113.3 $\pm$ 3.5	120.8 $\pm$ 4.3	5.4 $\pm$ 0.15	5.47 $\pm$ 0.27
P6	–	6	127.6 $\pm$ 3.4	140.3 $\pm$ 5.0	4.78 $\pm$ 0.17	4.36 $\pm$ 0.35
P7	–	9	172.3 $\pm$ 3.6	129.5 $\pm$ 4.9	3.97 $\pm$ 0.14	3.63 $\pm$ 0.37
P8	–	12	159.0 $\pm$ 3.8	86.0 $\pm$ 5.7	2.97 $\pm$ 0.12	2.08 $\pm$ 0.15

TABLE III  
Electrical Properties of Polyimide and Polyimide/MWNT Composites

Sample	Unmodified MWNT (wt %)	Modified MWNT (wt %)	Surface resistance( $\Omega/\text{cm}^2$ )		Volume resistance( $\Omega \text{ cm}$ )	
			<i>In situ</i>	Blending	<i>In situ</i>	Blending
PI	0	–	$1.40 \times 10^{14}$		$4.30 \times 10^{15}$	
P1	3	–	$3.50 \times 10^{12}$	$6.30 \times 10^{12}$	$1.74 \times 10^{14}$	$1.60 \times 10^{14}$
P2	6	–	$1.20 \times 10^{11}$	$2.00 \times 10^{11}$	$2.83 \times 10^{13}$	$1.30 \times 10^{13}$
P3	9	–	$1.40 \times 10^{10}$	$1.70 \times 10^{10}$	$9.74 \times 10^9$	$7.60 \times 10^9$
P4	12	–	$1.80 \times 10^9$	$3.50 \times 10^9$	$1.42 \times 10^9$	$4.20 \times 10^9$
P5	–	3	$3.90 \times 10^{11}$	$1.70 \times 10^{11}$	$9.81 \times 10^{13}$	$1.20 \times 10^{14}$
P6	–	6	$1.60 \times 10^{10}$	$2.10 \times 10^{10}$	$3.94 \times 10^{12}$	$7.00 \times 10^{13}$
P7	–	9	$4.20 \times 10^8$	$2.20 \times 10^9$	$5.54 \times 10^9$	$4.80 \times 10^9$
P8	–	12	$8.50 \times 10^7$	$7.20 \times 10^8$	$2.98 \times 10^8$	$7.40 \times 10^8$

(C=O symmetric stretching) and  $1358 \text{ cm}^{-1}$  (C–N–C imide ring stretching, the functional group of polyimide). Whether to use *in situ* polymerization or blending, adding MWNT into PI matrix will not change the chemical structure of MWNT.

The TEM images shown in Figure 4 present the morphology of the PI/MWNT composite films. The aggregation of unmodified MWNT can be observed easily, which reveals the poor interaction between the unmodified MWNT and PI. On the other hand, modified MWNT can be found to have better dispersion in PI matrix. Because modified MWNT has carboxyl acid group and shorter length, it can form the hydrogen bonding with polymer matrix to achieve better interaction with PI. These TEM images suggest the *in situ* polymerization can achieve better dispersion than blending method in this study. In addition, the cross-section SEM images shown in Figure 5 present morphology of the fracture surface of the hybrid films. Modified MWNT is found to have better dispersion in PI matrix. Bundled unmodified MWNT is exposed outside the surface

of PI, which further reveals the poor interaction between them.

Thermal properties of PI/MWNT composites were examined by TGA analysis as listed in Table I. Pristine polyimide exhibits the good thermal stability and prevents itself from thermal decomposition until  $563^\circ\text{C}$ . The thermal decomposition temperature ( $T_d$ ) of the PI/MWNT composites increases as the content of MWNT is increased. By adding modified MWNT, better thermal stability can be achieved than by adding the unmodified MWNT using *in situ* polymerization, because the modified MWNT with carboxyl acid group can form the hydrogen bonding with PI to achieve better dispersion in PI matrix. The composites prepared by *in situ* polymerization have higher thermal decomposition temperature than prepared by blending, because the pretreatment step under ultra-sonication makes the MWNT networks looser to have better dispersion in PI matrix. The highest thermal decomposition temperature of  $575^\circ\text{C}$  can be achieved, when the composite is added with 9% of modified MWNT. For the composites

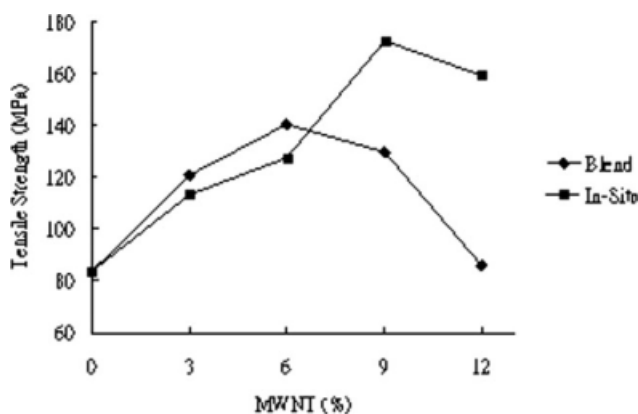


Figure 6 Tensile strength of the PI/ modified MWNT composites.

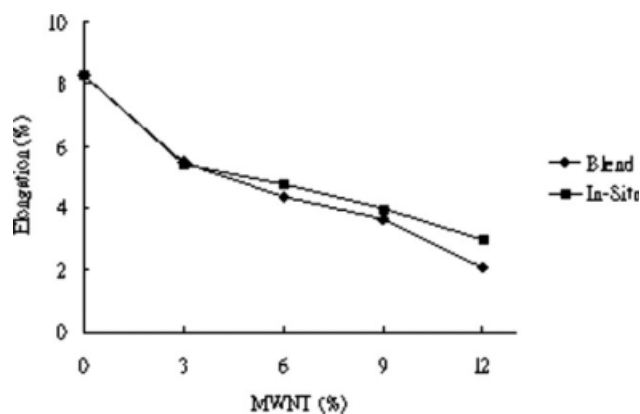


Figure 7 Elongation at break of the PI/ modified MWNT composites.

made by blending, thermal stability can not be improved by adding modified MWNT than unmodified MWNT. It is because that the viscosity of PAA with high molecular weight is so high that MWNT can not pass through polymer matrix easily to obtain well dispersed composites by blending.

Electrical conductivity should be optimized to meet the criterion of the electrostatic charge (ESC) mitigation to avoid electrostatic charge build-up in the materials. Both the surface and volume resistances of the PI/MWNT composites were measured at room temperature with the results presented in Table II. The data show that adding unmodified MWNT or modified MWNT into PI will reduce the surface and volume resistances, which indicates the high aspect ratio of carbon nanotube has significant effect on promoting the electrical conductivity. The criterion for electrostatic charge mitigation ( $10^6$ – $10^8$   $\Omega$ /square) can be met when PI is prepared by *in situ* polymerization with modified MWNT loading of 9 wt %. This result suggests that the loose network structure and better dispersion of modified MWNT in PI composites made by *in situ* polymerization can achieve an effective conductive path. As MWNT loading exceeds 9 wt %, the electrical conductivity increases slowly with the increase of MWNT.

Table III summarizes the tensile strength and elongation break for the PI composite films with various content of modified and unmodified MWNT. The MWNT can reduce the mobility of PI matrix and therefore increase the strength, but decrease the elongation of PI. The tensile strength of the composites can be much more increased by modified MWNT than unmodified MWNT. Figures 6 and 7 compare the tensile strength and elongation for PI/modified MWNT prepared by blending or *in situ* polymerization. The tensile strength can be increased about 1.5 times to 140 MPa with 6 wt % modified MWNT by blending, but decreased slightly with further increase of MWNT content. On the other hand, the best mechanical property can be obtained from the PI composites with modified MWNT by *in situ* polymerization. The tensile strength is increased about two times to 172 MPa for PI composites with 9 wt % modified MWNT by *in situ* polymerization. Better dispersion and interaction as the result of hydrogen bonding between the modified MWNT and PI matrix can be achieved in this composition. This result again supports that the modified MWNT has better dispersion in polyimide composite by *in situ* polymerization.

## CONCLUSIONS

The composites based on polyimide/MWNT hybrids have been successfully prepared by *in situ*

polymerization and blending. The PI/MWNT composites have excellent thermal stability, mechanical and electrical properties. To obtain homogeneous dispersion of MWNT in polyimide matrix, acid treatment of MWNT is chosen in this study. During the acid treatment process, carboxyl acid and hydroxyl groups can be formed at defect sites along the surface of MWNT or at the end of MWNT. The TEM results show that MWNT can be cut into short length with mixed-acid. These functional groups can form hydrogen bond with the polyimide chain to enhance the dispersion of MWNT in the polymer matrix. The thermal property of the composites is therefore higher than pure polyimide because of adding modified MWNT. And this can much more improve the mechanical properties of the composites than adding unmodified MWNT. Furthermore, the electrical conductivity can be increased by more than six orders when PI/MWNT composites are prepared by *in situ* polymerization with adding 9 wt % modified MWNT because of the effective conductive path formed by better dispersion of modified MWNT in PI. From the earlier results, we can conclude that better dispersion and interaction between modified MWNT and PI matrix can be achieved by *in situ* polymerization.

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