

# Investigation of MWNTs/PBO Nanocomposite Polymerization Mechanism with Model Compound

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**ABSTRACT:** A model compound was obtained by reaction of benzoic acid and 4,6-diamino-1,3-dihydroxybenzene dihydrochloride (DADHB · 2HCl) in the presence of functionalized multiwall carbon nanotubes (FMWNTs). FMWNTs were formed on raw multiwall carbon nanotubes (MWNTs) by chemical modification. The model compound was rinsed by chloroform and MWNTs were separated by centrifuge. The sediment yielded was denoted as graft multiwall carbon nanotubes (GMWNTs). Then X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and Fourier-transform infrared (FTIR) were used to investigate the existence of covalent bond between DADHB and FMWNTs. The results of XPS showed that nitrogen atoms amounted to about 3.3%

except for oxygen and carbon on the surface of GMWNTs. Meantime, the reaction of —COOH of the FMWNTs and the monomer DADHB occurred, and benzoxazole was formed predominantly by Raman spectroscopy analysis. FTIR spectroscopy confirmed the covalent grafting of monomer to FMWNTs in the processing procedure. As a result, the mechanism of the reaction of the poly(*p*-phenylenebenzoxazole) (PBO) oligomer and FMWNT composites was deduced according to the reaction of the model compound. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 893–898, 2007

**Key words:** Raman spectroscopy; FTIR; oligomers

## INTRODUCTION

Poly(*p*-phenylene benzoxazole) (PBO) fibers are a rigid-rod polymer with excellent thermal stability and remarkable tensile strength and modulus.<sup>1–3</sup> The tensile strength and modulus of commercial PBO fibers (Zylon™ HM) are 5.8 GPa and 270 GPa, respectively.<sup>4</sup> However, the axial compressive strength of PBO fibers is ~ 10–15% of their tensile strength. The poor compressive strength of high-performance fibers restricts their application in composites. A number of investigations have been performed to improve lateral interactions in rigid polymers including morphology modification.<sup>5</sup> Interfibrillar entanglements are introduced by twisting and drawing the polymer dope during fiber spinning. The compressive strength of PBO fibers is also improved.<sup>6</sup> Inorganic components are incorporated into PBO fibers and films by coating or infiltration. While no significant improvement of compressive

strength was observed.<sup>7</sup> Single-wall carbon nanotubes (SWNTs) and PBO composites are synthesized by in situ polymerization in some investigations. PBO fiber tensile strength has been increased by about 50% when the content of SWNT addition is 10 wt %.<sup>8</sup> However, there has been limited research on polymerization mechanism of CNTs/PBO.

The PBO polymerization mechanism has been reported in poly(phosphoric acid).<sup>9–11</sup> PBO oligomers are not statistically end-capped with the two monomers. Only 4,6-diamino-1,3-dihydroxybenzene (DADHB) is found at the PBO oligomer chain ends due to the extremely low solubility of terephthalic acid (TA) in PPA. A model compound was prepared with DADHB · 2HCl and benzoic acid. The chemical structures 2,6-diphenylbenzo[1,2-*d*;4,5-*d'*]bisoxazole and the PBO oligomer are shown in Figure 1.

The present work investigates the polymerization mechanism of multiwall carbon nanotube (MWNT)/PBO nanocomposites by means of a model compound. DADHB · 2HCl and benzoic acid were chosen as two monomers of the model compound in the presence of functionalized multiwall carbon nanotubes (FMWNTs). FMWNTs were chosen as a starting model nanotube because the surface of FMWNTs was found to contain —COOH groups by X-ray photoelectron spectroscopy (XPS) analysis. From the viewpoint of molecular design, DADHB could react with carboxyl groups on the FMWNTs.

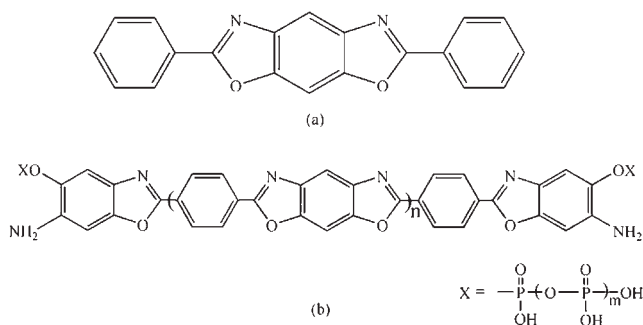
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**Figure 1** Chemical structure of (a) 2,6 bisphenylbenzo [1,2-d:5,4-d']bisoazole; and (b) PBO oligomer.

## EXPERIMENTAL

### Synthesis of GMWNTs

Raw MWNTs (Shenzhen Nanotech Port Co., Ltd., Shenzhen, China; 95% purity) (1.5 g) were treated by a reflux process in a 200-mL mixture acid concentrated  $\text{H}_2\text{SO}_4$ /concentrated  $\text{HNO}_3$  of solution (1 : 3, v/v) at boiling point temperature for 4 h. The treated MWNTs were then washed with distilled water until no residual acid was present. Subsequently, the samples were dried at  $80^\circ\text{C}$  under vacuum. The sample was referred to as functionalized multiwall carbon nanotubes (FMWNTs).

DADHB  $\cdot$  2HCl was prepared through a three-step reaction from trichlorobenzene<sup>12</sup> and was purified by recrystallization from diluted hydrochloric aqueous solution with  $\text{SnCl}_2$ . All glassware and stirring bars were oven-dried before use; 10 mmol DADHB  $\cdot$  2HCl and 20 mmol benzoic acid were mixed together with newly prepared 83.5 wt % polyphosphoric acid (PPA) (80 g) in a 100-mL glass flask equipped with a mechanical stirred and two gas ports. Removal of HCl from DADHB  $\cdot$  2HCl was performed under  $100^\circ\text{C}$  for 20 h under nitrogen atmosphere; subsequently, a 4.6-g mixture containing  $\text{H}_3\text{PO}_4$  and FMWNTs by ultrasonic bath (38 kHz), for 30 min under room temperature, was added to the reaction flask. The mixture was heated at  $160^\circ\text{C}$  for 24 h and  $180^\circ\text{C}$  for 24 h with constant, strong stirring. The mixture was finally heated to  $200^\circ\text{C}$  for 6 h with stirring. The dope was poured into the distilled water and then washed to remove the PPA completely. The model compound was then dried under vacuum at  $100^\circ\text{C}$ .

Model compound powders were dispersed in chloroform for 30 min, then separated by centrifugal at 4000 rpm for 20 min once and again. Each centrifugal solution was tested by FTIR until the signal of the model compound could no longer be detected, showing that the CNTs were completely washed. The graft multiwall carbon nanotubes (GMWNTs) were obtained.

### Characterization

XPS was adopted to measure the surface compositions of several kinds of CNT. The measurements were performed using a Thermo ESCALAB 250 spectrometer equipped with a monochromatic AlK $\alpha$  (1486.6 eV). The instrument was operated with an analyzer chamber pressure of  $3.0 \times 10^{-8}$  Pa, and with the axis of the energy analyzer at  $90^\circ$  relative to the nominal plane of the sample surface and operated in a fixed transmission mode. The high-resolution C1s were curve-fitted by built-in software to analyze the chemical bonding states of atoms.

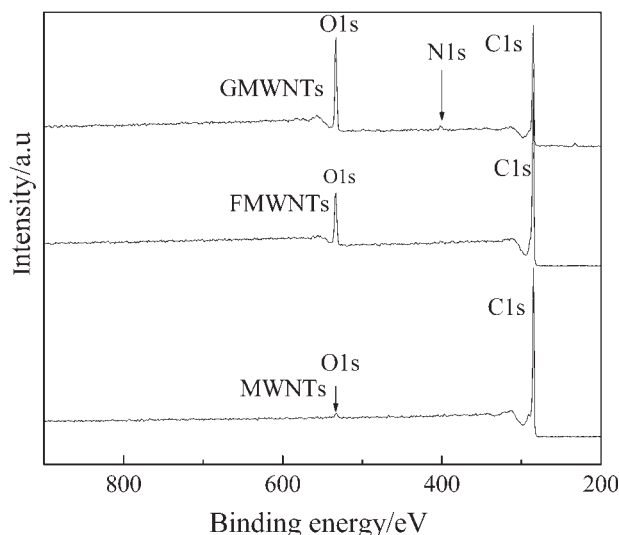
The Raman spectrum was recorded with a T64000 Raman spectrometer from the France JY Company, (Villeneuve d'Ascq, France) equipped with an Ar<sup>+</sup> gas laser (514.5 nm). The Raman band of a silicon wafer at  $520\text{ cm}^{-1}$  was used to calibrate the spectrometer. The laser power at the sample was 100 mW. The laser beam was focused on the samples, using an optical microscope with a  $50\times$  objective lens. The spectral resolution was  $0.15\text{ cm}^{-1}$ .

The Fourier-transform infrared (FTIR) spectra of MWNTs, FMWNTs, and GMWNTs were measured with a spectral resolution of  $4\text{ cm}^{-1}$  on a Nicolet Nexus 670 FT-IR spectrophotometer, using KBr disks or pellets at room temperature.

## RESULTS AND DISCUSSION

### X-ray photoelectron spectroscopy analysis

X-ray photoelectron spectroscopy (XPS) proved to be a powerful tool for chemical analysis. The composition of CNTs, MWNTs, FMWNTs, and GMWNTs is characterized by XPS in Figure 2. The chemical compositions of the surface of CNTs are shown in



**Figure 2** XPS survey spectrum of CNTs.

**TABLE I**  
Chemical Composition of the CNTs Determined by XPS Analysis

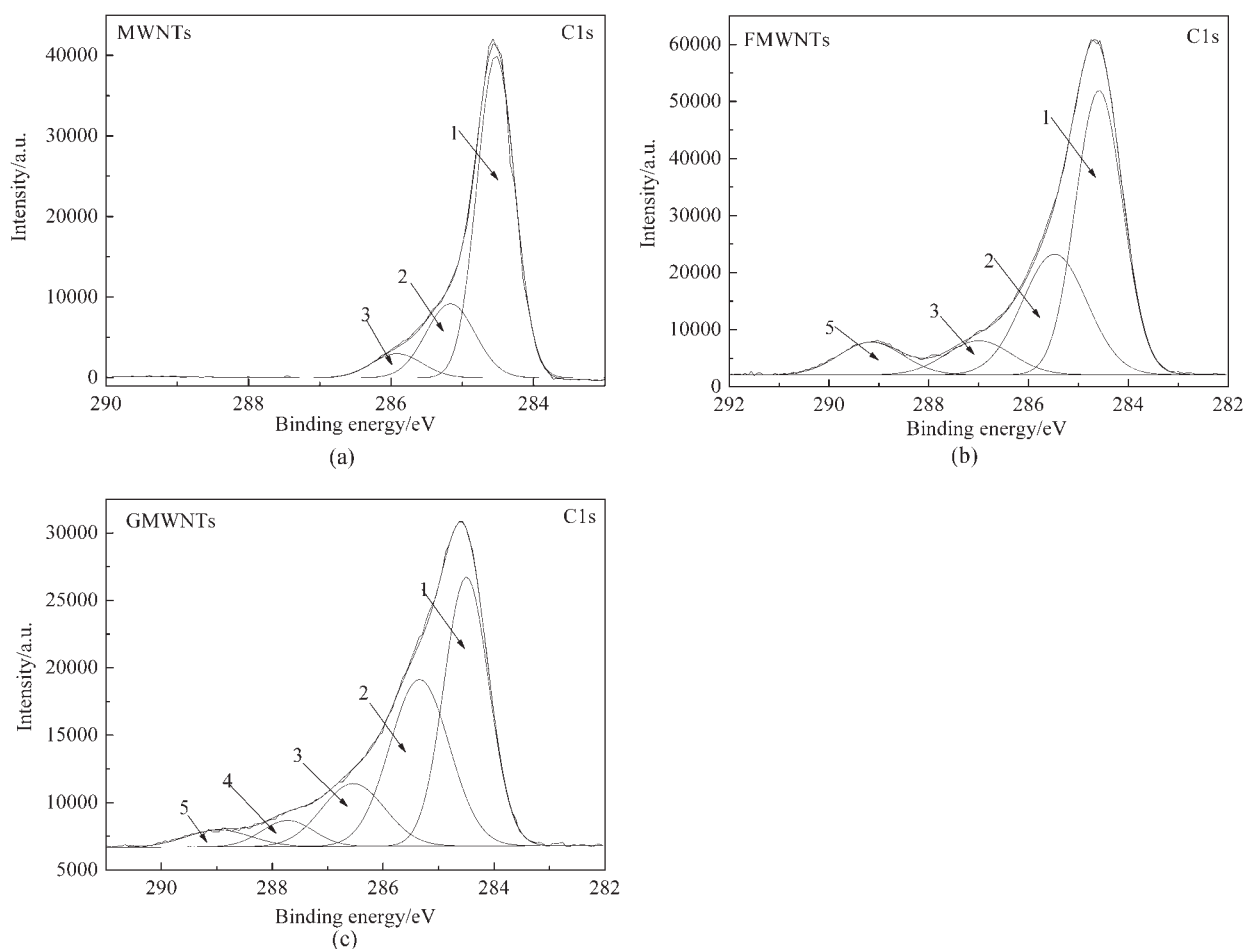
Sample	at%			O/C
	C	O	N	
MWNTs	97.6	2.4	—	0.024
FMWNTs	85.3	14.7	—	0.171
GMWNTs	66.4	30.3	3.3	0.456

Table I. After the MWNTs were treated with acid, the oxygen content was raised to 14.7%, but no nitrogen appeared. After the FMWNTs were reacted with monomers, the oxygen content was raised to 30.32%, and that of nitrogen introduced by DADHB was about 3.3%.

In the MWNT spectrum [Fig. 3(a)], the C1s core level could be curve-fitted with three components, with binding energy at 284.5 eV for C—C, 285.4 eV for —C—O—C—, and 286.4 eV for —C—OH, respectively. The —C—O—C— and —C—OH species were attributed to atmospheric oxidation or residual oxides that resulted from the MWNT purification process.

The XPS C1s spectrum of FMWNTs is shown in Figure 3(b). This spectrum clearly consists of four components. The peak at 284.5 eV for C—C is due to the graphite-like carbon atoms of the tube walls. The signal at 289.1, 287.0, and 285.5 eV is assigned to the O—C=O—, —C—O—C—, and —C—OH species, respectively. Compared with Figure 3(a), Figure 3(b) shows a new peak at 289.1 eV, assigned to O—C=O after acid treatment, and the comparative content of O—C=O is 8.2%. After the MWNTs were treated with acid, carboxyl was introduced and hydroxyl functional groups increased on the surface.<sup>13</sup> These groups will be reacted with the DADHB.

The C1s spectrum of the GMWNT surface is shown in Figure 3(c). The C1s core level spectrum contained five components. Besides 284.5 eV for the C—C, the additional higher binding energies are 285.3 eV for the N—C and C—O—C species, 286.5 eV for the C—OH species, 287.7 eV for O—C=N, and 289.0 eV for O=C—N; the results are shown in Table II. The [N—C=O]/[N=C—O] is 19/24, as measured by their area ratio. The results indicate that primarily benzoxazole formed.



**Figure 3** XPS C1s, divide chart. (a) MWNTs C1s; (b) FMWNTs C1s; (c) GMWNTs C1s.

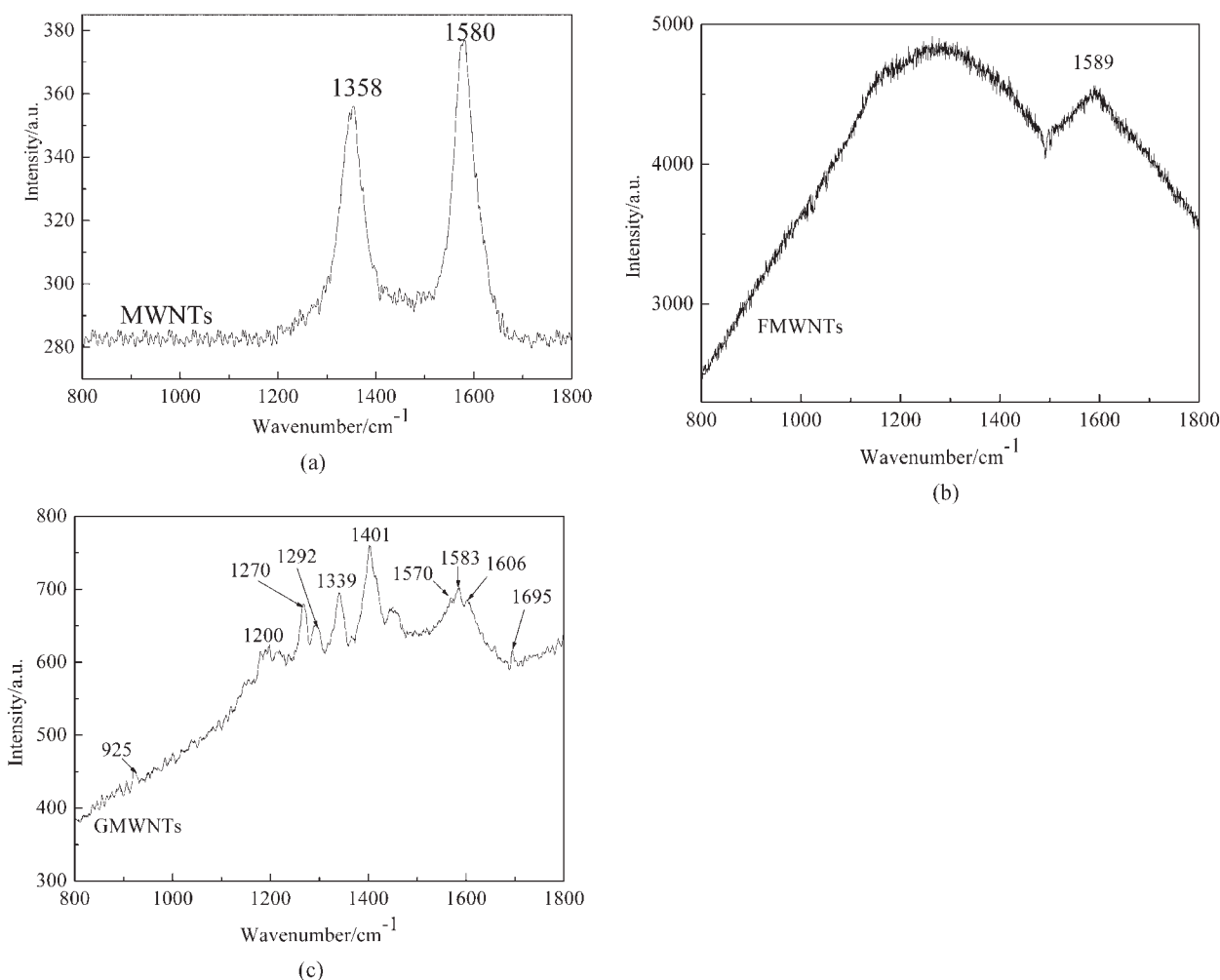
**TABLE II**  
**Fraction of Carbon Functional Groups from High-Resolution C1s XPS Peaks**

Samples	C1s				
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
MWNTs					
Binding energy (eV)	284.5	285.1	286.0	—	—
Content of functional groups (mol%)	71.5	21.3	7.1	—	—
FMWNTs					
Binding energy (eV)	284.5	285.5	287.0	—	289.1
Content of functional groups (mol%)	52.4	30.6	8.8	—	8.2
GMWNTs					
Binding energy (eV)	284.5	285.3	286.5	287.7	289.0
Content of functional groups (mol%)	42.4	35.1	13.9	4.8	3.8
Functional groups	C—C	C—O—C or C—N	C—OH	O—C=N	O—C=O or N—C=O

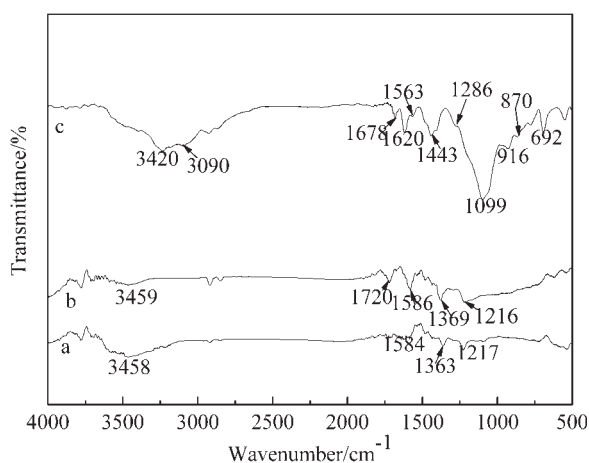
### Raman spectroscopy analysis

The Raman spectrum of CNTs is shown in Figure 4. There were two dominant optically active phonon modes in the Raman spectrum of raw MWNTs, as shown in Figure 5(a), where the line at  $1580\text{ cm}^{-1}$  is the G line, corresponding to the optically active in-

plane  $E_{2g}$  vibrational mode; the D line at  $1358\text{ cm}^{-1}$  is related to the defects in the curved graphite sheets.<sup>14</sup> After acid treatment, the wide speak centered at  $1350\text{ cm}^{-1}$  indicated that the sidewalls of the carbon nanotubes were covalently modified in the FMWNT spectrum in Figure 5(b). The clear evidence of the MWNT graft is given by Raman spectroscopy in Fig-



**Figure 4** Raman spectra. (a) MWNTs; (b) FMWNTs; (c) GMWNTs.



**Figure 5** FTIR spectra. (a) MWNTs; (b) FMWNTs; (c) GMWNTs.

ure 5(c). There are characteristic peaks of CNTs at  $1339\text{ cm}^{-1}$  (D line) and  $1583\text{ cm}^{-1}$  (G line). The peak at  $1695\text{ cm}^{-1}$  is the amide group for  $\text{N}-\text{C}=\text{O}$ .<sup>16</sup> The characteristic peaks of PBO are at  $1620\text{ cm}^{-1}$ , along with prominent peaks at  $928$ ,  $1178$ ,  $1207$ ,  $1278$ ,  $1306$ , and  $1543\text{ cm}^{-1}$ .<sup>15</sup> The peak at  $1606\text{ cm}^{-1}$  in Figure 5(c) is also considered the vibration mode of the *p*-phenylene ring backbone. The peaks at  $1570\text{ cm}^{-1}$  are the ring-stretching vibration of the phenylene group coupled with the ring deformation vibration of benzene in benzobisoxazole group. The peak at  $1292\text{ cm}^{-1}$  in Figure 5(c) is the  $\text{C}-\text{C}$  stretching of the carbons linking heterocycle and phenyl ring. Moreover, the peak at  $1200\text{ cm}^{-1}$  is the ring deformation of the whole phenylene benzobisoxazole groups; and the peak at  $925\text{ cm}^{-1}$  is the  $\text{C}-\text{H}$  out-of-plane bending vibrations in the phenylene ring,<sup>17</sup> indicating that the benzoxazole group and amine formed during the reaction process.

#### Fourier transform infrared analysis

Figure 5 shows the FTIR spectra of MWNT, FMWNT, and GMWNT powder. The appearance of a wide band centered at  $3459\text{ cm}^{-1}$  was attributed to the presence of  $\text{O}-\text{H}$  groups on the surface of the raw MWNTs. The peaks of  $1586\text{ cm}^{-1}$ ,  $1363\text{ cm}^{-1}$  and  $1216\text{ cm}^{-1}$  were attributed to  $\text{C}=\text{C}$ ,  $\text{C}-\text{H}$ , and  $\text{C}-\text{O}$ , respectively. After the MWNTs were treated in  $\text{H}_2\text{SO}_4/\text{HNO}_3$ , the characteristic bands generated by the polar functional groups, i.e.,  $-\text{OH}$  and  $-\text{COOH}$ , were observed at  $3458\text{ cm}^{-1}$  and  $1720\text{ cm}^{-1}$  in the FTIR spectrum of the CNTs.<sup>18</sup> The characteristic peaks of GMWNTs were assigned<sup>19</sup> as follows: a wide band centered at  $3420\text{ cm}^{-1}$  for  $\text{N}-\text{H}$  and  $\text{O}-\text{H}$  stretching vibrations of amine and hydroxyl end groups;  $1678\text{ cm}^{-1}$  for the  $\text{C}=\text{O}$  group of the amide functionality;  $1620\text{ cm}^{-1}$  for  $\text{C}=\text{N}$  bonds of benzoxazole;  $1563\text{ cm}^{-1}$  for stretching

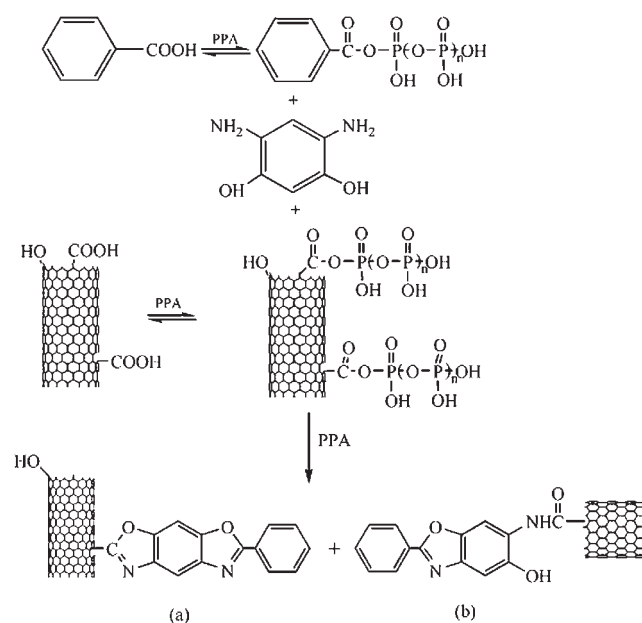
vibration  $\text{C}-\text{N}$  of amide;  $1443\text{ cm}^{-1}$  for skeletal vibrations of the conjugated system;  $1286\text{ cm}^{-1}$  for  $\text{C}-\text{N}$  band;  $1099\text{ cm}^{-1}$  for  $\text{C}-\text{H}$  in-plane deformations in the substituted aromatic rings; and  $925\text{ cm}^{-1}$  for  $\text{C}-\text{O}-\text{C}$  stretching vibration;  $870\text{ cm}^{-1}$  and  $692\text{ cm}^{-1}$  out-of-plane  $\text{C}-\text{H}$  vibrations of aromatic rings. FTIR results verified the existence of the benzoxazole group and amine, and confirmed the covalent grafting of monomer to the MWNTs in the processing procedure.

#### Dispersal of MWNTs

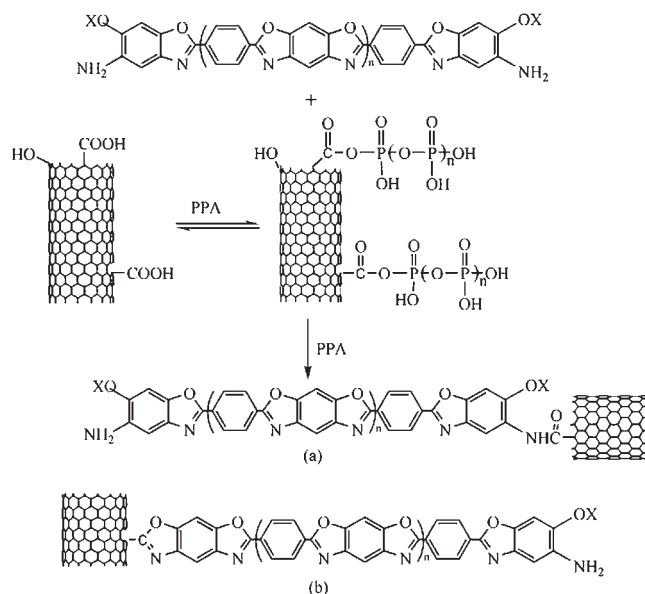
MWNT dispersability changed after grafting polymerization, clearly demonstrating that the benzoxazole chains were chemically bonded to MWNTs and could not be removed during the washing step. While MWNTs could not be well dispersed in chloroform (a good solvent for 2,6-diphenylbenzo[1,2-d;4,5-d']bisoxazole), a very stable MWNT suspension was formed in chloroform after the polymer grafting. This finding suggested that the graft groups were able to modify the properties of MWNTs to the extent that the material became dispersible.

#### Mechanism of polymerization

The proposed mechanism for the grafting polymerization is illustrated in Figure 6. According to the results of XPS analysis, Raman spectroscopy, and FTIR, the carboxylic acid functionalities will react with the amine of DADHB. This led to model compound chain grafting onto the MWNTs by the formation of a covalent



**Figure 6** Reaction route of DADHB, benzoic acid, and GMWNTs.



**Figure 7** Reaction route of FMWNTs and PBO oligomer.

lent bond. Because the PBO oligomer chain ends were capped with DADHB.<sup>9</sup> The mechanism of the reaction of PBO oligomer and FMWNTs composites could be deduced in Figure 7. This type of nanotube structure with the head linked to the side was in favor of the improvement of compressive strength. The focus of the present work is on the polymerization mechanism.

## CONCLUSIONS

The model consisting of DADHB and benzoic acid was prepared by in situ polymerization in the presence of MWNTs. MWNTs, FMWNTs, and GMWNTs were characterized by means of several techniques. XPS demonstrated that 3.3 at% nitrogen appeared on

the surface of GMWNTs. The high-resolution XPS and Raman spectra indicated the formation of the benzoxazole group and amine. FTIR confirmed the existence of a covalent bond between the FMWNTs and DADHB. The reaction mechanism of the model compound is suggested by analysis, which is helpful in understanding the mechanism of PBO/MWNTs nanocomposite polymerization.

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