

# Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) multi-bonded carbon nanotube (CNT): Preparation and formation of PPO/CNT nanocomposites

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## ARTICLE INFO

### Article history:

Received 13 August 2008  
Received in revised form 14 October 2008  
Accepted 15 October 2008  
Available online 21 October 2008

### Keywords:

Carbon nanotube  
Poly(2,6-dimethyl-1,4-phenylene oxide)  
Nanocomposites

## ABSTRACT

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) multi-bonded carbon nanotube (CNT) (CNT-PPO) was prepared using brominated PPO under the condition of atom transfer radical polymerization. The structure and properties of CNT-PPO were characterized with FTIR, Raman spectroscopy and thermal analyzer. The PPO layer in a thickness of about 4.5 nm was observed covering on the side wall of CNT with a high-resolution TEM. The PPO modification warrants the good dispersion of CNTs in PPO in the formation of PPO/CNT nanocomposites, which demonstrated enhanced mechanical properties and increases in electrical conductivity. The developed approach of CNT modification with engineering plastics can be applied to other polymers and preparation of functional polymer/CNT nanocomposites.

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## 1. Introduction

Modification of carbon nanotubes (CNTs) with organic moieties brings interfacial compatibility between CNTs and organic materials, to enhance their solubility in organic solvents and compatibility in organic polymeric materials [1–3]. Massive studies have been reported on the incorporation of polymeric chains to CNTs via chemical linkages. Both “grafting-to” [4–6] and “grafting-from” [6–8] approaches have been widely discussed. The first step in most modifications is to create reactive sites on CNT surfaces by treatment of CNTs with strong acids such as sulfuric acid and nitric acid [9,10]. However, this treatment is somewhat dangerous in operation [11,12]. CNT cut and structure destruction might also accompany with acid treatment. Therefore, some reports focused on modifications of CNTs without acid treatments [5,13]. One major reaction utilized in these non-acid treatment modifications is between free radicals and CNTs. Besides the modification methods, the types of polymers to be incorporated onto CNTs are also of interest. Controlled radical polymerizations are widely utilized in CNT modifications. However, this modification is limited to polymers which can be obtained with radical polymerizations.

One major purpose of CNT modification is to achieve a homogeneous dispersion of CNTs in polymer matrix for the preparation

of polymer–CNT nanocomposites [14]. It is noteworthy that functionalization of CNTs with the matrix polymer of the as-prepared polymer–CNT nanocomposites is an ideal approach to result in high-quality nanocomposites [14–16]. Therefore, polyurea [17], polyether [18], and polyurethane [19] have been covalently linked to CNTs via addition polymerizations for preparation of nanocomposites. On the other hand, engineering plastics are relatively important materials in applications. The nanocomposites of CNTs and engineering plastics are therefore attractive. However, the nanocomposites of engineering thermoplastics and CNTs were not widely reported [20–22], due to the lack of a good approach to prepare engineering plastic-functionalized CNTs.

From the above it can be seen that polymer-functionalized CNTs have been widely reported. The major limits of the previous arts are involving polymer synthesis in the modification procedures. Direct functionalization of CNTs with commercial engineering plastics is attractive to extend the scopes of CNT modification and applications. However, an effective approach is still not reported. Therefore, in this work, we report the first attempt to modify CNTs with commercial engineering plastics. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was used as an example based on its excellent electrical and thermal properties and wide applications in electrical, electronics, business machines, and vehicles. The PPO modification on CNTs warrants the good dispersion of CNTs in PPO in formation of PPO/CNT nanocomposites. This approach can be applied to functionalize CNTs with other polymers and to prepare functional polymer/CNT nanocomposites.

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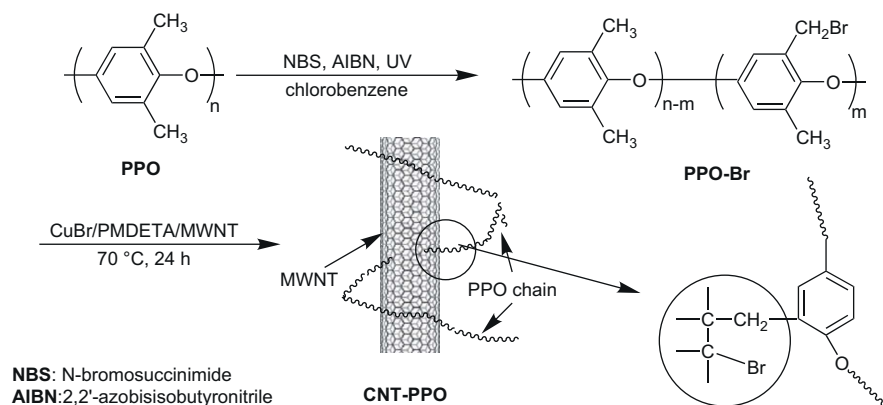


Fig. 1. Synthesis route of PPO-modified carbon nanotubes.

## 2. Experimental

### 2.1. Materials

PPO with an inherent viscosity of 0.4 dL/g (in chloroform at 25 °C) was received from General Electric Plastics Co. Brominated PPO (PPO-Br) was prepared in our lab according to the reported method [23]. The bromination degree (the group ratio of  $-\text{CH}_2\text{Br}/(-\text{CH}_3 + -\text{CH}_2\text{Br})$  in PPO-Br) calculated from  $^1\text{H}$  NMR analysis is 31%. Multi-walled carbon nanotube (MWNT), the

average diameters of 10–50 nm and the length of 1–25  $\mu\text{m}$ , was received from the Carbon Nanotube (CNT) Co., Ltd., Incheon, Korea, was used as received. The purity of the received MWNT is 93%. MWNT was washed with dimethylsulfoxide prior to use. 1,1,4,7,7-Pentamethyldiethyltri-amine (PMDETA, Aldrich, 99% in purity) and copper(I) bromide (CuBr, Aldrich, 99.999% in purity) were used as ligand and catalyst in atom transfer radical reaction for the preparation of PPO modified CNTs. The chemical reagents were used as received without further purification.

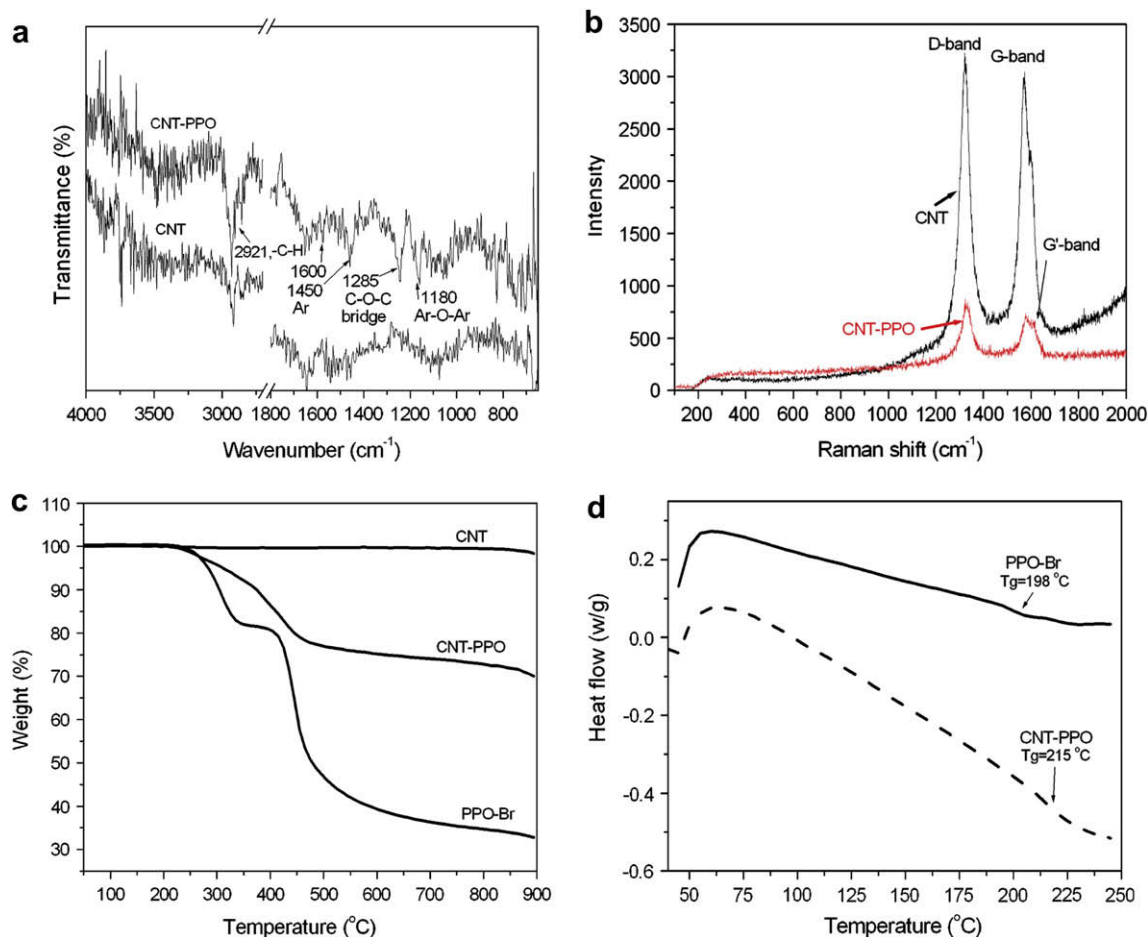


Fig. 2. Characterization on CNT-PPO: (a) FTIR spectra of CNT and CNT-PPO, (b) Raman spectra of CNT and CNT-PPO, (c) TGA thermograms showing the presence of organic PPO part in CNT-PPO, and (d) DSC thermograms showing the glass transition temperatures of PPO part in CNT-PPO.

## 2.2. Characterization

Raman spectra were obtained using a Renishaw Raman spectrometer employing a He–Ne laser of 1 mW radiating on the sample operating at 632.8 nm. FTIR-ATR spectra were obtained with a Perkin Elmer Spectrum One FTIR equipped with a multiple internal reflectance apparatus and a ZnSe prism as an internal reflection element. High-resolution transmission electron microscopy (HRTEM) was conducted with a JEOL JEM-2010 HRTEM. Scanning electron micrographs (SEM) were obtained with a Hitachi S-4800 field-emission SEM. Thermogravimetric analysis (TGA) was performed with an instrument from Thermal Analysis Incorporation (TA-TGA 2050) at a heating rate of 10 °C/min under nitrogen atmosphere. The glass transition temperatures of prepared materials were measured with a differential scanning calorimeter (DSC, TA-DSC Q100) at a heating rate of 20 °C/min. Mechanical property of materials was analyzed with an Instron 5543 analyzer at an elongation rate of 0.5 mm/min. AC electrical conductivity was measured with a Solartron 1296A Dielectric Interface equipped with a Solartron 1255B Frequency Response Analyzer at a frequency range of 0.1 Hz to 1 MHz.

## 2.3. Preparation of PPO modified CNT (CNT–PPO)

PPO-Br (0.2 g) was dissolved in 10 mL toluene. The solution was purged with argon gas flow for 15 min. After addition of MWNT (0.2 g), CuBr (0.065 g), PMDETA (0.27 g), the reaction system was purged with argon for another 15 min. The reaction system was then de-gassed for 3 times and then reacted at 70 °C for 24 h. The reaction mixture was poured into excess THF. CNTs were collected with filtration, washed with tetrahydrofuran (THF) and hot water for several times to remove the physically adsorbed compounds, and then dried under vacuum to give the product of CNT–PPO (0.22 g).

## 2.4. Preparation of PPO/CNT nanocomposites

Desired amount of CNT–PPO was added into the solution of PPO in chloroform (10 wt%). The obtained solution was put in an ultrasonic bath for 1 h and then cast on a glass plate with a casting knife. The thickness set for the casting knife was 300  $\mu\text{m}$ . After drying at ambient condition for 24 h, self-standing PPO/CNT nanocomposite film was obtained. The samples were named as PPO/CNT–PPO-*X*, in which *X* indicates the content (wt%) of CNT–PPO in the nanocomposites. In this work, PPO/CNT–PPO-*X* nanocomposites having *X* values of 0, 0.2, 0.5, 0.7, 1.0, and 2.0 were prepared.

## 3. Results and discussion

### 3.1. Preparation of PPO functionalized CNT

PPO, which is not a reactive polymer, can be introduced with some reactive bromomethyl groups by a bromination reaction [23]. The brominated PPO (PPO-Br) could serve as a macro-initiator for atom transfer radical polymerization (ATRP) using the benzylbromide groups as initiating sites [24]. The initiating reaction of ATRP generates carbon free radicals associating with the benzylbromide groups. Our previous work demonstrated that the active sites of ATRP reactive towards CNT surfaces through the atom transfer radical addition. After the reaction, the organic moieties covalently bond to CNT surface with the halogen atom transferring to CNTs [6]. This reaction is utilized in this work to incorporate PPO chains to CNT surfaces (Fig. 1). The benzylbromide groups of PPO-Br are utilized as reactive groups towards CNT surfaces for the preparation of PPO-modified CNT (CNT–PPO)

under the ATRP reaction condition. In the resulted CNT–PPO, PPO is multi-bonded to and wind around CNT. This reaction route opens a new window to functionalization of CNTs with engineering plastics.

The presence of organic PPO part and inorganic CNT part in the CNT–PPO nanohybrid is characterized with FTIR and Raman spectroscopy, respectively. Comparing to pristine CNT, the PPO chains in CNT–PPO exhibit absorption peaks in FTIR spectrum at 2921 (C–H), 1600 (phenyl group), 1285 (C–O) and 1180 (Ar–O–Ar)  $\text{cm}^{-1}$  (Fig. 2a) [23]. On the other hand, graft of PPO onto CNT side wall results in a structure change in CNT surface and brings an alternation to Raman spectrum (Fig. 2b). The signals at 1315 and 1590  $\text{cm}^{-1}$  represent the disorder  $\text{sp}^3$  mode (D band) and the tangential mode (G band) of CNTs, respectively. The relatively high ratio of D/G band intensity observed with CNT–PPO, which indicates the formation of  $\text{sp}^3$  hybridized carbon on CNTs with PPO modification, as well as the appearance of the D' band at 1614  $\text{cm}^{-1}$  both demonstrates the success of bonding PPO-Br to CNT side walls [17]. The organic PPO

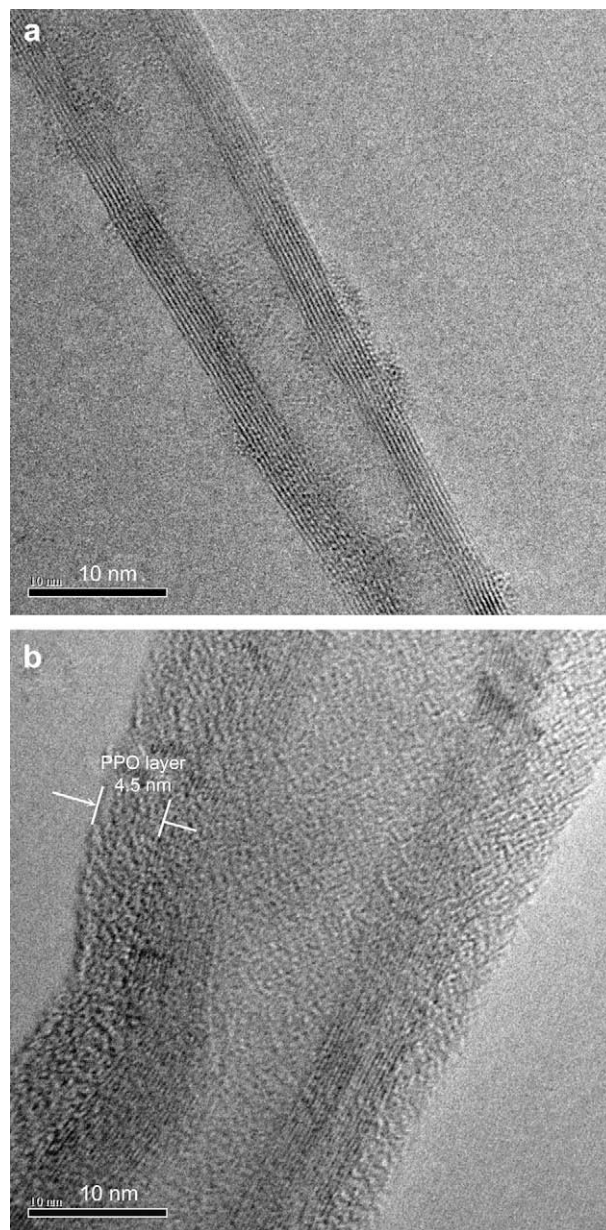
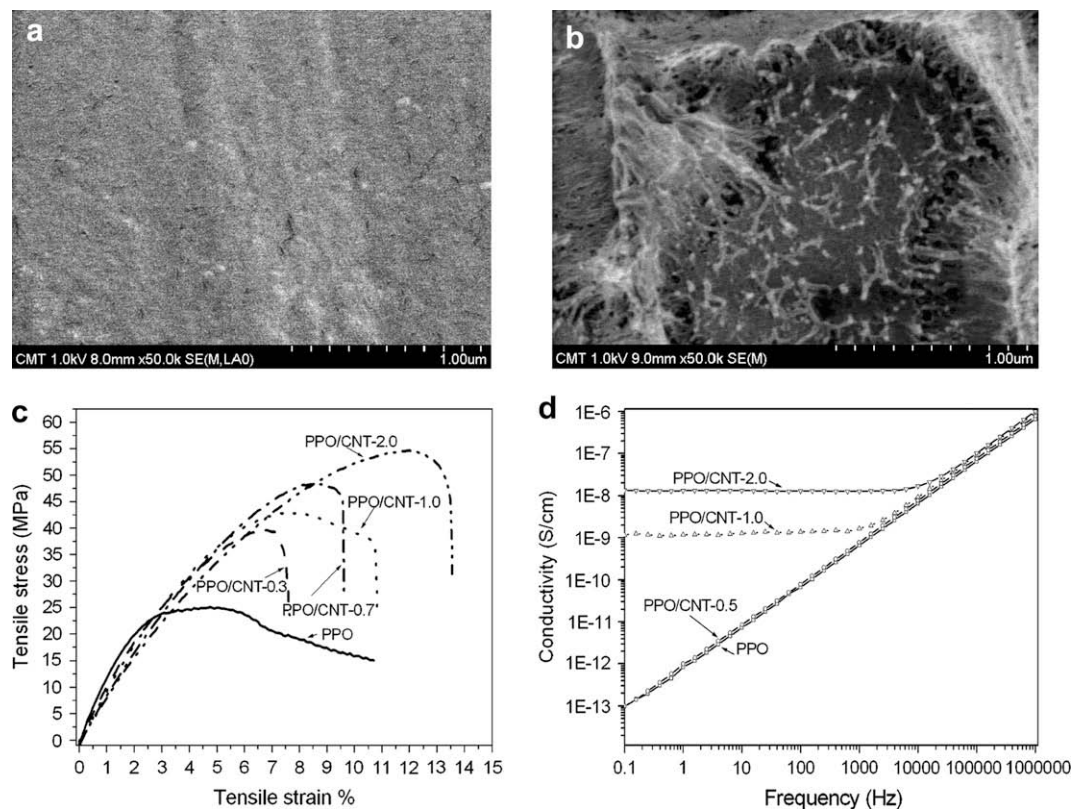


Fig. 3. High-resolution TEM micrographs of (a) CNT and (b) CNT–PPO.





**Fig. 4.** Characterization on PPO/CNT nanocomposites: (a) SEM micrograph of pristine PPO film, (b) SEM micrograph of PPO/CNT-PPO-2.0 nanocomposite film, (c) stress-strain curves of PPO/CNT nanocomposite films measured with an Instron, (d) AC electrical conductivity measurements on PPO/CNT nanocomposite films.

part in CNT-PPO contributes to the weight loss (about 25 wt%) in TGA analysis, as pristine CNT does not exhibit obvious weight loss till 900 °C (Fig. 2c). The weight loss of CNT-PPO appears in the temperature range similar to that observed with PPO-Br. In DSC analysis (Fig. 2d), PPO-Br exhibits a glass transition temperature ( $T_g$ ) at about 198 °C. The chain mobility of the CNT-bonded PPO is highly restricted with the  $T_g$  value of CNT-PPO (215 °C) increased by 17 °C in comparison with that of PPO-Br. Fig. 3 shows the HRTEM micrographs of CNT and CNT-PPO. The multiwall bundles of CNT in a diameter of about 12 nm can be clearly observed. After PPO modification, an amorphous layer in thickness of about 4.5 nm was observed covering on the outer surface of CNT. The presence of the amorphous layer demonstrates the success of bonding PPO chains onto CNT side wall. In addition, incorporation of organic PPO chains to CNTs also increases the solubility of CNT-PPO in organic solvents like THF and chloroform.

### 3.2. PPO/CNT nanocomposites

The enhancement of CNT-PPO solubility in solvents warrants its well dispersion in PPO solution and good compatibility with PPO matrix. CNT-PPO is then used as a nano-additive to PPO for the preparation of PPO/CNT nanocomposites. The SEM images of the nanocomposite fracture surfaces show the dispersion of CNTs in PPO matrix [23]. Contrasting to the pristine PPO film showing a dense and homogeneous crosssection in SEM micrograph (Fig. 4a), the presence of CNT in PPO/CNT nanocomposites possessing 2 wt% CNT-PPO (PPO/CNT-PPO-2.0) can be clearly seen in its SEM cross-sectional micrograph (Fig. 4b). Separated CNT bundles dispersed in the PPO matrix. No aggregation formation in the PPO/CNT-PPO-2.0 nanocomposite could also be indicative of the effects of PPO-functionalization on the enhancements of the

CNT compatibility to PPO matrix [25]. In addition, the bundle lengths of CNTs in the nanocomposite were relatively short, indicating some of them have broken during nanocomposite fracture. The strong interfacial interaction between PPO-CNT and PPO matrix is demonstrated [13]. The good compatibility and interfacial interactions of PPO-CNT in the nanocomposites attribute to enhance the physical properties of the nanocomposites. The mechanical properties and electrical conductivity of the PPO/CNT nanocomposites are measured to investigate the effect of loading CNT-PPO in PPO. Although not demonstrating significant increases in Young's modulus of PPO, formation of PPO/CNT nanocomposites shows increases in their tensile strain and tensile stress (Fig. 4c). The significant increase in tensile strength could be due to the good compatibility between CNT-PPO and PPO matrix. Although there is no chemical bonding between CNT-PPO and PPO, the polymer chains in CNT-PPO and in PPO matrix entangle each other with no interfaces to result in strengthening. Similar results were reported to polyurethane/CNT nanocomposites [26]. Moreover, with the addition of CNT-PPO, the significant enhancement on the toughness of PPO is noteworthy.

As an insulating material, the AC electrical conductivity of PPO is about  $10^{-13}$  S/cm at 0.1 Hz and increases with increase in frequency. The homogeneous dispersion of CNT-PPO in PPO matrix also results in an increase in the electrical conductivity by several orders of magnitude (Fig. 4d, DC conductivity of about  $10^{-8}$  S/cm). The frequency-independent plateau region observed for PPO-CNT-1.0 and PPO-CNT-2.0 is consistent with "Johnscher Universal Power Law" for solids [27]. The wide range of the frequency-independent conductivity observed for PPO-CNT-2.0 also indicates that a percolating network-like structure of CNTs forms in PPO/CNT-PPO-2.0 nanocomposite [28]. The CNT bundles in PPO-CNT-2.0 shown in Fig. 4b also provide a support to this result.

#### 4. Conclusions

A facile route to modify CNTs with commercial-available engineering plastics is reported using PPO as an example. Modification was demonstrated with FTIR, Raman, and HRTEM observation. The multi-bonded PPO chains in CNT–PPO significantly improve the compatibility and dispersion ability of CNT in PPO matrix, so as to increase the mechanical properties and electrical conductivity of the resulting PPO/CNT nanocomposites. The developed approach of CNT modification with engineering plastics can be applied to other polymers and preparation of functional polymer/CNT nanocomposites. Further results will be reported in the near future.

#### Acknowledgements

Financial support on this work from the Center-of-Excellence (COE) Program on Membrane Technology from the Ministry of Education (MOE), Taiwan is appreciated.

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