

# Polybenzoxazine/single-walled carbon nanotube nanocomposites stabilized through noncovalent bonding interactions



Chih-Chiao Yang<sup>a</sup>, Yung-Chih Lin<sup>a</sup>, Po-I. Wang<sup>b</sup>, Der-Jang Liaw<sup>b</sup>, Shiao-Wei Kuo<sup>a,\*</sup>

<sup>a</sup>Department of Materials and Optoelectronic Science, Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung 804, Taiwan

<sup>b</sup>Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan

## ARTICLE INFO

### Article history:

Received 3 October 2013

Received in revised form

16 February 2014

Accepted 24 February 2014

Available online 5 March 2014

### Keywords:

Polybenzoxazine

Carbon nanotube

Hybrid complex

## ABSTRACT

In this study we prepared a new class of pyrene-functionalized benzoxazines (Py-BZ) through reactions of phenol, paraformaldehyde, and pyren-1-amine (Py-NH<sub>2</sub>) in toluene and EtOH. We prepared Py-NH<sub>2</sub> through catalytic reduction of 1-nitropyrene (Py-NO<sub>2</sub>), which we had synthesized through electrophilic aromatic substitution of pyrene, using HNO<sub>3</sub> as the nitration agent. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectroscopy and Fourier transform infrared (FTIR) spectroscopy confirmed the chemical structure of this new monomer; differential scanning calorimetry (DSC) and FTIR spectroscopy revealed the curing behavior of the Py-BZ polymers. The presence of the pyrene-functionalized benzoxazine enhanced the solubility of single-walled carbon nanotubes (SWCNTs) in THF, leading to the formation of highly dispersible Py-BZ/SWCNT organic/inorganic hybrid complex materials. Fluorescence emission spectroscopy revealed significant  $\pi$ - $\pi$  stacking interactions between the Py-BZ and the SWCNTs in these complexes. In addition, differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical analysis revealed that incorporating the SWCNTs into the Py-BZ matrix significantly enhanced the thermal stability of the polymer after thermal curing.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Benzoxazines are intriguing heterocyclic compounds that are attracting considerable attention for use as cyclic monomers that undergo near-zero shrinkage upon polymerization and provide polymers exhibiting tunable glass transition temperatures and high char yields [1,2]. Furthermore, polybenzoxazines (PBZs) have unique properties not found in traditional phenolic and epoxy resins, such as excellent dimensional stability, flame retardance, stable dielectric constants, and low surface free energies [3–7]. Modifications of benzoxazine resins, through the appending of alkylnyl or allyl side groups or strong hydrogen bonding functional groups, can lead to new and interesting materials for the development of useful products [8–10]. These functionalized benzoxazines can be polymerized into materials possessing three-dimensional networks exhibiting high thermal and mechanical stabilities and high resistance to solvents and moisture. Blending with other polymers [11–14], including polyurethane,

poly(ethylene oxide), and poly(*N*-vinyl-2-pyrrolidone), or organic/inorganic hybrid systems, including clay [15–17], and polyhedral oligomeric silsesquioxane (POSS) [18–26], allows further modification of the properties of benzoxazine resins.

In addition to PBZ/clay and PBZ/POSS nanocomposites [15–26], covalent surface functionalization of carbon nanotubes (CNTs) [27–29] with PBZs has also received much attention recently [30–37]. Yu et al. described the first examples of PBZ-modified multiwalled carbon nanotubes (MWCNTs) [30]. They covalently modified MWCNTs, through treatment with HNO<sub>3</sub> followed by toluene-2,4-diisocyanate (TDI), to introduce –OH, –CO<sub>2</sub>H, and –N=C=O groups on their surfaces. The surface –CO<sub>2</sub>H groups catalyzed the ring-opening reactions of benzoxazine and, thereby, decreased the curing temperature of the system. Huang et al. treated MWCNTs with H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> to introduce surface –OH and –CO<sub>2</sub>H groups [33]. These –CO<sub>2</sub>H groups hydrogen bonded with the phenolic –OH groups after ring opening of benzoxazine, resulting in improved adhesion between PBZ and the MWCNTs. Liu et al. prepared MWCNTs modified with Diels–Alder adducts using benzoxazine functional groups [34]. Nevertheless, covalent functionalization of CNTs typically changes the orbital hybridization of some of the carbon atoms from sp<sup>2</sup> to sp<sup>3</sup>, thereby deteriorating the optical, electronic, and mechanical

\* Corresponding author. Fax: +886 7 5254099.

E-mail address: [kuosw@faculty.nsysu.edu.tw](mailto:kuosw@faculty.nsysu.edu.tw) (S.-W. Kuo).

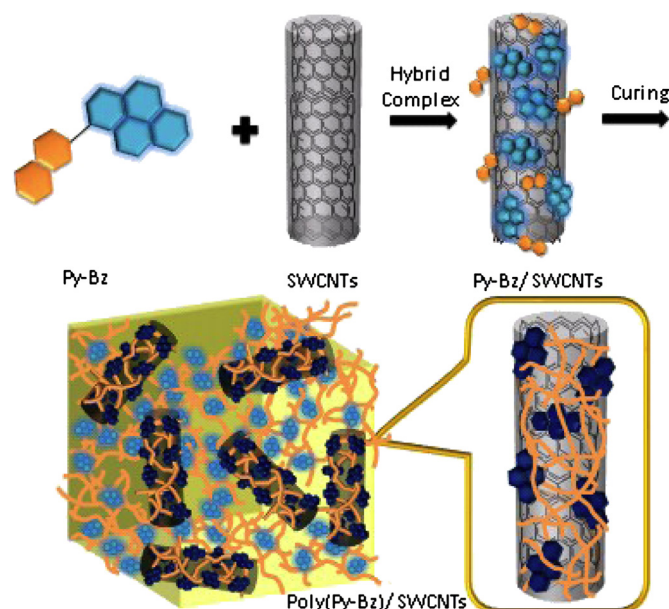
properties. Noncovalent approaches toward the modification of CNTs do not destroy the electronic conjugation, can enhance dispersibility, and can maintain the electronic and mechanical properties. Dumas et al. reported the dispersion of untreated MWCNTs in a *p*-phenylenediamine-based benzoxazine (P-pPDA) [37].  $\pi$ -Stacking interactions between the CNTs and P-pPDA led to the formation of a reinforced network exhibiting enhanced thermal and mechanical properties. Most noncovalent approaches toward the modification of CNTs, however, have exploited the strong  $\pi$ - $\pi$  interactions of pyrene with CNT surfaces [38].

Therefore, in this study we prepared a pyrene-based benzoxazine precursor that we then used to form PBZ/CNT nanocomposites, especially with single-walled carbon nanotubes (SWCNTs), stabilized through strong  $\pi$ - $\pi$  interactions between the pyrene groups and the CNT surfaces. Electrophilic aromatic substitution of pyrene with  $\text{HNO}_3$  as the nitration agent provided 1-nitropyrene (Py- $\text{NO}_2$ ), which we subjected to catalytic reduction to obtain pyren-1-amine (Py- $\text{NH}_2$ ). Next, we prepared a pyrene-based benzoxazine (Py-BZ) through the reaction of phenol, paraformaldehyde, and Py- $\text{NH}_2$  in toluene and EtOH (Scheme 1). Finally, we obtained PBZ/SWCNTs nanocomposites after mixing Py-BZ with SWCNTs and then curing. Because of the strong  $\pi$ - $\pi$  interactions between the SWCNTs and the PBZ polymers, the systems exhibited significantly improved thermal stability, as evidenced using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). In addition, we used fluorescence spectroscopy and transmission electron microscopy (TEM) to investigate the interactions and dispersion of SWCNTs in Py-BZ solutions Scheme 2.

## 2. Experimental

### 2.1. Materials

Paraformaldehyde (96%) and pyrene were purchased from Acros.  $\text{K}_2\text{CO}_3$  (10 wt%) was purchased from Aldrich. Phenol (99%) was purchased from Showa.  $\text{HNO}_3$  acid (65%) and AcOH (99.8%) were purchased from Scharlau. Hydrazine monohydrate (98%) was purchased from Alfa Aesar. SWCNTs were purchased from Centron

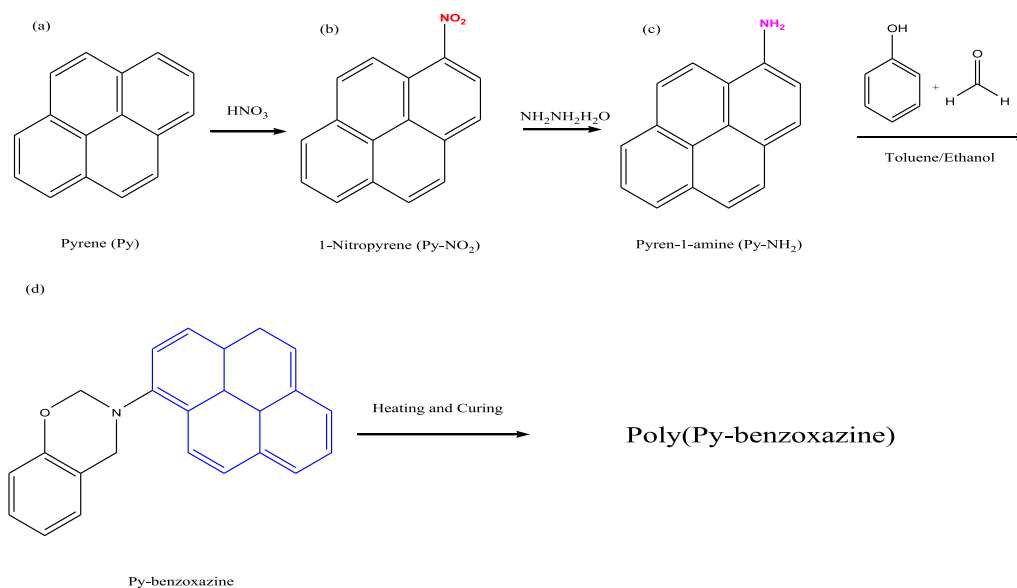


**Scheme 2.** Preparation of Py-BZ/SWCNT and Poly(Py-BZ)/SWCNT hybrid complexes, stabilized through  $\pi$ - $\pi$  interactions.

Biochemistry Technology. All other chemicals were of reagent grade and used as received.

### 2.2. Pyren-1-amine (Py- $\text{NH}_2$ )

A mixture of 1-nitropyrene (10 g, 4.04 mmol)—which had been prepared as yellow crystals (95%) through the nitration of pyrene with  $\text{HNO}_3$  in AcOH and evaporation of the solvent—and palladium on carbon (0.21 g) was heated under reflux in EtOH (200 mL) for 1 h. Hydrazine hydrate (13 mL) was added and then the mixture was heated for another 1 h. After cooling, the precipitated crystals of Py- $\text{NH}_2$  were filtered off. The filtrate was concentrated on a vacuum rotary evaporator; cooling of the concentrate gave a second



**Scheme 1.** Synthesis of (b) Py- $\text{NO}_2$ , (c) Py- $\text{NH}_2$ , and (d) Py-BZ.

Download English Version:

<https://daneshyari.com/en/article/5181317>

Download Persian Version:

<https://daneshyari.com/article/5181317>

[Daneshyari.com](https://daneshyari.com)