Polym. Bull. (2011) 67:1731–1739
DOI 10.1007/s00289-011-0476-1

ORIGINAL PAPER

Synthesis of novel single-walled carbon nanotubes/poly (*p*-phenylene benzobisoxazole) nanocomposite

**Zhen Hu · Yudong Huang · Feng Wang ·
Yuhuan Yao · Shaofan Sun · Yanwei Li ·
Zaixing Jiang · Huifang Xu · Peiyi Tang**

Received: 29 December 2010 / Revised: 22 February 2011 / Accepted: 13 March 2011 /

Abstract Poly (*p*-phenylene benzobisoxazole) (PBO) fibers are some of the strongest organic polymer fibers. However, the introduction of single-walled carbon nanotubes (SWNT) into the PBO backbone might lead to improvements in their alignment and physical properties. Therefore, SWNT was cut and functionalized by three oxidative cutting methods. After cutting, three different types of SWNT were obtained. Furthermore, copolymerization of SWNTs with PBO polymer was successfully carried out in a mixed solvent of polyphosphoric acid and methanesulfonic acid. The SWNTs were homogeneously distributed throughout the films of copolymerized products, as determined by Raman spectroscopy. The benzoxazole moieties could be formed between the carboxyl of SWNTs and *o*-aminophenol derivatives of PBO polymer. The length of SWNTs affected the dispersion and reaction activity. Short SWNTs could react with the PBO polymer more easily and form more covalent bonds.

Keywords Carbon nanotubes · Nanostructured materials · Composites · Fiber technology

Introduction

Today's polymeric fibers are up to ten times as strong as that available half a century ago. Poly (*p*-phenylene benzobisoxazole) (PBO) is one of the polybenzoxazoles containing an aromatic heterocyclic ring. Fibers prepared with PBO have superior mechanical properties, excellent thermal, thermo-oxidative stability, and

---

Z. Hu (✉) · Y. Huang (✉) · F. Wang · Y. Yao · S. Sun · Y. Li · Z. Jiang · H. Xu · P. Tang
School of Chemical Engineering and Technology, Harbin Institute
of Technology, Harbin 150001, China
e-mail: huzhen@hit.edu.cn

Y. Huang
e-mail: ydhuang.hit1@yahoo.com.cn

good flame retardance. The tensile strength and the tensile modulus of as-spun PBO fiber can reach up to 5.8 and 180 GPa, respectively. The tensile modulus, in particular, is much higher than that of carbon, steel, Kevlar, and other super fibers. However, even for commercial high modulus PBO fibers, there is still a large gap between the actual tensile modulus and the theoretical tensile modulus. Improvements in fiber orientation and molecular chain packing order have been suggested as the main methods to overcome this gap [1].

Carbon nanotubes (CNTs) are a family of new materials with unique structure and excellent mechanical, electrical, and optical properties. Theoretical and experimental investigations have shown that CNTs possess remarkable mechanical properties. CNTs can be ideal reinforcing agents for kinds of materials especially for polymers. Since then, many efforts have been made to explore the potential usage of CNTs as reinforcing agents [2–8]. In addition, CNTs can also act as a nucleating agent for polymer crystallization and as a template for polymer orientation, enhancing the physical properties of the formed materials [9]. No other nucleating agents are as narrow and long as single-walled carbon nanotubes (SWNT). Experts working in this field suggest that even stronger fibers can be made using carbon nanotubes. Thus, both PBO and CNTs share some important properties. The opportunity to combine CNTs and PBO appears as a desirable way to develop nanocomposites provided with properties that are inherent in both components.

To fully exploit these CNTs characteristics in macroscopic functional fibers or composites, one must overcome the critical issue of limited dispersion that can affect the performance of CNTs-infused materials. Due to their high aspect ratio and the strong van der Waals attraction between them, full-length purified CNTs tend to aggregate into a dense, robust network of ropes, usually 10–50 nm in diameter and several micrometers in length. In addition to the dispersion problem, the presence of rigid full-length CNTs increases the steric hindrance and decreases the reactivity [10]. It has been shown, however, that the solubility of SWNTs can be improved by shortening their length and through chemical functionalization [11–15]. In this study, we prepared a new block copolymer system wherein short functionalized SWNTs are covalently bonded to acid-soluble polybenzazoles, a commercial family of materials (PBO). The key concept is to synergistically combine the unprecedented properties of short SWNTs with the processibility of PBO. In addition, we expect that the SWNTs–PBO copolymer will lead to better alignment of the polymer fibers, enhancing the physical properties of the formed materials. In the previous studies [16, 17], the covalent modification of PBO polymer with SWNT has not been reported. Moreover, the effect of SWNTs length and functional degree on polymerization was not clear. In this study, copolymerization of SWNTs (with different length and functional degree) with PBO polymer was successfully carried out in a mixed solvent of polyphosphoric acid and methanesulfonic acid (MSA) in the presence of P_2O_5 (Fig. 1).

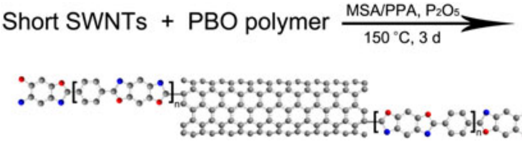

Fig. 1 Preparation of SWNT/PBO copolymer

Experimental

Materials

1,4-Diaminoresorcinol dihydrochloride (DADHB) was synthesized in our laboratory from 1,2,3-trichlorobenzene by a modified method. The SWNT was provided by Shenzhen NANO Tech. Port. Co. Ltd. and were fabricated by catalytic pyrolysis of hydrocarbons. Terephthalic acid (TPA), phosphoric acid, and MSA were purchased from Aldrich Chemical Company. MSA was distilled under vacuum in the presence of P_2O_5 before use.

Preparation of SWNT 1 (average length was 49 nm)

The SWNT was first disentangled in oleum (20% SO_3) for 72 h by an immersion blender to ensure complete superacid intercalation. Subsequently, a mixture of oleum and 70% nitric acid was slowly added into the SWNT/oleum dispersion to make a mixed solvent of oleum/nitric acid at volume ratio of 3:1. The SWNT dispersion was stirred at 70 °C for 4 h to cut the SWNT.

Preparation of SWNT 2 (average length was 124 nm)

Piranha solutions (v/v 96% H_2SO_4:30% $H_2O_2 = 4:1$) were prepared immediately before use to maintain their activity. The SWNT was then added to the solution (1 mL piranha: 1 mg of SWNT) for 12 h once the solution was heated to the 70 °C.

Preparation of SWNT 3 (average length was 192 nm)

Ammonium persulfate solutions were prepared by dissolving 4 g salt in 50 mL of 96% H_2SO_4. The SWNT was then added to the persulfate solution (1 mL solution: 1 mg of SWNT) for 12 h at 70 °C.

Synthesis of PBO polymer

NaOH (0.4 mol) was dissolved in 500 mL distilled water, and then 0.2 mol TPA was added. DADHB (0.2 mol) and a small mount $SnCl_2$ were dissolved in 250 mL distilled water. Mixed the above aqueous solutions with stirring, and heated up to 80 °C for 30 min under the nitrogen atmosphere, then cooling to room temperature and filter. The DADHB/TPA complex salt was obtained after vacuum drying. PBO polymer was prepared from DADHB/TPA complex salt in polyphosphoric acid using solution polycondensation in kneader.

Copolymerization of PBO polymer with SWNTs

In a typical procedure, PBO (4.75 g) polymer was dissolved with stirring in 100 mL of MSA. P_2O_5 (193.34 g) was added to the phosphoric acid (145.55 g, 85%) to generate polyphosphoric acid (83.5% P_2O_5). And then 0.25 g SWNT was homogeneously dispersed with sonication in polyphosphoric acid at 150 °C for 3 h. Mixed the above solutions with stirring and the copolymerization was carried out at 150 °C for 3 days.

Characterization

The transmission electron microscopy (TEM) sample was prepared by sonicating SWNTs in methanol. The length distribution of SWNTs was obtained by the dynamic light scattering. Light scattering experiments were performed on a Horiba DLS particle-size analyzer LB550. Raman spectra were recorded on a Renishaw Raman microscope. ATR-IR spectra were collected on thin films. A powder was pressed onto 0.5 mm thick soft indium foil, and X-ray photon-electron spectrum (XPS) data were collected on a PHI Quantera SXM Scanning X-ray Microscope with monochromatic Al KR X radiation (1486.6 eV). The film of SWNT/PBO copolymer mounted on a metal sample board were coated with gold using an ion sputter and then observed by SEM (Netherlands Philips FEI Sirion). TG analyses were performed with a thermo gravimetric analyzer (Netzsch STA449C) from room temperature to 1000 °C in air atmosphere at a heating rate of 10 °C/min.

Results and discussion

Preparation and characterization of functionalized SWNTs

The block copolymerization is a condensation reaction between carboxylic acid moieties at the ends and defect sites of SWNTs and the *o*-aminophenol end groups of PBO polymer. The preparation scheme is shown in Fig. 1. It has been reported that block copolymerizations of PBO oligomer with aromatic oligomers can be carried out in a mixed solvent of PPA and MSA with P_2O_5 [17]. In this study, purified SWNTs were cut into short lengths and carboxylated by oxidation of the defect sites. Figure 2a, b, and c shows TEM images of SWNTs. Similar to prior studies, the rough edges of the SWNTs in the TEM images were indications of the high level of functionalization at the ends of the SWNTs. Figure 2d shows the corresponding length distributions of the SWNTs after oxidation. After oxidation, the histograms showed a decrease in the number of longer nanotubes and an increase in the number of shorter nanotubes. The average size of SWNT 1, 2, and 3 was 49, 124, and 192 nm, respectively.

The Raman spectra of the SWNTs were obtained on a Renishaw Ramascope with 785 cm^{-1} diode laser (Fig. 3a). Compared with the pristine SWNT, the D/G ratio of the disorder mode (D band at around 1350 cm^{-1}) and the tangential mode (G band at 1580 cm^{-1}) had increased. This indicated that there was a high level of functionalization after oxidation. Moreover, the D/G ratio of SWNTs was in the order of SWNT 1 $>$ SWNT 2 $>$ SWNT 3, which indicated SWNT 1 had the highest level of functionalization. The XPS (Fig. 3b) indicated a high concentration of covalently bonded carboxylic acid groups (–COOH, binding energy 288 eV) on the surface and ends of these SWNTs [18, 19]. Elemental analysis based on the XPS

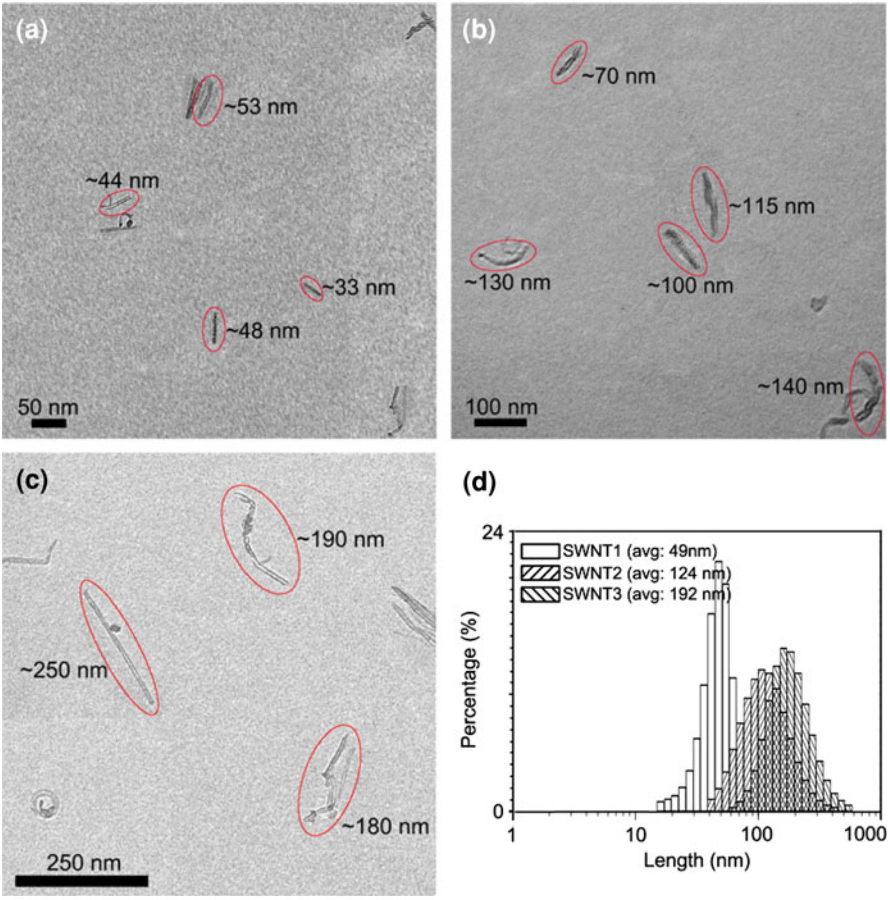

Fig. 2 TEM images of **a** SWNT1, **b** SWNT 2, and **c** SWNT 3. **d** Length distribution of functionalized SWNTs

data supported the findings that the functional degree of SWNTs was in the order of SWNT 1 > SWNT 2 > SWNT 3.

Copolymerization of short SWNTs and PBO polymer

Cutting of SWNTs was carried out to increase the dispersion in PPA and improve the reactivity with PBO polymer. The precipitate of SWNTs/PBO copolymer did not dissolve in DMF and NMP, while the SWNTs were dispersed well in both solvents [20, 21]. The change in solubility of the nanotubes before and after the copolymerization indicated covalent bonding of the PBO polymer to the SWNTs. After copolymerization, a thin film was made by press-forming the product. Various areas of the films were examined by the focused beam of a 633 nm laser of the Raman spectroscope as shown in Fig. 4a. Raman spectra of the copolymerized products were almost the same in all of the 50 examined areas of the film for SWNT

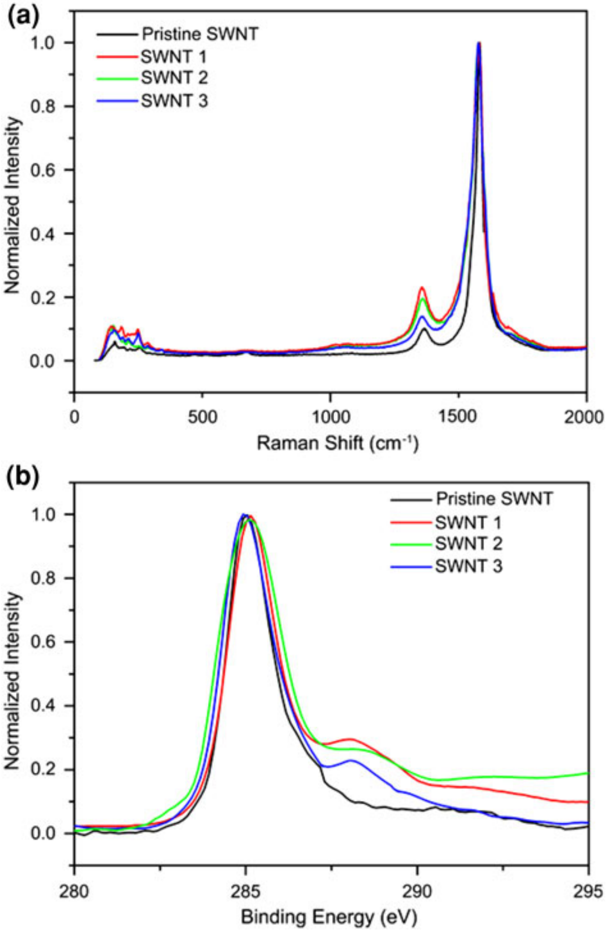

Fig. 3 **a** Raman spectra of functionalized SWNTs. **b** XPS spectra of functionalized SWNTs

1 and 2. These results indicated that SWNT 1 and 2 with the characteristic RBM, D band, and G band were homogeneously distributed throughout the films. It has been reported that SWNT aggregates or bundles were not observed in SWNT/PBO (10/90) composite fibers, suggesting SWNTs exfoliation as individuals [22]. For the control experiment, Raman spectra of the SWNT 3/PBO film showed the presence of RBM, D band, and G band in almost 80% of the 50 examined areas. The other areas exhibited fluorescence from PBO. This result indicated that a certain amount of SWNT 3 aggregated or bundled in the copolymer. The Raman spectroscopy results indicated that the length of the SWNT influenced its dispersion, the shorter the length of SWNT, the better dispersion in the copolymer.

The XPS spectra are shown in Fig. 4b. In the XPS spectra of SWNT 1/PBO and SWNT 2/PBO, the peak of the carboxylic acid moiety O=C–O at 288 eV disappeared after the copolymerization, which was indicative of the covalent

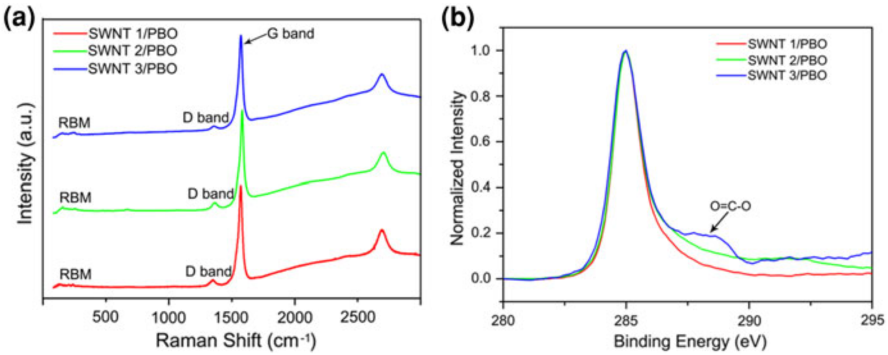

Fig. 4 **a** Representative Raman spectra of copolymerized products. **b** XPS spectra of copolymerized products

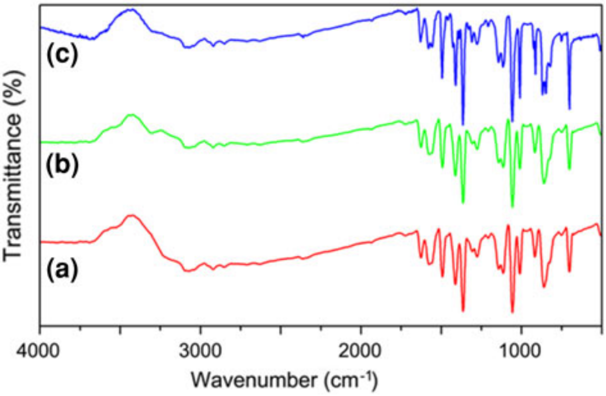

Fig. 5 ATR-IR spectra of (*a*) SWNT 1/PBO, (*b*) SWNT 2/PBO, and (*c*) SWNT 3/PBO copolymerized products

bonding between short SWNTs and PBO polymer. In comparison, the XPS spectrum of SWNT 3/PBO copolymer remained the O=C–O peak. The result indicated that the long length nanotubes reduced the reactivity of SWNT 3, which makes low rate conversion of the carboxyl. ATR-IR spectra of the copolymerized products showed the presence of peaks characteristic of PBO as shown in Fig. 5. A C=N stretch at ~1620 cm^{-1}, =C–O–C stretch at ~1050 cm^{-1} and an aromatic C–H stretch at ~3050 cm^{-1} were observed in all three spectrum. In the IR spectra of SWNT 1/PBO and SWNT 2/PBO, the peak of the –OH at ~3600 cm^{-1} disappeared after the copolymerization, which was indicative of the covalent bonding between short SWNTs and PBO polymer. On the other hand, the IR spectrum of SWNT 3/PBO copolymer remained the –OH peak. These data supported the findings concluded from XPS spectra. IR spectra showed that copolymerization did not change the properties of PBO and generated SWNT/PBO copolymer.

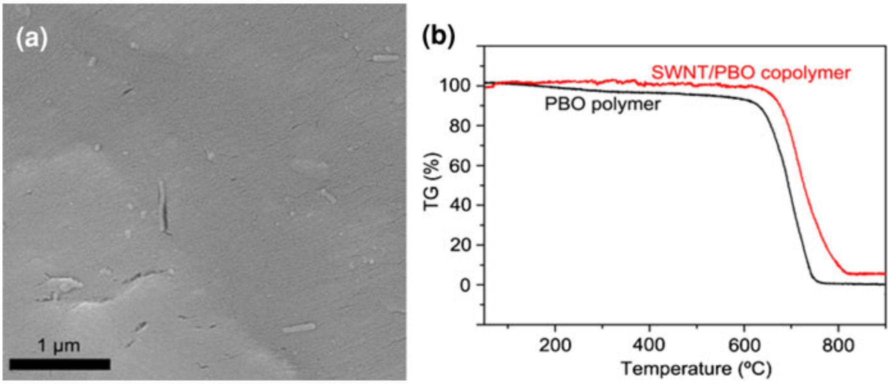

Fig. 6 **a** Representative SEM photograph of SWNT/PBO copolyme and **b** TG curves of PBO and SWNT/PBO copolymer in air

Because the SEM photos and TG curves of the three copolymers were almost the same, we gave the representative SEM photo and TG spectrum in Fig. 6. Figure 6a showed the representative SEM photo of PBO/SWNT copolymer films. It could be observed from Fig. 6a that the outer surface of the copolymer was smooth. The SWNT dispersed well in the PBO polymer matrix. Thermal degradation behavior of PBO/SWNT in air atmosphere (Fig. 6b) was compared with the pure PBO. It can be seen from Fig. 6b that the TG curve of PBO decreased slightly in the initial stages, the thermal degradation occurred at 615 °C and the significant changes happened between 620 and 750 °C. On the other hand, for SWNT/PBO copolymer, the thermal degradation happened at about 640 °C, and finally left about 6 mass% residues at 900 °C with significant changes between 650 and 820 °C. It can be found that PBO/SWNT copolymer had better heat resistance in the atmosphere of air.

Conclusions

In this study, SWNT was cut and functionalized by three oxidative cutting methods. After cutting, three different types of SWNT were obtained. Copolymerization of SWNTs with PBO polymer was successfully carried out in a mixed solvent. The study tested the reaction activity of the PBO polymer with oxidative SWNTs. The covalent bonds could be formed between the carboxyl of SWNTs and *o*-aminophenol derivatives of PBO polymer. After copolymerization, the SWNTs were homogeneously distributed in the films of copolymerized products. Furthermore, the length of SWNTs affected the dispersion and reaction activity. Short SWNTs had better dispersion, which could react with the PBO polymer more easily and form more covalent bonds. SWNT dispersed well in the PBO matrix. The thermal resistance of the SWNT/PBO copolymer was better than PBO. Moreover, this study will provide a new way to prepare novel PBO/SWNT super performance fibers.

Acknowledgments The project was supported by Special Foundation of China Postdoctoral Science (No. 201003436), China Postdoctoral Science Foundation (No. 20090450981), Heilongjiang Province Postdoctoral Foundation (No. LRB08-452), Science and Technology Projects Fund for Innovative Talent of Harbin (No. 2009RFQXG044), Development Program for Outstanding Young Teachers in Harbin Institute of Technology (No. HITQNJS.2009.56) and KOTO innovation foundation (HIT(SCET)-KOTO - 20100604).

References

1. Chae HG, Kumar S (2008) Making strong fibers. Science 319:908–909
2. Zhang Q, Li J, Zhao X, Chen D (2009) Preparation and characterization of alkylated carbon nanotube/polyimide nanocomposites. Polym Int 58:557–563
3. Choi YJ, Hwang SH, Hong YS, Kim JY, Ok CY, Huh W, Lee SW (2004) Preparation and characterization of PS/multi-walled carbon nanotube nanocomposites. Polym Bull 53:393–400
4. Philip B, Xie J, Abraham JK, Varadan VK (2004) Polyaniline/carbon nanotube composites: starting with phenylamino functionalized carbon nanotubes. Polym Bull 53:127–138
5. Ko SW, Hong MK, Park BJ, Gupta RK, Choi HJ, Bhattacharya SN (2009) Morphological and rheological characterization of multi-walled carbon nanotube/PLA/PBAT blend nanocomposites. Polym Bull 63:125–134
6. Clayton LM, Gerasimov TG, Cinke M, Meyyappan M, Harmon JP (2004) Gamma radiation effects on the glass transition temperature and mechanical properties of PMMA/soot nanocomposites. Polym Bull 52:259–266
7. Coleman JN, Khan U, Gun'ko YK (2006) Mechanical reinforcement of polymers using carbon nanotubes. Adv Mater 18:689–706
8. Ma W, Liu L, Zhang Z et al (2009) High-strength composite fibers: realizing true potential of carbon nanotubes in polymer matrix through continuous reticulate architecture and molecular level couplings. Nano Lett 9:2855–2861
9. Minus ML, Chae HG, Kumar S (2006) Single wall carbon nanotube templated oriented crystallization of poly(vinyl alcohol). Polymer 47:3705–3710
10. Cui S, Canet R, Derre A, Couzi M, Dehaes P (2003) Characterization of multiwall carbon nanotubes and influence of surfactant in the nanocomposite processing. Carbon 41:797–809
11. Stephenson JJ, Hudson JL, Azad S, Tour JM (2006) Individualized single walled carbon nanotubes from bulk material using 96% sulfuric acid as solvent. Chem Mater 18:374–377
12. Liang F, Sadana AK, Peera A, Chattopadhyay J, Gu Z, Hauge RH, Billups WE (2004) A convenient route to functionalized carbon nanotubes. Nano Lett 4:1257–1260
13. Coleman KS, Bailey SR, Fogden S, Green MLH (2003) Functionalization of single-walled carbon nanotubes via the bingel reaction. J Am Chem Soc 125:8722–8723
14. Banerjee S, Hemraj-benny T, Wong SS (2005) Covalent surface chemistry of single-walled carbon nanotubes. Adv Mater 17:17–29
15. Liu Y, Yao Z, Adronov A (2005) Functionalization of single-walled carbon nanotubes with well-defined polymers by radical coupling. Macromolecules 38:1172–1179
16. Kumar S, Dang TD, Arnold FE et al (2002) Synthesis, structure, and properties of PBO/SWNT composites. Macromolecules 35:9039–9043
17. Kobashi K, Chen Z, Lomeda J, Rauwald U, Hwang WF, Tour JM (2007) Copolymer of single-walled carbon nanotubes and poly(*p*-phenylene benzobisoxazole). Chem Mater 19:291–300
18. Kovtyukhova NI, Mallouk TE, Pan L, Dickey EC (2003) Individual single-walled nanotubes and hydrogels made by oxidative exfoliation of carbon nanotube ropes. J Am Chem Soc 125:9761–9769
19. Rosario-Castro BI, Contes EJ, Perez-Davis ME, Cabrera CR (2005) Attachment of single-wall carbon nanotubes on platinum surfaces by self-assembling techniques. Rev Adv Mater Sci 10:381–386
20. Boul PJ, Liu J, Mickelson ET et al (1999) Reversible sidewall functionalization of buckytubes. Chem Phys Lett 310:367–372
21. Ausman KD, Piner R, Lourie O, Ruoff RS, Korobov MJ (2000) Organic solvent dispersions of single-walled carbon nanotubes: toward solutions of pristine nanotubes. Phys Chem B 104:8911–8915
22. Uchida T, Kumar S (2005) Single wall carbon nanotube dispersion and exfoliation in polymers. J Appl Polym Sci 98:985–989