Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Polymer 47 (2006) 3961–3966
polymer
www.elsevier.com/locate/polymer

Nylon 610 and carbon nanotube composite by in situ interfacial polymerization

Minsung Kang, Seung Jun Myung, Hyoung-Joon Jin *

Department of Polymer Science and Engineering, Inha University, Incheon 402-751, South Korea

Received 5 October 2005; received in revised form 27 January 2006; accepted 18 March 2006
Available online 18 April 2006

Abstract

Poly(hexamethylenesebacamide) (nylon 610) nanocomposites containing well dispersed multi-walled carbon nanotubes (MWNTs) were successfully produced via the in situ interfacial polymerization of two liquid phases, one containing hexamethylenediamine in the presence of MWNTs and the other containing sebacoyl chloride. The processing consisted of dispersing acid-treated MWNTs in an aqueous phase containing a Triton X-100 surfactant. Scanning and transmittance electron microscopies showed that the individual MWNTs were uniformly dispersed in the nylon 610 matrix. Tensile tests of the composite sheet showed a 170% increase in the Young's modulus with slight increases in the tensile strength and the elongation at break (about 40 and 25%, respectively). This suggests an interaction between the acid-treated MWNTs and nylon 610. The thermal stability of the composite was also enhanced by the incorporation of MWNT into nylon 610 matrix.

Keywords: Carbon nanotube; Interfacial polymerization; Nylon 610

1. Introduction

Interfacial copolymerization occurs at an interface between two immiscible, low molecular weight fluids, each containing a different reactant. The dissolved monomers diffuse to the interface, where they undergo a copolymerization reaction. The resulting copolymer is usually incompatible with the liquid phases and a polymer film grows at the interface. The interfacial technique has several advantages. Bulk stoichiometry is not necessary to produce high-molecular-weight polymers and fast reactions can be used. The low temperatures allow the synthesis of polymers that might be unstable at the high temperatures generally required in the typical step polymerization [1–3]. This technique has been used to synthesize polyamides, polyesters, polycarbonates, polyurethanes, and many other macromolecules [4,5]. Interfacial polymerization of two immiscible liquids has also been used to fabricate nanocapsules for the controlled drug-release and thin-film type porous membranes for filtration [5–16]. Recently, the technological requirements for applying interfacial polymerization have prompted many theoretical studies aimed at predicting the kinetics of thin film formation and the molecular weight distribution of polymer [16–21].

Since their discovery by Ijima, carbon nanotubes (CNTs) have gained increasing interest on account of their unique structure and extraordinary mechanical and electronic properties [22,23]. Theoretical and experimental studies have shown that CNTs have an extremely high Young's moduli that is similar to that of the graphite in-plane (∼1000 GPa) [24,25]. Therefore, CNT-reinforced polymer composites have potential defense and aerospace applications, where high strength and lightweight components are of prime importance. In addition to their mechanical properties, the electrical properties of CNTs can be used to impart conductivity to non-conducting polymers, thereby improving the electrostatic charge dissipation and electromagnetic shielding efficiency [26,27]. Accordingly, many polymers are currently under investigation for their potential as host matrices for CNTs. The resulting composites have been reported to show improved mechanical and electrical properties [28–30]. The techniques commonly used to fabricate CNT-composite materials rely on solution casting [31–33], melt processing [34,35], wet spinning [36–38] and electrospinning [39–41].

This study used a new and simple processing route to incorporate multi-walled carbon nanotubes (MWNTs) into a polymer matrix via in situ interfacial polymerization.

---

* Corresponding author. Tel.: +82 32 860 7483; fax: +82 32 865 5178.
E-mail address: hjjin@inha.ac.kr (H.-J. Jin).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.03.073

Poly(hexamethylenesebacamide) (nylon 610)/MWNT composite was prepared using two liquid phases containing the reactants and MWNTs. One phase contained a solution of sebacoyl chloride in carbon tetrachloride and the other contained a solution of hexamethylenediamine and MWNTs in water, which was prepared by sonication with a surfactant. The MWNTs-incorporated nylon 610 exhibited enhanced mechanical properties with a small amount of MWNTs.

2. Experimental sections

2.1. Materials

Sebacoyl chloride (TCI, Japan) and hexamethylenediamine (JUNSEI, Japan) were used as received and were stored in a refrigerator and in an oven at 60 °C for 2 h prior to use, respectively. Carbon tetrachloride (DC Chemical Co. Ltd, Korea) was used as the reaction medium for sebacoyl chloride. The carbon nanotubes used in this study were MWNT (Iljin Nanotech Co., Korea), which were synthesized via a thermal chemical vapor deposition (CVD) method.

2.2. Purification of cabon nanotubes

The purity of the as-received MWNT was 97%. In order to remove the impurities (such as the metallic catalysts) in the MWNT, the MWNT were treated with 3 M HNO_3 at 60 °C for 12 h, followed by refluxing in 5 M HCl at 120 °C for 6 h. Thermogravimetric analysis (TGA, Polymer Lab., TGA1000, UK) confirmed the purity of the acid-treated MWNT to be 99%.

2.3. Preparation of carbon nanotube dispersion

The purified MWNTs were dispersed in pure water containing Triton X-100 (non-ionic). Ultrasound was then applied to the MWNT dispersion using an ultrasonic generator (Kyungill Ultrasonic Co., Korea), which has a nominal frequency of 28 kHz, with power of 600 W for 7 h at 25 °C.

2.4. Nylon 610/MWNT composite synthesis

The nylon 610/MWNT composite synthesis by interfacial polymerization was accomplished using an organic phase comprised of 5.4 mL (6.048 g, 25.2 mM) sebacoyl chloride in 180 mL carbon tetrachloride in an 1 L beaker. Over this solution, 90 mL of an aqueous MWNT dispersion containing 7.95 g of hexamethylenediamine and 2.16 g of sodium hydroxide was added. The polymerization reaction began immediately upon adding the MWNT dispersion and a film of nylon 610/MWNT formed at the liquid interface. The film was grasped with tweezers and raised as a rope of continuously forming nylon 610/MWNT film on a glass rod roller. The nylon 610/MWNT composite was washed well with distilled water. The damp sample was partly air-dried, which was followed by drying in a vacuum oven at 80–100 °C.

2.5. Characterizations

The surface morphology was observed using a field emission scanning electron microscopy (FESEM, S-4300, Hitachi, Japan). The FESEM images were obtained by collecting the samples on an aluminum SEM disk, which was then coated with platinum. The acceleration voltages and the working distances for each image were 15 kV and 6 mm, respectively. High-resolution transmission electron microscopy (TEM) was performed using a Philips CM 200 unit, which was operated at an acceleration voltage of 120 kV. For the observation of the nylon 610/MWNT composites, a fragment of the composites were sonicated in water for 12 h and a drop of sample was then placed onto a 300 mesh carbon-coated copper grid. Approximately 2 min after deposition, the grid was tapped softly with filter paper to remove the surface water, which was followed by air-drying. The samples were vacuum-dried for 24 h at room temperature before the measurement. The tensile properties of the nylon 610/MWNT composite were determined using a universal test machine (Model no. 4200, Instron, USA) at a cross-head speed of 25.4 mm/min according to the ASTM D 638 at room temperature. Sheet type specimens for the tensile test were prepared by hot pressing (Lab Press, CARVER) at 250 °C for 1 min under a pressure of 2.0 atm. Viscosity determinations on the polymer solutions are reported here as inherent viscosities ($\eta_{inh} = [\ln \eta_{rel}]/c$) determined at 25 °C in *m*-cresol with $c = 0.5$ g polymer/100 mL of solution using Ubbelohde viscometer [3].

3. Results and discussion

3.1. Purification of MWNTs

The individual as-synthesized CNTs were found in the amorphous material in the form of bundles that were several 100 μm long. These CNTs were entangled with impurities such as metal catalysts to form large submicron aggregates [42], which had to be separated into individual CNTs that could then be used as reinforcing materials in the polymer nanocomposites [26]. In order to prepare the MWNTs with a high purity, a two-step purification procedure including oxidation was used, as described in the Section 2. Oxidation in nitric acid can modify the side walls and substitute the ends of the CNTs with oxygen containing groups [43,44]. Using this two-step procedure, the CNT could be separated form the impurities such as metal particles. Although direct evidence for an oxidized surface on the CNTs is not provided in this report, the modification of the side walls and ends of the CNTs via oxidation has been reported [45–48].

3.2. Dispersion of MWNTs in water

The ultrasonication of MWNTs with a surfactant in aqueous media provided a dispersion of individually separated nanotubes, which prevented the nanotubes from aggregating via van der Waals interactions [48–53]. At the optimum

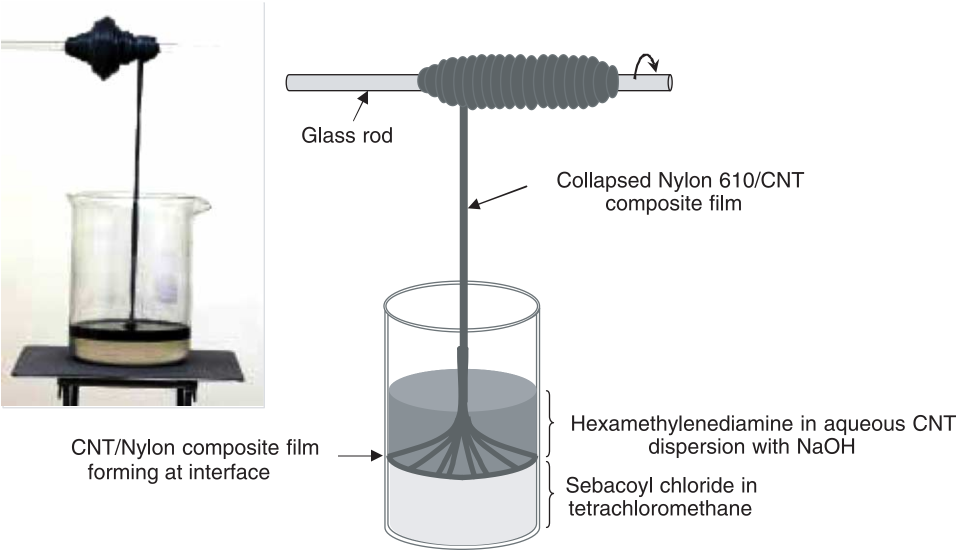

Fig. 1. Collapsed nylon 610/MWNT composite film forming at and being withdrawn from a liquid interface.

surfactant concentration in aqueous solution, a homogeneous dispersion of nanotubes formed into a single phase. Large and dense clusters of nanotubes formed in solution after sonication when the amount of surfactant was either too low or high [48–56]. The optimum concentration of the surfactant was approximately 0.3 wt% and the nanotube concentration was 0.05 wt%. Triton X-100 was used as surfactant to disperse the purified MWNTs resulting in homogenous black ink-like solutions being obtained, which was stable and could be stored at room temperature for several months without significant precipitation [45,56].

3.3. Interfacial polymerization

Polymerization of the two reactants was carried out at the interface between the two liquid phases, one containing an aqueous solution of hexamethylenediamine and the other containing an organic solution of sebacoyl chloride in carbon tetrachloride. Hexamethylenediamine reacts with sebacoyl chloride to yield poly(hexamethylenesebacamide) (nylon 610), which can be synthesized at room temperature using the fast Schotten–Baumann reactions of acid chlorides. Polymerization for the composite was carried out by placing an aqueous solution of the diamine containing the MWNTs on top of the organic phase containing the acid chlorides. Sodium hydroxide was added to the aqueous phase to neutralize the hydrogen chloride by-product, which would reduce the reaction rates by tying up the diamines. The precipitated nylon 610/MWNT composite product was continuously withdrawn as a continuous film in filament form due to its sufficient mechanical strength, as shown in Fig. 1. The collected composites were washed twice with water to extract the remaining salts, and the vacuum-dried samples were then molded into a sheet type for further characterization. Fig. 2 shows the color difference between the pure nylon 610 sheet and the nylon 610/MWNT composite sheet with the incorporated MWNTs.

3.4. Morphology of nylon 610/MWNT composites

The uniform dispersion of CNTs in the polymer matrix is one of the most important factors for reinforcing a composite because any non-uniformity can result in structural defects. The composite film was fractured in liquid nitrogen and the fracture surface of the composite was observed by FESEM (Fig. 3). The bright regions in the images were attributed to the MWNTs due to their high conductivity, and the MWNTs were found to be uniformly distributed in the nylon 610 matrix without aggregation. The interfacial adhesion between the polymer matrix and the reinforcements is also another important factor for enhancing the mechanical properties of the composite. Although direct evidence of an oxidized surface on MWNTs is not provided in this report, the modification of the side walls and ends of the nanotubes by oxidation during

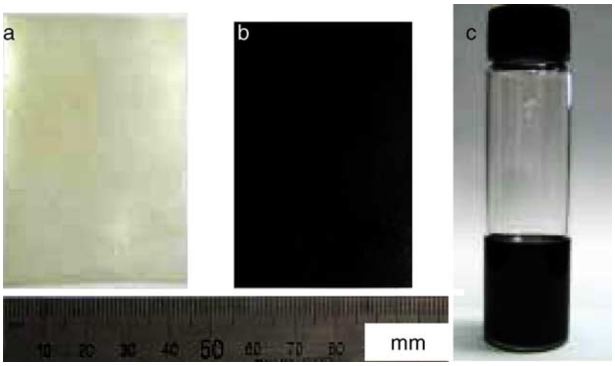

Fig. 2. Image of (a) nylon 610 and (b) nylon 610/MWNT composite sheets, and (c) the solution of the composite dissolved in *m*-cresol at 25 °C (c = 0.5 g/100 mL).

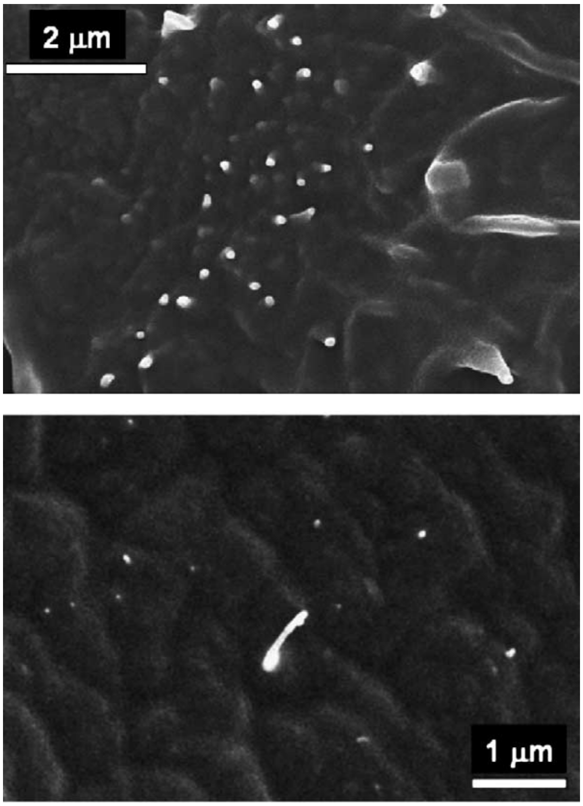

Fig. 3. FESEM images of fractured surface of nylon 610/MWNT composite sheet.

the purification of CNTs has been reported [43–48,57]. TEM showed the individual MWNTs were coated by nylon 610 (Fig. 4). A thin layer of nylon 610 with a thickness of 5–10 nm was observed on the surface of MWNT. We believe that the molecules of nylon 610 might be adsorbed on the surface of MWNT during polymerization by the potential interaction of nylon 610 and acid-purified MWNT. It should be noted that the sample for TEM observations was prepared by sonicating the composite in water for 12 h.

3.5. Thermal properties of nylon 610/MWNT composites.

The concentration of MWNTs incorporated into the nylon 610 after polymerization and purification was determined using TGA analysis. The TGA curves were obtained by heating the sample up to 600 °C at a rate of 20 °C/min with N_2 gas purging (Fig. 5). Nylon 610 began to degrade at approximately 400 °C and was completely decomposed at 525 °C, and approximately 1.5 wt% of the MWNTs in the composites remained above 550 °C. Furthermore, Fig. 5 indicates that the composites decompose at higher temperature, which suggests that the incorporation of MWNTs increases the thermal stability of the composite. It is well-known that the enhanced thermal conductivity of a composite can facilitate heat transport and increase its thermal stability through the incorporation of high thermal conducting CNTs [58–61].

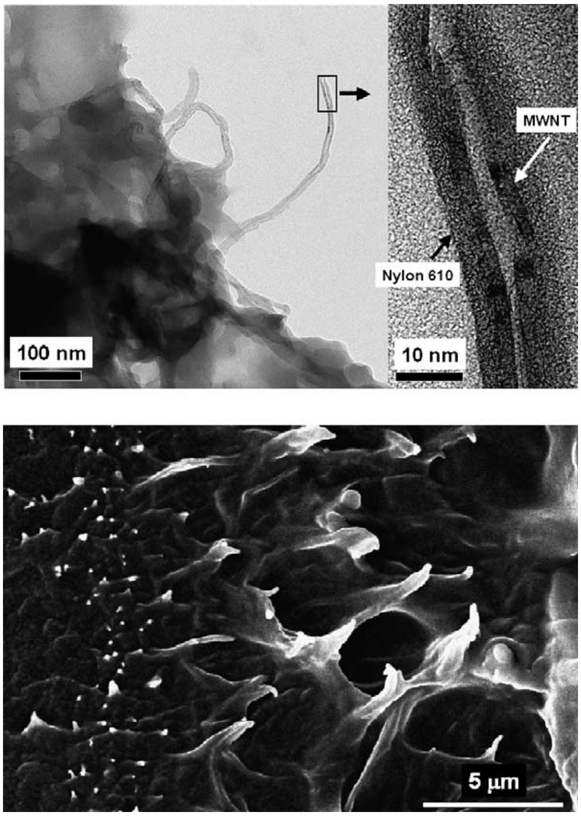

Fig. 4. High-resolution TEM (above) and FESEM (below) images of nylon 610/MWNT composite.

3.6. Mechanical properties and inherent viscosity of nylon 610/MWNT composites.

After incorporating the MWNTs into the nylon 610, the Young's modulus and tensile strength of the composite films increased (Table 1). The composite film shows a Young's modulus of 2.4±0.3 GPa, which is approximately 170% higher than that of the pure nylon 610 film. However, the tensile strength and the elongation at the break of the composite film were slightly higher (approximately 40 and 25%, respectively) than that of the nylon 610 film. The incorporation

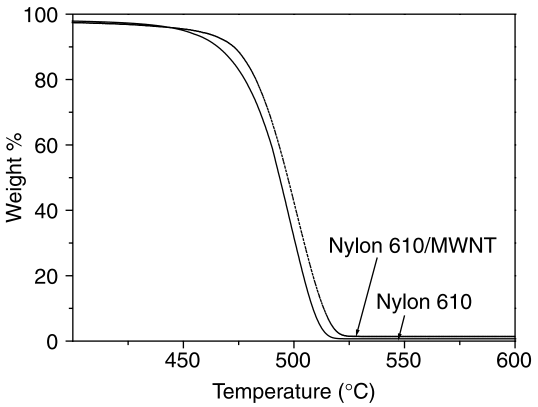

Fig. 5. TGA curves of nylon 610 and nylon 610/MWNT composite.

Table 1
Mechanical properties of nylon 610/MWNT composite

Samples	Tensile modulus, E^{a} (GPa)	Tensile strength, $\sigma_y^{a,b}$ (MPa)	Elongation^{a} (%)	η_{inh} (dL/g)
Nylon 610	0.9 ± 0.1	35.9 ± 0.5	10.2 ± 0.3	1.06
Nylon 610/MWNTs	2.4 ± 0.3	51.4 ± 1.7	12.7 ± 0.7	1.40

[a] $N=5$, average ± standard deviation.
[b] Strength at yield.

of MWNTs into nylon 610 increased the tensile properties, which suggests that the composite is apparently stronger than nylon 610 as a result of the incorporation of only a small amount (1.5 wt%) of MWNTs. The inherent viscosities of nylon 610 and the composite were measured by dissolving them in *m*-cresol. The solution of the composite was homogeneous and stable at room temperature as shown in Fig. 2(c). The MWNTs did not separate and make sedimentation in the solution during 2 weeks. The inherent viscosity of the composite was higher than that of nylon 610 because the small portion of added surfactants for dispersion of MWNTs in aqueous solution might assist the transfer of both diamine and salt across the interface during polymeriazation [1–3]. Note that polycondensation is dependent only on the conditions near the interface [1–3].

4. Conclusions

Nylon 610/MWNT composites were prepared by dispersing MWNTs via an in situ interfacial polymerization of two liquid phases, one containing hexamethylenediamine and the other containing sebacoyl chloride in the presence of MWNTs with Triton X-100. It was found that the interfacial polymerization process was not only useful for dispersing the MWNTs in the nylon 610 matrix but was also efficient in enhancing the mechanical properties (170% increase in the Young's modulus) of the matrix polymer with a small amount of MWNTs (1.5 wt%). High-resolution TEM provided evidence of an interfacial adhesion between the oxidized MWNTs and the amide group of nylon 610. The incorporation of MWNTs into nylon 610 matrix also increases the thermal stability of the composite.

Acknowledgements

The authors of this paper would like to thank the Korea Science and Engineering Foundation (KOSEF) for sponsoring this research through the SRC/ERC program of MOST/KOSEF (R11-2005-065).

References

[1] Wittbecker EL, Morgan PW. J Polym Sci 1959;40:289–97.
[2] Morgan PW, Kwolek SL. J Polym Sci 1959;40:299–327.
[3] Morgan PW, Kwolek SL. J Polym Sci, Part A 1963;1:1147–62.
[4] Odian G. Principles of polymerization. 3rd ed. New York: Wiley; 1991.
[5] Morgan PW. In: Mark HF, Kroschwitz JI, editors. Encyclopedia of polymer science and engineering, 2nd ed, vol. 8. New York: Wiley; 1985. p. 221–37.
[6] Couvreur P, Barrat G, Fattal E, Legrand P, Vauthier C. Crit Rev Ther Drug Carrier Syst 2002;19:99–134.
[7] Ji J, Dickson JM, Childs RF, McCarry BE. Macromolecules 2000;33: 624–33.
[8] Janssen LJJM, te Nijenhuis K. J Membr Sci 1992;65:59–68.
[9] Janssen LJJM, te Nijenhuis K. J Membr Sci 1992;65:69–75.
[10] Janssen LJJM, te Nijenhuis K. J Membr Sci 1993;79:11–26.
[11] Ji J, Childs RF, Mehta M. J Membr Sci 2001;192:55–70.
[12] Mikos AG, Kiparissides C. J Membr Sci 1991;59:205–17.
[13] Ji J, Mehta M. J Membr Sci 2001;192:41–54.
[14] Petersen RJ. J Membr Sci 1993;83:81–150.
[15] Cadotte J, King R, Majerle R, Petersen R. J Macromol Sci, Chem 1981; A15:727–55.
[16] Freger V, Srebnik S. J Appl Polym Sci 2003;88:1162–9.
[17] Freger V. Langmuir 2003;19:4791–7.
[18] Yashin VV, Balazs AC. J Chem Phys 2004;121:2833–43.
[19] Yashin VV, Balazs AC. J Chem Phys 2004;121:11440–54.
[20] Karode SK, Kulkarni SS, Suresht AK, Mashelkar RA. Chem Eng Sci 1998;53:2649–63.
[21] Karode SK, Kulkarni SS, Suresht AK, Mashelkar RA. Chem Eng Sci 1997;52:3243–55.
[22] Iijima S. Nature 1991;354:56–8.
[23] Saito R, Dresselhause G, Dresselhause MS. Physical properties of carbon nanotubes. London: Imperial College Press; 1998.
[24] Salvetat JP, Briggs GAD, Bonard JM, Basca RR, Kulik AJ, Stockli T, et al. Phys Rev Lett 1999;82:944–7.
[25] Yu MF, Files BS, Arepalli S, Ruoff RS. Phys Rev Lett 2000;84: 5552–5.
[26] Baughman RH, Zakhidov AA, de Heer WA. Science 2002;297:787–92.
[27] Harris PJF. Int Mater Rev 2004;49:31–43.
[28] Ajayan PM, Stephan O, Colliex C, Trauth D. Science 1994;265: 1212–4.
[29] Ajayan PM, Schadler LS, Giannaris C, Rubio A. Adv Mater 2000;12: 750–3.
[30] Meincke O, Kaempfer D, Weickmann H, Friedrich C, Vathauer M, Warth H. Polymer 2004;45:739–48.
[31] Shaffer MSP, Windle AH. Adv Mater 1999;11:937–41.
[32] Qian D, Dickey EC, Andrews R, Rantell T. Appl Phys Lett 2000;76: 2868–70.
[33] Safadi B, Andrews R, Grulke EA. J Appl Polym Sci 2002;84:2660–9.
[34] Zhang WD, Shen L, Phang IY, Liu T. Macromolecules 2004;37:256–9.
[35] Potschke P, Fornes TD, Paul DR. Polymer 2002;43:3247–55.
[36] Vigolo B, Penicaud A, Coulon C, Sauder C, Pailler R, Journet C, et al. Science 2000;290:1331–4.
[37] Vigolo B, Poulin P, Lucas M, Launois P, Bernier P. Appl Phys Lett 2002; 81:1210–2.
[38] Kumar S, Dang TD, Arnold FE, Bhattacharyya AR, Min BG, Zhang X, et al. Macromolecules 2002;35:9039–43.
[39] Sen R, Zhao B, Perea D, Itkis ME, Hu H, Love J, et al. Nano Lett 2004;4: 459–64.
[40] Ko F, Gogotsi Y, Ali A, Naguib N, Ye H, Yang G, et al. Adv Mater 2003; 15:1161–5.
[41] Sung JH, Kim HS, Jin HJ, Choi HJ, Chin IJ. Macromolecules 2004;37: 9899–902.
[42] Chen XH, Chen CS, Chen Q, Cheng FQ, Zhang G, Chen ZZ. Mater Lett 2002;57:734–8.
[43] Yang Y, Zhang J, Nan X, Liu Z. J Phys Chem B 2002;106:4139–44.
[44] Liu J, Casavant MJ, Cox M, Walters DA, Boul P, Lu W, et al. Chem Phys Lett 1999;303:125–9.
[45] Liu J, Rinzler AG, Dai H, Hafner JH, Bradley RK, Boul PJ, et al. Science 1998;280:1253–6.
[46] Kong H, Gao C, Yan D. Macromolecules 2004;37:4022–30.
[47] Niyogi S, Hamon MA, Hu H, Zhao B, Bhowmik P, Sen R, et al. Acc Chem Res 2002;35:1105–13.

[48] Chen J, Hamon MA, Hu H, Chen Y, Rao AM, Eklund PC, et al. Science 1998;282:95–8.

[49] Sun YP, Fu K, Lin Y, Huang W. Acc Chem Res 2002;35:1096–104.

[50] Yurekli K, Mitchell CA, Krishnamoorti R. J Am Chem Soc 2004;126: 9902–3.

[51] Islam MF, Rojas E, Bergey DM, Johnson AT, Yodh AG. Nano Lett 2003; 3:269–73.

[52] Matarredona O, Rhoads H, Li Z, Harwell JH, Balzano L, Resasco DE. J Phys Chem B 2003;107:13357–67.

[53] Star AD, Steuerman W, Heath JR, Stoddart JF. Angew Chem, Int Ed 2002;41:2508–12.

[54] Bandyopadhyaya R, Nativ-Roth E, Regev O, Yerushalmi-Rozen R. Nano Lett 2002;2:25–8.

[55] Saran N, Parikh K, Suh DS, Muñoz E, Kolla H, Manohar SK. J Am Chem Soc 2004;126:4462–3.

[56] Vigolo B, Pénicaud A, Coulon C, Sauder C, Pailler R, Journet C, et al. Science 2000;290:1331–4.

[57] Hamon MA, Chen J, Hu H, Chen Y, Itkis ME, Rao AM, et al. Adv Mater 1999;11:834–40.

[58] Gao J, Itkis ME, Yu A, Bekyarova E, Zhao B, Haddon RC. J Am Chem Soc 2005;127(11):3847–54.

[59] Benedict LX, Louie SG, Cohen ML. Solid State Commun 1996;100: 177–80.

[60] Berber S, Kwon YK, Tomanek D. Phys Rev Lett 2000;84:4614–6.

[61] Huxtable ST, Cahill DG, Shenogin S, Xue L, Ozisik R, Barone P, et al. Nat Mater 2003;2:731–4.