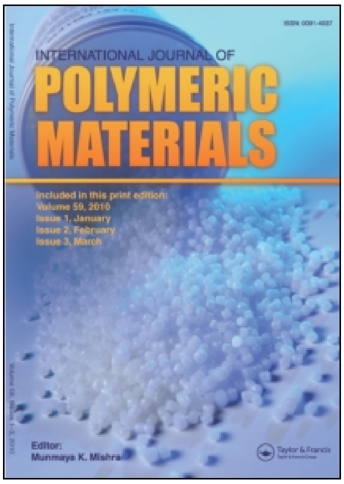

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

PET-SWNT Nanocomposite Fibers through Melt Spinning

K. Anoop Anand[a]; T. Sunil Jose[a]; U. S. Agarwal[b]; T. V. Sreekumar[b]; Bhawna Banwari[b]; Rani Joseph[a]
[a] Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin, India [b] Reliance Technology Group, Patalganga, India

To cite this Article Anand, K. Anoop , Jose, T. Sunil , Agarwal, U. S. , Sreekumar, T. V. , Banwari, Bhawna and Joseph, Rani(2010) 'PET-SWNT Nanocomposite Fibers through Melt Spinning', International Journal of Polymeric Materials, 59: 6, 438 — 449

To link to this Article: DOI: 10.1080/00914030903538587

URL: http://dx.doi.org/10.1080/00914030903538587

International Journal of Polymeric Materials, 59:438–449, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030903538587

PET-SWNT Nanocomposite Fibers through Melt Spinning

K. Anoop Anand,[1] T. Sunil Jose,[1] U. S. Agarwal,[2]
T. V. Sreekumar,[2] Bhawna Banwari,[2] and Rani Joseph[1]

[1]Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin, India
[2]Reliance Technology Group, Patalganga, India

Poly(ethylene terephthalate)-single-walled carbon nanotube (PET-SWNT) nanocomposite fibers have been prepared through melt spinning and drawing. While acting as effective nucleating agents for PET melt crystallization, SWNTs also provide significant reinforcement to PET fibers. For example, the tenacity and initial modulus of the composite fiber with 1 wt% SWNTs were, respectively, 1.8 times and 3.2 times higher as compared to those of the pristine PET fiber prepared under identical conditions. When the draw ratio was increased, tenacity and modulus of the fibers increased, indicating that drawing induced orientation of the polymer molecules and SWNTs. Thermal stability of the fibers was not significantly affected by the presence of SWNTs at low concentrations.

Keywords Mechanical properties, nanocomposite fibers, nucleating agents, poly(ethylene terephthalate), SWNTs

INTRODUCTION

Today, polyester fibers are used in a wide variety of applications ranging from textiles to automobiles. They are known for their high resilience, resistance to wrinkling, high durability, dimensional stability, and resistance to chemical and environmental attack. Poly(ethylene terephthalate) fiber accounts for

---

Received 18 November 2009; in final form 23 November 2009.
We are thankful to Ms. Priyanka Katiyar (DMSRDE, Kanpur) for her assistance in the fiber spinning processes.

Address correspondence to T. V. Sreekumar, Reliance Technology Centre, B-4 MIDC Industrial Area, Patalganga-410 220, India. E-mail: sreekumar.veedu@ril.com

over 97% of all polyester fibers manufactured today. Only small amounts of other types of polyester fibers are presently or have been produced commercially, of which the larger volume materials include poly(1,4-cyclohexane dimethylene terephthalate), poly(butylene terephthalate), and poly(trimethylene terephthalate) [1].

Scientists all over the world have made several attempts in the past to modify the performance characteristics of polymer fibers, mostly PET fibers [2–4]. Carbon nanotubes have recently been considered as attractive candidates for imparting several properties to polymer fibers [5,6]. For example, multi-walled carbon nanotubes (MWNTs) have been incorporated to nylon 6 and PET fibers by Xushan et al. [7]. They observed that, when adding 0.03 wt% MWNTs into nylon 6 fiber, the strength and modulus of the nylon fiber enhanced by 33 and 74%, respectively. Adding 0.1 wt% MWNTs into PET fiber made the latter fairly conducting. The breaking strength of this conducting PET fiber showed almost no decrease and the initial modulus was slightly enhanced in comparison with pure PET fiber. Poly(p-phenylene benzobisoxazole) (PBO)-based nanocomposite fibers with SWNTs have been prepared by Kumar et al. [8]. They reported that the fibers containing 10 wt% SWNTs exhibited 50% higher tensile strength as compared to the control PBO fiber. Sandler et al. also observed that carbon nanotubes act as effective reinforcements in melt spun polyamide-12 fibers [9]. Sreekumar et al. have prepared polyacrylonitrile-SWNT nanocomposite fibers through solution spinning [10]. The spun nanocomposite fibers containing 10 wt% SWNTs exhibited a 100% increase in tensile modulus at room temperature, and it increased by an order of magnitude at 150°C. They also observed a significant reduction in thermal shrinkage and the glass transition temperature was increased by 40°C as compared with control PAN fiber. Crystallization and orientation in polypropylene-SWNT nanocomposite fibers have been studied by Bhattacharyya et al. [11]. Using WAXD and Raman spectroscopy, the authors established that SWNTs have higher orientation than PP in drawn PP-SWNT nanocomposite fibers. This report also claims that even with a limited dispersion, SWNTs could act as nucleating agents for PP crystallization. PP fiber modulus has also been reported as increased by 50% with the addition of 5 wt% carbon nanofibers [12]. It is anticipated that the shear forces during melt spinning can induce alignment of SWNTs in the fiber axis direction to impart significant reinforcement to the polymer matrix. Indeed, several other groups have demonstrated improvement in the properties of polystyrene and poly(methyl methacrylate), as a result of melt/wet spinning various amounts of nanotubes with the polymer matrix [13–15].

Ma et al. have prepared PET-based composite fibers reinforced with various grades of carbon nanofibers [16]. They reported that the tensile moduli of the composite fibers were marginally higher than that of the pristine PET fiber. On the other hand, the tensile strength of the composite fibers was either comparable to or lower than the control fiber.

Although several types of fiber spinning methods are commercially used, polyester fibers are usually produced by melt spinning [17]. Melt spinning is the least complex spinning method; it simply involves forcing a polymer melt through a spinneret and into air to cause the polymer to solidify. It does not involve the problems associated with the use of solvents and is therefore the preferred method provided that the polymer gives a stable melt. The homogenized and filtered melt is extruded through the spinneret and can solidify anywhere from a few centimeters from the spinneret plate to as far away as several meters.

In the present work, we have prepared PET-SWNT nanocomposites through a simple melt compounding method; they were melt spun with subsequent drawing to yield nanocomposite fibers. The role of carbon nanotubes in nucleating melt crystallization of PET has been studied using differential scanning calorimetry. The effect of fiber formation conditions on the development of their mechanical properties has also been investigated.

EXPERIMENTAL

Materials

Poly(ethylene terephthalate) pellets (characteristic cylindrical diameter $\approx 2.5\,\text{mm}$, length $\approx 3\,\text{mm}$) were obtained from Acordis Research (Arnhem, the Netherlands). The intrinsic viscosity of the polymer was determined to be 0.98 dL/g in 1/1 phenol/1,1,2,2-tetrachloroethane at 30°C. SWNTs were purchased from CarboLex Inc. (Lexington, U.S.A.). They were prepared by arc discharge method. The average diameter of an individual tube was 1.4 nm and length was in the range of 2–5 µm.

Preparation of the PET-SWNT Nanocomposite Fibers

A simple melt-compounding route was adopted for the preparation of PET-SWNT nanocomposites. The polymer and SWNTs were vacuum-dried at 150°C for 12 h to avoid moisture-induced degradation. The melt compounding was performed using a laboratory scale ($60\,\text{cm}^3$) Thermo Haake Polylab system operating at 40 rpm for 4 min at 270°C. A mixing time of 4 min was fixed since the torque stabilized to constant value during this time [18]. The stabilization of torque may be related to the attainment of a stable structure. Nanocomposites at different concentrations (0–2 wt%) of SWNTs were prepared. Melt compounded nanocomposites of PET and SWNTs were ground using a cryo grinder (Lloyd Instruments Ltd.) and were dried at 150°C under vacuum for at least 12 h. They were spun into fibers using a small scale spinning machine manufactured by Bradford University Research Ltd., UK, using a single-hole spinneret. The conditions of spinning were as follows:

- Spinneret: Single hole, dia = 1 mm, length = 7 mm
- Cylinder temperature: 265 (±0.5)°C
- Piston speed: 3 (±0.02) mm/min
- Winding speed: 70 (±0.2) m/min
- Filament type: mono filament

The spun fibers were subsequently drawn using a laboratory single zone drawing machine. PET fibers are typically drawn above 80°C; additional heat is necessary because it provides the fiber molecules with the mobility to rearrange. The specifications and conditions of drawing were as follows:

- Speed of the feed roller: 4 rpm
- Outer diameter of the rollers: 11.2 cm
- Speed of the take up roller: variable
- Length of the heating plate: 20.5 cm
- Heater temperature: 100 (±0.5)°C

Optical Microscopy

Optical micrographs of the nanocomposite fibers were recorded on a Leica polarizing microscope mounted with a hot stage assembly.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC Q-100, TA Instruments) was employed to study the effect of SWNTs on the crystallization characteristics of PET. Indium was used for temperature calibration ($T_m = 156.6$°C, $\Delta H_m = 28.4$ J/g). The samples were dried prior to the measurements and analyses were done in a nitrogen atmosphere using standard aluminum pans. Calorimetric measurements on neat PET and the 1 wt% PET-SWNT nanocomposite were done while the samples (4–5 mg) were exposed to the following temperature scans: heating at a rate of 20°C/min to 310°C, holding for 10 min to erase thermal history effects and then cooling to 50°C at a rate of 20°C/min during which the peak of crystallization exotherm was taken as the crystallization temperature, T_c. For analysis of the isothermal crystallization characteristics, the samples were subsequently reheated to 310°C at a rate of 20°C/min, held at 310°C for 2 min, and then cooled rapidly (60°C/min) to the desired temperature for isothermal crystallization (210, 215, 220 or 225°C). The heat of fusion (ΔH_m) and the heat of crystallization (ΔH_c) were determined from the areas of the melting and crystallization peaks, respectively.

Mechanical Properties of the Fibers

Mechanical properties of the PET-SWNT nanocomposite fibers were determined using a Favimat Fiber Testing machine (Textechno-textile testing technology) with a load cell of 1,200 cN capacity. The distance between the jaws at the start of each test was 20 mm and the test speed was 20 mm/min. The pre-tension was set at 0.50 cN/tex and the test temperature was maintained at 25 ± 1°C. At least 20 measurements were taken to represent each data point.

Thermal Stability

Thermogravimetric analyzer (TGA, Q-50, TA Instruments) was used to study the effect of SWNTs on the thermal stability of PET fibers. Approximately 5 mg of the samples were heated at a rate of 20°C/min from ambient to 700°C. The chamber was continuously swept with nitrogen at a rate of 60 mL/min.

RESULTS AND DISCUSSION

Optical Microscopy of the Nanocomposite Fibers

Optical microscopy images of the nanocomposite fibers are shown in Figure 1. While the control neat PET fiber is smooth and transparent (not shown), the introduction of SWNTs turns the color of the fibers gradually to dark black. With an increase in the nanotube content, the fiber surface becomes more uneven. It is evident from the images of the molten nanocomposite fibers that there are nanotube chunks as large as 50 to 100 μm. This is due to the poor dispersion of the SWNTs in the PET matrix as they were dispersed by simple melt compounding. It is interesting that the chunks seem to be elongated and oriented along the fiber axis direction with an L/D of nearly 3–4. It may be noted that these fibers were subjected to a draw ratio of 4. During this process the circular nanotube agglomerates might have undergone elongational shear flow along with the polymer matrix.

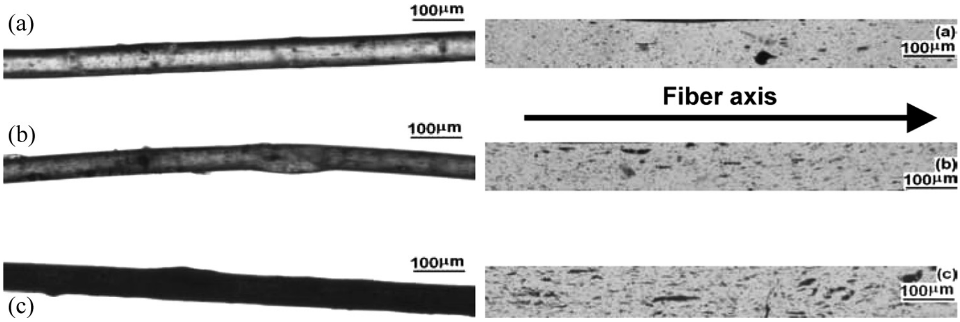

Figure 1: Optical microscopy images of PET-SWNT nanocomposite filaments with DR = 4 in the solid and molten form; (a) 0.5 wt% SWNTs, (b) 1 wt% SWNTs, (c) 2 wt% SWNTs.

Crystallization Characteristics

Carbon nanotubes have been evaluated as additives to polymers, especially thermoplastics, for imparting faster crystallization resulting in lower cycle times, which are critical in injection molding, etc. [19–24]. Results on the crystallization characteristics of our melt-compounded PET-SWNT nanocomposites (0 and 1 wt% SWNTs) are given in Figure 2. During cooling from the melt, the SWNT containing sample shows crystallization exotherm earlier than neat PET. It is found that the nanocomposite sample containing SWNTs at a concentration as low as 1 wt% crystallizes ~14°C earlier than neat PET, indicating that SWNTs are acting as effective nucleating agents for PET crystallization (Figure 2a).

DSC-determined crystallization data shown in Table 1 also indicate that the melting temperature as well the enthalpies remain unaffected with SWNTs in PET at least up to a concentration of 1 wt%. The degree of supercooling ($\Delta T = T_m - T_c$), which is a measure of the crystallizability is also lower for the nanocomposite, indicating that its crystallizability is greater than that of neat PET [25].

Figure 2b shows typical isothermal crystallization curves of the samples at four temperatures (210, 215, 220 and 225°C). The time corresponding to the maximum in the heat flow rate (exotherm) was taken as peak time of crystallization (t_{peak}). Such peaks are seen at different isothermal crystallization temperatures for the 1 wt% SWNT containing nanocomposite, with the earlier or faster crystallization (smaller t_{peak}) corresponding to the lower temperature of isothermal crystallization. For the case of neat PET, no peak is seen at the highest temperature of 225°C because crystallization is very slow and would require longer time than the 4 min employed in our DSC program. On the other hand, for the nanocomposite sample, the rate of crystallization is so fast near the lowest temperature (210°C) that most of the crystallization occurs already during the cooling scan (60°C/min) employed to reach that temperature, resulting in absence of exothermic peaks in the heat flow curves at that temperature.

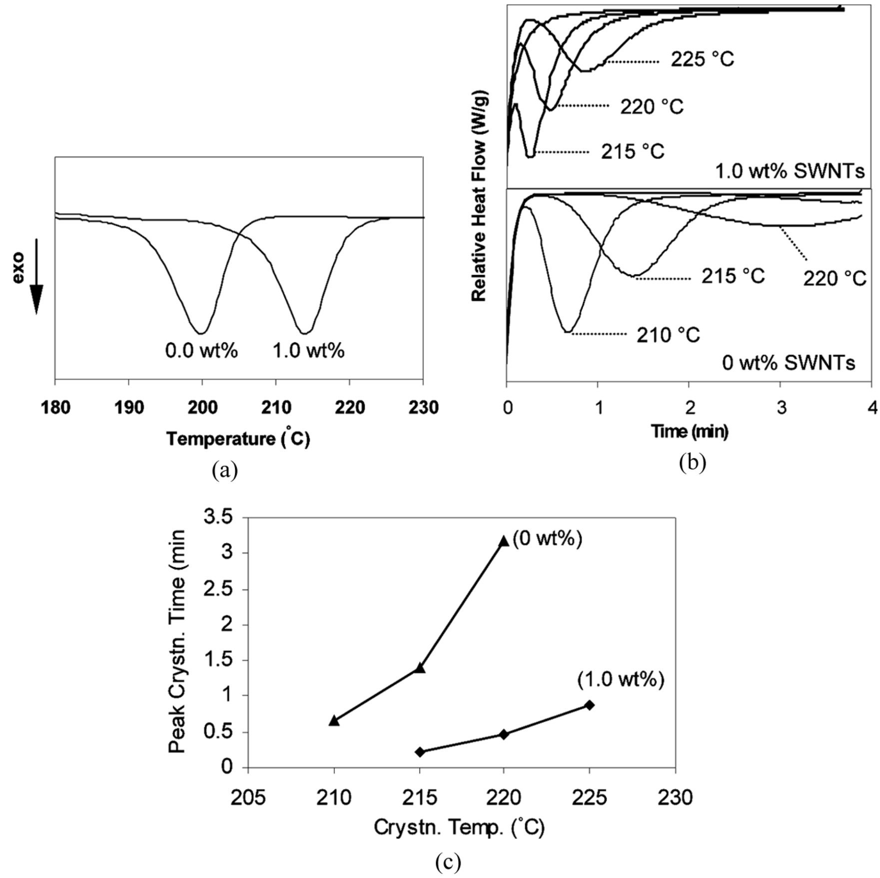

Figure 2: (a) Normalized DSC cooling scans (20°C/min from 310°C melt) of neat PET and PET-SWNT 1 wt% nanocomposite (b) heat flow during isothermal crystallization (c) effect of SWNTs on the peak crystallization time of PET at different isothermal crystallization temperatures.

The peak times of crystallization at each of the temperatures for both neat PET and 1 wt% SWNT nanocomposite are plotted against the isothermal crystallization temperature (Figure 2c). We notice that the t_{peak} values for the nanocomposite sample reduce dramatically as compared to neat PET

Table 1: Crystallization characteristics of neat PET and PET-SWNT 1 wt% nanocomposite.

Concn. of SWNTs (wt%)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	ΔT (°C)
0	199.9	38.2	253.0	37.5	53.1
1	214.3	37.3	251.1	37.7	36.8

due to the presence of SWNTs. These results indicate that SWNTs are acting as promising nucleating agents for the melt crystallization of PET.

Mechanical Properties of PET-SWNT Nanocomposite Fibers

Mechanical properties of the drawn PET-SWNT nanocomposite fibers (draw ratio, D.R. = 4,5,6) are given in Table 2. It is evident that the presence of SWNTs substantially reinforces the fiber. For example, the tenacity of the composite fiber with 2.0 wt% SWNTs is roughly 2.5 times higher the tenacity of pristine PET fiber. The modulus at 2% elongation is about five times higher as compared to that of the pristine PET fiber. However, the elongation of the fibers is reduced by the presence of SWNTs. This is due to the embrittlement of the polymer matrix in the presence of the nanofiller.

These results reveal that SWNTs offer a substantial level of reinforcement to PET fibers, and are in good agreement with several literature reports which have demonstrated that the fibers containing SWNTs, in which the nanotube alignment in the fiber direction was induced by shear forces during melt extrusion and fiber drawing, exhibited significantly higher mechanical properties [26]. The improved mechanical properties of the nanocomposite fibers can be attributed to the effective matrix-filler interaction enabling load transfer from the polymer matrix to the SWNTs. Table 2 also shows the effect of increasing draw ratio on the mechanical properties of the filaments. As the draw ratio increases, so do the tenacity and modulus. This is mainly due to the increasing macromolecular alignment at higher draw ratios [27]. Elongation at break, however, is reduced at higher draw ratios. Typical force-elongation diagrams of PET-SWNT nanocomposite fibers are compared with that of the pristine PET fiber in Figure 3.

However, a comparison of the theoretically predicted values of the fiber modulus with those of the experimental data shows that the method adopted for dispersing nanotubes in the polymer matrix is not really efficient to render

Table 2: Mechanical properties of PET-SWNT nanocomposite fibers.

SWNT content (wt%)	Tenacity (GPa)			Modulus (GPa)			Elongation (%)		
	DR-4	DR-5	DR-6	DR-4	DR-5	DR-6	DR-4	DR-5	DR-6
0	0.195	0.426	0.563	2.21	8.70	11.70	208.2	44.2	31.1
0.5	0.201	0.429	0.577	2.72	8.83	11.68	170.7	57.9	44.5
1.0	0.345	0.433	0.719	7.18	13.25	15.92	82.0	63.0	19.0
2.0	0.509	–	–	11.69	–	–	48.4	–	–

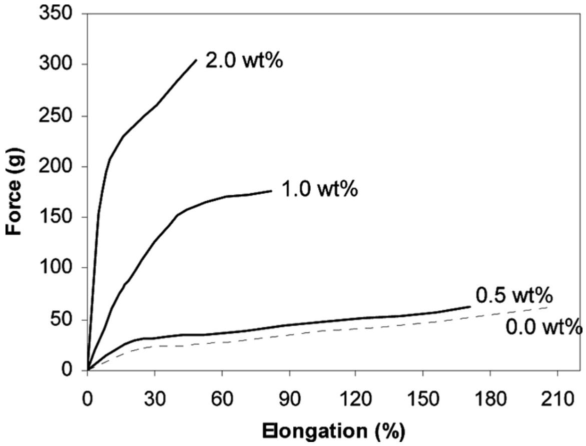

Figure 3: Representative force-elongation plots of pristine PET and PET-SWNT nanocomposite fibers (draw ratio = 4).

the maximum extent of reinforcement that are expected to be offered by SWNTs. Theoretical data of the fiber modulus as per Eq. (1) are compared with the experimental results in Table 3 [28].

$$E_{composite} = E_{PET} \times V_{PET} + E_{SWNT} \times V_{SWNT} \qquad (1)$$

where $E_{composite}$ is the modulus of the nanocomposite, and E_{PET} and E_{SWNT} are the modulii of the neat PET fiber (2.2 GPa) and SWNTs (640 GPa), respectively [29], and V_{PET} and V_{SWNT} are the respective volume fractions.

Effect of SWNTs on the Thermal Stability of Nanocomposite Fibers

There are several literature reports that have presented the effect of carbon nanotubes on the thermal stability of polymers [30–32]. Temperature dependence of weight loss characteristics of our PET-SWNT nanocomposite fiber samples has been studied using thermogravimetric analysis. TGA plots

Table 3: Comparison of theoretical and experimental data of the modulus of nanocomposite fibers.

Concn. of SWNTs (wt%)	Theoretical modulus (GPa)	Experimental data (GPa)
0.5	5.63	2.76
1	9.01	7.29
2	15.77	11.86

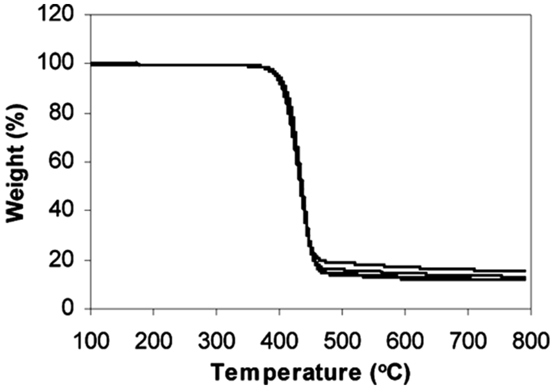

Figure 4: Typical TGA traces of neat PET (lowest curve) and PET-SWNT nanocomposite fibers.

of the fiber samples in Figure 4 indicate that decomposition of all samples starts at around 420°C irrespective of the SWNT content and thus the thermal stability of PET fibers is inferred to be unaffected by the presence of SWNTs up to a concentration of 2 wt%.

CONCLUSIONS

PET-SWNT nanocomposite fibers have been prepared through melt spinning followed by subsequent drawing. DSC studies of the nanocomposites reveal that SWNTs are acting as effective nucleating agents for the melt crystallization of PET. The mechanical properties indicated that SWNTs provide significant reinforcement to PET fibers. The tenacity and modulus values of the fibers increased with draw ratio, the reason being the increased molecular orientation and crystallization induced by drawing. Thermogravimetric analysis pointed out that thermal stability of the fibers is not significantly affected with SWNTs at low concentrations.

REFERENCES

[1] Gupta, V. B., and Kothari, V. K. (1997). *Manufactured Fibre Technology*, Chapman and Hall.

[2] Zeng, J., Kumar, S., Iyer, S., Schiraldi, D. A., and Gonzalez, R. I. *High Performance Polymers* **17**, 403 (2005).

[3] Jin, X., Xiao, C., An, S., and Jia, G. *J. Appl. Polym. Sci.* **102**, 4144 (2006).

[4] Kim, M. S., Kim, H. K., Byun, S. W., Jeong, S. H., Hong, Y. K., Joo, J. S., Song, K. T., Kim, J. K., Lee, C. J., and Lee, J. Y. *Synth. Met.* **126**, 233 (2002).

[5] Iijima, S. *Nature* **56**, 354 (1991).

[6] Ajayan, P. M. *Chem. Rev.* **99**, 1787 (1999).

[7] Xushan, G., Yan, T., Shuangyan, H., and Zhenfu, G. *Chemical Fibers International* **55**, 170 (2005).

[8] Kumar, S., Dang, T. D., Arnold, F. E., Bhattacharyya, A. R., Min, B. G., Zhang, X. F., Vaia, R. A., Park, C., Adams, W. W., Hauge, R. H., Smalley, R. E., Ramesh, S., and Willis, P. A. *Macromolecules* **35**, 9039 (2002).

[9] Sandler, J. K. W., Pegel, S., Cadek, M., Gojny, F., van Es, M., Lohmar, J., Blau, W. J., Schulte, K., Windle, A. H., and Shaffer, M. S. P. *Polymer* **45**, 2001 (2004).

[10] Sreekumar, T. V., Liu, T., Min, B. G., Guo, H., Kumar, S., Hauge, R. H., and Smalley, R. E. *Adv. Mater.* **16**, 58 (2004).

[11] Bhattacharyya, A. R., Sreekumar, T. V., Liu, T., Kumar, S., Ericson, L. M., Hauge, R. H., and Smalley, R. E. *Polymer* **44**, 2373 (2003).

[12] Kumar, S., Doshi, H., Srinivasrao, M., Park, J. O., and Schiraldi, D. A. *Polymer* **43**, 1701 (2002).

[13] Andrews, R., Jacques, D., Rao, A. M., Rantell, T., Derbyshire, F., Chen, Y., Chen, J., and Haddon, R. C. *Appl. Phys. Lett.* **75**, 1329 (1999).

[14] Qian, D., Dickey, E. C., Andrews, R., and Rantell, T. *Appl. Phys. Lett.* **76**, 20 (2000).

[15] Haggenmueller, R., Gommans, H. H., Rinzler, A. G., Fischer, J. E., and Winey, K. I. *Chem. Phys. Lett.* **330**, 219 (2000).

[16] Ma, H., Zeng, J., Realff, M. L., Kumar, S., and Schiraldi, D. A. *Compos. Sci. Technol.* **63**, 1617 (2003).

[17] Gurudatt, K., De, P., Rakshit, A. K., and Bardhan, M. K. *J. Appl. Polym. Sci.* **90**, 3536 (2003).

[18] Anand, K. A., Agarwal, U. S., and Joseph, R. *J. Appl. Polym. Sci.* **104**, 3090 (2007).

[19] Grady, B. P., Pompeo, F., Shambaugh, R. L., and Resasco, D. E. *J. Phys. Chem. B* **106**, 5852 (2002).

[20] Valentini, L., Biagiotti, J., Kenny, J. M., and Santucci, S. *J. Appl. Polym. Sci.* **87**, 708 (2003).

[21] Nogales, A., Broza, G., Roslaniec, Z., Schulte, K., Sics, I., and Hsiao, B. S. *Macromolecules* **37**, 7669 (2004).

[22] Probst, O., Moore, E. M., Resasco, D. E., and Grady, B. P. *Polymer* **45**, 4437 (2004).

[23] Anand, K. A., Agarwal, U. S., and Joseph, R. *Polymer* **47**, 3976 (2006).

[24] Anand, K. A., Agarwal, U. S., Nisal, A., and Joseph, R. *Euro. Polym. J.* **43**, 2279 (2007).

[25] Qu, M. H., Wang, Y. Z., Wang, C., Ge, X. G., Wang, D. Y., and Zhou, Q. *Euro. Polym. J.* **41**, 2569 (2005).

[26] Siochi, E. J., Working, D. C., Park, C., Lillehei, P. T., Rouse, J. H., Topping, C. C., Bhattacharyya, A. R., and Kumar, S. *Composites: Part B* **35**, 439 (2004).

[27] Doi, M., and Edwards, S. F. (1986). *The Theory of Polymer Dynamics*, Oxford University Press.

[28] Liu, T., and Kumar, S. *Nano Lett.* **3**, 647 (2003).

[29] Chae, H. G., Sreekumar, T. V., Uchida, T., and Kumar, S. *Polymer* **46**, 10925 (2005).

[30] Ou, C. F. *J. Appl. Polym. Sci.* **89**, 3315 (2003).

[31] Park, C., Ounaies, Z., Watson, K. A., Crooks, R. E., Smith, J., Park, C., Ounaies, Z., Watson, K. A., Crooks, R. E., Smith, J., and Clair, T. L. *Chem. Phys. Lett.* **364**, 303 (2002).

[32] Kashiwagi, T., Grulke, E., Hilding, J., Groth, K., Harris, R., Butler, K., Shields, J., Kharchenko, S., and Douglas, J. *Polymer* **45**, 4227 (2004).