

다중벽 탄소나노튜브/리오셀 복합섬유의 제조 및 특성조사

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(2007년 5월 23일 접수, 2007년 7월 25일 채택)

Preparation and Characterization of Multiwalled Carbon Nanotubes/Lyocell Composite Fibers

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(Received May 23, 2007; Accepted July 25, 2007)

Abstract : In this work, the multiwalled carbon nanotubes(MWNTs) were functionalized with sodium dodecylbenzene sulfonate(SDBS) and then MWNTs/Lyocell composite fibers were prepared. The properties of MWNTs, the functionlization on the surface of MWNTs and their dispersion in the cellulose matrix were characterized by TEM, SEM, WAXD and FT-IR. The results showed that SDBS has been coated successfully onto the surface of the MWNTs by functionlization. This can improve effectively the dispersion uniformity of MWNTs in NMMO aqueous solution and is helpful to prepare a spinnable spinning dope. Moreover, the resultant MWNTs/Lyocell composite fibers still have cellulose II crystal structure, and their tensile strength and initial modulus increased with the increasing draw ratio and reached the optimal value with adding 1 wt% MWNTs. The thermal stability of the composite fiber was also improved by the addition of the MWNTs.

Keywords : multiwalled carbon nanotubes, lyocell, composite fibers.

Introduction

Since carbon nanotubes (CNTs) were discovered by Iijima in 1991,¹ they have received much attention due to their remarkable properties such as high tensile strength, superior modulus and exceptional electrical conductivity.² Recently it has been reported that incorporation of CNTs in polymer matrix may increase modulus and hardness of the composite material by stress transfer between the CNTs and the polymer matrix. Zhang *et al.* reported that the tensile modulus, tensile strength and hardness of the CNTs/PA6 composites with the addition of 1 wt% CNTs were increased about 115, 120 and 67%, respectively.³ Wang and his colleagues also found that comparing with the UHMWPE fiber, the mechanical and thermal properties of CNTs/UHMWPE composite fibers were improved significantly since the functionalized CNTs can be dispersed homogeneously in the UHMWPE matrix and become effective in the reinforcement.⁴

However, the research about CNTs/cellulose composite fiber has not been reported. On the other hand, Lyocell fiber is a new kind of cellulose fiber developed in the 1990s.⁵ It is expected to replace the rayon fiber in the future due to its simple, advanced and environmentally friendly process. Lyocell fiber has lots of excellent properties such as high strength, good hand-feeling and water-absorbing properties, and so on. Therefore, it is not only used in the textile field, but also expectantly used as tire cord, precursor of carbon fiber and conducting fiber etc. after being modified and will have wide potential applications in some fields such as industry and aerospace. At present, there are a few reports on modified Lyocell fiber and no work has been done on Lyocell fiber modified with CNTs.^{6,7}

In this paper, the multiwalled carbon nanotubes(MWNTs) were used as an additive of Lyocell process. The functionalization of MWNTs with sodium dodecylbenzene sulfonate (SDBS) and its dispersion in the solvent system (i.e. *N*-methylmorpholine-*N*-oxide aqueous solution) of Lyocell process were studied. The structure and properties of

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MWNTs/Lyocell composite fibers were also investigated.

Experimental

Materials. Cellulose pulp (DP=488, α -cellulose content 98%) used in this work was obtained from Baoding Chemical Fiber Co., China. *N*-Methylmorpholine-*N*-oxide (NMMO) aqueous solution (50 wt%) was purchased from BASF AG, Germany. *n*-Propyl gallate and SDBS were reagent grade. They were purchased from Shanghai Chemical Co. and Farco chemical supplies, respectively. MWNTs having purity greater than 95% were prepared by chemical vapor deposition process and provided by Shanghai Applied Nanotechnologies Co., Ltd..

Purification and Functionalization of MWNTs. In this work, the as-received MWNTs were purified by being refluxed in 2.6 M HNO₃ for 36 h. On cooling, the refluxing mixture was washed with deionized water on a sintered glass filter until the washing showed no acidity. To modify the surface of MWNTs, the purified MWNTs were homogeneously dispersed in 1 wt% SDBS aqueous solution by ultrasonication for 30 min and the obtained suspension was filtered with membrane with a large pore size of 5 μ m. The functionalized MWNTs treated with SDBS were obtained by further rinsing and drying.

Preparation of MWNTs/Lyocell Composite Fibers. NMMO aqueous solution distilled to 74 wt% and a certain amount of functionalized MWNTs were mixed and ultrasonicated for about 2 h. Then the MWNTs/NMMO aqueous solution, cellulose pulp and *n*-propyl gallate (antioxidant) were mixed and transferred to a spinning tank, for which the temperature was set at 90 ~95 °C. The extra water in the mixture was distilled under vacuum to obtain a homogeneous cellulose/NMMO · H₂O/MWNTs spinning dope in which cellulose content was 10 wt%.

Figure 1 was the schematic drawing of the spinning equipment. The spinning dope with the temperature of 90 ~93 °C was extruded from a spinneret with 100 orifices (0.08 mm in diameter). After being passed through an air gap of 50 mm in length it was immersed into a coagulation bath and a washing bath successively, and then taken-up

at a certain spinning speed to obtain the MWNTs/Lyocell composite fibers. Because no MWNTs was found in the coagulation bath and the washing bath, which indicated that MWNTs were retained in the Lyocell fiber completely, the MWNTs content in the Lyocell fiber could be determined according to the initial addition amount of MWNTs.

Transmission Electron Microscopy (TEM). The morphologies of the MWNTs were observed by a Hitachi H800 transmission electron microscope with an accelerating voltage of 200 kV.

FT-IR Spectroscopy. FT-IR spectrophotometer model NEXUS-670 (Nicolet, USA) was used for FT-IR measurements of MWNTs and SDBS in the range from 500 to 4000 cm⁻¹.

Optical Microscopy Measurements. The morphology of the spinning dope containing a certain amount of MWNTs was observed with a Olympus XP51 optical microscope (Olympus, Japan).

Wide Angle X-ray Diffraction (WAXD) Measurements. Wide angle X-ray diffraction patterns for Lyocell fiber and MWNTs/Lyocell composite fibers were obtained by a D/MAX-2500PC diffractometer (Rigaku, Japan) using a X-ray beam wavelength of 0.154 nm (Cu K α).

Thermal Gravimetric Analysis (TGA). TGA of Lyocell fiber and MWNTs/Lyocell composite fibers were performed on a STA 449 C TGA balance (Netzsch, Germany) in the range of temperature from 50 to 800 °C under a nitrogen atmosphere. The scan rate was maintained at 10 °C/min.

Scanning Electron Microscopy (SEM). The cross-sections morphology of MWNTs/Lyocell composite fibers were investigated using JSM-5600LV SEM (JEOL Co., Japan). The MWNTs/Lyocell composite fibers were fractured in liquid nitrogen and coated with a thin gold by using a sputter coater prior to microscopy to avoid charge buildup.

Mechanical Test for Lyocell Fibers. The mechanical properties of Lyocell fiber and MWNTs/Lyocell composite fibers were measured with an XQ-1 Tensile Tester (Donghua University, China). The sample length was 20 mm and the extension rate was set at 5 mm/min. All measurements were performed at 20 °C and 65% relative humidity.

Results and Discussion

Morphology of MWNTs. As-produced CNTs were usually contaminated with residual metal catalyst and some carbon species such as carbon nanoparticles, graphitic and amorphous carbons. Because the presence of these impurities may significantly affect the properties of CNTs and CNTs/polymeric matrix composite materials, it was necessary to remove the impurities from CNTs. It had been reported that some chemical purification methods such as acid treat-

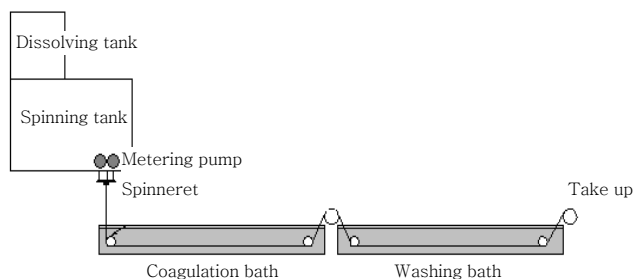


Figure 1. Schematic drawing of the spinning equipment.

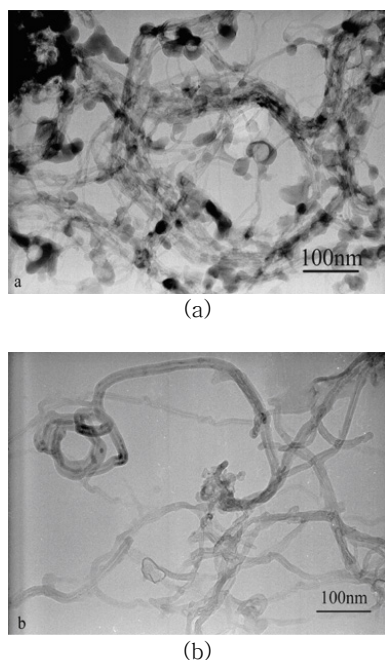


Figure 2. TEM images of the as-received and purified MWNTs. (a) as-received MWNTs and (b) purified MWNTs.

ment can effectively eliminate metallic species as well as any other carbonaceous materials than CNTs.⁸ They are also effective in breaking the tube caps and introducing oxygen-containing functional groups onto the surface of CNTs, which are helpful for the materials with good properties.^{9,10} In this paper, the acid treatment was used to purify the MWNTs.

Figure 2 shows the TEM images of the as-received and purified MWNTs. It indicates that after purification, the surface of the MWNTs becomes glabrous and no particle-like impurities are found. The diameters of MWNTs are between 20 and 40 nm and the length of MWNTs is about several microns.

The FT-IR spectra for as-received, purified, functionalized MWNTs (treated with SDBS) and SDBS are shown in Figure 3. It can be seen that compared with the curve (a), the FT-IR spectrum of the purified MWNTs (curve (b)) exhibits an expected C=O stretching band near 1700 cm^{-1} and an obvious hydroxyl stretching band at about 3400 cm^{-1} arising from the carboxylic acid groups introduced by purification. From curve (d) it can be found SDBS exhibits two C=C stretching vibration bands for benzene ring at 1602 and 1497 cm^{-1} , respectively, and the characteristic band associated with SO_4^{2-} group at 1220 cm^{-1} .¹¹ From curve (c) it is further found the functionalized MWNTs (treated with SDBS) exhibit some characteristic bands which are similar to those of SDBS and two C=C stretching

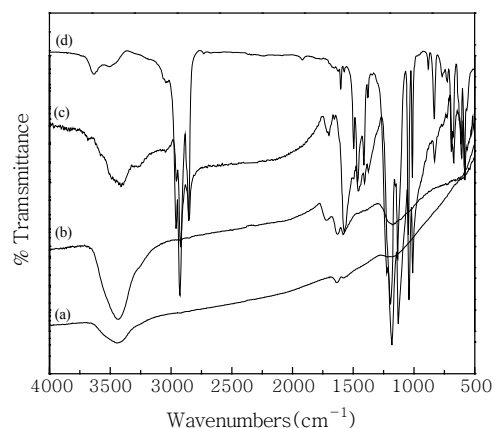


Figure 3. FT-IR spectra of (a) as-received MWNTs, (b) purified MWNTs, (c) functionalized MWNTs, and (d) SDBS.

vibration bands of benzene ring shifted from 1602 cm^{-1} to 1565 cm^{-1} and 1497 cm^{-1} to 1458 cm^{-1} , respectively. Moreover, compared with the curve (b), it is also found the band at 3400 cm^{-1} for functionalized MWNTs become weaker and less sharp than that of the purified sample. These results imply that SDBS has been coated successfully onto the surface of the MWNTs by functionalization. SDBS is an anionic surfactant containing a sulfonate hydrophilic segment, a hydrocarbon hydrophobic segment and a benzene ring moiety. It is a good dispersant for carbon nanotubes.¹² Naturally the adsorption of the surfactant has an effect on the wetting behavior and the interfacial adhesion, which in turn has an impact on the surfactant's ability to disperse the carbon nanotubes.¹³

The Dispersion of MWNTs in NMMO Aqueous Solution and Lyocell Composite Fibers. It is well known that the dispersion uniformity of the CNTs in the polymeric matrix can influence the spinnability and the properties of the composite fibers. Therefore, in this work, the dispersion of the functionalized MWNTs in NMMO aqueous solution and Lyocell composite fibers were further investigated. Figure 4 shows the optical microscope photographs of the NMMO aqueous solutions containing 0.5 wt% purified MWNTs and containing the functionalized MWNTs with the content of 0.5, 1, 3 and 5 wt%, respectively. It can be found that when the purified MWNTs without functionalization were mixed in NMMO aqueous solution, the aggregation of the MWNTs were observed obviously (see Figure 4(a)), even though the content of the MWNTs was very low (e.g. 0.5 wt%). On the other hand, the functionalized MWNTs treated by SDBS could be dispersed homogeneously with a higher content (e.g. 5 wt%, see Figure 4(e)) in NMMO aqueous solution and no obvious aggregation of MWNTs occurs. This means the treatment of MWNTs with SDBS can improve effectively

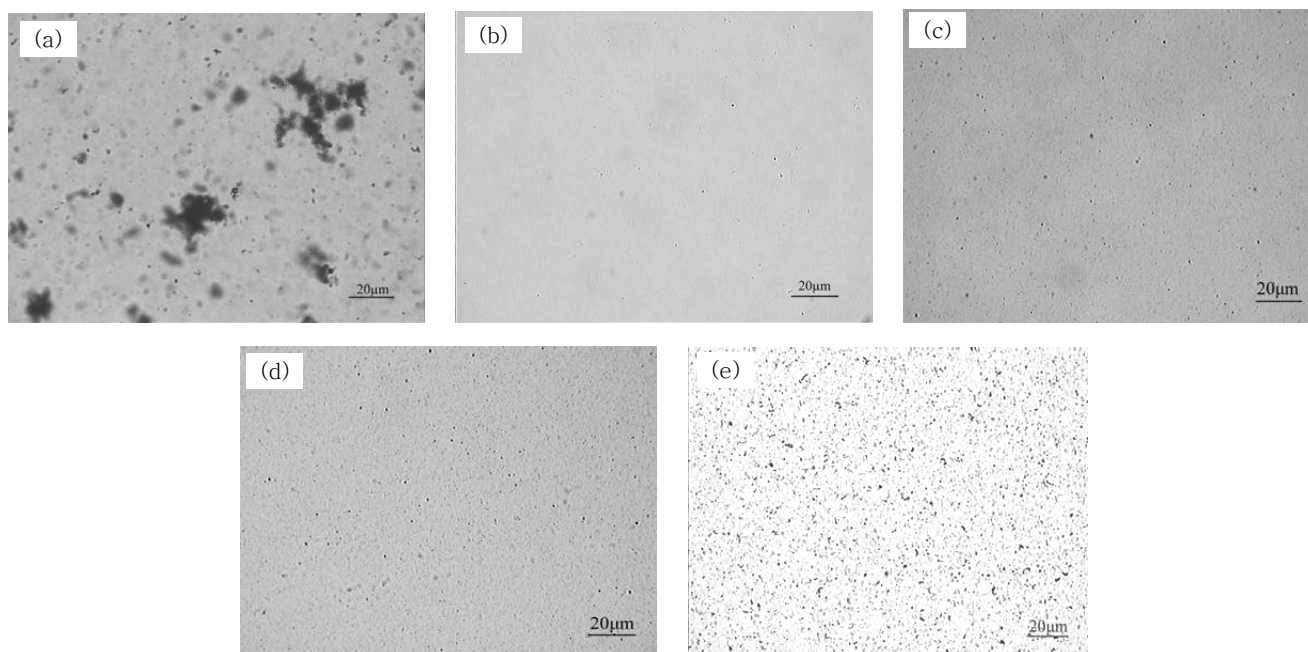


Figure 4. Optical microscope photographs of NMMO aqueous solutions containing 0.5 wt% purified MWNTs (a) and containing the functionalized MWNTs with the content of 0.5 (b), 1 (c), 3 (d), and 5 wt% (e), respectively.

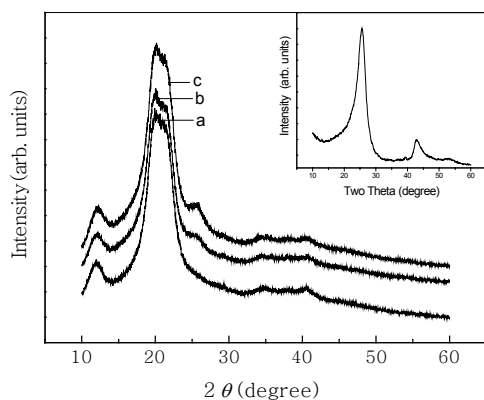


Figure 5. WAXD patterns of Lyocell (a) and MWNTs / Lyocell composite fibers with different MWNTs contents (b) 3 wt%, and (c) 5 wt%. Inset: WAXD pattern of MWNTs.

the dispersion uniformity of MWNTs in NMMO aqueous solution and is helpful to prepare a spinnable spinning dope of good quality.

The WAXD patterns of Lyocell fibers containing various amounts of functionalized MWNTs are illustrated in Figure 5. They show obvious diffraction peaks at $2\theta = 12.1^\circ$, 20.1° and 21.1° , corresponding to the characteristic reflections of (101), $(10\bar{1})$ and (002) planes of the monoclinic cell of cellulose II, respectively. The WAXD pattern of MWNTs exhibits two characteristic diffraction peaks (see the inset in Figure 5). The stronger one is at $2\theta = 25.6^\circ$, corresponding

to (002) plane reflection of graphite. It can be found from Figure 5 the MWNTs/Lyocell composite fibers also have a diffraction peak at $2\theta = 25.6^\circ$ and the intensity of this peak increased with the addition amount of MWNTs. These results indicate that the MWNTs have been added into the cellulose fiber and MWNTs filled Lyocell fibers still have cellulose II crystal structure.

Structure and Properties of MWNTs/Lyocell Composite Fibers.

Figure 6 shows SEM images of cross-sections for MWNTs/Lyocell composite fibers containing 0.5(a), 1(b), 3(c) and 5 wt% (d) MWNTs, respectively. The bright dots and lines, which are the embedded MWNTs, are observed to disperse homogeneously in Lyocell matrix in the case of lower MWNTs content (see Figures 6(a)–(c)). However, when the amount of MWNTs filled in the fiber is higher the aggregation of MWNTs can be obviously observed (see Figure 6(d)).

Figure 7 shows the TGA results for Lyocell fiber and MWNTs/Lyocell composite fibers. It is found that both Lyocell fiber and MWNTs/Lyocell composite fiber exhibit an onset degradation temperature near 300°C . And the degradation temperature for the latter is a little higher than that of the former, indicating that the thermal stability of the composite fiber was improved by the addition of the MWNTs. It may be attributed to both the excellent stability of carbon nanotubes and their interactions with the cellulose matrix.¹⁴

The tensile strength and initial modulus of Lyocell fiber

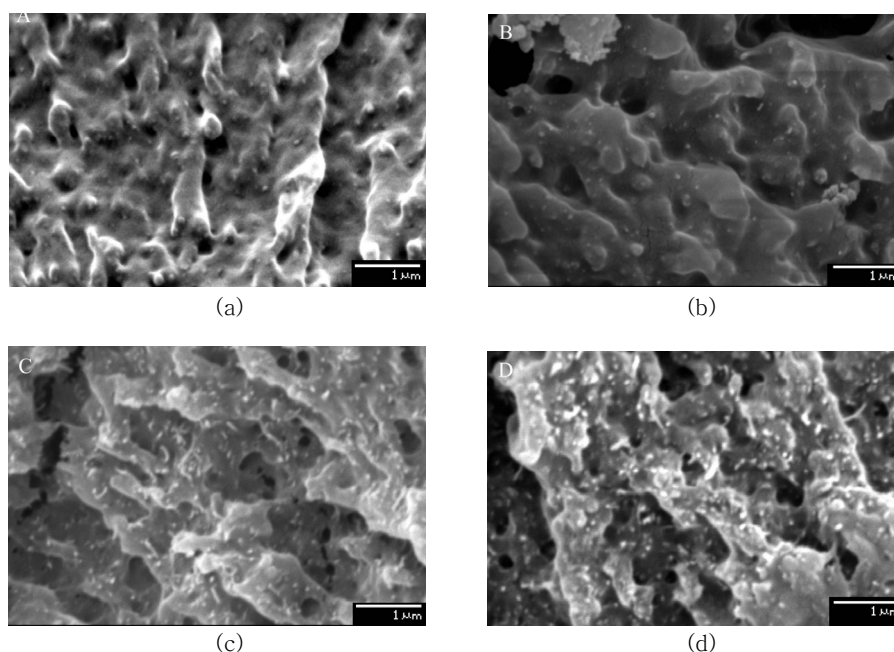


Figure 6. SEM images of cross-sections for MWNTs/Lyocell composite fibers containing 0.5 (a) , 1 (b) , 3 (c), and 5 wt% (d) MWNTs , respectively.

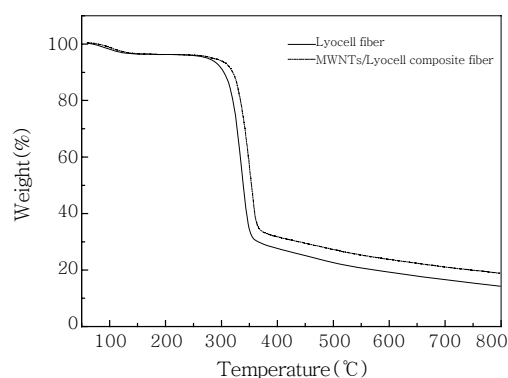


Figure 7. TGA curves of Lyocell fiber and MWNTs /Lyocell composite fiber containing 5 wt% MWNTs.

and MWNTs/Lyocell composite fibers are listed in Table 1 and Table 2, respectively. It is found that the mechanical properties of Lyocell fiber were improved with the increase of the draw ratio, which resulted mainly from the orientation of the polymer chains. Moreover, compared with the pure Lyocell fiber, the mechanical properties of MWNTs/Lyocell composite fibers were increased significantly, which means the carbon nanotubes in cellulose matrix play a vital role in load transfer.¹⁵

Furthermore, it is also found that the tensile strength and initial modulus of MWNTs/Lyocell fibers were increased firstly with the addition of MWNTs and reached the highest value with adding 1 wt% MWNTs, then decreased with the

Table 1. Tensile Strengths of Lyocell Fiber and MWNTs/ Lyocell Composite Fibers

Draw ratio	Tensile strength (cN/dtex)					
	0%	0.2%	0.5%	1%	3%	5%
	MWNTs	MWNTs	MWNTs	MWNTs	MWNTs	MWNTs
2.82	3.76	4.24	4.35	4.43	4.30	4.12
3.17	3.85	4.38	4.47	4.52	4.41	4.32
3.48	3.92	4.50	4.58	4.79	4.53	4.50

Table 2. Initial Modulus of Lyocell Fiber and MWNTs/Lyocell Composite Fibers

Draw ratio	Initial modulus (cN/dtex)					
	0%	0.2%	0.5%	1%	3%	5%
	MWNTs	MWNTs	MWNTs	MWNTs	MWNTs	MWNTs
2.82	31.0	42.3	45.7	46.9	45.6	42.5
3.17	33.3	44.4	47.1	48.2	46.9	43.9
3.48	36.5	46.1	48.9	51.8	48.8	46.4

further addition of MWNTs. The better mechanical properties of the composite fibers with 1 wt% MWNTs is attributed to the homogeneous dispersion of MWNTs in the cellulose matrix. The decrease in mechanical properties for the composite fiber with a high addition amount of MWNTs such as 5 wt% could be ascribed to the increase of localized clusters or aggregations of MWNTs.¹⁶⁻¹⁸

Conclusions

MWNTs functionalized with SDBS can be used as an

additive of Lyocell process to prepare MWNTs/Lyocell composite fibers. It was found that SDBS has been coated successfully onto the surface of the MWNTs by functionalization. This can improve effectively the dispersion uniformity of MWNTs in NMMO aqueous solution and is helpful to prepare a spinnable spinning dope. Moreover, the resultant MWNTs/Lyocell composite fibers still have cellulose II crystal structure, and their tensile strength and initial modulus increased with the increasing draw ratio and reached the optimal value with adding 1 wt% MWNTs. The thermal stability of the composite fiber was also improved by the addition of the MWNTs.

Acknowledgements. We acknowledge the financial support of the National Natural Science Foundation of China (Grant No. 50673016) and Program of Shanghai Subject Chief Scientist (05XD14025).

References

1. S. Iijima, *Nature*, **354**, 56 (1999).
2. H. Dai, E. Wong, and C. Lieber, *Science*, **272**, 523 (1996).
3. W. Zhang, L. Shen, I. Phang, and T. Liu, *Macromolecules*, **37**, 256 (2004).
4. Y. P. Wang, R. L. Cheng, L. L. Liang, and Y. M. Wang, *Compos. Sci. Technol.*, **65**, 793 (2005).
5. H. P. Fink, P. Weigel, H. J. Purz, and J. Ganster, *Progress in Polymer Science*, **26**, 1473 (2001).
6. F. Meister, D. Vorbach, Ch. Michels, R. Maron, K. Berghof, and E. Taeger, *Chemical Fibers Intern.*, **48**, 32 (1998).
7. H. H. Zhang, L. W. Guo, H. L. Shao, and X. C. Hu, *J. Appl. Polym. Sci.*, **99**, 65 (2006).
8. S. Porroa, S. Mussoa, M. Vinante, L. Vanzetti, M. Anderle, F. Trotta, and A. Tagliaferro, *Physica E*, **37**, 58 (2007).
9. Y. Lin, B. Zhou, and K. Fernando, *Macromolecules*, **36**, 7199 (2003).
10. I. Chiang, B. Brinson, R. Smalley, J. Margrave, and R. Hauge, *J. Phys. Chem. B*, **6**, 1157 (2001).
11. K. Nakashiki and P. Solomon, *Infrared Absorption Spectroscopy*, Holden-Day, Oakland, CA, 1977.
12. V. C. Moore, M. S. Strano, E. H. Haroz, R. H. Hauge, and R. E. Smalley, *Nano. Lett.*, **10**, 269 (2003).
13. X. Gong, J. Liu, S. Baskaren, R. Voise, and J. Young, *Chem. Mater.*, **12**, 1049 (2000).
14. M. Shaffer and A. Windle, *Adv. Mater.*, **1**, 937 (1999).
15. G. Hwang, Y. Shieh, and K. Hwang, *Adv. Funct. Mater.*, **14**, 487 (2004).
16. P. Potschke, T. Fornes, and D. Paul, *Polymer*, **43**, 3247 (2002).
17. M. D. Frogley, D. Ravich, and H. D. Wagner, *Comp. Sci. Technol.*, **63**, 1647 (2003).
18. J. W. Ning, J. J. Zhang, Y. B. Pan, and J. K. Guo, *Mater. Sci. Eng. A*, **357**, 392 (2003).