Properties and Structure of MWNTs/Cellulose Composite Fibers Prepared by Lyocell Process

Jiang Lu,[1,2] Huihui Zhang,[1] Yihui Jian,[1] Huili Shao,[1] Xuechao Hu[1]

[1]*State Key Laboratory for Modification of Chemical Fiber and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai 201620, People's Republic of China*
[2]*College of Chemical and Environmental Engineering, Hubei University of Technology, Wuhan 430064, People's Republic of China*

Received 4 January 2010; accepted 20 March 2011
DOI 10.1002/app.34543
Published online 9 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Lyocell fiber is a new kind of regenerated cellulose fiber and expected to replace the Rayon fiber to be not only used in the textile field but also used in the fields of industry and aerospace after being modified. In this work, the multi-walled carbon nanotubes (MWNTs)/Lyocell composite fibers were prepared under different draw ratios by dry-wet spinning and their electrical properties, mechanical properties, and structure were investigated. It was found that an appropriate amount of MWNTs could be dispersed homogeneously in the Lyocell matrix and could improve the mechanical and thermal properties of composite fiber. The results of wide angle X-ray diffraction (WAXD) showed that the MWNTs in the composite fiber almost aligned along the axis of the fibers and the orientation of MWNTs increased with the increasing draw ratio. Furthermore, it was found that more MWNTs content and lower draw ratio could improve the electrical conductance of the composite fiber. The composite fiber containing 5 wt % MWNTs has a volume conductivity of 8.8×10^{-4} S/cm, which is five orders higher than that of pure Lyocell fiber. These results indicate that the MWNTs/Lyocell composite fiber has potential applications in the areas of precursor of carbon fiber and conductive fiber. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 956–961, 2012

Key words: carbon nanotubes; Lyocell; composite fiber; electrical properties

INTRODUCTION

Lyocell process is a new technique developed in the end of last century for the production of regenerated cellulose fiber. In this process, cellulose pulp is dissolved in *N*-methylmorpholine-*N*-oxide (NMMO) directly to form Lyocell fiber by a dry-wet spinning method. Lyocell fiber has attracted much more attention in the field of textiles than the conventional Rayon fiber due to its simple and environmentally friendly process. Moreover, it has lots of outstanding characteristics such as high strength, round cross-section and compact structure.[1] Therefore, it is expected to replace the Rayon fiber to be not only used in the textile field, but also used as tire cord, precursor of carbon fiber etc. after being modified and will have wide potential applications in the fields of industry and aerospace.[2,3]

On the other hand, carbon nanotubes (CNTs) are a new kind of lightweight materials which exhibit excellent mechanical and electrical properties.[4] One of the most intriguing applications of CNTs is CNTs/polymer composite in which the nanotube architecture is established with a host polymer matrix. The mechanical and novel electrical characteristics of CNTs make them an ideal candidate as fillers in lightweight polymer composites designed for structural or functional applications. Some researches on fabrication of various CNTs/polymer composite films and fibers have been reported. Polymers such as polyacrylonitrile,[5] polycarbonate,[6] poly (vinyl alcohol)[7] and polystyrene[8] as well as nylon-6,[9] have been used as matrices. However, only few studies on Lyocell fiber modified with CNTs has been reported till now.[10] In this work, the multi-walled carbon nanotubes (MWNTs) were used to modify the Lyocell fiber using a dry-wet spinning process. And the structure, mechanical property, and volume conductivity of the resultant composite fibers were investigated.

EXPERIMENTAL

Materials

Cellulose pulp used in this work has an average degree of polymerization (DP) of 488 and an

Correspondence to: H. Shao (HLShao@dhu.edu.cn).
Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 50873024, 50673016.
Contract grant sponsor: Hi-Tech Research and Development Program of China (863 Project); contract grant number: No. 2009AA03Z425.

α-cellulose content of 98%. *n*-propyl gallate with reagent grade was provided by Shanghai Chemical Co., China. NMMO aqueous solution (50 wt %) and sodium dodecylbenzene sulfonate (SDBS, reagent grade) were purchased from BASF AG, Germany and Farco Chemical Supplies, Hongkong, respectively. MWNTs having a purity higher than 95% were obtained from Shanghai Applied Nanotechnologies Co., China.

Methods

The MWNTs were purified by refluxing in HNO_3 to remove impurities such as carbon black and graphite nanoparticles. The purified MWNTs were further functionalized with SDBS. The detail of this method has been reported previously.[10]

The above functionalized MWNTs were mixed homogeneously with the concentrated NMMO aqueous solution by ultrasonication. Then the cellulose pulp and *n*-propyl gallate(stabilizer) were blended into MWNTs/NMMO aqueous solution and the extra water in the mixture was removed under vacuum to obtain a homogeneous cellulose/NMMO H_2O/MWNTs spinning dope with a cellulose content of 10 wt %. The spinning dope was extruded from a spinneret with 100 orifices (0.08 mm in diameter). After being passed through a 50-mm long air gap, the dope was immersed into water and then taken-up under different draw ratios to obtain various MWNTs/Lyocell composite fibers.

Characterization

The volume resistivity or conductivity of MWNTs/Lyocell composite fibers was measured by a Keithley 236 electrometer (Keithley Source). The measured segment of each specimen consisted of 1000 composite fibers and had a length of 5 cm. Each sample was tested five times. The diameters of the fibers were measured by an Olympus XP51 optical microscope (Olympus, Japan). The morphologies of the fibers were observed with a SIRION 200 field emission scanning electron microscope (FESEM) (FEI). Wide angle X-ray diffractions (WAXD) for the fibers were performed with a D/MAX-2500PC diffractometer (Rigaku, Japan) (CuKα, λ = 0.154 nm). The two-dimensional x-ray diffraction at a fixed azimuthal angle of 25.6° was used to determine the orientation angle of MWNTs in the composite fibers. The tensile tests for the fibers were carried out using an XQ-1 Tensile Tester (Donghua University, China) at 20°C and 65% relative humidity with the sample length of 20 mm and an extension rate of 5 mm/min. The 30 specimens were tested for each sample and the average value was calculated.

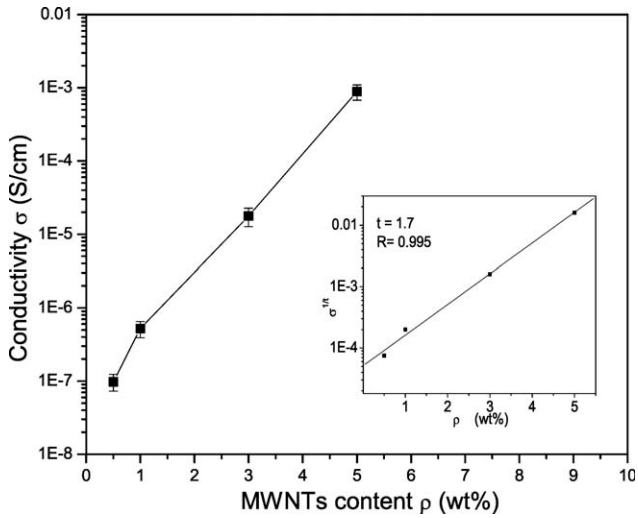

Figure 1 The volume conductivity of MWNTs/Lyocell composite fibers as a function of MWNTs content (draw ratio = 3.48). The insert shows the relationship between $\sigma^{1/t}$ and MWNTs content ρ in composite fibers.

RESULTS AND DISCUSSION

The electrical property of MWNTs/Lyocell composite fibers

The volume conductivity σ for MWNTs/Lyocell composite fiber can be calculated by

$$\sigma = 4L/R\pi d^2 n \quad (1)$$

wherein L is the length of measured segment of MWNTs/Lyocell composite fiber, d is its diameter, R is the measured electrical resistance, and n is the number of the composite fibers.

Figure 1 shows the volume conductivity σ of MWNTs/Lyocell composite fiber as a function of MWNTs weight fraction ρ. It was clear that the volume conductivity of the composite fiber increased with the increasing MWNTs content. The insert shown in Figure 1 represents the linear relationship between $\sigma^{1/t}$ with a scaling exponent t of 1.7 and MWNTs content ρ in composite fibers, which indicates that the volume electrical conductivities of MWNTs/Lyocell composite fibers with different MWNTs contents follow the percolation scaling law well, i.e., $\sigma = \sigma_f (\rho\text{-}\rho_c)^t$, wherein σ_f is the filler conductivity and ρ_c is the percolation threshold. The scaling exponent t of 1.7 for the MWNTs/Lyocell composite fiber is similar to those for some other CNTs/polymer composites reported in literatures.[11–13]

Figure 2 shows a relationship between the volume conductivity and the draw ratio for MWNTs/Lyocell composite fibers with different MWNTs contents. It indicated that the pure Lyocell fibers obtained under different draw ratios almost had constant volume conductivity. But with the addition of MWNTs, the

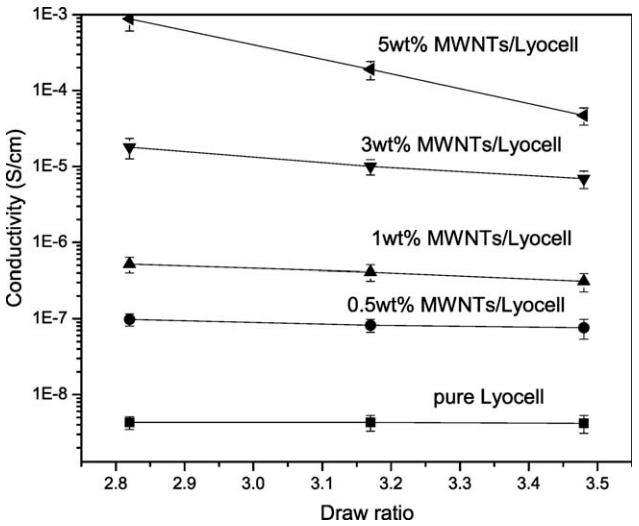

Figure 2 The relationship between the volume conductivity and the draw ratio for MWNTs/Lyocell composite fibers with different MWNTs contents.

volume conductivity of the composite fibers depended on the draw ratio gradually. Especially for the MWNTs/Lyocell composite fibers having a higher MWNTs content, its volume conductivity was obviously increased when the draw ratio was decreased, therein the 5 wt % MWNTs/Lyocell composite fiber prepared under a draw ratio of 2.82 had a volume conductivity of 8.8×10^{-4} S/cm, which was five orders higher than that of pure Lyocell fiber. This can attribute to the orientation characteristic of MWNTs in the fiber. The lower draw ratio results in lower orientation degree of MWNTs. When the draw ratio is increased, the orientation of MWNTs along the fiber is enhanced (see the discussion in the following related paragraph). Therefore, the probability for the MWNTs to touch each other and form a conducting pathway through the fiber is reduced with the increasing draw ratio, which leads to the decrease of volume conductivity of the composite fiber. This is in accordance with the result of CNTs/polymethyl methacrylate films reported by Haggenmueller et al.[14]

Mechanical property of MWNTs/Lyocell composite fibers

Figure 3 shows the mechanical properties of MWNTs/Lyocell composite fibers with different MWNTs contents. It was found both the tensile strength and initial modulus of the composite fibers were improved firstly with the addition of MWNTs and reached the maximum with a MWNTs content of 1 wt %, then decreased with the further addition of MWNTs. Compared with the pure Lyocell fiber, the tensile strength and modulus of the composite fiber containing 1 wt % MWNTs were increased by 22 and 42%, respectively. The decrease in mechanical property for MWNTs/Lyocell composite fibers with higher MWNTs content may be ascribed to the agglomeration of MWNTs.

Theoretical predictions on the mechanical properties of nanocomposites are still in their infancy. According to the rule of mixture for the strength of the CNTs/polymer composite material,[15,16] the strength of MWNTs/Lyocell composite fiber with lower volume fraction of MWNTs can be represented by the following formula,

$$\sigma^*_C = \eta\varphi_{CNT}\sigma_{CNT}' + \sigma^*_L(1-\varphi_{CNT}) \text{ for low } \varphi_{CNT} \text{ and } \varepsilon^*_L < \varepsilon_{CNT}^*. \quad (2)$$

where ε, σ, η, and φ are the strain at break, tensile strength, effectiveness parameter, and volume fraction, respectively. The subscripts L, CNT and C represent the properties of the pure Lyocell fiber, the MWNTs and MWNTs/Lyocell composite fiber, respectively. The superscripts * and $'$ refer to the ultimate and maximum property values, respectively. The effectiveness parameter η varies from 1 for the unidirectional reinforcement to 5/8 for reinforcement in two-dimensional random orientations. In our work, it was found the MWNTs in MWNTs/Lyocell composite fiber almost aligned along the axis of the fibers (see the following Table I) and therefore an estimated η of 0.96 is used in Eq. (2). The other experimentally measured properties are also used here, i.e., at draw ratio = 3.48, σ_L^* = 3.92cN/dtex = 0.59GPa, $\varepsilon_L^* \approx \varepsilon_C^* \approx 9\%$. The volume fraction ($\varphi_{CNT}$) of the MWNTs in 1 wt % MWNTs/Lyocell composite fiber is estimated to be 0.75%. And the theoretical maximum tensile strength and the ultimate strain at break (ε_{CNT}^*) for the MWNTs are reported to be 63 GPa and 12%, respectively.[17]

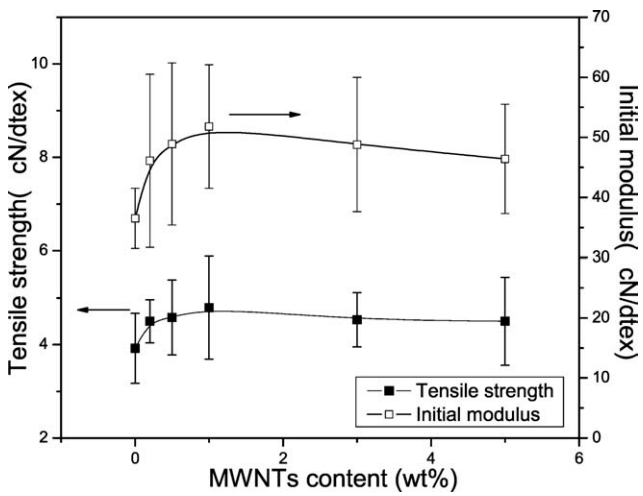

Figure 3 Tensile strength and initial modulus of MWNTs/Lyocell composite fibers with different MWNTs contents (draw ratio = 3.48).

TABLE I
The Relationship Between Draw Ratio and Orientation Angle of MWNTs in MWNTs/Lyocell Composite Fiber

Draw ratio	Orientation angle
2.82	±10.3°
3.17	±10.1°
3.48	±9.9°

According to these theoretical values and ε_L*, the σ_{CNT}' of the MWNTs at a strain of 9% shown in Eq. (2) can be estimated to be 47.25 GPa. Using above data and based on the rule of mixture [Eq. (2)], the calculated strength for 1 wt % MWNTs/Lyocell fiber can be obtained, i.e., σ_C* = 0.93 GPa. The value is higher than our experimental result shown in Figure 3 (4.79cN/dtex = 0.72 GPa), which may be ascribed to some factors, such as agglomeration of the MWNTs, mutual compatibility of the MWNTs and cellulose matrix, and the structural faults in the composite fiber formed during the spinning process etc.

Thermal property of MWNTs/Lyocell composite fiber

The thermal properties of Lyocell fiber and MWNTs/Lyocell composite fibers were characterized by TGA under a N_2 atmosphere and shown in Figure 4. It is clear that the onset decomposition temperature shifts from 298°C for the pure Lyocell fiber to 319°C for the MWNTs/Lyocell composite fiber with 5 wt % MWNTs, implying that the thermal stability of the composite fiber was improved by the addition of the MWNTs. This is because that the thermal degradation of polymer generally begins with chain cleavage and radical formation. The MWNTs in the composite fiber may act as radical scavengers and hence delay the onset of thermal degradation.[18]

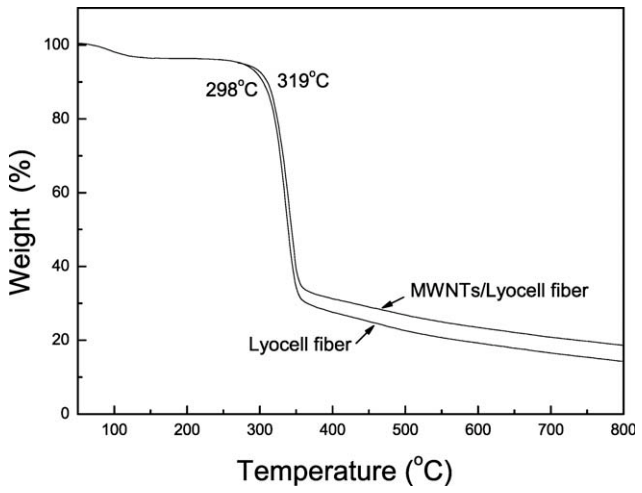

Figure 4 TGA curves of pure Lyocell fiber and MWNTs/Lyocell composite fiber with 5 wt % MWNTs.

Structure of MWNTs/Lyocell composite fiber

The WAXD patterns of pure Lyocell fiber, MWNTs/Lyocell composite fiber containing 5 wt % MWNTs and MWNTs are illustrated in Figure 5. It is found both pure Lyocell fiber and MWNTs/Lyocell composite fiber have obvious diffraction peaks at 2θ = 12.1°, 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. And the latter has another stronger diffraction peak at 2θ = 25.6°, which is the characteristic diffraction peak for MWNTs (see the curve c). These results indicate that the MWNTs have been added into the MWNTs/Lyocell composite fiber and the composite fiber still has cellulose II crystal structure. Furthermore, from the above WAXD results and by using the peakfit software (4.12 version, Seasolve Co.), the crystallinities for the pure Lyocell fiber and 5 wt % MWNTs/Lyocell composite fiber were calculated to be 55.8% and 55.1%, respectively, which implies that these two fibers almost have the same crystallinity.

It was reported that two-dimensional x-ray diffraction could be used to assess the orientation of MWNTs in nanocomposites.[19] According to this method, the orientation of MWNTs in MWNTs/Lyocell composite fibers obtained under different draw ratios were further investigated and the results were shown in Table I. It was found the MWNTs in the composite fibers almost aligned along the axis of the fibers and the orientation of MWNTs increased with the increasing draw ratio. As indicated above, the enhanced orientation of MWNTs along the fiber axis resulted in the decreasing volume conductivity of MWNTs/Lyocell composite fibers.

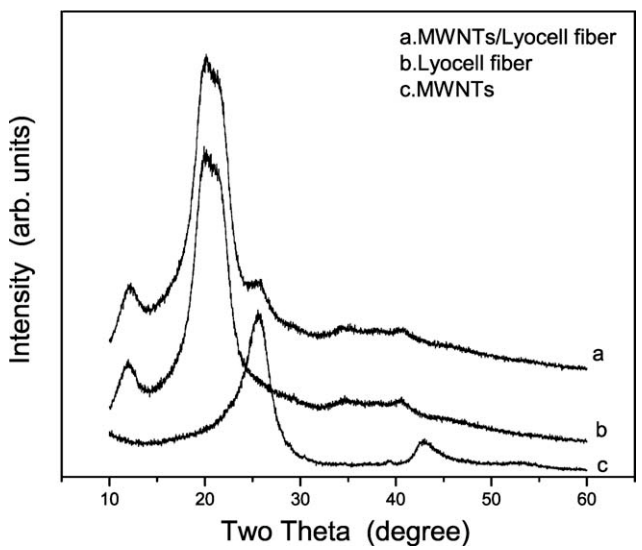

Figure 5 WAXD patterns of pure Lyocell fiber, MWNTs/Lyocell composite fiber containing 5 wt % MWNTs and MWNTs.

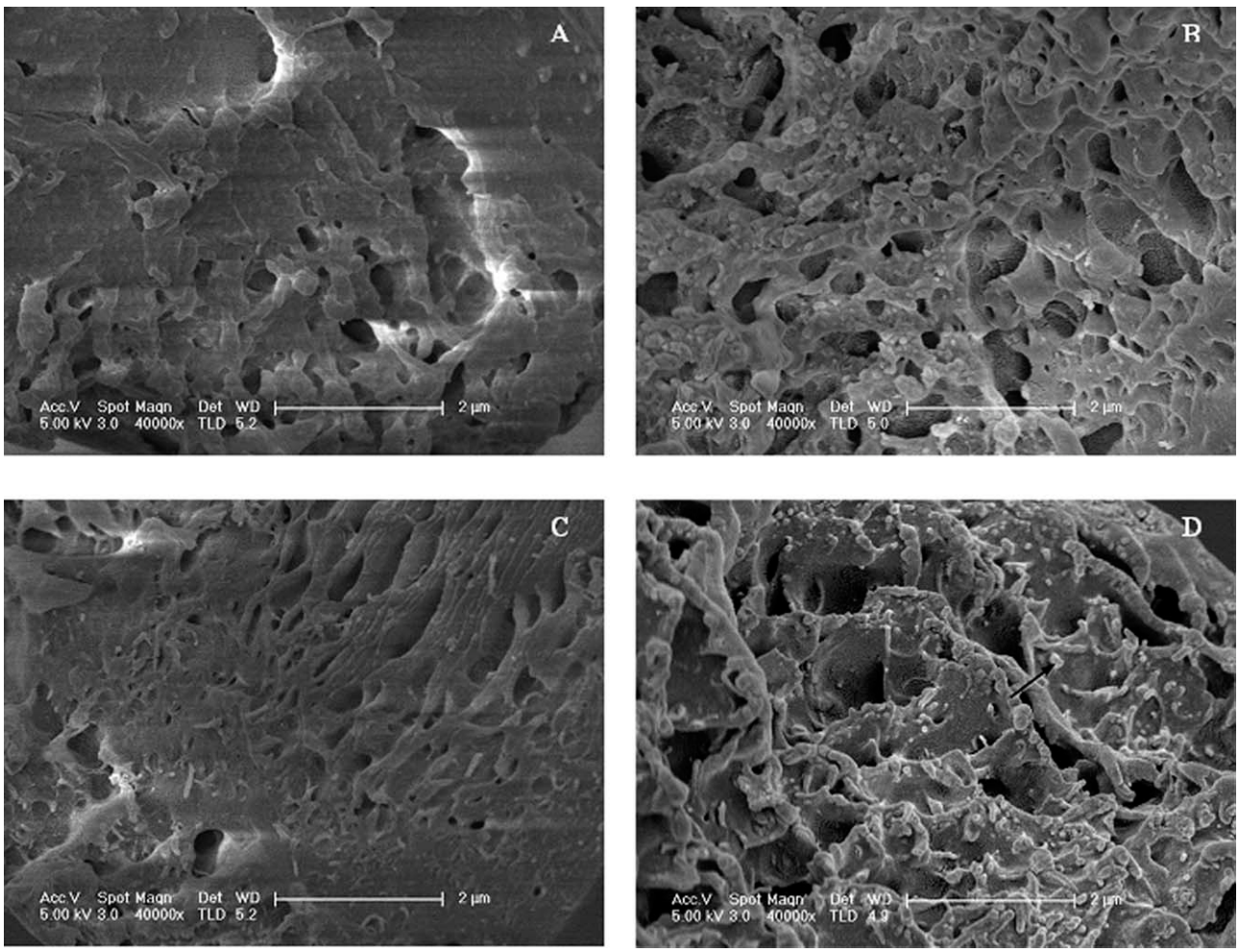

Figure 6 FESEM images of cross-sections for MWNTs/Lyocell composite fibers containing (A) 0.5 wt %, (B) 1 wt %, (C) 3 wt % and (D) 5 wt % MWNTs, respectively.

Figure 6 illustrates FESEM images of cross-sections for MWNTs/Lyocell composite fibers containing 0.5 (A), 1 (B), 3 (C), and 5 wt % (D) MWNTs, respectively. It was found that the MWNTs could be dispersed homogeneously in Lyocell matrix in the case of lower MWNTs content [e.g., Fig. 6 (A,B)], while the MWNTs aggregations occurred in the fiber in the case of higher MWNTs content [e.g., Fig. 6(D), in which one of the MWNTs aggregations was pointed out by the arrow].

CONCLUSIONS

The MWNTs/Lyocell composite fibers having the cellulose II crystal structure can be prepared by dry-wet spinning process. An appropriate amount of MWNTs could be dispersed uniformly in the Lyocell matrix and could improve the mechanical and thermal properties of composite fiber. Compared with the pure Lyocell fiber, the modulus and tensile strength of the composite fiber containing 1 wt % MWNTs were increased by 42 and 22%, respectively. Moreover, the MWNTs in the composite fiber almost aligned along the axis of the fiber and their orientation increased with the increase of draw ratio. In addition, more MWNTs content and lower draw ratio could improve the electrical conductance of the composite fiber. The composite fiber containing 5 wt % MWNTs has a volume conductivity of 8.8×10^{-4} S/cm, which is five orders higher than that of pure Lyocell fiber. These results indicate that the MWNTs/Lyocell composite fiber has potential applications in the areas of precursor of carbon fiber and conductive fiber.

The authors thank the Fundamental Research Funds for the Central Universities.

References

1. Fink, H. P.; Weigel, P.; Purz, H. J. Ganster, J. Prog Polym Sci 2001, 26, 1473.
2. Vorbach, D.; Taeger, E. Chem Fiber Int 1998, 48, 120.
3. Zhang, H. H.; Guo, L. W.; Shao, H. L.; Hu, X. C. J Appl Polym Sci 2006, 99, 65.
4. Poulin, P.; Vigolo, B.; Launoise, P. Carbon 2002, 40, 1741.

5. Chae, H. G.; Sreekumar, T. V.; Uchida, T.; Kumar, S. Polymer 2005, 46, 10925.
6. Fornes, T. D.; Baur, J. W.; Sabba, Y.; Thomas, E. L. Polymer 2006, 47, 1704.
7. Lin, Y.; Zhou, B.; Fernando, K. A. S.; Liu, P.; Allard, L. F.; Sun Y. P. Macromolecules 2003, 36, 7199.
8. Hill, D. E.; Lin, Y.; Rao, A. M.; Allard, L. F.; Sun, Y. P. Macromolecules 2002, 35, 9466.
9. Liu, T.; Phang, I. Y.; Shen, L.; Chow, S. Y.; Zhang, W. D. Macromolecules 2004, 37, 7214.
10. Lu, J.; Zhang, H. H.; Shao, H. L.; Hu, X. C. Polymer (Korea) 2007, 31, 436.
11. Martin, C. A.; Sandler, J. K. W.; Shaffer, M. S. P.; Schwarz, M. K.; Bauhofer, W.; Schulte, K.; Windle, A. H. Compos Sci Technol 2004, 64, 2309.
12. Schmidt, R. H.; Kinloch, I. A.; Burgess, A. N.; Windle, A. H. Langmuir 2007, 23, 5707.
13. Regev, O.; ElKati, P. N. B.; Loos, J.; Koning, C. E. Adv Mater 2004, 16, 248.
14. Haggenmueller, R.; Gommans, H. H.; Rinzler, A. G.; Fischer, J. E. Winey, K. I. Chem Phys Lett 2000, 330, 219.
15. McCrum, N. G. L.; Buckley, C. P.; Bucknall, C. B. Principles of Polymer Engineering; Oxford University Press: New York, 1988.
16. Ruan, S. L.; Gao, P.; Yu, T. X. Polymer 2006, 47, 1604.
17. Yu, M. F.; Lourie, O.; Dyer, M. J. Moloni, K.; Kelly, T. F.; Ruoff, R. S. Science 2000, 287, 637.
18. Watts, P. C. P.; Fearon, P. K.; Hsu, W. K.; Billingham, N. C.; Kroto, H. W.; Walton, D. R. M. J Mater Chem 2003, 13, 491.
19. Jin, L.; Bower, C.; Zhou, O. Appl Phys Lett 1998, 73, 1197.