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Elastic deformation of multiwalled carbon nanotubes in electrospun MWCNTs–PEO and MWCNTs–PVA nanofibers

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Abstract

Polyethylene oxide (PEO) and polyvinyl alcohol (PVA) nanofibers (NFs) containing multiwalled carbon nanotubes (MWCNTs) have been prepared by electrospinning method. The elastic deformation of MWCNTs in these NFs, compared with the well-dispersed pristine MWCNTs, has been evaluated by statistically measuring the tortuosity change of MWCNTs, by adopting the tortuosity factor (TF) and calculating scale (CS) method. The average TFs of the well-dispersed MWCNTs increase nearly linearly with the increasing of CSs in the range of 30–500 nm. Comparatively, the TFs of MWCNTs in the PEO and PVA NFs first increase, then decrease with CSs and have an inflection point at the CS in 300 nm. The results indicate the elastic deformation of MWCNTs in electrospinning process, which is partly kept in the solidified MWCNTs–polymer NFs. The data comparison of MWCNTs–PEO and MWCNTs–PVA indicate that the polymers with relatively high elastic modulus can keep the elastic deformation of MWCNTs in relatively large degree. Finally, a simplified mechanical model is proposed to explain the interaction between MWCNTs and the polymer matrix. The calculated elastic modulus of the MWCNTs is in the order of magnitude of 100 GPa, in agreement with that of the AFM measurement.

Keywords: Electrospinning; MWCNTs–polymer composite; Elastic deformation

1. Introduction

Carbon nanotubes (CNTs) [1], with extraordinary mechanical and electronic properties, have the potential application as the reinforced materials in CNTs–polymer composite [2–8]. Using the electrospinning method, Chang et al. [9] has prepared single-walled CNTs (SWNTs)/polyvinylidene fluoride fiber mats and investigated the percolation threshold for the insulator-to-conductor transition of the composite mats. Ko et al. [8] has prepared the continuous CNTs-filled nanofibers (NFs) and reported that the modulus was improved 120% in NFs containing 4 wt% SWNTs. Dror and Salalha et al. [10,11] have achieved well-dispersed MWCNTs and SWNTs, and successfully prepared the electrospun MWCNTs/PEO NFs in which MWCNTs can be observed using transmission electron microscopy (TEM). Recently, Ge and Hou et al. [12,13] have prepared highly-oriented, large area continuous MWCNTs -polyacrylonitrile (PAN) NF composite sheets and reported that, for the first time, the orientation of the MWCNTs within the NFs was much higher than that of the PAN polymer crystal matrix.

However, though CNTs–polymer NFs exhibit relatively good mechanical properties to some degree, there are still big challenges in increasing the mechanical strength of CNTs–polymer composite close to that of the CNT itself. The situation is partly due to the poor understanding of the structure of CNTs inside, and the interaction between the CNTs and the polymer. In order to address part of these problems, it is necessary to find a convenient system to study the interaction between CNTs and polymers. Here, we propose the electrospinning process to study these problems. This method provides strong elongation of a CNTs–polymer solution and produces random fiber mats or continuous yarns [14,15] with the fiber diameter in the nanometer range. So far, great progress has been made in the fabrication of electrospun polymer/CNTs NFs, and a lot of reports on the morphologies of pure electrospun NFs have been found [16–19]. However, the morphologies of electrospun NFs embedded with CNTs and

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Table 1
Parameters of solutions used in the electrospinning

MWCNTs solution	Polymer solution		Electrospinning solution composition
0.07 (w/w)% MWCNTs	PEO	6 (w/w)% PEO ($M_w = 900{,}000$ g/mol)	50 (v/v)% PEO solution
		40:60 (v/v)% ethanol/water	50 (v/v)% MWCNTs solution
1 (w/w)% SDS	PVA	8 (w/w)% PVA	80 (v/v)% PVA solution
		($M_w = 75{,}000$–$79{,}000$ g/mol, hydrolysis 98–99%)	20 (v/v)% MWCNTs solution

the interaction between CNTs and the polymer matrix have not been understood in the depth. Since the NF is only several tens to hundreds nanometers in diameter, it can be easily observed by high-resolution transmission electron microscopy (HRTEM) [10]. Thus, it is possible to study the orientation of MWCNTs in the polymer and the interaction between MWCNTs and the polymer matrix, two most important factors in determining the reinforcement effect of MWCNTs in polymer fiber, especially in increasing their mechanical and/or electronic conductive properties.

Specifically, we use this method to prepare MWCNTs–PEO and MWCNTs–PVA composite NFs. Since, this method provides a very large driving force to stretch the fibers by adopting a very high electrostatic voltage, the deformation of the polymer matrix and probably also the MWCNTs can be expected. By introducing two parameters, tortuosity factor (TF) and calculating scale (CS), we are able to quantitatively determine the tortuosities of the pristine individual MWCNTs and the MWCNTs in MWCNTs–polymer NFs. Such comparison is useful for the evaluation of the elastic deformation of MWCNTs and the interaction between MWCNTs and the polymer matrix. Finally, a mechanical model is presented and is useful for understanding of the interaction between MWCNTs and the polymer matrix.

2. Experimental

The MWCNTs are prepared from the decomposition of hydrocarbons over Fe/Mo/Al_2O_3 catalyst using a fluidization method and have average outer diameter of 10–20 nm [20,21]. Generally, these MWCNTs were entangled to form some agglomerate structures. First, such MWCNTs agglomerates were broken by acid under the assistance of ultrasound and become all individual MWCNTs in a well-dispersed state [22]. Secondly, the modified MWCNTs and sodium dodecyl sulfate (SDS, dispersing agent) were dispersed in water and treated by ultrasound for 30 min. Thus, MWCNTs were well dispersed and the resulting solution liked homogeneous and stable dark ink. Thirdly, such solution was mixed with PEO/ethanol/water solution or PVA/water solution to achieve viscoelastic spinnable solution. The PEO and PVA served as the polymer matrix of the electrospun NFs embedded with the MWCNTs after solvent evaporation. The compositions of the dispersions and processing solutions are summarized in Table 1.

A typical electrospinning setup was used for this experiment. Electrospinning was carried out using air pressure of 10–30 kPa to force the solution spraying out of a syringe with the diameter of 1 mm at a voltage difference of 30 kV. The distance between the positive electrode and the grounded metal collector was 20 cm. A copper grid, coated by a holey carbon film, was pasted on the grounded metal collector and used for the collection of the NFs samples. Such samples can be directly used for the characterization of HRTEM (JOEL 2010, exciting at 200 kV), without any morphological changes in the normal sample preparation. In order to make comparisons with the MWCNTs in polymer NFs, the specimens of well-dispersed MWCNTs were also prepared on the copper grid for HRTEM observation. Large amount of HRTEM images, from many samples, were taken for the morphological analysis.

3. Results and discussion

During the electrospinning process, the electrified jet (solution of MWCNTs–polymer) under a high electrostatic field is continuously stretched and split into multiple branches, due to the complicated actions such as bending instability and the high frequency of whipping. With the solvent evaporation, the MWCNTs–polymer solidify to

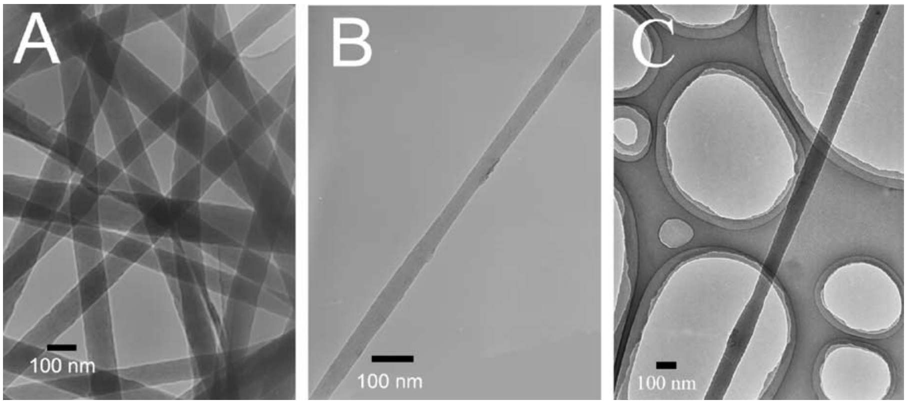

Fig. 1. (A) Electrospun pure PEO mat; (B) a single PEO NF without MWCNTs; (C) a single PVA NF without MWCNTs.

become filaments with its diameter decreasing sharply from several microns to several hundreds nanometers. It is observed that, without any MWCNTs, the pure PEO and PVA NFs have uniform diameters and are very straight (Fig. 1). However, when the solution of MWCNTs mixed with PEO or PVA is used, the case is of significant difference. Generally, there are three main kinds of NFs. First, when the MWCNTs are relatively straight, the NFs of MWCNTs–PEO or MWCNTs–PVA will also be very straight (Fig. 2). Secondly, when the curvature of MWCNTs is relatively serious, the morphologies of MWCNTs–PEO or MWCNTs–PVA NFs, however, will be changed by these large curvatures or knots (Fig. 3). The last kind of NFs appears to be curved with MWCNTs (Fig. 4). It is clear that the MWCNTs influence the morphologies of MWCNTs–PEO or MWCNTs–PVA NFs significantly. The order of magnitude of the elastic modulus of MWCNTs is up to 1 TPa [23], while that of PEO or PVA is only 100 MPa. Thus, the morphological difference in the NFs with and without MWCNTs is attributed to the significant difference between the elastic modulus of the MWCNTs and those of PEO and PVA.

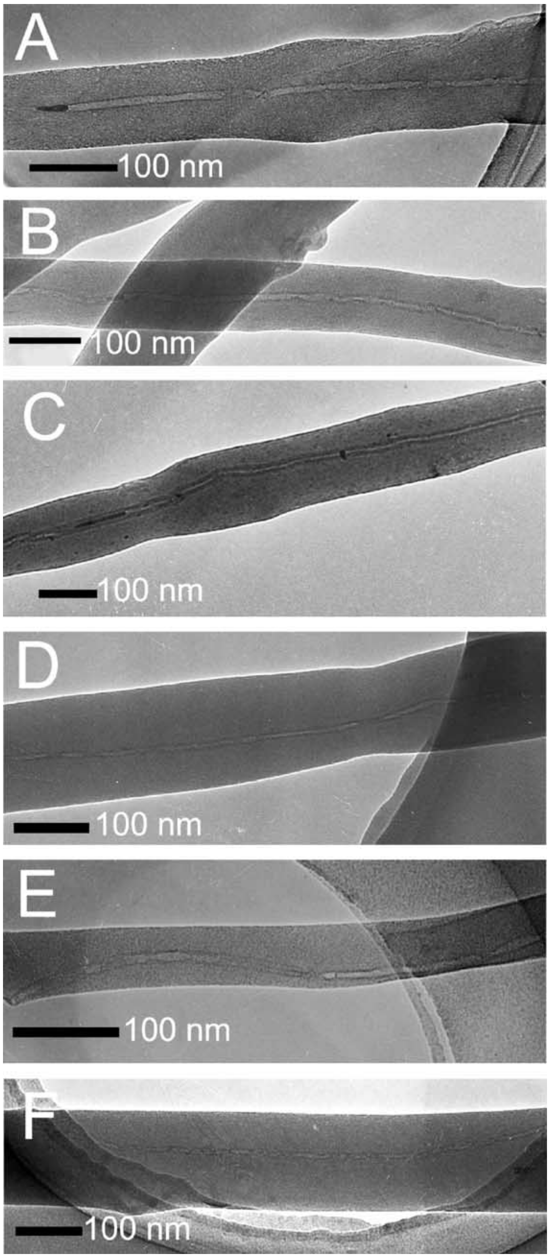

Fig. 2. Well-oriented MWCNTs in polymer NFs: (A–C) PEO NFs; (D–F) PVA NFs.

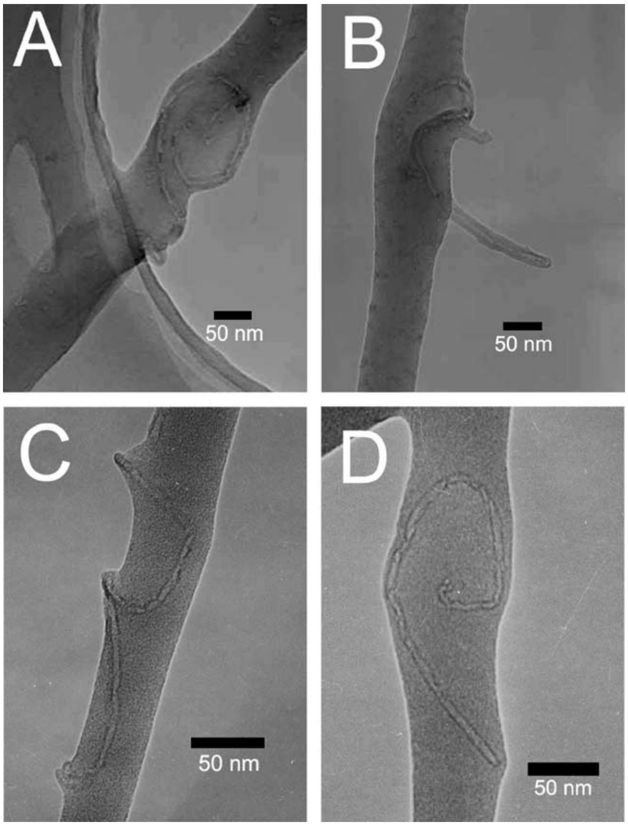

Fig. 3. Irregular MWCNTs in polymer NFs: (A,B) PEO NFs; (C,D) PVA NFs.

However, such qualitative comparison is insufficient for the evaluation of the interaction between MWCNTs and polymers. Since the modified MWCNTs used for electrospinning is acidic treated, there are many functional groups including the OH, COOH or C=O groups on the surface of modified MWCNTs, as confirmed by FTIR spectra [22,24]. These groups of the modified MWCNTs easily interact with the functional groups on PEO and PVA molecular chain, to form hydrogen bonds in the interface of MWCNTs and the polymer matrix. Such interaction between the modified MWCNTs and polymers is relatively strong, as compared with the physical interaction between the untreated MWCNTs with polymers. Thus, it can be expected that such interaction may be strong enough to influence the morphologies of MWCNTs embedded in the polymer matrices. Comparing the morphologies of well-dispersed MWCNTs with the morphologies of MWCNTs in polymer

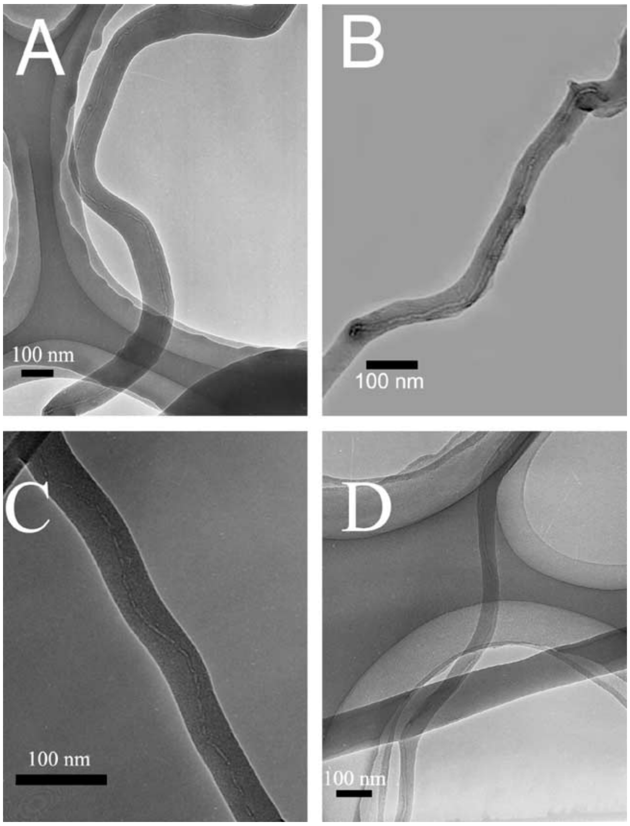

Fig. 4. Polymer NFs embedded with MWCNTs, the morphologies of which are affected by the interaction between them: (A,B) PEO NFs; (C,D) PVA NFs.

NFs, it is possible to examine the morphological changes of MWCNTs and the interaction between MWCNTs and polymer matrices. Generally, it can be seen in Fig. 5 that the morphologies of well-dispersed CNTs are similar to those of CNTs embedded in polymer NFs: straight, twisted and even looped. So it is necessary to develop a method to quantitatively compare the tortuosities of these MWCNTs. In order to achieve this, two parameters, tortuosity factor (TF) and calculating scale (CS), are introduced. TF is defined as:

$$\mathrm{TF} = \frac{\text{Length of the curve line between two points}}{\text{Distance between two points}}.$$

It is noted that, since the length distributions of MWCNTs are relatively broad, the direct comparison of the TFs of the different MWCNTs seems meaningless. So another parameter, CS, must be introduced to achieve the rational results. As shown in Fig. 6, for the measurement of the same curving line, the TFs of a given CS can be calculated by segment one after another. Thus, a series of TFs at changing CSs can be obtained. When large amount of samples are measured, the average TFs at the same CS can be determined and is reliable for the comparison of the tortuosities of the well-dispersed MWCNTs and MWCNTs embedded in NFs.

In detail, the TFs of MWCNTs are calculated, under different CSs, as measuring HRTEM images of 169 individual well-dispersed MWCNTs, 154 individual MWCNTs embedded in PEO NFs and 150 individual MWCNTs embedded in PVA NFs. The statistical results indicate that the lengths of the three kinds of MWCNTs follow the same lognormal distribution (Fig. 7). Considering the average length of these MWCNTs is 560 nm, the maximal CS is determined to 500 nm in order to ensure the sufficient sample size. As shown in Fig. 8, changing the CSs from 30 to 500 nm, the average values of TFs of the three kinds of MWCNTs follow different trends. The well-dispersed MWCNTs satisfy the linear equation: $\mathrm{TF} = 1 + 4.8 \times 10^{-4}\,\mathrm{CS}$. That means their TFs increase monotonously linearly with the CSs. Comparatively, the TFs of MWCNTs in NFs only increase with CSs in the range of 30–300 nm. There is an inflection point when the CS is at 300 nm. The TFs of MWCNTs embedded in PEO and PVA NFs are notably smaller than those of well-dispersed MWCNTs, when the CS is beyond 350 nm. The results indicate that the MWCNTs in NFs have been stretched and oriented to some degree. Though the crystallization behavior of PEO and PVA is different, the similar deformation tendency of MWCNTs in MWCNTs–PEO and MWCNTs–PVA NFs indicates that the deformation of MWCNTs is a general phenomenon in the electrospinning process. Furthermore, the changes of TFs between well dispersed MWCNTs and MWCNTs in PVA are much more significant than those of TFs between well dispersed MWCNTs and MWCNTs in PEO, as shown in Fig. 8. Considering the relatively large elastic modulus of PVA than that of PEO, it indicates that the different polymers present different elastic deformation results of MWCNTs. Thus, it can be further deduced that the elastic deformation of MWCNTs in the electrospinning process may

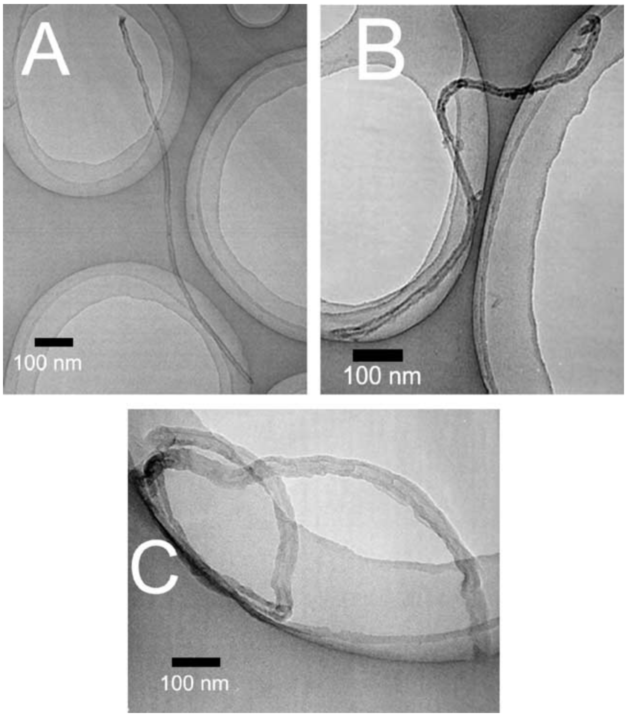

Fig. 5. Well-dispersed MWCNTs (A–C).

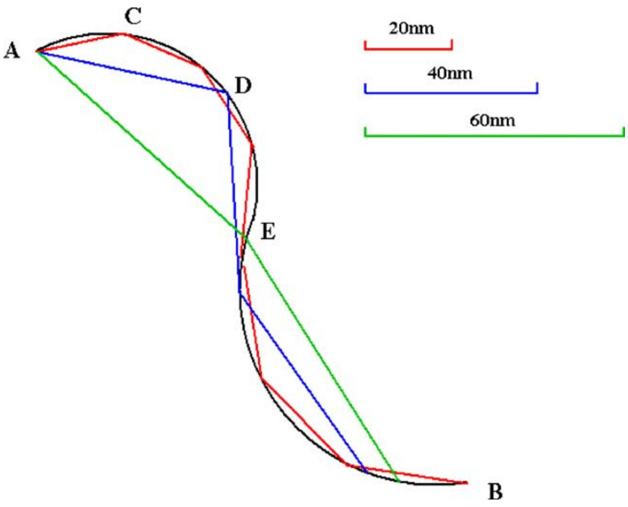

Fig. 6. Schematic diagram of calculating scale.

be relatively large and only part of these elastic deformation is kept in the solidified NF samples, considering the modulus of MWCNTs far larger than that of polymer matrices. Also from our results, it can be rationally anticipated that the deformation may be relatively easily kept and relatively large in the polymer with high modulus than that in the polymer with low modulus, as using other polymers.

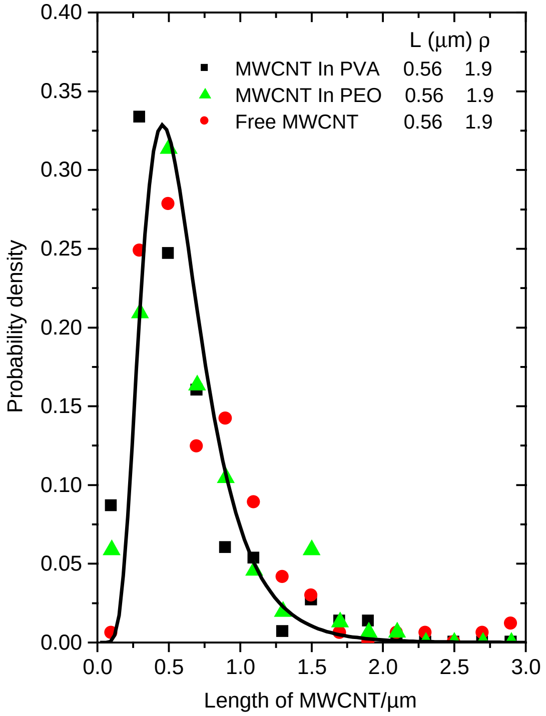

Fig. 7. Probability distributions of the lengths of the three kinds of MWCNTs.

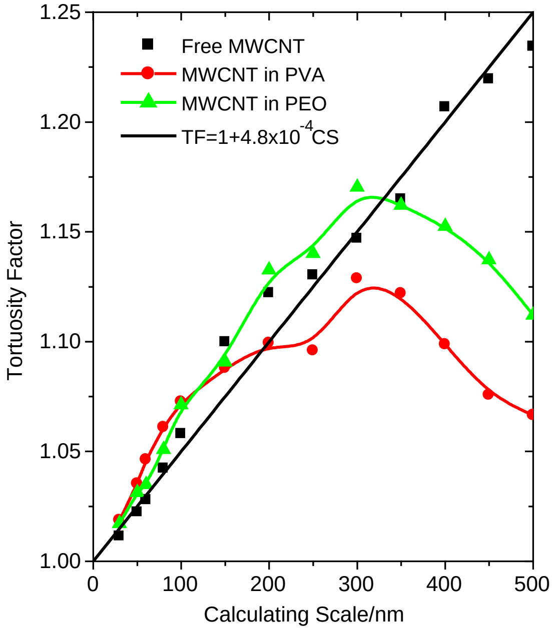

Fig. 8. Average TFs of the three kinds of MWCNTs at different CSs.

Furthermore, according to the difference in TFs, the interaction between MWCNTs and the polymer matrix can be examined. Though electrospinning process is complicated and dynamic, MWCNTs–polymer NFs in HRTEM images can be considered in a static state in which MWCNTs and the polymer matrix is under the mechanical balance. Thus, the interaction between MWCNTs and polymer matrix can be calculated by force analysis. In previous report, the elastic modulus of MWCNTs has been measured by using atomic force microscopy (AFM, Fig. 9) [23]. The deflection δ of an isotropic beam as a function of applied load is known from small deformation theory given in Eq. (1),

$$\delta = F\left(\frac{L^3}{\alpha EI}\right) \tag{1}$$

where F is the applied force, L is the suspended length, E is the elastic modulus, I is the second moment of area of the beam (usually called moment of inertia), and the constant α is 192. For a hollow cylinder, $I = \pi(r_0^4 - r_i^4)/4$, where r_0 and r_i are the outer and inner radii, respectively. For materials with elastic deformation, the deformations of the MWCNT and the polymer NF both follow the rule as shown in Eq. (1). Here, to achieve a simplified model, the well-dispersed MWCNTs and the MWCNTs in polymer NFs are considered as the initial state and the final state experiencing an elastic deformation, respectively. It is further hypothesized that the circular arc represents the tortuosity of the MWCNT. Thus, the interaction of MWCNT with the polymer matrix in NFs can be quantitatively determined. As shown in Fig. 10, L_0 is the CS, subscript 1 represents the initial state, and subscript 2 represents the final state. Using the TFs of the two kinds of MWCNTs at the same CS such as 400, 450 or 500 nm,

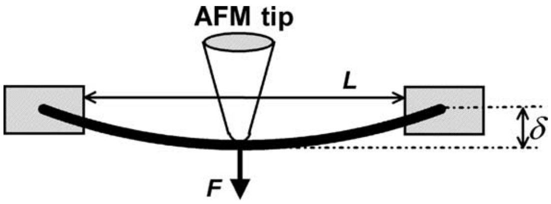

Fig. 9. Measurement of the elastic modulus of MWCNTs by the AFM.

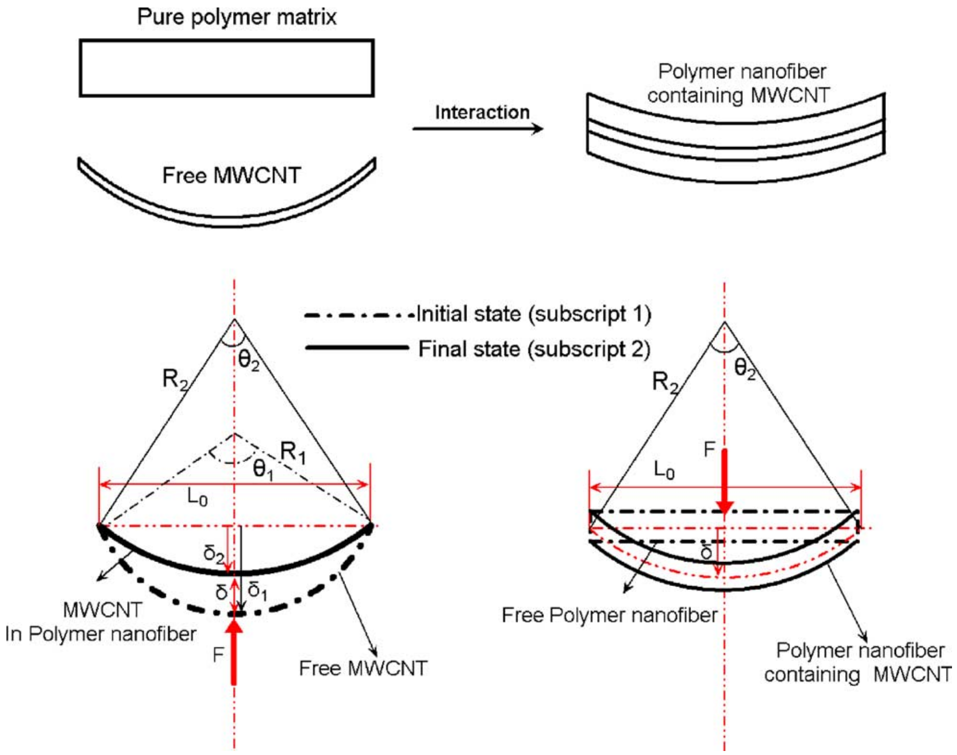

Fig. 10. Mechanical analysis of MWCNTs in polymer NFs.

the parameters of R_1, R_2, θ_1, θ_2, δ_1, δ_2 can be calculated. Then δ_{CNTs} can be obtained through $\delta_1 - \delta_2$. Similarly, it can also be supposed that the pure polymer NF is the initial state and the polymer NF containing the MWCNTs is the final state. Thus, δ_{polymer} is obtained using the same method as that for the MWCNT. According to the hypothesis above, the relationship between the modulus of MWCNTs and that of the polymer can be described in Eq. (2) as follows:

$$\frac{E_{\text{CNTs}}}{E_{\text{polymer}}} = \frac{I_{\text{polymer}}}{I_{\text{CNTs}}} \frac{\delta_{\text{polymer}}}{\delta_{\text{CNTs}}} \tag{2}$$

Table 2 shows the statistical results of r_0 and r_i of MWCNTs and PEO and PVA NFs in this work. As assuming the r_i value of polymer NFs equals to the r_0 value of MWCNTs, the values of $E_{\text{CNTs}}/E_{\text{polymer}}$ at the CSs in 400, 450 or 500 nm can be obtained, respectively (Table 3). The average value of $E_{\text{CNTs}}/E_{\text{polymer}}$ is at the order of magnitude of 10^3. Since the order of magnitude of the elastic modulus of PEO and PVA is about 100 MPa, the elastic modulus of MWCNTs in the present work is estimated at the order of magnitude of 100 GPa, in agreement with the result of Salvetat [23]. This similarity also indicates the validity of our method. Notably, our method is not only useful for the understanding the interaction between MWCNTs and polymers, but also effective to gain the quantitative data of the range of

Table 2
The statistical results of r_0 and r_i

	MWCNTs	PEO NFs	PVA NFs
r_0 (nm)	8	36	46
r_i (nm)	3	8	8

Table 3
Calculated results of $E_{\text{MWCNTs}}/E_{\text{polymer}}$

L_0 (nm)	δ_{MWCNT} (nm)	δ_{Polymer} (nm)		$I_{\text{PEO}}/I_{\text{MWCNT}}$		$E_{\text{MWCNT}}/E_{\text{Polymer}}$ ($\times 10^3$)		Average value of $E_{\text{MWCNT}}/E_{\text{Polymer}}$ ($\times 10^3$)	
		PEO	PVA	PEO	PVA	PEO	PVA	PEO	PVA
400	17	98	78	519.3	1319.3	3.04	2.81	2.05	2.02
450	29	104	77			1.87	1.81		
500	46	107	80			1.24	1.44		

elastic modulus of MWCNTs. Also our method is in relatively a macroscopic scale and does not require the strict operating conditions, as compared with that of AFM. Thus, the present method provides convenience for study of the related materials.

4. Conclusions

In the present work, MWCNTs–PEO and MWCNTs–PVA NFs are successfully fabricated in the electrospinning process. The elastic deformation of MWCNTs in these NFs, resulting from the electrospinning process and the strong interaction between MWCNTs and the polymer matrix, has been studied by comparing TFs of the three kinds of MWof CNTs. It can be seen that the TFs of MWCNTs embedded in polymer NFs decrease, indicating that MWCNTs have been stretched and oriented along the NF axis during the electrospinning processing to some degree. The results are both observed in two polymers with different crystallization behaviors, suggesting a generalized phenomenon irrelevant to the kind of polymers. The degree of elastic deformation of MWCNTs kept after the solidification of NFs increases with the increasing modulus of the polymer matrix. Furthermore, a simplified model is proposed to estimate the elastic modulus ratio of MWCNTs to polymers (at the order of magnitude of 10^3). The result, in agreement with that from AFM measurement, confirms the validity of the method in the present work, which is useful for the further understanding the interaction between MWCNTs and the polymer matrix quantitatively.

Acknowledgements

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References

[1] Iijima S. Nature 1991;354:56–8.
[2] Qian D, Dickey EC, Andrews R, Tantell T. Appl Phys Lett 2000;76(20): 2868–70.
[3] Ajayan PM, Stephan O, Colliex C, Trauth D. Science 1994;265:1212.
[4] Curran SA, Ajayan PM, Blau WJ, Carroll DL, Coleman JN, Dalton AB, et al. Adv Mater 1998;10(14):1091–3.
[5] Coleman JN, Blau WJ, Dalton AB, Munoz E, Collins S, Kim BG, et al. Appl Phys Lett 2003;82(11):1682–4.
[6] Vigolo B, Penicaud A, Coulon C, Sauder C, Pailler R, Journet C, et al. Science 2000;290:1331.
[7] Dalton AB, Collins S, Munoz E, Razal JM, Ebron VH, Ferraris JP, et al. Nature 2003;423:703.
[8] Ko F, Gogotsi Y, Ali A, Naguib N, Ye H, Yang G, et al. Adv Mater 2003; 15(14):1161–5.
[9] Chang S, Kim Y, Bake CK. J Polym Sci, Part B: Polym Phys 2003;41(13): 1572–7.
[10] Dror Y, Salalha W, Khalfin RL, Cohen Y, Yarin AL, Zussman E. Langmuir 2003;19(17):7012–20.
[11] Salalha W, Dror Y, Khalfin RL, Cohen Y, Yarin AL, Zussman E. Langmuir 2004;20(22):9852–5.
[12] Ge JJ, Hou HQ, Li Q, Graham MJ, Greiner A, Reneker DH, et al. JACS 2004;126(48):15754–61.
[13] Hou HQ, Ge JJ, Zeng J, Li Q, Reneker DH, Greiner A, et al. Chem Mater 2005;17(5):967–73.
[14] Smit E, Buttner U, Sanderson RD. Polymer 2005;46:2419–23.
[15] Katta P, Alessandro M, Ramsier RD, Chase G. Nano Lett 2004;4(11): 2215–8.
[16] Fong H, Chun I, Reneker DH. Polymer 1998;40:4585–92.
[17] Zong XH, Ran SF, Fang DF, Hsiao BS, Chu B. Polymer 2003;44: 4459–67.
[18] Zarkoob S, Eby RK, Reneker DH, Hudson SD, Ertley D, Adams WW. Polymer 2004;45:3973–7.
[19] Park WH, Jeong L, Yoo DI, Hudson S. Polymer 2004;45:7151–7.
[20] Wang Y, Wei F, Luo GH, Yu H, Gu GS. Chem Phys Lett 2002;364(5): 568–72.
[21] Qian WZ, Yu H, Wei F, Zhang QF, Wang ZW. Carbon 2002;40(15): 2968–70.
[22] Wang Y, Wu J, Wei F. Carbon 2003;41(15):2939–48.
[23] Salvetat JP, Kulik AJ, Bonard JM, Andrew G, Briggs D. Adv Mater 1999; 11(2):161–5.
[24] Jiang LQ, Gao L. J Inorg Mater 2003;18(5):1135–8.