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The Effect of Multi-walled Carbon Nanotubes on the Molecular Orientation of Poly(vinyl alcohol) in Drawn Composite Films

Xiao Wang, Soo Young Park[1], Kwan Han Yoon, Won Seok Lyoo[2], and Byung Gil Min*

School of Advanced Materials and System Engineering, Kumoh National Institute of Technology, Gumi 730-701, Korea
[1]Department of Polymer Science, Kyungpook National University, Daegu 702-701, Korea
[2]School of Textiles, Yeungnam University, Gyeongsan 712-749, Korea
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Abstract: Poly(vinyl alcohol) (PVA)/multi-walled carbon nanotube (MWNT) composite films were prepared by casting a DMSO solution of PVA and MWNTs, whereby the MWNTs were dispersed by sonication. A significant improvement in the mechanical properties of the PVA drawn films was achieved by the addition of a small amount of MWNTs. The initial modulus and the tensile strength of the PVA drawn film increased by 30 % and 45 %, respectively, with the addition of 1 wt% MWNTs, which are close to those calculated from the rule of mixtures, and were strongly dependent upon the orientation of the PVA matrix. The mechanical properties, however, were not improved with a further increase in the MWNT content. The orientation of MWNTs in the composite was not well developed compared to that of the PVA matrix. This result suggests that the improvement of the molecular orientation of the PVA matrix plays a major role in the increase of the mechanical properties of the drawn PVA/MWNT composite films.

Keywords: Carbon nanotubes, Carbon composites, Molecular orientation, X-ray diffraction, Poly(vinyl alcohol)

Introduction

Since they were discovered in 1991 by Iijima [1], carbon nanotubes (CNTs) have drawn a lot of interest because of their unique mechanical, electrical, and thermal properties. Polymer/CNT composites have been researched to exploit the extraordinary properties of CNTs such as low density, high stiffness and high strength, which make them ideal as reinforcements in composite materials. These composites, however, still have many processing related problems such as dispersion, alignment and load transfer between the CNTs and matrix which have to be improved if they are to be considered as structural materials for a variety of applications. Consequently, a fundamental understanding of the reinforcing mechanism between the CNTs and matrix is essential for both the manufacturing and the application of composite materials.

Poly(vinyl alcohol) (PVA) has recently been established as a suitable matrix material for CNT composites due to its water solubility, which enables composite fibers to be successfully processed via water and surfactants [2-9]. PVA is also widely used for the fabrication of polarized sheets after mechanical stretching [2]. However, most studies on PVA/CNT composites are mainly focused on either the reinforcing effect on the bulk state of composites or on the alignment of CNTs in the composites [3,4]. There was little discussion on the effect of CNTs on the molecular orientation of the matrix polymer in drawn composites.

The aim of the present paper is to investigate the effect of MWNTs on the molecular orientation of PVA matrices in drawn films, for the better understanding of the reinforcing mechanism of CNTs in composites in the drawn state.

*Corresponding author: bgmin@kumoh.ac.kr

Experimental

The PVA used in this study was obtained from DuPont© with a degree of hydrolysis of 99.5 % and a degree of polymerization of 1700 and the MWNTs were purchased from Iljin©. Two methods were used to make PVA/MWNT composite films. First, the MWNTs in DMSO were sonicated for four hours with a bath sonicator. The mixtures were stirred at one-hour intervals for at least 5 minutes during sonication and then PVA was dissolved in the mixtures at 120 °C for 3 hours. The 99/1, 97/3 and 95/5 (w/w) PVA/MWNT solutions in DMSO with a 15 wt% PVA concentration were prepared for this study. The cast films were put into a coagulation bath containing 70/30 (w/w) ethanol/DMSO at 5 °C for 30 minutes, and then they were transferred into another coagulation bath containing ethanol at room temperature for 9 hours. After they had been left to dry for 10 hours, the films were drawn with a ratio of 8 on a hot plate. The same preparation and drawing condition was applied to both the neat PVA and composite films. Second, to regard the comparison of the miscibility between the MWNTs and PVA, MWNT/DMSO and PVA/DMSO solutions were prepared separately. The MWNT/DMSO solutions were first sonicated for 2 hours. Then, both solutions were mixed and sonicated further for an additional 2 hours.

Morphology of the composite films was examined using a Hitachi S-4300 Scanning Electron Microscope (SEM). The films fractured in liquid nitrogen were mounted on the SEM stub using conductive tape and then coated with gold before scanning. The mechanical properties of the composite films were measured using Instron 4467 UTM. The gauge length and crosshead speed were 20 mm and 20 mm/min, respectively. Wide-angle X-ray diffraction patterns were recorded onto a

phosphor image plate in a Statton camera. A Rigaku rotating anode X-ray generator, operated at 40 kV and 240 mA and producing CuK_α radiation, was monochromated with a flat monochromator (Huber© Model 151). The sample-to-film distance was calibrated by SiO_2 powders. For differential scanning calorimetry studies, DSC 910 (TA instruments) was applied. The samples were heated at a rate of 10 °C/min from 30 to 250 °C under a Nitrogen atmosphere and cooled at the same rate. The second heating and cooling processes were used for analysis.

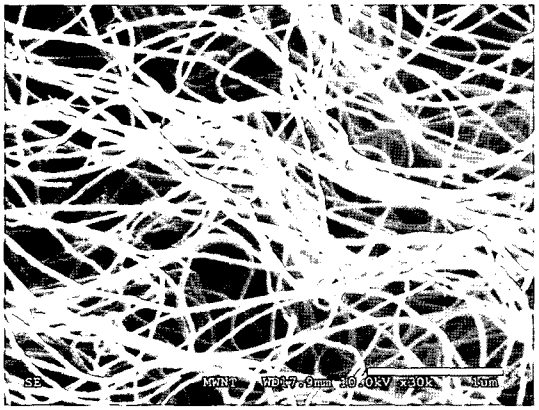

Figure 1. SEM micrograph of the MWNT powders used in the study.

Results and Discussion

Morphology of the MWNTs and Composite Films

DMSO is a good solvent, not only for PVA in making high performance fibers or films, but also for the dispersion of CNTs [3,10]. Transparent PVA films could be obtained from PVA/DMSO solutions, whereas it was difficult to get dimensionally stable and transparent films from aqueous PVA solutions. The good dispersion of CNTs in a polymer matrix is one of major challenges in fabricating CNT-reinforced composites because the CNTs, in their manufactured state, cluster together in any suspension due to the strong van der Waals interactions in that scale [11,12]. It is difficult to disperse the MWNTs in a polymer matrix at the high concentration due to the entanglement of MWNTs in bulk state, as shown in Figure 1. Figure 2 shows the SEM micrographs of the fractured surfaces of the PVA/MWNT composites. The MWNTs were well dispersed in the PVA matrix (Figure 2a) at the low concentration of 1 wt% (Figure 2b), while some agglomerates were observed with the addition of 3 wt% (Figure 2c) and 5 wt% (Figure 2d) MWNTs.

Mechanical Properties of Composite Films

The reinforcing effect of the CNTs in the drawn state is meaningful for the practical application to fibers or stretched films. The mechanical properties of composites formed by a

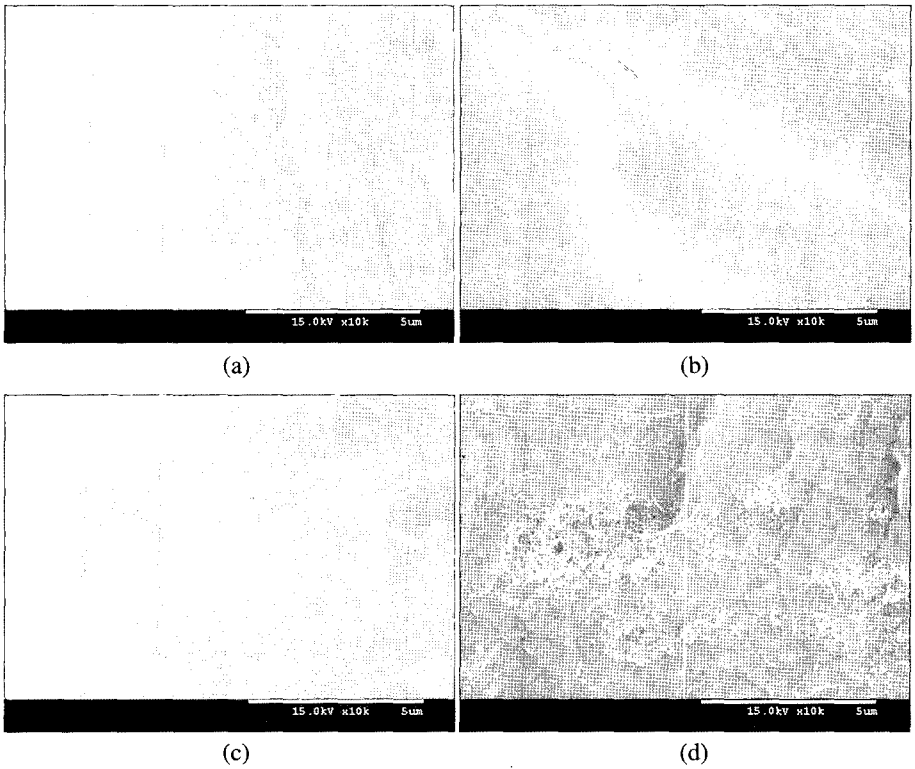

Figure 2. SEM micrographs of the fractured surfaces of the undrawn (a) neat PVA film and PVA/MWNT composite films containing, (b) 1 wt% MWNTs, (c) 3 wt% MWNTs, and (d) 5 wt% MWNTs.

PVA matrix and CNTs have been reported [4,5,13,14]. Cadek *et al.* [15] reported an increase of 78 % in Young's modulus for composite films containing 1 wt% weight of MWNTs. They concluded that this increase was mainly due to the increase in crystallinity. Zhang *et al.* [4] also achieved a 60 % improvement in mechanical properties in the modulus of PVA composites with the addition of 5 % HiPco single wall nanotubes. However, these results were obtained for the undrawn films.

Figure 3 shows the mechanical properties of the PVA/MWNT composite films with the drawing ratio of 8. The initial modulus of the PVA drawn film was increased by 30 % and the tensile strength was enhanced by 45 % with the addition of 1 wt% MWNTs. This indicated that the MWNTs effectively reinforced the PVA matrix. On the other hand, the elongation at break was slightly reduced by the presence of MWNTs in the composites. Moreover, it's clear that the first method of composite preparation was more effective in terms of reinforcements due to possible better dispersion of MWNTs. The values of theoretical modulus in Figure 3(a) were estimated by the rule of mixtures (equation 1), where E_c is the modulus of the composites, V_{NT} and V_{PVA} are volume fractions of the MWNTs and PVA, and E_{NT} is presumed to be 1 TPa [16].

$$E_c = V_{NT}E_{NT} + V_{PVA}E_{PVA} \quad (1)$$

The E_{PVA} was obtained from the experimental data in Figure 3(a) [13,14,17]. The modulus of the composite film containing 1 wt% of MWNTs was close to the calculated ideal value, while the improvement for larger amounts of MWNTs was not as great. These deviations from the calculated ideal values for the higher contents of MWNTs may be due to the poor dispersion of the MWNTs in the matrix, as shown in Figure 2.

Effect of Molecular Orientation on Mechanical Properties by WAXD Analyses

The WAXD patterns of the drawn PVA and PVA/MWNT composite films show well-crystalline and well-oriented PVA structures (Figure 4). The diffraction from MWNTs (d = 3.2 Å) is clearly distinguished from those from PVA, as shown by an arrow in Figure 4. However, the diffraction of the MWNTs was hardly seen in the equatorial 2θ scans due to their low intensity. The number of walls in the MWNTs used in the study was approximately 50, which was estimated from the

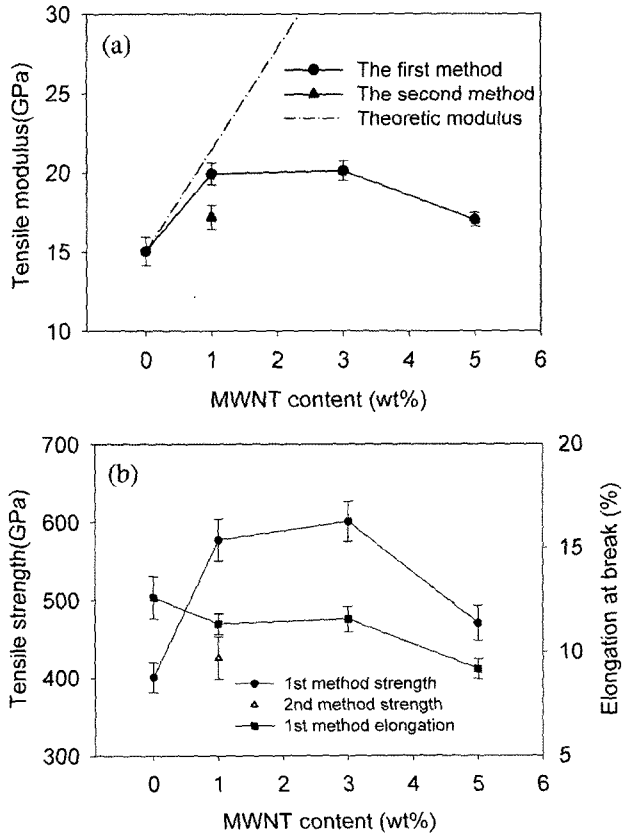

Figure 3. Mechanical properties of the drawn PVA and PVA/MWNT composite films; (a) initial modulus, (b) tensile strength and elongation at break.

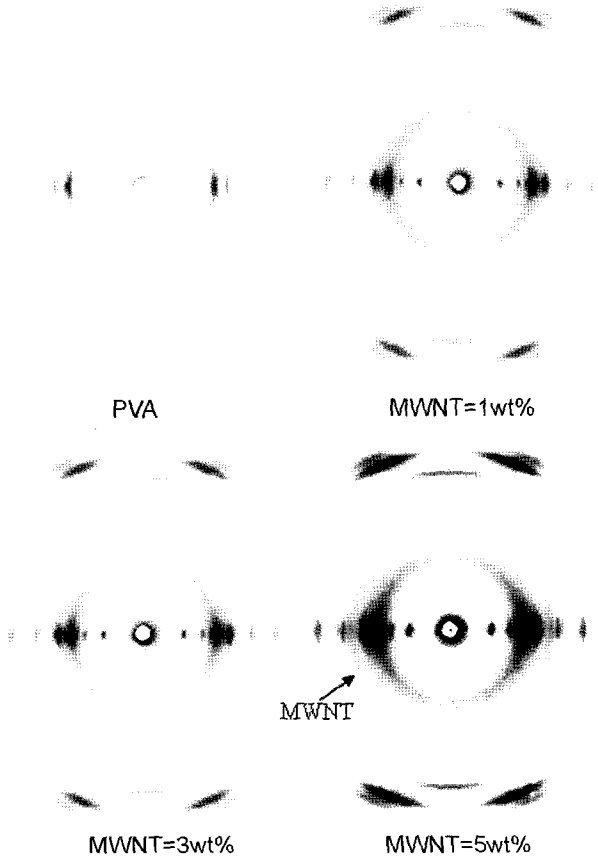

Figure 4. Wide-angle X-ray patterns of drawn PVA and PVA/MWNT composite films.

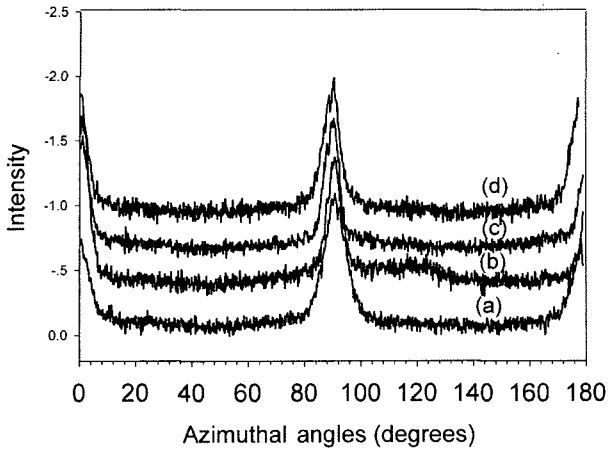

Figure 5. Azimuthal scans of the peak at $2\theta = 13^\circ$ in Figure 4; (a) 0 wt%, (b) 1 wt%, (c) 3 wt%, and (d) 5 wt% MWNT content.

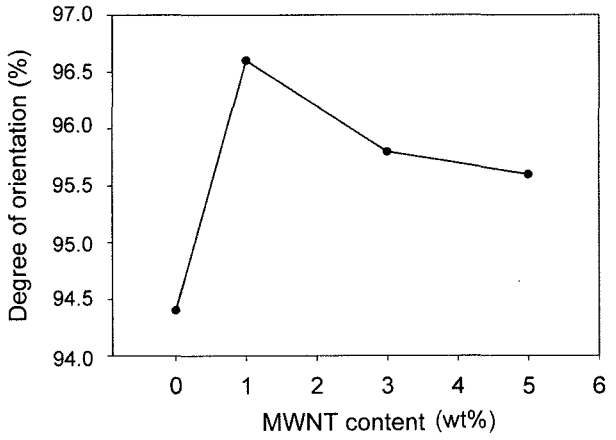

Figure 6. The degree of orientations of the drawn PVA/MWNT composite films versus MWNT content.

ratio of the interlayer distance (*ca.* 0.32 nm from X-ray diffraction) and the average thickness of the MWNTs (*ca.* 30-40 nm from Figure 1).

Figure 6 shows the degree of orientation (*D.O.*) of the PVA molecules of the drawn films, which was calculated using equation 2, where FWHM is the full-wide-at-half-maximum of the azimuthal scan (Figure 6) of the peak at $2\theta = 13^\circ$ (an arrow in Figure 5).

$$D.O. = \frac{180^\circ - FWHM}{180^\circ} \times 100\% \quad (2)$$

The orientation of the PVA is at its maximum at 1 wt% MWNTs, which is similar to the trend of the initial modulus in Figure 3(a). A small increase in the molecular orientation can lead to a significant improvement of the mechanical properties. On the other hand, the orientation of the MWNTs was almost isotropic compared to that of the PVA matrix, as shown in Figure 4. Unfortunately, the azimuthal scan for the diffraction of the MWNTs was not available due to its low intensity. These results strongly suggest that the molecular orientation of the matrix PVA improved with the addition of MWNTs and that it plays an important role in the increase of the mechanical properties of the drawn PVA/MWNT composites. Therefore, the good reinforcement of MWNT due to good dispersion and good orientation of PVA lead to favorable mechanical properties of PVA/MWNT composite films with 1 wt% MWNTs, compared with other samples.

Thermal Properties of the Composite Films

The thermal properties were also discussed to seek the relationship between them and mechanical properties. It can be only observed that the crystallization of PVA occurs faster with the addition of 1 wt% MWNTs due to the induced nucleation effect of the MWNTs [18,19]. However, there was no further increase in the crystallization rate above 1 wt% of the MWNT content and no crystallinity change was found.

Conclusion

A significant improvement in the mechanical properties of the PVA drawn films, i.e. the 30 % and 45 % increase in the initial modulus and tensile strength, respectively, was achieved with the addition of 1 wt% MWNTs. This improvement is caused not only by the better dispersion of MWNTs in the PVA matrix but also in the improved molecular orientation of the PVA matrix with the addition of MWNTs. At the higher MWNT content the improvement in the mechanical properties of the drawn composite films was not satisfactory due to not only poor dispersion of MWNT but also poor MWNT orientation by agglomeration of nanotubes.

Acknowledgement

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References

1. S. Iijima, *Nature*, **354**, 56 (1991).
2. A. G. Rozhin, Y. Sakakibara, H. Kataura, S. Matsuzaki, K. Ishida, Y. Achiba, and M. Tokumoto, *Chem. Phys. Lett.*, **405**, 288 (2005).
3. X. F. Zhang, T. Liu, T. V. Sreekumar, S. Kumar, X. D. Hu, and K. Smith, *Polymer*, **45**, 8801 (2004).
4. X. Zhang, T. Liu, T. V. Srekumar, S. Kumar, V. C. Moore, R. H. Hauge, and R. E. Smalley, *Nano Lett.*, **3**, 1285 (2003).
5. M. S. P. Shaffer and A. H. Windle, *Adv. Mater.*, **11**, 937 (1999).
6. A. B. Dalton, S. Collins, E. Munoz, J. M. Razal, V. H. Ebron, J. P. Ferraris, J. N. Coleman, B. G. Kim, and R. H.

Baughman, *Nature*, **423**, 703 (2003).
7. A. G. Rozhin, Y. Sakakibara, M. Tokumoto, H. Kataura, and Y. Achiba, *Thin Solid Film*, **464-465**, 368 (2004).
8. A. Chatterjee, *Fibers and Polymers*, **3**, 134 (2002).
9. S. H. Kim, B. G. Min and S. C. Lee, *Fibers and Polymers*, **6**, 108 (2005).
10. K. D. Ausman, R. Piner, O. Lourie, R. S. Ruoff, and M. Korobov, *J. Phys. Chem. B*, **104**, 8911 (2000).
11. Z. H. Fan, K. T. Hsiao, and S. G. Advani, *Carbon*, **42**, 871 (2004).
12. Z. H. Fan and S. G. Advani, *Polymer*, **46**, 5232 (2005).
13. K-T. Lau and D. Hui, *Compos. Part B-Eng.*, **33**, 263 (2002).
14. T. V. Screekumar, T. Liu, B. G. Min, H. Guo, S. Kumar, R. H. Hauge, and R. E. Smalley, *Adv. Mater.*, **16**, 58 (2004).
15. M. Cadek, J. N. Coleman, V. Barron, K. Hedicke, and W. J. Blau, *Appl. Phys. Lett.*, **81**, 5123 (2002).
16. M. Cadek, J. N. Coleman, K. P. Ryan, V. Nicolosi, G. Bister, A. Fonseca, J. B. Nagy, K. Szostak, F. Beguin, and W. J. Blau, *Nano lett.*, **4**, 353 (2004).
17. B. G. Demczyk, Y. M. Wang, J. Cumings, M. Hetman, W. Han, A. Zettl, and R. O. Ritchie, *Mater. Sci. Eng. A-Struct.*, **334**, 173 (2002).
18. E. Assouline, A. Lustiger, A. H. Barber, C. A. Cooper, E. Klein, E. Wachtel, and H. D.Wagner, *J. Polym. Sci. Part B: Polym. Phys.*, **41**, 520 (2003).
19. A. R. Bhattacharyya, T. V. Sreekumar, T. Liu, S. Kumar, L. M. Ericson, R. H. Hauge, and R. E. Smalley, *Polymer*, **44**, 2373 (2003).