

Rheological and electrical properties of polycarbonate/multi-walled carbon nanotube composites

Y.T. Sung^a, M.S. Han^a, K.H. Song^a, J.W. Jung^a, H.S. Lee^b, C.K. Kum^b, J. Joo^c, W.N. Kim^{a,*}

^a Department of Chemical and Biological Engineering, Korea University, Anam-dong, Seoul 136-701, South Korea

^b Tech. Center, LG Chemical Ltd, 84, Jang-dong, Yusong-ku, Daejeon 305-343, South Korea

^c Department of Physics, Korea University, Anam-dong, Seoul 136-701, South Korea

Received 24 August 2005; received in revised form 28 March 2006; accepted 8 April 2006

Available online 5 May 2006

Abstract

Rheological and electrical properties of the polycarbonate (PC)/multi-walled carbon nanotube (MWNT) were studied. The MWNT was functionalized by treating with the hydrogen peroxide (H_2O_2). The H_2O_2 treated MWNT was dried by thermal and freeze drying methods. From the morphological studies, the degree of entanglement of the MWNT was decreased after treating with the H_2O_2 . For the H_2O_2 treated MWNT (thermal drying), the length of the MWNT was shortened compared that of the H_2O_2 treated MWNT (freeze drying). The rheological and electrical properties of the PC/MWNT (H_2O_2 treated) composites increased compared that of the PC/MWNT (untreated) composites. Also, the electrical conductivity showed higher value for the PC/MWNT (H_2O_2 treated, freeze drying) composites compared that of the PC/MWNT (H_2O_2 treated, thermal drying) composites. From the results of the morphological, rheological, and electrical properties of the PC/MWNT composites, it is suggested that the electrical and rheological properties of the PC/MWNT composites are affected by the MWNT–MWNT network structure, which is related with the MWNT morphologies such as the degree of aggregation and aspect ratio of the MWNT.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Multi-walled carbon nanotube composite; Rheological properties; Electrical properties

1. Introduction

Development of the polymer/carbon nanotube (CNT) composites has been widely studied because of its superior mechanical and electrical properties since the discovery by Iijima in 1991 [1–15]. The CNT has Young's modulus up to 1 TPa [16] and has very large aspect ratio. Also, the CNT showed high electrical conductivity up to 10^3 S/cm [17].

In the polymer/CNT composites, the rheological properties could be changed by the structure of the composites. Pötschke et al. [1] reported the increase of the storage and loss modulus of the polycarbonate (PC)/multi-walled carbon nanotube (MWNT) composites at the low frequency region. Also, Mitchell et al. [2] reported the increase of the rheological properties at the low frequency region for the polystyrene (PS)/single-walled carbon nanotube (SWNT) composites. According to the Pötschke et al. [1] and Mitchell et al. [2], it has been proposed that the increase of the rheological properties at the

low frequency region was related to the network structure of the CNT.

However, the rheological properties of the polymer/CNT composites could be influenced by the polymer chain confinement by the CNT [3–5]. For example, Pötschke et al. [4] and Abdel-Goad and Pötschke [5] analyzed the rheological properties of the PC/MWNT composites by the MWNT–PC interaction. Also, in our previous study, we reported the chain confinement of the PC in the PC/MWNT composites by the dynamic mechanical thermal analysis (DMTA) [3].

In this study, the rheological and electrical properties of the PC/MWNT composites are reported by the measurements of the dynamic rheology and electrical conductivity, respectively. In particular, the effects of the MWNT functionalization by hydrogen peroxide (H_2O_2) on the rheological and electrical properties of the PC/MWNT composites are reported.

2. Experimental

2.1. Materials

A MWNT was supplied by the Iljin Nanotech Ltd. The MWNT was synthesized by chemical vapor grown method.

* Corresponding author. Tel.: +82 2 3290 3296; fax: +82 2 924 1793.

E-mail address: kimwn@korea.ac.kr (W.N. Kim).

Table 1
Characteristics of polycarbonate and multi-walled carbon nanotube used in this study

Sample	\bar{M}_n	\bar{M}_w	MWD	T_g (°C) ^a	Diameter (nm)	Length (μm)
PC ^b	11,000	30,000	2.7	156.6	–	–
MWNT ^c	–	–	–	–	10–12	10–15

^a Measured in our laboratory by DMTA.

^b Supplied by LG Chemical Ltd (PC 201 15).

^c Supplied by Iljin Nanotech Ltd.

Typical diameter of MWNT ranged from 10 to 12 nm, while length is between 10 and 15 μm. The PC was supplied by LG Chemical Ltd with the commercial designation of PC 201 15. The characteristics of the PC and MWNT are summarized in Table 1.

2.2. Composite preparations

The MWNT was treated by H₂O₂ with an aid of the sonication. The 1.0 g MWNT was treated with the 400 ml of H₂O₂ at 50 °C for 90 min. The treated MWNT and H₂O₂ mixture was dried by two different methods: (i) thermal drying, which is the MWNT and H₂O₂ mixture was dried for 12 h at 80 °C in the drying oven. (ii) Freeze drying, which is the MWNT and H₂O₂ mixture was centrifuged for 1 h, then the mixture was washed with distilled water until the MWNT and H₂O₂ mixture contained almost no acidity (pH 6.0–6.5). Then, the MWNT and H₂O₂ mixture was freeze dried at –60 °C for 72 h. For the preparation of the PC/MWNT composites, a total of 10.0 g of PC/MWNT mixture, ranged from 1 to 7 wt%, was dissolved in the 300 ml of tetrahydrofuran (THF) at 60 °C for 6 h under the sonication process. The PC/MWNT composites were pressed in the hot press at 260 °C. All the PC/MWNT composites were dried at least 12 h at 80 °C before pressing in the hot press. Also, the PC/MWNT composites without H₂O₂ treatment were prepared in order to compared with the H₂O₂ treated PC/MWNT composites.

2.3. FR-IR

Infrared spectra (400–4000 cm⁻¹) of the MWNT were obtained with Perkin–Elmer FT-IR. Scans of 32 were averaged with a scan rate of 2 cm⁻¹. The FT-IR samples were prepared by pressing the MWNT with potassium bromide (KBr).

2.4. Transmission electron microscopy (TEM)

The images of the microstructure of the MWNT with H₂O₂ treatment were obtained by JEOL transmission electron microscopy (model: JEM-2000EX/T) without staining the specimen.

2.5. Rheology

Dynamic measurements were carried out using advanced rheometric expansion system (ARES). The frequency sweep

from 0.1 to 100 rad/s were performed at 260 °C under dry nitrogen condition. For all the measurements, the PC/MWNT samples were tested within the linear viscoelastic strain range.

2.6. Electrical conductivity

For measuring the electrical conductivity, the four-probe method was used to eliminate the contact resistance. Four thin gold wires (0.05 mm thick and 99% gold) were attached in parallel on the samples by conducting graphite paint [18].

3. Results and discussion

Fig. 1 shows the IR spectra of the H₂O₂ treated and untreated MWNT. From Fig. 1(b) and (c), the H₂O₂ treated MWNT shows the C–C peak at 1220 cm⁻¹ and the C=O stretching peak at about 1730 cm⁻¹, which are not shown in the untreated MWNT. In Fig. 1(b) and (c), the MWNT shows the two peaks at about 1650 and 1220 cm⁻¹ for its carbon skeleton, which are associated with C=C and C–C, respectively. The appearance of the C–C peak at 1220 cm⁻¹ and C=O peak at 1730 cm⁻¹ suggested that the MWNT was functionalized by treating with the H₂O₂.

Fig. 2 shows the TEM images of the H₂O₂ treated and untreated MWNT. From Fig. 2(a), the untreated MWNT is shown to entangled and appeared to be aggregated. From Fig. 2(b) and (c), the entanglement of the MWNT is loosened after treating the MWNT by the H₂O₂. The degree of entanglement of the MWNT is decreased by treating with the

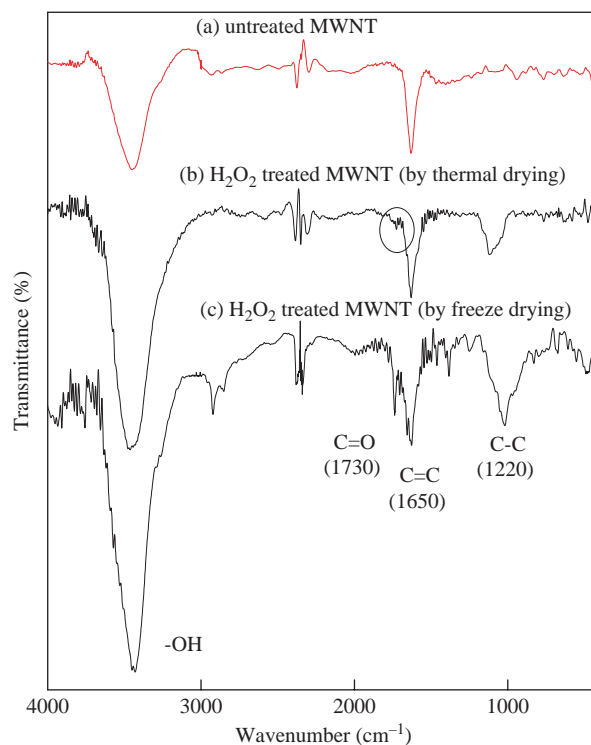


Fig. 1. IR spectra of the H₂O₂ treated and untreated MWNT: (a) untreated MWNT; (b) H₂O₂ treated MWNT (by thermal drying); (c) H₂O₂ treated MWNT (by freeze drying).

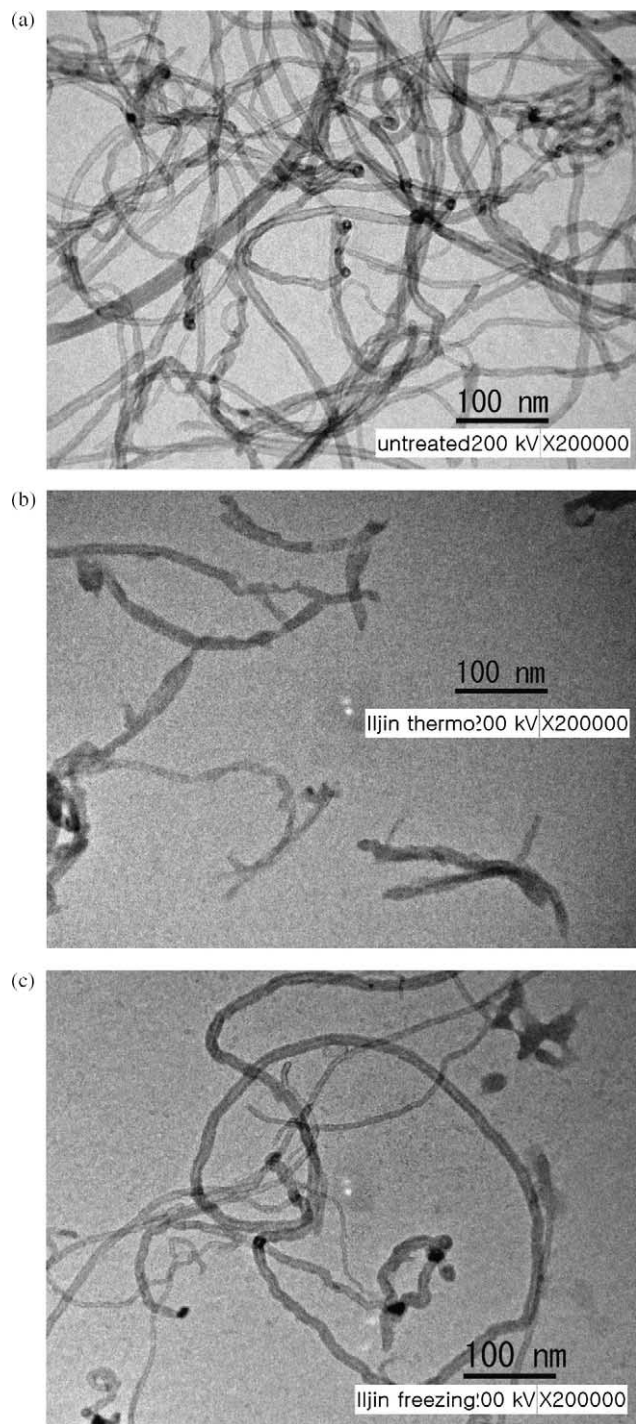


Fig. 2. TEM images of the H_2O_2 treated and untreated MWNT: (a) untreated MWNT; (b) H_2O_2 treated MWNT (by thermal drying); (c) H_2O_2 treated MWNT (by freeze drying).

H_2O_2 , therefore, the H_2O_2 treatment may be used to improve the dispersion of the MWNT in the PC/MWNT composites. In addition, from Fig. 2(b) and (c), the length of the MWNT is observed to be shortened for the MWNT by thermal drying than that of the MWNT by freeze drying. This behavior may be due to the continuous chopping by the thermal effect.

Fig. 3 shows the storage modulus (G') of the PC and PC/MWNT composites at 260 °C. From Fig. 3(a), the storage

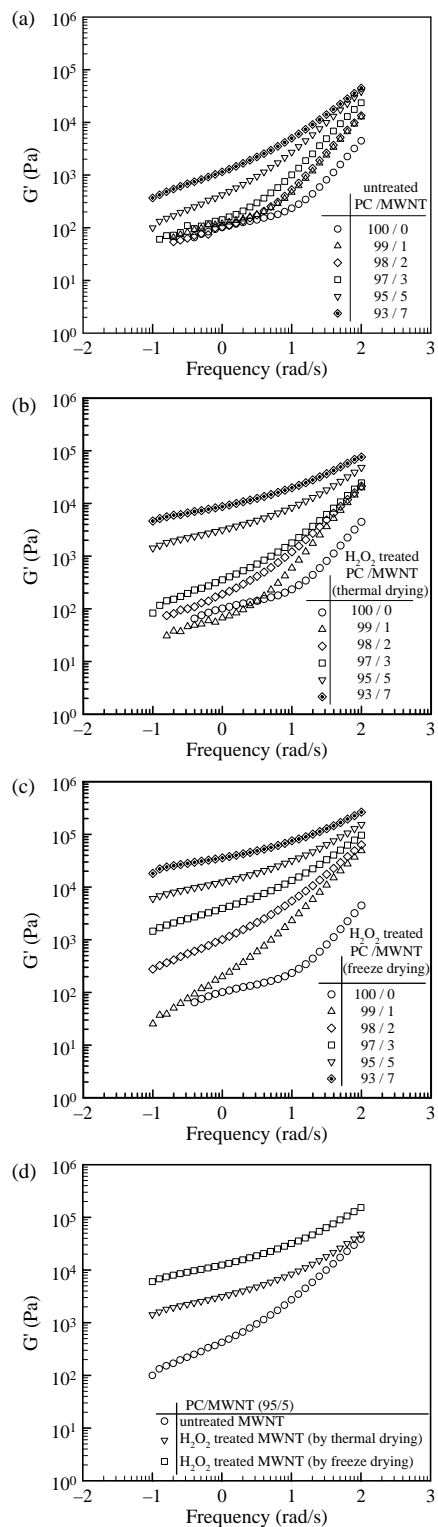


Fig. 3. Storage modulus (G') of the PC and PC/MWNT composites at 260 °C: (a) untreated MWNT; (b) H_2O_2 treated MWNT (by thermal drying); (c) H_2O_2 treated MWNT (by freeze drying); (d) untreated vs H_2O_2 treated MWNT for the PC/MWNT (95/5 wt%) composites.

modulus (G') of the PC/MWNT (untreated) composites increases with increasing the MWNT content. From Fig. 3(b) and (c), it is also shown that the storage modulus of the PC/MWNT (H_2O_2 treated) composites increases with increasing

the MWNT composites. In Fig. 3(d) shows the storage modulus (G') of the PC/MWNT (95/5) composites with frequency. For the PC/MWNT (95/5, H_2O_2 treated) composites, the increase of the storage modulus shows more significant at the low frequency compared the PC/MWNT (95/5, untreated) composites. From Fig. 3(d), the storage modulus of the PC/MWNT (95/5, H_2O_2 treated, freeze drying) composites increase more significantly than that of the PC/MWNT (95/5, H_2O_2 treated, thermal drying) composites, which suggests that the rheological properties of the PC/MWNT composites are influenced by the treatment of the MWNT. For the 98/2, 97/3, and 93/7 PC/MWNT composites, similar behavior are observed at the low frequency. Detail explanation of the increase of storage modulus at low frequency will be discussed later in this study.

Fig. 4 shows the loss modulus (G'') of the PC and PC/MWNT composites at 260 °C. From Fig. 4(a)–(c), the loss modulus (G'') increases with the increase of the MWNT content for the PC/MWNT (untreated and H_2O_2 treated) composites. In Fig. 4(d), for the PC/MWNT (95/5, H_2O_2 treated) composites, the increase of the loss modulus shows more significant at the low frequency compared the PC/MWNT (95/5, untreated) composites. Also, it is observed that the loss modulus of the PC/MWNT (95/5, H_2O_2 treated, freeze drying) composites increase more significantly than that of the PC/MWNT (95/5, H_2O_2 treated, thermal drying) composites. From the results of the Figs. 3 and 4, it is observed that the increase of the storage modulus of the PC/MWNT composites is greater than the increase of the loss modulus of the PC/MWNT (untreated and H_2O_2 treated) composites. Since, the structure of the polymer composites is more sensitively reflected on the storage modulus (G') than on the loss modulus (G'') [1,2].

Fig. 5 shows the complex viscosity (η^*) of the PC and PC/MWNT composites at 260 °C. From Fig. 5(a)–(c), the complex viscosity (η^*) increases with the increase of the MWNT content for the PC/MWNT (untreated and H_2O_2 treated) composites. From the results of the storage and loss modulus shown in Figs. 3 and 4, the increase of the complex viscosity of the PC/MWNT composites is mainly due to the increase of the storage modulus (G'). The complex viscosity (η^*) is related to both the storage (G') and loss modulus (G'') ($\eta^* = [(G')^2 + (G'')^2]^{1/2}/\omega$, ω = frequency). In Fig. 5(d), for the complex viscosity of the PC/MWNT (95/5, H_2O_2 treated) composites, shear-thinning behavior is observed compared the PC/MWNT (95/5, untreated) composites. The shear-thinning behavior and long time relaxation suggest the pseudo-solid-like behavior of the PC/MWNT (95/5, H_2O_2 treated) composites shown in Fig. 5(d).

From Figs. 3–5, it has shown that the rheological properties of the PC/MWNT (H_2O_2 treated) composites such as storage and loss modulus, and complex viscosity increase significantly at low frequency with MWNT content. The rheological properties of polymer composites at low frequency region (terminal region) reflect the hydrodynamically percolated filler–filler network structure [1,2]. Therefore, it is suggested that the increase of rheological properties of the PC/MWNT (H_2O_2 treated) composites at low frequency is related to the

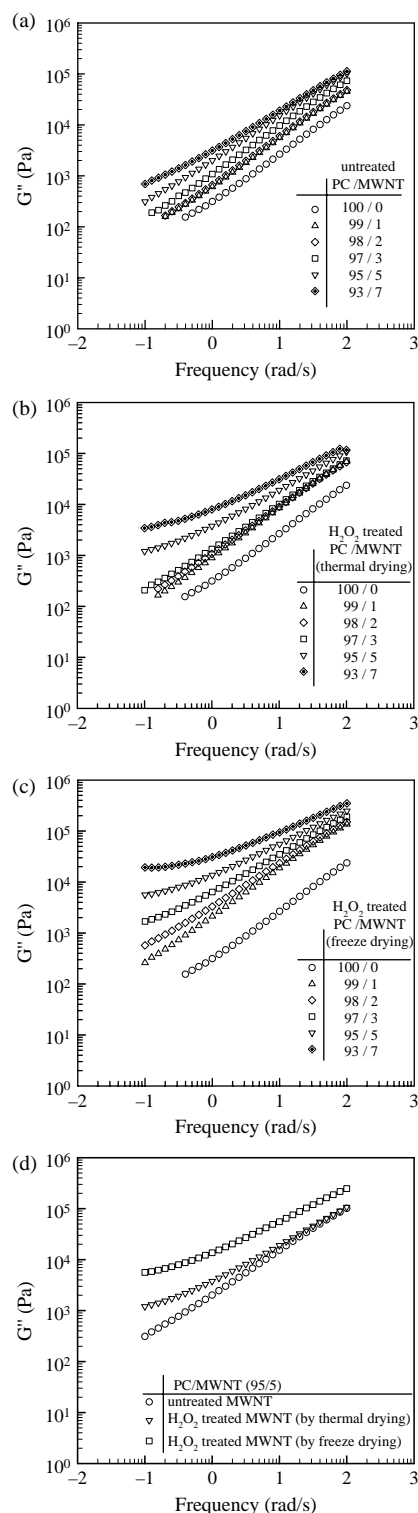


Fig. 4. Loss modulus (G'') of the PC and PC/MWNT composites at 260 °C: (a) untreated MWNT; (b) H_2O_2 treated MWNT (by thermal drying); (c) H_2O_2 treated MWNT (by freeze drying); (d) untreated vs H_2O_2 treated MWNT for the PC/MWNT (95/5 wt%) composites.

increase of the MWNT–MWNT network structure. Similar results were reported by Pötschke et al. [1] and Mitchell et al. [2] for the PC/MWNT and PS/SWNT composites, respectively. From Figs. 3–5, for the PC/MWNT (95/5, H_2O_2 treated,

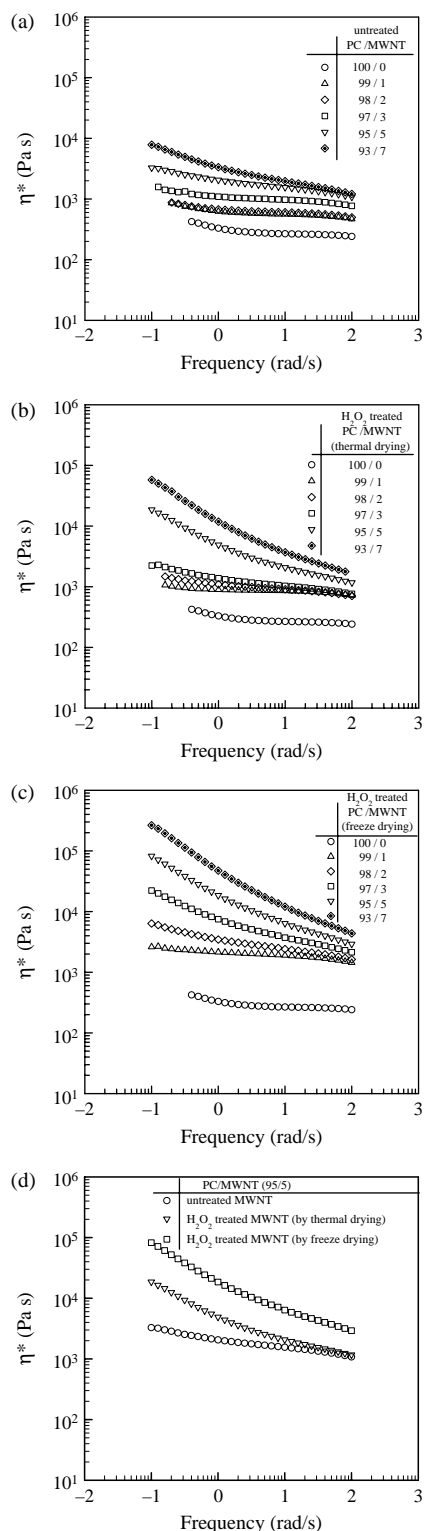


Fig. 5. Complex viscosity (η^*) of the PC and PC/MWNT composites at 260 °C: (a) untreated MWNT; (b) H_2O_2 treated MWNT (by thermal drying); (c) H_2O_2 treated MWNT (by freeze drying); (d) untreated vs H_2O_2 treated MWNT for the PC/MWNT (95/5 wt%) composites.

freeze drying) composites, the rheological properties increase significantly compared the PC/MWNT (95/5, H_2O_2 treated, thermal drying), which suggest that the rheological properties of the PC/MWNT composites are influenced by the

morphological behavior of the MWNT. From the above results of the morphological and rheological properties of the PC/MWNT composites, it is suggested that the rheological properties of the PC/MWNT composites are affected by the hydrodynamically percolated MWNT–MWNT network structure, which is related with the MWNT morphologies such as the degree of aggregation and aspect ratio of the MWNT.

From Figs. 3–5, for the PC/MWNT (untreated) composites, it has shown that the rheological properties such as storage and loss modulus, and complex viscosity increase with the MWNT content. At low frequency, the increase of the rheological properties of the PC/MWNT (untreated) composites is not as much as that of the PC/MWNT (H_2O_2 treated) composites. At high frequency, the rheological data shown in Figs. 3(d)–5(d) did not show significant difference between the PC/MWNT H_2O_2 treated and untreated composites compared that at low frequency. The increase of the rheological data of the PC/MWNT composites at high frequency suggests that the PC/MWNT interaction may exist between the PC and MWNT in the PC/MWNT composites. The rheological properties of polymer composites at high frequency region reflect the dynamics of polymer entanglement [2]. In our earlier studies, Sung et al. [3] reported the chain confinement of the PC in the PC/MWNT composites by the DMTA. Pötschke et al. [4] and Abdel-Goad and Pötschke [5] reported the temperature dependence of the rheological properties and the PC/MWNT interaction in the PC/MWNT composites. In their studies, Pötschke et al. [4] and Abdel-Goad and Pötschke [5] used the commercial masterbatch of the PC/MWNT composites. In this study, however, the rheological properties of the PC/MWNT composites were able to observe with the treatment of the MWNT in the PC/MWNT composites.

Fig. 6 shows the electrical conductivity of the PC/MWNT composites with the MWNT content. For the PC/MWNT (untreated) composites, the electrical conductivity shows the percolation threshold at about 5 wt% MWNT content. For the H_2O_2 treated MWNT (freeze drying) and H_2O_2 treated MWNT (thermal drying) composites with the PC, the electrical conductivity shows the percolation threshold at about 2 and 3 wt% MWNT content, respectively. Also, the values of the electrical conductivity of the PC/MWNT composites (H_2O_2 treated) show higher compared that of the PC/MWNT (untreated) composites with the MWNT composites. The behavior of the higher value of the electrical conductivity of the PC/MWNT (H_2O_2 treated) composites could be explained by the behavior of the rheological properties of the PC/MWNT (H_2O_2 treated) composites such that the increase of the rheological properties at low frequency is related to the increase of the percolated MWNT–MWNT network structure. In addition, the values of the electrical conductivity of the H_2O_2 treated MWNT (freeze drying) composites with the PC show higher compared that of the H_2O_2 treated MWNT (thermal drying) composites with the PC. From the above results of the morphological, rheological, and electrical properties of the PC/MWNT composites, it is suggested that the electrical and rheological properties of the PC/MWNT composites are affected by the MWNT–MWNT network

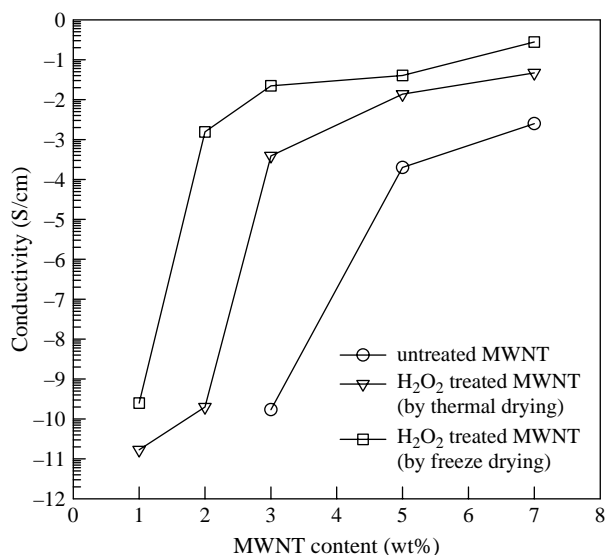


Fig. 6. Electrical conductivity of the PC/MWNT composites with MWNT content: (○) untreated MWNT; (▽) H₂O₂ treated MWNT (by thermal drying); (□) H₂O₂ treated MWNT (by freeze drying).

structure, which is related with the MWNT morphologies such as the degree of aggregation and aspect ratio of the MWNT.

4. Conclusions

In this study, the rheological and electrical properties of the PC/MWNT composites were investigated with the MWNT treatment and content. From the results of the TEM images of the H₂O₂ treated and untreated MWNT, it was observed that the degree of entanglement of the MWNT was decreased by treating with the H₂O₂. Also, the length of the H₂O₂ treated MWNT (thermal drying) observed to be shortened than that of the H₂O₂ treated MWNT (freeze drying) depending on the drying condition of the MWNT.

From the results of the rheological properties of the PC/MWNT composites, the storage and loss modulus, and complex viscosity of the PC/MWNT composites were increased with the MWNT content. For the PC/MWNT (H₂O₂ treated) composites, the rheological properties of the PC/MWNT composites increased significantly at low frequency, which suggested that the increase of rheological properties at low frequency could be due to the increase of the MWNT–MWNT network structure. For the PC/MWNT (H₂O₂ treated, freeze drying) composites, the rheological properties was increased compared that of the PC/MWNT (H₂O₂ treated, thermal drying) composites.

From the results of the electrical properties of the PC/MWNT composites, the values of the electrical conductivity of the PC/MWNT (H₂O₂ treated) composites showed

higher compared that of the PC/MWNT (untreated) composites with the MWNT content. The higher value of the electrical conductivity of the PC/MWNT (H₂O₂ treated) composites could be explained by the behavior of the rheological properties of the PC/MWNT (H₂O₂ treated) composites such that the increase of the rheological properties at low frequency is related to the increase of the percolated MWNT–MWNT network structure. From the preparation methods of the MWNT, the values of the electrical conductivity of the PC/MWNT (H₂O₂ treated, freeze drying) composites showed higher compared that of the PC/MWNT (H₂O₂ treated, thermal drying) composites.

From the above results of the morphological, rheological, and electrical properties of the PC/MWNT composites, it can be concluded that the rheological and electrical properties of the PC/MWNT composites are affected by the MWNT–MWNT network structure, which is related with the MWNT morphologies such as the degree of aggregation and aspect ratio of the MWNT.

Acknowledgements

This study was supported by research grants from the Ministry of Commerce, Industry, and Energy through the Materials and Component Technology Development Program.

References

- [1] Pötschke P, Fornes TD, Paul DR. *Polymer* 2002;43:3247–55.
- [2] Mitchell CA, Bahr JL, Arepalli S, Tour JM, Krishnamoorti R. *Macromolecules* 2002;35:8825–30.
- [3] Sung YT, Kum CK, Lee HS, Byon NS, Yoon HG, Kim WN. *Polymer* 2005;46:5656–61.
- [4] Pötschke P, Abdel-Goad M, Alig I, Dudkin S, Lellinger D. *Polymer* 2004; 45:8863–70.
- [5] Abdel-Goad M, Pötschke P. *J Non-Newton Fluid Mech* 2005;128:2–6.
- [6] Iijima S. *Nature* 1991;354:56–8.
- [7] Friend SO, Barber JJ. US Patent No. 5,611,964 March 18, 1997.
- [8] Shaffer MSP, Fan X, Windle AH. *Carbon* 1998;36:1603–12.
- [9] Shaffer MSP, Windle AH. *Adv Mater* 1999;11:937–41.
- [10] Sandler J, Shaffer MSP, Prasse T, Bauhofer W, Schulte K, Windle AH. *Polymer* 1999;40:5967–71.
- [11] Gong X, Liu J, Baskaran S, Voise RD, Young JS. *Chem Mater* 2000;12: 1049–52.
- [12] Jin Z, Pramoda KP, Xu G, Goh SH. *Chem Phys Lett* 2001;337:43–7.
- [13] Star A, Stoddart JF. *Macromolecules* 2002;35:7516–20.
- [14] Kumar S, Dang TD, Arnold FE, Bhattacharyya AR, Min BG, Zhang X, et al. *Macromolecules* 2002;35:9039–43.
- [15] Barrau S, Demont P, Peigney A, Laurent C, Lacabanne C. *Macromolecules* 2003;36:5187–94.
- [16] Treacy MMJ, Ebbesen TW, Gibson JM. *Nature* 1996;381:678–80.
- [17] Fischer JE, Dai H, Thess A, Lee R, Hanjani NM, Dehaas DL, et al. *Phys Rev B* 1997;55:R4921–R4.
- [18] Joo J, Lee CY. *J Appl Phys* 2000;88:513–8.