

Preparation of Multiwalled Carbon Nanotube/Nylon-6 Nanocomposites by *In Situ* Polymerization

Khalid Saeed, Soo-Young Park

Department of Polymer Science, Kyungpook National University, Buk-gu, Daegu 702-701, Republic of Korea

Received 11 March 2007; accepted 12 June 2007

DOI 10.1002/app.26942

Published online 30 August 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Multiwalled carbon nanotube/nylon-6 nanocomposites (MWNT/nylon) were prepared by *in situ* polymerization, whereby pristine MWNTs (P-MWNTs) and purified MWNTs (A-MWNTs) were used as reinforcing materials. The A-MWNTs were purified by nitric acid treatment, which introduced the carboxyl groups (COOH) to the MWNTs. The SEM micrographs from the fractured surfaces of the nanocomposites showed that the A-MWNTs were well dispersed in A-MWNT/nylon as compared to the P-MWNTs in P-MWNT/nylon. The percolation thresholds of P-MWNT/nylon and A-MWNT/nylon, which were studied by rheological properties, were found at ~ 1 wt % of the MWNTs. The conductivity of P-MWNT/nylon and A-MWNT/nylon were 3.15×10^{-5} and 7.46×10^{-5} S/cm by the loading of 5 and 7 wt % of MWNTs, respectively. Differ-

ential scanning calorimetry (DSC) showed that the crystallization temperatures of P-MWNT/nylon and A-MWNT/nylon (195°C) increased more than that of pure nylon (189°C) due to the nucleation effect of MWNTs. Wide-angle X-ray analysis indicated that the incorporation of MWNTs into the nylon matrix resulted only in α -crystalline structure, which were quite different from those reported for the clay/nylon nanocomposite (show both α - and γ -crystals). It might be due to the different geometry between the MWNTs and the nanoclay platelets, which have one and two-dimensional geometry, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3729–3735, 2007

Key words: *in situ* polymerization; nylon-6; MWNTs; composite; WAXS

INTRODUCTION

Since their discovery,¹ carbon nanotubes (CNTs), including single-wall carbon nanotubes (SWNTs) and multiwall carbon nanotubes (MWNTs), have attracted a great deal of interest due to their unique chemical, electrical, thermal, and mechanical properties. The carbon nanotubes have high elastic modulus which is up to 1 TPa. The thermal conductivity is about twice that of diamonds and the electric current-carrying capacity is 1000 times higher than that of copper wires.² Because of these unique properties, researchers have paid a great deal of attention in utilizing these remarkable characteristics for applications such as polymeric composites, hydrogen storage,³ actuators,⁴ field-emission materials,⁵ chemical sensors,⁶ and nanoelectronic devices.⁷

The incorporation of CNTs into polymer matrix has remarkably improved the mechanical, electrical, and thermal properties of the resulting composites, compared to other reinforcing agents such as glass fibers, metal flakes, hollow microspheres, and carbon nanofibers due to their high aspect ratio.⁸ The development of CNT reinforced composites however, has been impeded due to difficulty in dispersing CNTs

into the polymer matrices. This is because they are present in the form of bundles and ropes due to a van der Waal attraction among the tubes in combination with their high surface area. In addition, polymeric materials, whose viscosity levels are relatively higher than low molar mass materials, have difficulty in penetrating the CNT bundles. To overcome this CNT dispersion problem, chemical functionalization on the CNT wall was used, which not only disperses CNTs in an organic solvent,⁹ water,^{10,11} or polymer matrix,¹² but also attaches polymeric materials chemically to the surfaces of CNTs.¹³ Other techniques such as the adsorption of amines,¹⁴ radiofrequency glow-discharge plasma modification,¹⁵ and wrapping¹⁶ are used in dispersing CNTs into polymer matrices.

Nylon-6 has been widely used as an important engineering plastic and synthetic fiber due to its excellent load bearing (strength and stiffness) capability at elevated temperature, resistance to chemical and abrasions, toughness and resistance to impact, and low-coefficient of friction.¹⁷ Nylon-6 displays interesting polymorphism behavior and its crystalline structure was found to be α -Phase and γ -phase crystals.¹⁸ The α -Phase is thermodynamically more stable than the γ -phase because it consists of fully extended planar zigzag chains, by which adjacent, antiparallel chains are joined by hydrogen bonds and can be obtained by slow cooling from the melt. The γ -phase is composed of pleated sheets of parallel chains,

Correspondence to: S.-Y. Park (psy@knu.ac.kr).

which are joined by hydrogen bonding. The γ -phase is due to fast cooling from the melt or fiber spinning at high speed.¹⁹ Various researchers incorporated fillers (like nanoclays, CNTs, etc.) into the nylon-6 in order to study their effect on the properties such as thermal, mechanical, electrical, and crystallization behavior of nylon-6. Goa et al.^{20,21} prepared single walled carbon nanotubes/nylon-6 (SWNT/nylon) composites by *in situ* polymerization, in which they used carboxyl and amide terminated single walled carbon nanotubes (SWNT-COOH and SWNT-CONH₂). They made the composite fibers using a custom-made spinneret assembly and their morphology and mechanical properties were studied. Young's modulus, tensile strength, and the thermal stability of the reinforced composite fibers improved significantly to those of neat nylon-6 fibers.

In the present study, we prepared nylon and its composites by *in situ* polymerization, whereby pristine MWNTs (P-MWNTs) and purified MWNTs (A-MWNTs) were used as reinforcing materials. The A-MWNTs were purified using nitric acid, which also introduced the carboxylic group (COOH) onto the MWNTs and showed better compatibility with nylon as compared to the P-MWNTs. Both composite systems were analyzed and properties such as thermal stability, electrical properties and crystallization behavior, were compared with those of neat nylon.

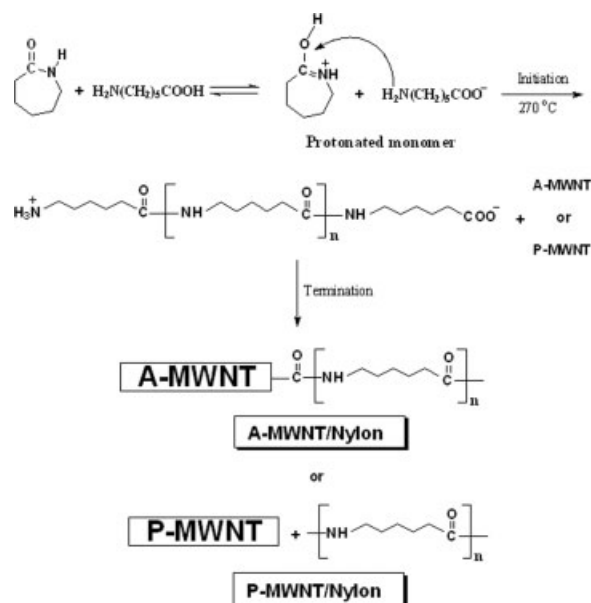
EXPERIMENTAL

Materials

ϵ -Caprolactam (99% purity) and 6-amino hexanoic acid (99% purity) were purchased from Aldrich and Sigma, respectively, and used as received. Nitric acid (64–66% purity) was purchased from Ducksan Chemicals. MWNTs (CVD MWNT) were supplied by Nanomirea[®] and manufactured by thermal chemical vapor deposition.²² The diameter and length of the CVD MWNTs were 20 ~ 40 nm and 30 ~ 40 μ m, respectively, and its purity was higher than 95 vol %.

Purification of MWNTs

MWNTs were purified by acid treatment, whereby 3 g of MWNTs were sonicated in 300 mL of 5M HNO₃ for 2 h and then refluxed at 120°C for 12 h. The A-MWNTs were separated from HNO₃ by filtration and then washed with distilled water until free from acid. The A-MWNTs were dried in a vacuum oven and stored for further use. Carboxyl groups were also introduced to the MWNTs during purification with HNO₃.²³



Scheme 1 *In situ* polymerization of P-MWNT/nylon and A-MWNT/nylon nanocomposites.

IN SITU POLYMERIZATION OF MWNT/NYLON NANOCOMPOSITES

Scheme 1 shows the *in situ* polymerization of P-MWNT/nylon and A-MWNT/nylon nanocomposites. The synthetic procedure for the P-MWNT/nylon nanocomposites is as follows: A known percentage of P-MWNT and 24 g of ϵ -caprolactam were taken in a three-neck round bottom flask. The mixture was sonicated for 1 h at 120°C to produce a homogeneous dispersion of P-MWNTs in ϵ -caprolactam, and then 2.4 g of 6-amino hexanoic acid were added to the suspension. The flask was transferred to a preheated oil bath (270°C) and heated for 6 h with mechanical stirring, under a nitrogen atmosphere. The same procedure was used for the A-MWNT/nylon nanocomposites.

CHARACTERIZATION

SEM analysis

The SEM micrographs of the platinum-coated fractured surfaces (broken in the liquid nitrogen) of the MWNT/nylon nanocomposites were analyzed using a Hitachi S-570 scanning electron microscope (SEM).

Thermal properties

The thermal properties of the nylon and the composites were studied by TGA and DSC. The TGA thermograms of the composites were obtained in a nitrogen atmosphere, at a heating rate of $20^\circ\text{C}/\text{min}$ between 25°C and 900°C , using a TA4000/Auto DSC 2910 System. The DSC analyses were carried out using a Dupont 2000 Thermal Analyzer. A specific

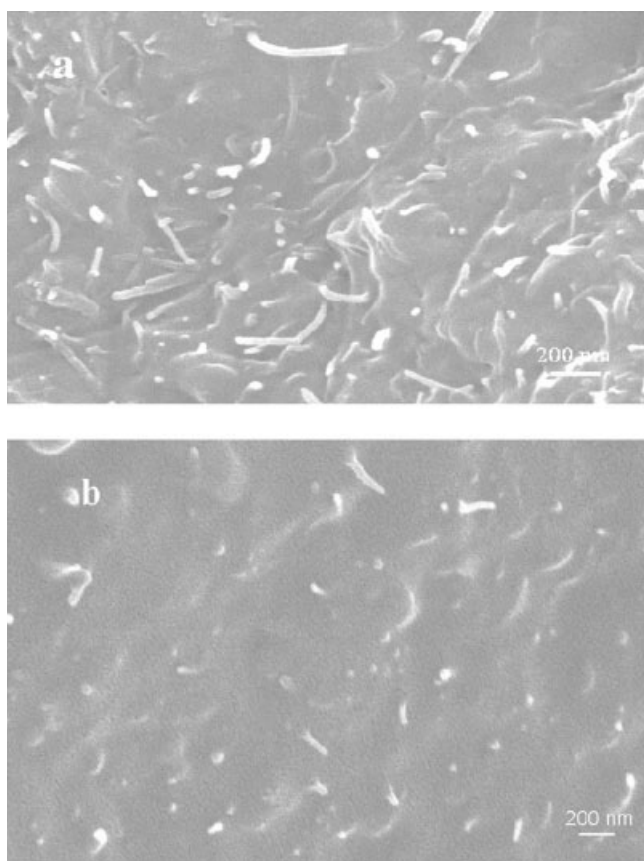


Figure 1 SEM images of the fractured surfaces of (a) P-MWNT(5 wt %)/nylon and (b) A-MWNT (5 wt %)/nylon.

amount of sample was sealed in an aluminum sample pan and prepared by compression molding. DSC thermograms were obtained at heating and cooling rates of 10°C/min, under a nitrogen atmosphere in order to diminish oxidation. The nylon and its composites were preheated to 250°C and the sample was maintained there for 5 min to remove the previous thermal history.

Rheometer measurements

The rheological properties were studied using a UDS 200 Rheometer (Physica[®]). The measurements were conducted using cone and plate geometry with the diameter of 25 mm and the cone angle of 1°. All samples (0.3-mm thick) were measured at 250°C in an angular frequency range between 0.1 and 100 rad/s and with 5% strain.

Electrical conductivity measurements

The conductivity of the film samples was measured at 25°C with a four-point probe method using a HMS-3000 (Ecopia[®]). The dimensions of the samples were ~ 15 (length) × 15 (width) × 0.15 (thickness) mm³ and their ends were coated with an indium paste to ensure good electrical contact. The measurable

conductivity range in this instrument was between 10³ and 10⁻⁶ S/cm.

Mechanical properties

The tensile properties were measured using an Instron (Model M 4465). The tests were carried out at room temperature with crosshead speed of 5 mm/min. The sample dimensions were 60 (gauge length), 5 (width), ~2 (thickness) mm³.

Wide angle X-ray scattering

Synchrotron wide angle X-ray scattering (WAXS) measurements were conducted on Beamline 4C2 at Pohang Light Source (Korea) where a W/B4C double multilayer monochromator delivered monochromatic X-rays with a wavelength (λ) of 0.1542 nm and a resolution of $\Delta\lambda/\lambda = 0.01$. A flat Au mirror was used to reject higher harmonics from the beam. A 2D CCD camera (Princeton Instruments, SCX-TE/CCD-1242) was used to collect the X-rays. The nylon and its composites were heated to 250°C, and maintained for 5 min, then cooled to room temperature, in order to remove the previous thermal history. Cooling experiments were performed on a Melter hot stage at a cooling rate of 6°C/min between 250 and 70°C. The sample thickness was about 5 mm, and exposure time was 10 s. Two-dimensional X-ray patterns were integrated along the azimuthal direction in order to provide one-dimensional curves at each temperature.

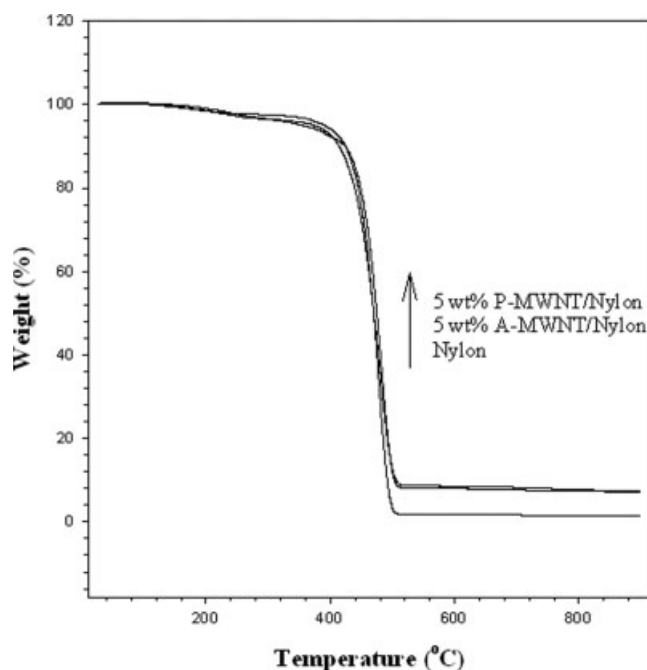


Figure 2 TGA thermograms of nylon, P-MWNT(5 wt %)/nylon, and A-MWNT(5 wt %)/nylon.

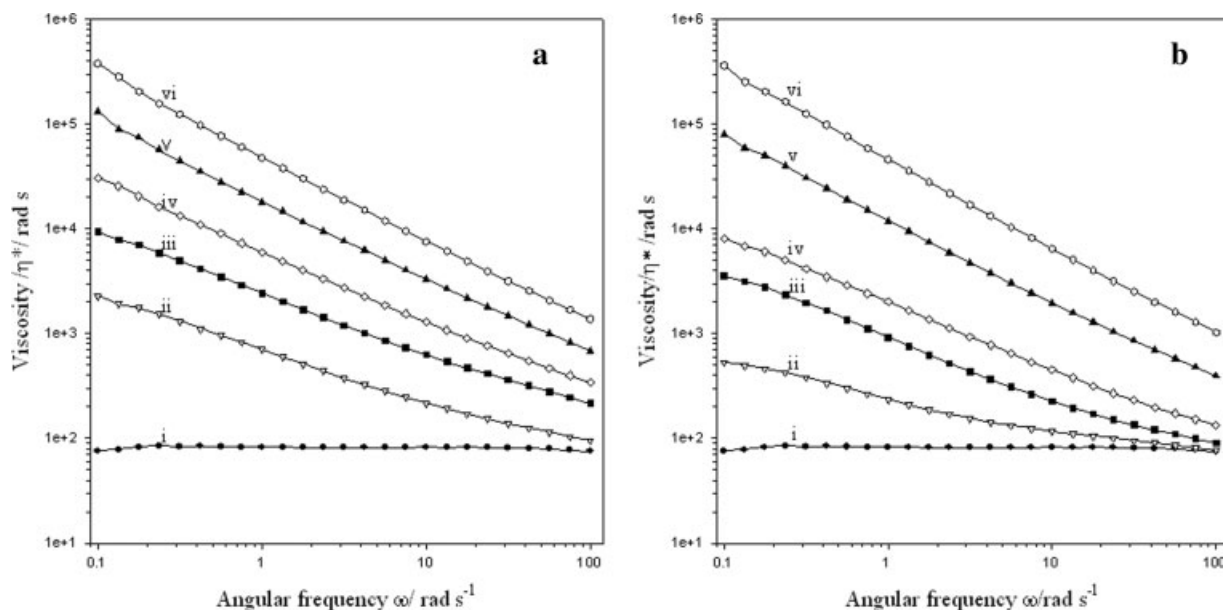


Figure 3 Complex viscosities (η^* s) of (a) P-MWNT/nylon and (b) A-MWNT/nylon; weight % of MWNTs (i) 0, (ii) 1, (iii) 2, (iv) 3, (v) 5, (vi) 7.

RESULTS AND DISCUSSION

Dispersion of MWNTs in nylon

Figure 1 shows the SEM microphotographs of the fractured surfaces of the P-MWNT(5 wt %)/nylon and A-MWNT(5 wt %)/nylon. It was found that the A-MWNTs in the A-MWNT(5 wt %)/nylon were well dispersed as compared to the P-MWNTs in the P-MWNT(5 wt %)/nylon. This dispersion of MWNTs in the A-MWNT/nylon is due to their chemical modification during purification with nitric acid treatment. This enables the MWNTs to be more compatible with nylon.^{10,24} Both P-MWNT/nylon and A-MWNT/nylon nanocomposites (contain 5 wt % MWNT) which was prepared by *in situ* polymerization, show better dispersion compared to the CNT/nylon prepared by melt compounding.^{25,26}

Thermal properties

The thermogravimetric analyses (TGA) of nylon, P-MWNT(5 wt %)/nylon and A-MWNT(5 wt %)/nylon were performed in a nitrogen atmosphere and the thermograms are shown in Figure 2. Pure nylon started to lose weight at about 400°C and was completely decomposed at 500°C. Both P-MWNT(5 wt %)/nylon and A-MWNT(5 wt %)/nylon composites were also decomposed approximately at about 500°C and the residual amount, which was contributed by the MWNTs in the composites, remained at higher temperatures.

Melt viscosities

Figure 3 shows complex viscosities (η^* s) of P-MWNT/nylon and A-MWNT/nylon, as a function of frequency with different amounts of MWNTs. The η^* s at low frequencies increased as the MWNT content increased for P-MWNT/nylon and A-MWNT/nylon. Both composite systems showed profound shear-thinning behavior when the amount of MWNTs increased. The percolation threshold, which represents a starting MWNT content of a three-dimensional network, was 1 wt % for both P-MWNT/nylon and A-MWNT/nylon.^{24,27,28} We found similar behavior for η' and η'' with η^* .

DC conductivity measurements

By using a four-point probe method, the conductivities of film samples were measured as a function of the MWNT loads (Table I). The P-MWNT/nylon and A-MWNT/nylon nanocomposite films showed electrical conductivities 3.15×10^{-5} and 7.46×10^{-5} S/cm when 5 and 7 wt % MWNTs were incorporated into

TABLE I
Conductivity of P-MWNT/Nylon and A-MWNT/Nylon Films as a Function of MWNT Amounts

Sample	Conductivity (S/cm)
5 wt % P-MWNT/nylon	3.15×10^{-5}
5 wt % A-MWNT/nylon	—
7 wt % P-MWNT/nylon	1.44×10^{-5}
7 wt % A-MWNT/nylon	7.46×10^{-5}

TABLE II
Mechanical Properties of Nylon and MWNTs/Nylon Nanocomposites

Samples	Tensile strength (MPa)	Modulus (MPa)	Elongation at the break (%)
Nylon	18.924 ± 0.34	471.09 ± 16.51	100.75 ± 9.21
P-MWNT/nylon			
1 wt % MWNTs	18.02 ± 4.156	573.17 ± 92.01	35.95 ± 15.22
2 wt % MWNTs	22.46 ± 0.64	657.76 ± 8.69	57.81 ± 16.61
5 wt % MWNTs	21.18 ± 1.80	747.90 ± 18.83	13.39 ± 6.28
7 wt % MWNTs	24.08 ± 1.87	921.30 ± 96.62	10.78 ± 2.47
A-MWNT/nylon			
1 wt % MWNTs	21.60 ± 2.08	631.87 ± 58.25	23.99 ± 7.23
2 wt % MWNTs	19.28 ± 2.61	703.97 ± 27.70	18.72 ± 9.07
5 wt % MWNTs	23.07 ± 7.56	834.61 ± 58.32	27.143 ± 11.99
7 wt % MWNTs	22.49 ± 2.67	869.20 ± 93.70	10.83 ± 1.12

the nylon matrix, respectively. Conductivity for neat nylon was not detected within detection limit (below 10^{-6} S/cm). A-MWNT/nylon showed electrical conductivity when 7 wt % MWNTs (higher than MWNT (5 wt %) used in P-MWNT/nylon) were incorporated into the nylon matrix. It might be due to the acid treatment, which destroyed the π -bonding of the surface of MWNTs during purification.

Mechanical properties

Table II shows the tensile properties of the neat nylon and the MWNT/nylon nanocomposites, which improved by incorporation of MWNTs into the nylon matrix. The tensile strength and modulus were increased from 18 (pure nylon-6) to 24 and 22 MPa (P-MWNT/nylon and A-MWNT/nylon) and from 471 (pure nylon-6) to 921 and 869 MPa (P-MWNT/nylon and A-MWNT/nylon), respectively, by the

incorporation of 7 wt % MWNTs into the nylon matrix. However, elongation at the break (which indicate the flexibility of the material) of neat nylon (100 MPa) was higher than MWNT/nylon nanocomposites. Also elongation at the break decreased gradually when the amount of MWNTs increased in the composites (7 wt % MWNT/nylon show 10 MPa). This implies that MWNTs make nylon stronger but less flexible. The increase in tensile strength and modulus, and decrease of elongation at the break for CNT/nylon was also reported by other researchers.^{20,29,30}

Effect of MWNTs on crystallization behavior

Figure 4 shows the DSC thermograms of nylon, P-MWNT/nylon and A-MWNT/nylon, as a function of the amount of MWNTs. Pure nylon showed only a melt-crystallization peak (T_{C1}) (crystallization from the melt state upon cooling) at about 189°C. The T_{C1} of

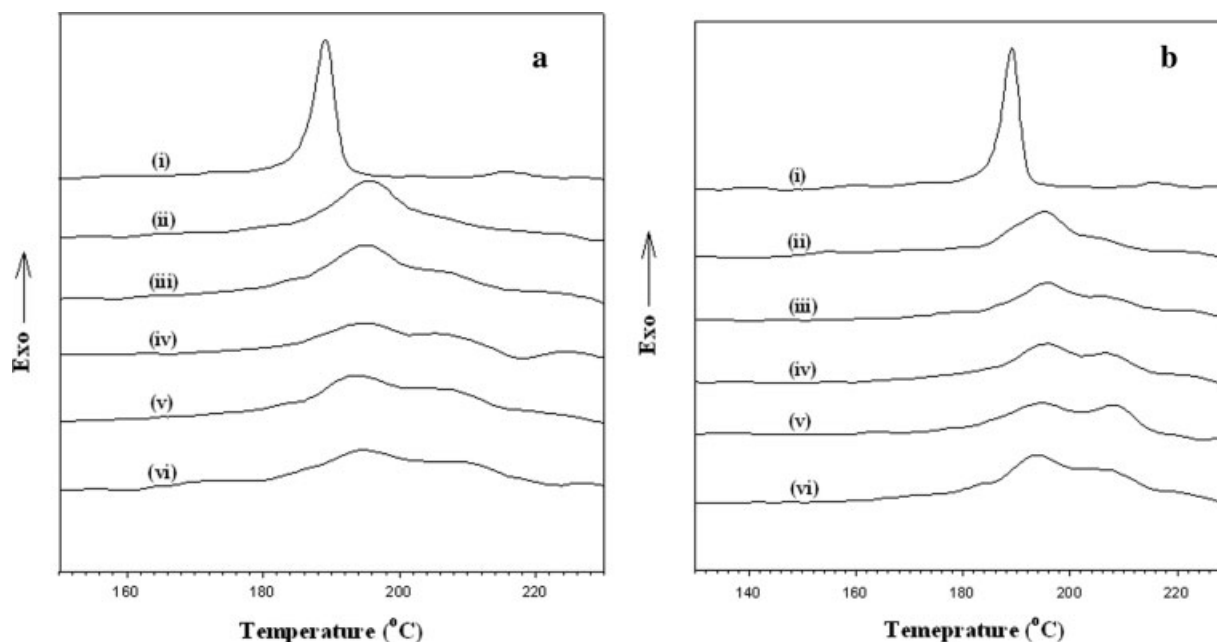


Figure 4 DSC cooling curves of (a) P-MWNT/nylon and (b) A-MWNT/nylon; (i) 0, (ii) 1, (iii) 2, (iv) 3, (v) 5, (vi) 7.

P-MWNT/nylon and A-MWNT/nylon shifted to a higher temperature (about 195°C). The increase of T_{C1} can be explained by the assumption that both MWNTs and A-MWNTs act as efficient nucleating agents for the crystallization of nylon matrix and the crystallization rate increased compared to that of neat nylon.^{31,32} In the case of composite samples, a new crystallization peak (T_{C2}) was observed at high temperature (about 208°C). Phang et al.³³ and Wu et al.³⁴ also observed similar crystallization behavior for nylon-6/MWNT and nylon-6/montmorillonite clay, respectively.

Figure 5 shows the wide-angle, X-ray patterns of pure nylon, P-MWNT/nylon and A-MWNT/nylon,

which were crystallized from the melt state (250°C) to 70°C. Pure nylon shows two peaks at about $2\theta = 20$ and 23°, which indicate that the α -crystalline phase is predominant in our experimental conditions.³⁵ The α -crystalline phase consists of an anti-parallel arrangement of chains, which is often attributed to crystallites consisting of folded chains. WAXS patterns of P-MWNT/nylon and A-MWNT/nylon [Fig. 5(b,c)] show similar peaks to those of pure nylon, which reveal that composite samples contain only the α -crystalline phase. By contrast, the γ -crystalline phase was clearly observed for the clay/nylon nanocomposites, with the addition of nanoclay in the

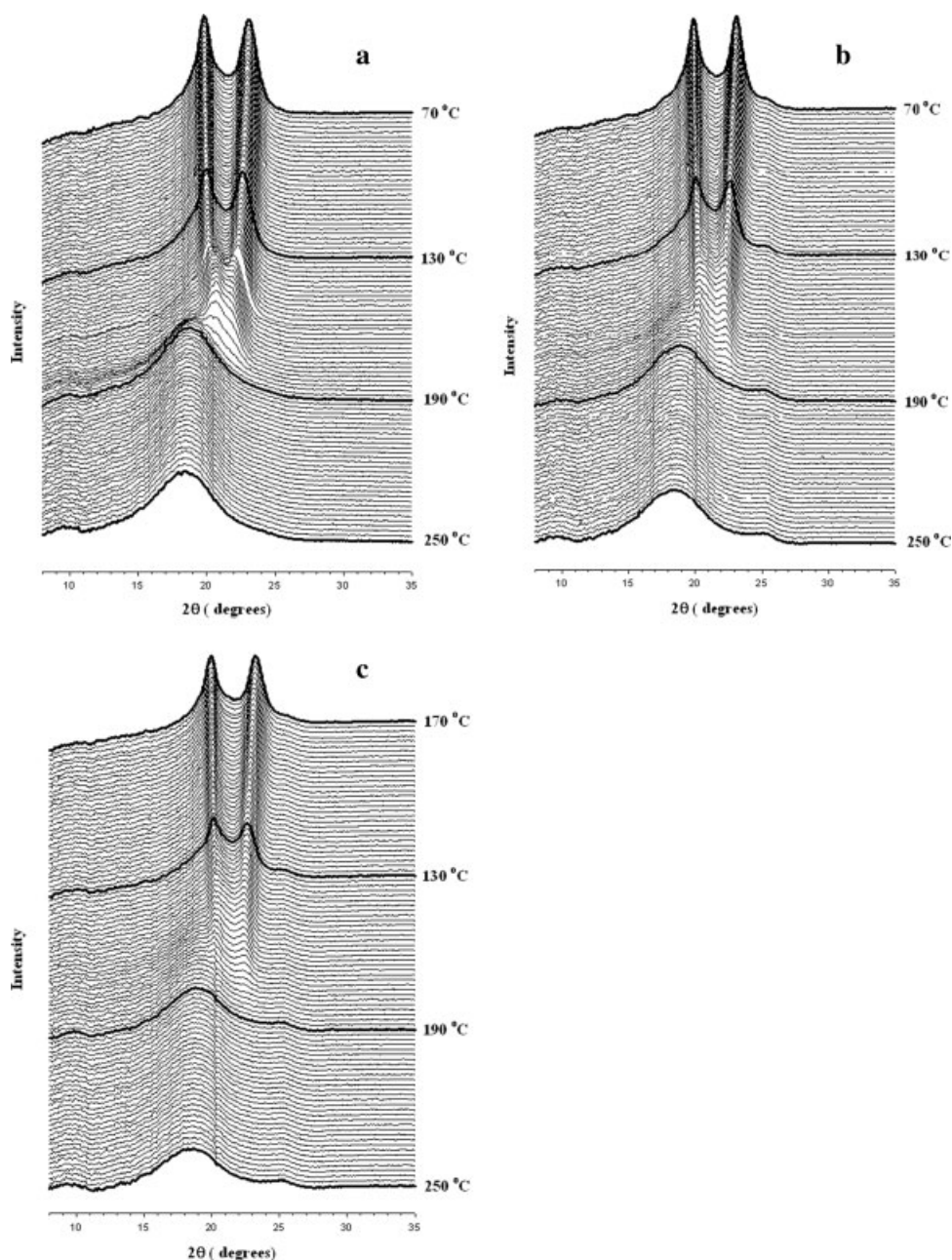


Figure 5 WAXS patterns of (a) Nylon, (b) P-MWNT(5 wt %)/nylon and (c) A-MWNT(5 wt %)/nylon.

nylon matrix.^{36–38} It is proposed that the presence of two-dimensional (2D) layered clay sheets disrupts the α -crystallite formation and results in the less ordered γ -crystal phase.³⁹ In the case of MWNT/nylon-6, however, the nanoscale confinement effect from the 1D geometry of CNTs, on the crystallization of nylon seems less pronounced than that of nanoclay platelets (2D geometry). That is, the constraints from the CNTs imposed on the polymer chains are less than those of the nanoclay sheets. The CNTs may only provide nucleation sites in the nylon matrix, which encourage the formation of α -crystalline phase.

CONCLUSION

MWNT-reinforced nylon (P-MWNT/nylon and A-MWNT/nylon) was prepared by an *in situ* polymerization method, in order to study the effect of the pristine MWNTs and purified MWNTs on the thermal, electrical properties, and crystallization behavior of nylon. The percolation thresholds of P-MWNT/nylon and A-MWNT/nylon, which were studied by rheological properties, were found to be ~ 1 wt % of the MWNTs. The conductivity of P-MWNT/nylon and A-MWNT/nylon was 3.15×10^{-5} and 7.46×10^{-5} S/cm, with the loading of 5 and 7 wt % of MWNTs, respectively. The crystallization behavior of nylon, P-MWNT/nylon and A-MWNT/nylon was studied by DSC and WAXS. The DSC results indicate that the crystallization temperature of nylon increased by the incorporation of MWNTs in the polymer matrix due to their heterogeneous nucleation effect. Also, a new crystallization peak T_{C2} , was observed at high temperatures (about 208°C) along with the main crystallization peak T_{C1} for P-MWNT/nylon and A-MWNT/nylon. These results are closely related to the incorporation of MWNTs. WAXS analysis indicated that the incorporation of MWNTs into the nylon matrix, resulted only α -crystalline structures which are quite different from those reported for clay/nylon nanocomposites (shows both α - and γ -crystals). Such differences might be due to the differences in nanofiller morphology or geometry.

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2006-311-D00426). And synchrotron work was supported in part by the Ministry of Science & Technology (MOST), by POSCO, by the Center for Integrated Molecular System (Korea Science & Engineering Foundation), by the KISTEP (Basic Research Grant of Nuclear Energy, MOST).

References

- Iijima, S. *Nature* 1991, 354, 56.
- Bin, Y.; Kitanaka, M.; Zhu, D.; Matsuo, M. *Macromolecules* 2003, 36, 6213.
- Liu, C.; Fan, Y. Y.; Liu, M.; Cong, H. T.; Cheng, H. M.; Dresselhaus, M. S. *Science* 1999, 286, 1127.
- Baughman, R. H.; Cui, C.; Zakhidov, A. A.; Iqbal, Z.; Barisci, J. N.; Spinks, G. M.; Wallace, G. G.; Mazzoldi, A.; Rossi, D. D.; Rinzler, A. G.; Jaschinski, O.; Roth, S.; Kertesz, M. *Science* 1999, 284, 1340.
- De Heer, W. A.; Chatelain, A.; Ugarte, D. *Science* 1995, 270, 1179.
- Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science* 2002, 287, 622.
- Tans, S. J.; Verschueren, A. R. M.; Dekker, C. *Nature* 1998, 393, 49.
- Cui, S.; Canet, R.; Derre, A.; Couzi, M.; Delhaes, P. *Carbon* 41, 2003, 797.
- Bahr, J. R.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J Am Chem Soc* 2001, 123, 6536.
- Pompeo, F.; Resasco, D. E. *Nano Lett* 2002, 2, 369.
- Shafer, M. S. P.; Fan, X.; Windle, A. H. *Carbon* 1998, 36, 1603.
- Lee, H.-J.; Oh, S.-J.; Choi, J.-Y.; Kim, J. W.; Han, J.; Tan, L.-S.; Baek, J.-B. *Chem Mater* 2005, 17, 5057.
- Baek, J.-B.; Lyons, C. B.; Tan, L.-S. *Macromolecules* 2004, 37, 8278.
- Kong, J.; Dai, H. *J Phys Chem B* 2001, 105, 2890.
- Chen, Q.; Dai, L.; Gao, M.; Huang, S.; Mau, A. *J Phys Chem B* 2001, 105, 618.
- O'Connell, M. J.; Boul, P.; Ericson, L. M.; Huffman, C.; Wang, Y.; Haroz, E. Kuper, C.; Tour, J.; Ausman, K. D.; Smalley, R. E. *Chem Phys Lett* 2001, 342, 265.
- Mark, J. E. *Polymer data handbook*; 1998, pp. 180.
- Bunn, C. W.; Garner, E. V. *Proc R Soc Lond A* 1947, 189, 39.
- Brucato, V.; Grippa, S.; Piccarolo, S.; Titomanlio, G. *Polym Eng Sci* 1991, 24, 1411.
- Goa, J.; Itkis, M. E.; Yu, A.; Bekyarova, E.; Zhao, B.; Haddon, R. C. *J Am Chem Soc* 2005, 127, 3847.
- Goa, J.; Zhao, B.; Itkis, M. E.; Bekyarova, E.; Hu, H.; Kranak, V.; Yu, A.; Haddon, R. C. *J Am Chem Soc* 2006, 128, 7492.
- [<http://www.nanomirea.co.kr>].
- Niyogi, S.; Hamon, M. A.; Hu, H.; Zhao, B.; Bhowmik, P.; Sen, R.; Itkis, M. E.; Haddon, R. C. *Acc Chem Res* 2002, 35, 1105.
- Saeed, K.; Park, S.-Y. *J Appl Polym Sci* 2007, 104, 1957.
- Li, J.; Fang, Z.; Tong, L.; Gu, A.; Liu, F. *J Appl Sci: Part B: Polym Phys* 2006, 44, 1499.
- Chen, G.-X.; Kim, H.-S.; Park, B. H.; Yoon, J.-S. *Polymer* 2006, 47, 4760.
- Pötschke, P.; Abdel-Goad, M.; Alig, I.; Dudkin, S.; Lellinger, D. *Polymer* 2004, 45, 8863.
- Liu, C.; Zhang, J.; He, J.; Hu, G. *Polymer* 2003, 44, 7529.
- Zhao, C.; Hu, G.; Justice, R. W.; Schaefer, D.; Zhang, S.; Yang, M. C.; Han, C. *Polymer* 2005, 46, 5125.
- Zhang, W. D.; Shen, L.; Phang, I. Y.; Liu, T. *Macromolecules* 2004, 37, 256.
- Valentini, L.; Biagiotti, J.; López-Manchado, M. A.; Santucci, S.; Kenny, J. M. *Polym Eng Sci* 2004, 44, 303.
- Liu, X.; Wu, Q. *Polymer* 2001, 42, 10013.
- Phang, I. Y.; Ma, J.; Shen, L.; Liu, T.; Zhang, W.-D. *Polym Int* 2006, 55, 71.
- Wu, Q.; Liu, X.; Berglund, L. A. *Macromol Rapid Commun* 2001, 22, 1438.
- Lincoln, D. M.; Vaia, R. A.; Wang, Z.-G.; Hsiao, B. S.; Krishnamoorti, R. *Polymer* 2001, 42, 9975.
- Park, S.-Y.; Cho, Y.-H. *Macromol Res* 2005, 13, 156.
- Lincoln, D. M.; Vaia, R. A.; Wang, Z.-G.; Hsiao, B. S. *Polymer* 2001, 42, 1621.
- Park, S.-Y.; Cho, Y.-H.; Vaia, R. A. *Macromolecules* 2005, 38, 1729.
- Liu, T.; Phang, I. Y.; Shen, L.; Chow, S. Y.; Zhang, W.-D. *Macromolecules* 2004, 37, 7214.