Macromol. Symp. **2005**, *224*, 287-295

Novel Carbon Nanotube/Poly(L-lactic acid) Nanocomposites; Their Modulus, Thermal Stability, and Electrical Conductivity

Sung-Il Moon,[1] *Fengzhe Jin,*[1] *Cheol-jin Lee,*[2] *Sadami Tsutsumi,*[1] *Suong-Hyu Hyon**[1]

[1] Institute for Frontier Medical Sciences, Kyoto University, 53 Kawahara-cho, Shogoin, Sakyo-ku, Kyoto 606-8507, Japan
Fax:(+81) 75 751 4141; E-mail: biogen@frontier.Kyoto-u.ac.jp
[2] Department of Nanotechnology Hanyang University, 17 Hanengdang-dong, Seongdong-gu, Seoul 133-791, Korea

Summary: The interest in poly(L-lactic acid)(PLLA) has been increasing in recent years because this polymer is made from renewable resources and its properties are benign to the environment. Carbon nanotubes(CNTs) have shown exceptional stiffness and strength and remarkable thermal and electrical properties, which make them ideal candidates for the development of multifunctional material systems. In this study, mechanical and thermal properties as well as the electrical conductivity of CNTs/PLLA nanocomposites were investigated. Our study of the mechanical properties of these nanocomposites indicates that the tensile strength and ultimate elongation decreased, but Young's modulus slightly increased from 1 GPa to 2.5 GPa. Embedding the CNTs into the polymer matrix improves the thermal stability of the polymer. The thermogravimetric analysis (TGA) results of PLLA and the 3 wt% CNTs/PLLA nanocomposites in air show initial weight loss at the same temperature as PLLA, but the decomposition temperature for the nanocomposite is approximately 10℃ higher than that of PLLA. Similar results were found for the other CNTs/PLLA composites (5, 10 wt%). In addition, electrical conductivity and electromagnetic wave shielding effect was also investigated.

Keywords: biodegradable; carbon nanotubes (CNTs); multiwalled carbon nanotubes (MWCNTs); nanocomposites; poly(L-lactic acid) (PLLA)

Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 by Sumio Iijima at NEC Laboratories, Japan, during their studies of fullerene material by TEM, carbon nanotubes have been found to exhibit outstanding physical properties for a wide range of potential applications.[1] CNTs exhibit remarkable intrinsic properties such as high mechanical strength,[2] structurally dependent electrical conductivity[3,4] and thermal conductivity.[5]

 DOI: 10.1002/masy.200550625

This combination of properties makes them a very interesting material. It is also believed that the incorporation of CNTs into polymer matrices should lead to composites with unique properties.[6] Accordingly, many polymers are presently being investigated as host matrices for CNTs and the resulting composites are being assessed for a number of properties such as flame-retardant behavior[7], electrical conductivity[8,9] and electrostatic charging behavior[10].

Recent experimental results[2,11,12] and theoretical studies[13,14] have demonstrated that individual CNTs have extremely high Young's modulus (about 1.2 TPa) and flexibility. Moreover, mechanical properties (bending modulus) depend on the quality[15] and the diameter[16] of the CNTs. It is thus tempting to use CNTs for mechanical reinforcement and to obtain new materials with unusual mechanical properties. However, the ultimate performance of such materials is expected to depend strongly on their ability to transfer the load from the host matrix to the CNTs.[10,17] This ability is directly related to the possibility of achieving homogeneously dispersed nanocomposites and the ability to control the nature of the interactions between the CNTs and the polymer chains.

Poly(L-lactic acid) (PLLA) is a crystalline polymer having its T_m around 180℃. This polymer is known to be a biocompatible and biodegradable polyester derived from renewable resources. Because of these characteristics, PLLA has been utilized for surgical implant materials and drug delivery systems[18-25] as well as commodity applications[26]. In both of these applications, it is important that PLLA has a broad range of physical properties and functions. PLLA has good mechanical properties, thermal plasticity and biocompatibility, and is readily fabricated. These characteristics make it a promising polymer for various end-use applications. Thus, the intrinsic properties of PLLA, coupled with knowledge of how such properties can be improved to achieve compatibility with thermoplastics processing, manufacturing, and end-use requirements has fuelled technological and commercial interest in PLLA.

In this paper, multiwalled carbon nanotube (MWCNTs)/PLLA nanocomposites have been prepared by direct application of ultrasonic energy in a solution of PLLA in chloroform. We wish to report various properties of MWCNTs/PLLA nanocomposites, including thermal and mechanical properties, along with their electrical properties.

Materials and Methods

Materials. L-lactic acid as a 90 wt% aqueous solution, was supplied by Wako Pure

Chemical Industries, Ltd. (Tokyo). Tin (II) chloride dihydrate ($SnCl_2$-$2H_2O$) was purchased from Nacalai Tesque Co. (Kyoto). The PLLA sample (weight-average molecular weight M_w = 3.0 x 10^5; polydispersity index M_w/M_n = 1.7) was prepared by a melt/solid state polycondensation method according to our previous papers[27-30]. The aligned MWCNTs sample have been synthesized by pyrolysis of iron pentacarbonyl ($Fe(CO)_5$) and acetylene (C_2H_2) mixtures in a simply designed horizontal quartz tube reactor. The growth rate and the crystallinity of carbon nanotubes were enhanced by increasing the flow rate of Ar carrier gas. It was noted that the growth rate was dramatically increased by adopting C_2H_2 direct bubbling, compared with Ar. A maximum length of 2000 μm was achieved[31] by this technique.

Carbon nanotubes (CNTs)/Poly (L-lactic acid)(PLLA) composites. Various amounts of multi-walled carbon nanotubes (MWCNTs) (specially, 0.5, 3, 5 wt%, and 10 wt%) were added to PLLA nanocomposite and films were prepared. Two methods were used to prepare these nanocomposite films. Method 1: a 10 wt% solution of PLLA in $CHCl_3$ was prepared, which was combined with dispersed MWCNTs and sonicated for 6 h. Subsequently, the mixtures were poured into Teflon dishes and dried at room temperature for 1 week. To insure full evaporation of the solvent, each MWCNTs/PLLA composite was vacuum-dried at 80℃ for 8 hours. Method 2: the as cast composite films from method 1 were folded and broken into pieces of 0.5 ~ 1.0 cm^2 and stacked between two metal plates. This stack was then hot pressed at 200℃ and 150 kgf/cm^2 for 15 min. As a result 100 ~ 200 μm thick films were obtained.

Characterization

Transmission light micrographs. Transmission light micrographs images of the MWCNTs/PLLA composite films were obtained using a Keyence Digital microscope VHX-100N.

Tensile properties. The tensile strengh of the compression-moulded samples, 5 x 50 x 0.4 mm^3, was measured using a Shimadzu Autograph SD-100-C, with 1kN load cell and a crosshead speed of 10 mm/min. Young's modulus, tensile strength and elongation at break were calculated from the load vs elongation curves. The results obtained were averaged over five Samples. The temperature and relative humidity were kept constant at 25℃ and 65 % RH, respectively.

Thermal properties. Decomposition, melting, glass transition and crystallization temperatures (T_d, T_m, T_g and T_c, respectively) of MWCNTs/PLLA composite samples were measured by a Shimadzu TGA 2950 thermogravimetric analyzer under nitrogen at 10℃ /min from 25℃ to 500℃ under nitrogen with samples cut from the composites, and by a Seiko Exstar 6000 differential scanning calorimeter (DSC) using Indium as standard. Heating was performed under nitrogen at 10℃/min.

Surface electrical conductivity. The electrical resistivity R_s (S/cm) of the specimens was measured by a four-probe method at room temperature with a Mitsubishi Chemical MCP-S311 surface resistivity meter, whereas smaller conductivities were measured by a two-probe method at room temperature with a Yokogawa-Hewlett-Packard 4329A high resistance meter.

Electromagnetic wave shielding effect. The electromagnetic wave shielding effectiveness in the frequency range of 0 ~ 1000 MHz was measured by a method developed by the Kansai Electronic Industry Development Center, Osaka, Japan (hereafter called the "KEC" method)[32,38]. Using an Advantest R3361A Spectrum analyzer, the resolution band width was 100 KHz and the video band width was 100 KHz.

Results and Discussion

At first, we investigated the MWCNTs/PLLA composite by transmission light micrograph. Figure 1 shows the transmission light micrograph images of the composites for 0.5 wt% MWCNTs/PLLA composite thin film fabricated by the hot compressing method followed by sonication. There are no obvious agglomerizations of MWCNTs indicating that the nanotubes are uniformly distributed within the polymer matrix on a micrometer scale. Results of tensile tests for MWCNTs/PLLA composite films are shown in Figure 2 (a) and (b). It is observed that the Young's modulus increases with MWCNTs loading in the composite films compare to homo-PLLA films, although an increase in the MWCNTs content do not cause a significant increase in Young's modulus. The average Young's modulus of the 5 wt% composite film is approximately 2.5 GPa, which is approximately 150 % higher than that of the pure PLLA film.

It was also observed that increasing the loading amount of nanotubes in these composites caused a significant increase in stiffness, which eventually led to brittle fracture, as indicated by the low elongation at break in the tensile test.

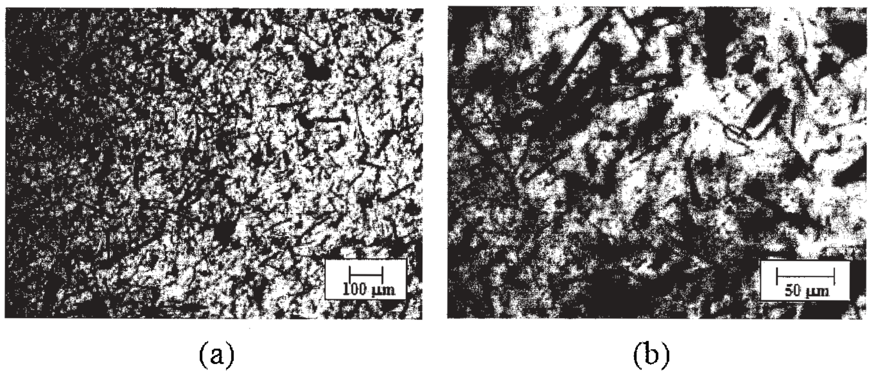

Figure 1. Transmission light micrograph images of a MWCNTs/PLLA composite thin film having 0.5 wt% MWCNTs content (a) 100 μm scale bar, (b) 50 μm scale bar.

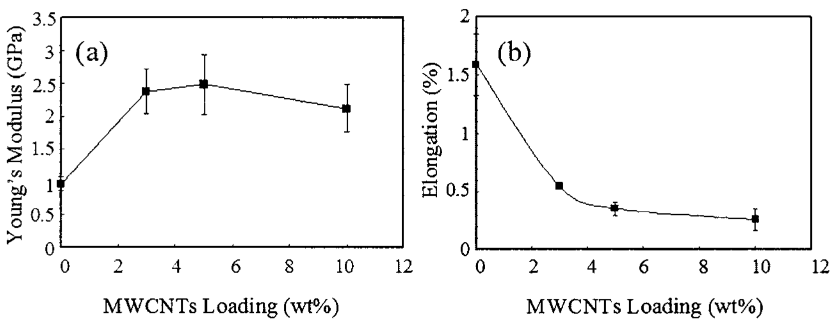

Figure 2. Young's modulus (a) and elongation at break (b) of MWCNTs composites plotted versus the MWCNTs contents.

As can be seen in Figure 3, the T_g and T_c of the composite slightly decreased except in the 10 wt% MWCNTs composite. This fact suggests that the MWCNTs fillers can work as the crystal nucleator of PLLA. These thermal phenomena should be induced by interaction between PLLA and MWCNTs.

Figure 4 provides a comparison of the mass loss curves for the degradation of virgin polymer and the nanocomposite under nitrogen. PLLA degrades without forming any residue. Degradation of our nanocomposites leaves 3 ~ 10 % between residue which remains practically constant. Assuming the PLLA has been completely volatilized, this number represents the amount of the MWCNTs phase in the nanocomposite. It is important to note, however, that the T_d at the point of 10 % weight loss increased by as much as 10 ~ 20℃.

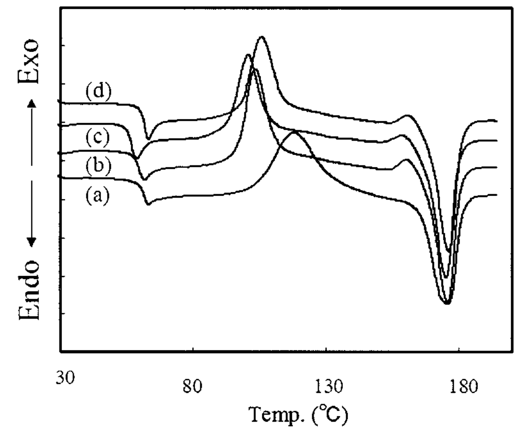

Figure 3. The DSC curves of PLLA and its blends with various MWCNTs contents recorded during the first heating scan; (a) PLLA (b) 3 wt% MWCNTs/PLLA (c) 5 wt% MWCNTs/PLLA (d) 10 wt% MWCNTs/PLLA.

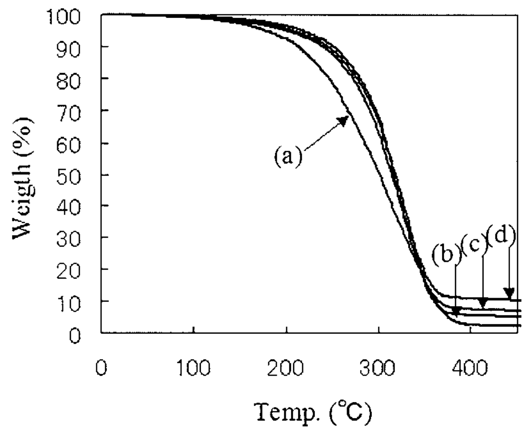

Figure 4. TGA curves of PLLA and its blends with various MWCNTs contents; (a) PLLA (b) 3 wt% MWCNTs/PLLA (c) 5 wt% MWCNTs/PLLA (d) 10 wt% MWCNTs/PLLA

Figure 5 demonstrates the electrical conductivities, which were measured by a four-probe method at room temperature. The dispersion of MWCNTs in the PLLA matrix resulted in substantial decrease in the electrical surface resistivity of the derived composite material as the MWCNTs loading was increased.

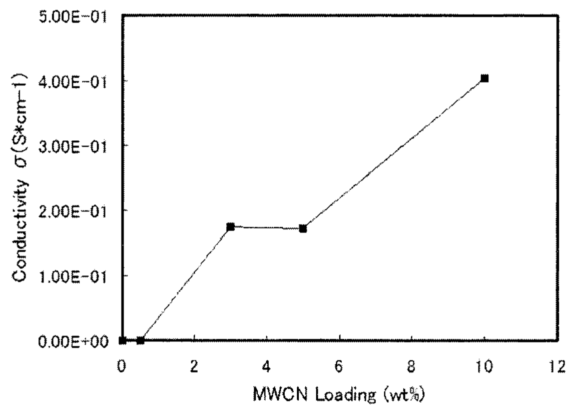

Figure 5. Surface electric conductivity of MWCNTs/PLLA composite films plotted versus the MWCNTs contents.

As highly advanced intergrated circuit networks are developed, electromagnetic waves generated from various kinds of electronic appliances cause interference noise resulting in erroneous operations and environmental problems. In order to eliminate the problems caused by these stray electromagnetic waves, it is required not to generate these electromagnetic waves or to keep the devices away. In either case, an electromagnetic wave shielding material can provide an effective countermeasure. For the electromagnetic wave shielding material, a conductive plastic becomes noteworthy since it can be readily formed into any configuration of a device housing. The conductive compound plastic for use in the electromagnetic wave shielding material is generally a mixture of a resin and a conductive filler including the powder, flake or fiber of a metal such as a copper, aluminum, zinc, stainless steel, and so on. However, the shielding materials employing the conductive metal material are still found to be unsatisfactory in that they cannot sufficiently shield a low frequency electromagnetic wave below 400 or 500 MHz as well as a high frequency electromagnetic wave above 600 or 700 MHz. It was found that a carbon powder such as a carbon nanotubes can be used as conductive filler. Our studies have revealed that electromagnetic wave shielding material comprising CNTs intermixed with the PLLA resin by means of a hot compressing method followed by sonication are effective and can improve the shielding similarly to or better than metallic conductive fillers. Nevertheless, such shielding material is found to be still insufficient in shielding

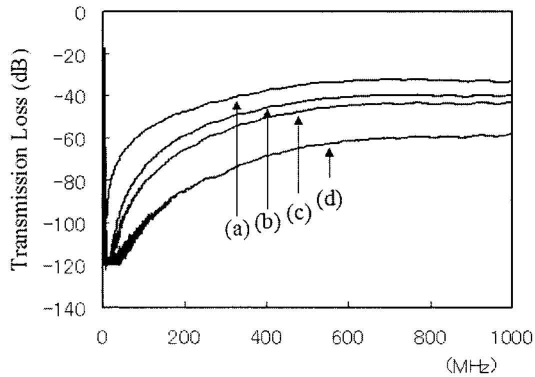

Figure 6. Electromagnetic wave shielding effectiveness of PLLA and its blends with various MWCNTs contents; (a) PLLA (b) 3 wt% MWCNTs/PLLA (c) 5 wt% MWCNTs/PLLA (d) 10 wt% MWCNTs/PLLA.

the low frequency electromagnetic waves below 400 or 500 MHz as well as the high frequency waves above 600 or 700 MHz.

Figure 6 shows the results of electromagnetic wave shielding effectiveness of MWCNTs/PLLA, measured by a KEC method in comparison to the original PLLA film. It is concluded that the composite MWCNTs/PLLA compounds exhibit superior electromagnetic shielding effect over a wide frequency range, from a low frequency of less than 400 or 500 MHz to a high frequency of above 600 or 700 MHz. As expected, the shielding effectiveness improved with increasing MWCNTs loading.

Conclusion

MWCNTs can be uniformly dispersed into polymers to produce significant changes to the physical properties of the host matrix. The dispersion of MWCNTs in a polymer matrix resulted in substantial decreases in the electrical surface resistivity of the derived composite material. Furthermore, it also improved the electromagnetic wave shielding effectiveness over a wide frequency range from a low frequency of less than 400 or 500 MHz to a high frequency of above 600 or 700 MHz. Incorporation of MWCNTs into PLLA polymer matrices also led to higher Young's modulus. Surface treatment of the CNTs could be used to improve interfacial bonding and increase tensile strength.

Acknowledgement

Thanks are due to the *Japan Society for the Promotion of Science* for awarding a postdoctoral fellowship and a research grant to Sung-Il Moon (ID No. 03311).

[1] S. Iijima, *Nature* **1991**, *354*, 56.
[2] M. M. J. Treacy, T. W. Ebessen, J. M. Gibson, *Nature* **1996**, *381*, 678.
[3] T. W. Ebbessen, *Ann. Rev. Mater. Science* **1994**, *24*, 235.
[4] J. W. Mintmire, B. D. Dunlap, C. T. White, *Phys. Rev. Lett.* **1992**, *68*, 631.
[5] J. che, T. Cagin, W. Goddard, *Nanotechnol.* **2000**, *11*, 65.
[6] R. Dagani, *Chem. Eng. News* **1999**, 77(23), June 7.
[7] H. D. Wagner, O. Lourie, Y. Feldman, R. Tenne, *Appl. Phys. Lett.* **1988**, *72*, 188.
[8] J. Coleman, S. Curran, A. Dalton, A. Davey, B. McCarthy, W. Blau, R. Barklie, *Phys. Rev.* B **1998**, *58*, 7492.
[9] K. Yoshino, H. Kajii, H. Araki, T. Sonoda, H. Take, S. Lee, *Fullerene Sci. Technol.* **1999**, *7*, 695.
[10] P. Calvert, *Nature* **1999**, *399*, 210.
[11] N. Chopra, A. Zettl, *Solid State Commun.* **1998**, *105*, 297.
[12] E. Wong, P. Sheehan, C. Lieber, *Science* **1997**, *277*, 1971.
[13] R. Ruoff, D. Lorents, *Carbon* **1995**, *33*, 925.
[14] E. Hernandez, C. Goze, P. Bernier, A. Rubio, *Phys. Rev. Lett.* **1998**, *80*, 4502.
[15] R. Gao, Z. Wang, Z. Bai, W. A. de Heer, L. Dai, M. Gao, *Rhys. Rev. Lett.* **2000**, *85*, 622.
[16] P. Poncharal, Z. Wang, D. Ugarte, W. A. de Hee, *Science* **1999**, *283*, 1513.
[17] M. Ajayan, L. Schadler, C. Giannaris, A. Rubio, *Adv. Mater.* **2000**, *12*, 750.
[18] H. R. Kricheldorf, I. Kreiser-Saunders, *Macromol. Symp.* **1996**, *103*, 85.
[19] A. R. Postema, A.J. Pennings, *J. Appl. Polym. Sci.* **1989**, *37*, 2351.
[20] B. Ething, S. Gogolewski, A. J. Pennings, *Polymer* **1982**, *23*, 1587.
[21] S.H. Hyon, K. Jamshidi, Y. Ikada, *Biomaterials*, **1997**, *18*, 1503.
[22] S.H. Hyon, K. Jamshidi, Y. Ikada, *Polym. Int.* **1998**, *46*, 196.
[23] S.H. Hyon, *Younsei Medical J.* **2000**, *41*, 720.
[24] F. Jin, S.H. Hyon, H.Iwata, S.Tsutsumi, *Macromol. Rapid. Commun.* **2002**, *23*, 909.
[25] S.H. Hyon, F. Jin, S. Tsutsumi, T. Kanamoto, *Macromol. Symp.* **2003**, *197*, 355.
[26] R. G. Sinclair, *J. Macromol. Sci. Pure Appl. Chem.* **1996**, *33*, 585.
[27] S. I. Moon, C. W. Lee, M. Miyamoto, Y. Kimura, *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 1673.
[28] S. I. Moon, Y. Kimura, *Polym. Int.* **2003**, *52*, 299.
[29] S. I. Moon, C. W. Lee, I. Taniguchi, M. Miyamoto, Y. Kimura, *Polymer* **2001**, *42*, 5059.
[30] S. I. Moon, C. W. Lee, I. Taniguchi, M. Miyamoto, Y. Kimura, *High Perform. Polym.* **2001**, *13*, S189.
[31] C. J. Lee, S. C. Lyu, H. W. Kim, C. Y. Park, C. W. Yang, *Chem. Phy. Lett.* **2002**, *359*, 109.
[32] E. Hariya, M. Umano, "Instruments for Measuring the Electromagnetic Shielding Effectiveness," 1984 IEEE International Symposium on Electromagnetic Compatibility, 2, 1984, Tokyo, Japan.
[33] E. Hariya, M. Umano, N. Morinaga Y. Nagasawa. "Experimental Investigation on the Electromagnetic Shielding Effectiveness" (in Japanese), *IECE Technical Report*, MW85-68, 9, 1985.