CONDUCTING COMPOSITE NANOFIBERS BASED ON CARBON NANOTUBES AND CONDUCTING POLYMERS

J. K. Kwon, S. Rana, H. J. Yoo, H. W. Lee, J. W. Cho*
Department of Textile Engineering, Konkuk University, Seoul, South Korea.
*jwcho@konkuk.ac.kr

Keywords: Composite nanofibers, Carbon nanotubes, Conductivity, Mechanical properties

1 Introduction

The composite fibers have been fabricated by single component and core-sheath bicomponent fibers using melt spinning, solution spinning, and electrospinning processes. Core-sheath morphology provides a unique template to develop and improve technologies while furthering the view of filler percolation in polymer composites.

Carbon nanotubes (CNTs) exhibit outstanding and unique mechanical and physical properties, and immediately after their discovery, those are regarded as new materials for future technologies [1]. Depending on their structure, diameter and preparation conditions CNTs may be single-walled, double-walled, and multi-walled and represent ballistic electron conductors. Individual tubes as well as ensembles of nanotubes are potential candidates as components in the area of electron field emission sources, scanning probes, nanoelectrical devices, components of electrochemical energy storage systems. They represent the ultimate carbon fiber, with the highest thermal conductivity, exceptional mechanical properties, and the highest tensile strength of any material, having Young's moduli of around 1 TPa and being up to 100 times stronger than steel. CNTs are the excellent conducting filler for polymer composites in addition to their superior mechanical and magnetic properties.

Conducting polymers are also one of the most widely used conducting materials. Recently, conducting polymer nanofibers have drawn much attention from the viewpoint of fundamental science and application [2, 3], in particular, areas such as electrochromic devices [4], active coating [5], actuator [6], sensor, and energy storage devices. However the molecular weight is not good enough to form fibers on its own through the elctrospinning process. Although the elctrospinning process is not suitable for direct fabrication of conducting polymers into nanofibers, the electospun nanofiber webs can be used as a template for polypyrrole grown since they provide high surface to volume ratio. Particularly some soluble polymers, including polypyrrole (PPy) and poly(3-hexylthiophene) (P3HT) can be grown onto fibers via reactive chemical vapor deposition (CVD) method [7].

Pristine polypyrrole without any bulky side groups is not easily soluble in any solvent. An addition of bulky side chains to polypyrrole backbone can make it soluble, however, the molecular weight may be not good enough to form fibers on its own through the elctrospinning process. Even though the elctrospinning process is not suitable for direct fabrication of conducting polymers into nanofibers, the electrospun nanofiber webs can be used as a template for polypyrrole grown since they provide high surface to volume ratio. Polypyrrole can be grown onto nonwoven fibers via reactive chemical vapor deposition (CVD) method.

In this study, the composite nanofibers of CNTs and conducting polymers are prepared and their properties are investigated.

2 Experimental Sections

2.1 Materials

Polyurethane (PU) was synthesized from a reaction of poly(ε-caprolactone)diol, 1,4-butanediol, and 4,4'-methylene bis(phenylisocynate). Pyrrole and 3-hexylthiophene monomers were purchased from Aldrich. Ferric chloride ($FeCl_3$) was received from Samchun Pure Chemical Co. Ltd., Korea.

2.2 Electrospinning of Nanofibers

PU solution of 20 wt% in dimethylsulfoxide (DMF) was used to produce the PU nanofibers by electrospinning. The tip of the needle and the collector was connected to the high-voltage power supply. The tip-to-collector distance was 15-20 cm, and the electrical potential was 15-20kV.

2.3 Conducting Polymer Coated Nanofibers

The coating of nanofiber webs was accomplished using the vapor phase deposition of conducting polymer. The electrospun nanofiber webs were dipped into 10 wt% aqueous solution of ferric chloride. The excess of $FeCl_3$ solution was gently wiped off with a tissue and the coated mat was then introduced in a reactor where nitrogen was bubbled through the liquid monomer. The monomer vapor get polymerized when comes in contact with the $FeCl_3$-coated nanofibers, producing a thin conducting polymer coating as shown in Fig. 1.

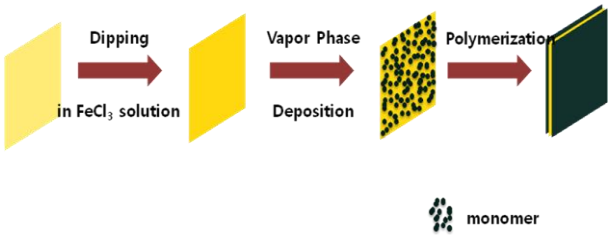


Fig. 1. Vapor phase conducting polymer coating process on nanocomposite fibers.

2.4 Conducting Polymer Coated Nanofibers

The dc conductivity of the samples at 25 ^{o}C was measured by the standard spring-loaded pressure contact four-probe method. A constant current (I) was passed from a constant direct current source electrometer through two adjacent leads of the four probes, and the voltage (V) across the other two leads was measured using a multimeter. The electrical conductivity (σ) was calculated using the van der Paw relation,

$$\sigma = (\ln 2/\pi d)\,(I/V) \qquad (1)$$

where d, the thickness of the film, was taken as the average of four measurements at different places using a screw gauge. Conductivity of two films of same sample, each with two trials, was measured, and the average of four such measurements was taken.

3 Results and Discussion

Scanning electron microscopy measurements were analyzed for PPy and P3HT coating nanofibers. The pure PU fibers show smooth surface, and after vapor phase polymerization, the fiber porosity was almost filled and very thick PPy coating was observed. We observed that PPy coating get thicker with time and the fiber diameter increased with increasing the polymerization time (Fig. 2). It is interesting to note the difference in coating morphology obtained with PPy and P3HT. PPy produced uneven nodular coating, whereas P3HT coating was very smooth and dense, even it is hard to distinguish from the SMPU nanofiber at low magnitude SEM analysis.

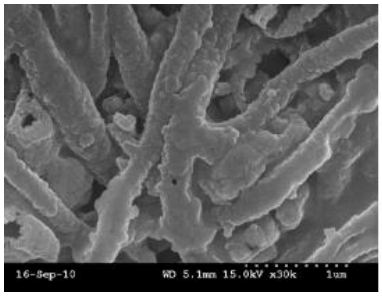
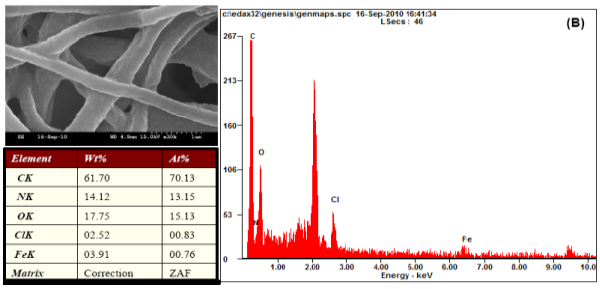


Fig. 2. SEM image of polypyrrole-coated nanofiber web after 6 h reaction.

The chemical composition of the spun nanofiber mats was analyzed by EDX spectrometer attached with FE-SEM. Fig. 3 shows the EDX spectra of the PPy coated PU fibers. For PPy coated PU fibers, the EDX spectra revealed the presence of N, C, Cl, and Fe supports the coated of PPy alone with some amount of oxidizing agent. The same phenomenon was observed for the P3HT coated nanofiber web, where the new peak of S was found, which supports the presence of thiophene onto the nanofibers surface in Fig. 4.

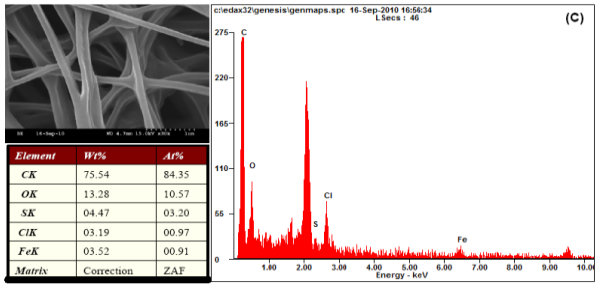
The sheet conductivity was measured using a 4-probe method. The conductivity of porous fiber mat could be affected by several reasons. Higher conductivity was observed for P3HT compared to polypyrrole, and it may be due to relatively well oriented coating of P3HT. Compared to P3HT, the conductivity value of PPy was initially higher,

indicating high coating of PPy in short period as supported by SEM and IR data. The conductivity of porous fiber mat could be affected by several reasons. These include conducting polymer/polymer matrix ratio, doping, and monomer vaporizing time. It has been simply assumed that the higher conductivity arises from a chain orientation along the longitudinal direction of the nanofiber. Higher conductivity was observed for P3HT compared to polypyrrole, and it may be due to relatively well oriented coating of P3HT, as observed from the SEM images. It has been shown that compared to P3HT, the conductivity value of PPy was initially higher, indicating high coating of PPy in short period, and it was supported by SEM and IR measurements.



Element	Wt%	At%
CK	61.70	70.13
NK	14.12	13.15
OK	17.75	15.13
ClK	02.52	00.83
FeK	03.91	00.76
Matrix	Correction	ZAF

Fig. 3. SEM-EDX spectrum of polypyrrole coated PU fiber.



Element	Wt%	At%
CK	75.54	84.35
OK	13.28	10.57
SK	04.47	03.20
ClK	03.19	00.97
FeK	03.52	00.91
Matrix	Correction	ZAF

Fig. 4. SEM-EDX spectrum of P3HT coated PU fiber.

The multi-walled carbon nanotubes (MWNTs) incorporating nanofibers were also prepared, followed by the CVD of conducting polymers to enhance the electrical conductivity due to synergetic effect [8,9]. Such composite nanofibers can offer not only the increased mechanical properties of conducting materials resulting from reinforcement of CNTs but also the smooth surface of the nanofiber webs. So they may have potential application as the conducting fabric sensors having good contact sensing with other materials as well as electrical heating materials.

4 Conclusions

Conducting polypyrrole and poly(3-hexylthiophene) coated shape memory block copolymer polyurethane nanofiber webs were prepared successfully. After vapor phase polymerization, the fiber porosity was almost filled and very thick polypyrrole coating was observed. The morphology of polypyrrole and P3HT coated fibers changed significantly with time during the vapor phase polymerization of polypyrrole and P3HT. However, a very smooth surface was observed for the P3HT coated nanofibers. Compared to P3HT, the initial polymerization rate was wery fast for polypyrrole, whereas regular controlled coating was observed for P3HT.

Acknowledgement: This work was supported by the grant from the Industrial technology development program of the Ministry of Knowledge Economy (MKE) of Korea (No KEIT 10033449-2009-11), and Seoul Future Contents Convergence (SFCC) Cluster established by Seoul R&BD Program (ST090826).

References

[1] N. G. Sahoo, S. Rana, J. W. Cho, L. Li, and S. H. Chan "Polymer nanocomposites based on functionalized carbon nanotubes". *Prog. Polym. Sci.*, 35, 837-867, 2010.

[2] L. Liu, N. Jia, Q. Zhou, M. Yan, and Z. Jiang, "Electrochemically fabricated nanoelectode ensembles for glucose biosensors". Mater. Sci. Eng., 27, 57- 60 (2007).

[3] A. K. Wanedaya, M. A. Bangar, M. Yun, W. Chen, N. V. Myung, and A. Mulchandani, "Field-effect transistors based on single nanowires of conducting polymers". J. Phys. Chem. C, 111, 5218-5221 (2007)

[4] S. Y. Jang, V. Seshadri, M. S. Khil, A. Kumar, M. Marquez, P. T. Mather, and G. A. Sotzing "Welded electrochromic conductive polymer nanofibers by electrostatic spinning". Adv. Mater., 17, 2177-2180 (2005).

[5] Y. Zhu, L. Feng, F. Xia, J. Zhai, M. Wan, and L. Jiang, "Chemical dual-responsive wettability of

superhydrophobic PANI-PAN coaxial nanofibers". Macro. Rapid Commun., 28, 1135-1141 (2007)

[6] B. K. Gu, Y. A. Ismail, G. M. Spinks, S. I. Kim, I. So, S. and J. Kim, "A linear actuation of polymeric nanofibrous bundle for artificial muscles". Chem. Mater., 21, 511-515 (2009)

[7] J. P. Lock, S. G. Im, and K. K. Gleason "Oxidative chemical vapor deposition of electrically conducting poly(3,4-ethylenedioxythiophene) films". *Macromolecules*, 39, 5326-5329, 2006.

[8] N. G. Sahoo, Y. C. Jung, H. H. So, and J. W. Cho "Polypyrrole coated carbon nanotubes: synthesis, characterization, and enhanced electrical properties". *Synth. Met.*, 157, 374-379, 2007.

[9] L. Hu, H. S. Kim, J. Yo. Lee, P. Peumans, and Y. Cui "Scalable coating and properties of transparent, flexible, silver nanowire". ACS Nano, 4, 2955-2963, 2010.