

Electrical Properties of Transparent Conductive CNT Composite Films

Mun Ja Kim and Ji-Beom Yoo*

Department of Advanced Materials Science and Engineering, Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University, 300, Chunchun-dong, Jangan-gu, Suwon 440-746, Korea

CNTs have good individual conductivity but a bundle of CNTs has different electrical properties than their individual counterparts. Therefore, transparent conducting electrode and flexible display electrode materials containing carbon nanotubes (CNTs) are quite a challenge to realize their application. Good techniques for dispersing CNTs are required before the various proposed applications can be realized. Using polyvinyl alcohol (PVA) to change the surface properties of a substrate improved the dispersion of CNTs on substrates while providing suitable adhesion of the CNTs to the substrates. We analyzed the changes in physical configuration and electrical properties of CNTs dispersed on a PVA-coated polyethylene terephthalate (PET) surface after soft thermal aging of the PVA. The electrical properties were characterized by measuring the sheet resistance of films.

Keywords: transparent conductive film (TCF), polyvinyl alcohol (PVA), carbon nanotube (CNT) composite

1. INTRODUCTION

Changing the properties of the carbon nanotube (CNT) surface or substrate is important for dispersing CNTs. The hydroxyl functional group of polyvinyl alcohol (PVA) not only has a suitable adhesion to polyethylene terephthalate (PET) substrates, but also chemically soft bonding with acid-treated CNTs. Through an acid treatment, many types of functional groups can be placed on the outermost wall or tip sides of CNTs.^[1] In addition, the physical dimensions of CNTs, such as the diameter and length, can be controlled.^[2] It is expected that the electrical properties of CNT composite films can be improved using acid-treated CNTs because CNTs treated with sulfuric acid and nitric acid contain carboxyl functional groups on their surface and have a controlled length. Acid-treated CNTs show more hydrophilic properties than untreated CNTs. On PVA coated PET films, a good dispersion is expected using acid-treated CNTs. PET is the most challenging substrate material because a PET film requires a processing temperature < 120°C. In addition, PET is an acceptable substrate for transparent displays because PET is economical, flexible, transparent and lightweight.

2. EXPERIMENT

A CNT surface treatment was performed on raw CNTs in

an organic solution. The CNT (thin MWNTs: Iljin Nanotech Co., Ltd) surface was functionalized using a H₂SO₄: HNO₃ (vol. 3:1) solution. Details of the acid treatment are described elsewhere.^[3,4] Carboxyl functional groups were formed on the outermost side of the CNTs.^[1] Furthermore, the acid treatment controlled the length to approximately 0.1 μm.^[4] In order to make a CNT conductive film without any surfactants and binders, the acid-treated CNTs were dispersed in isopropyl alcohol (IPA). IPA has a relatively heavy evaporation coefficient and can be used to transfer CNTs to plastic substrates. A CNT film was formed by spraying the CNT-IPA solution on the PET film. The CNT (0.03~0.05%) content was calculated as the weight percentage in the IPA solvent. Sonication processing was carried out to disperse the CNTs.

PVA was selected to improve the adhesion between the CNT film and the PET substrate. PVA is so hydrophilic that it can be used to adsorb the acid-treated CNTs on the substrates. PVA (content, 9~1 wt.%) was desorbed in deionized (D.I) water. The PVA layer was formed on the PET film by bar coating (commercial SUS bar: No. 6) or spin coating (6000 rpm). The PVA-coated PET film was baked immediately in an oven at 90°C. As the IPA became volatilized, a transparent conductive CNT film consisting of only CNTs was formed on the PVA-coated PET films. A thermal aging process was carried out at 90°C for 1~3 hrs to modify the CNT network in the already processed CNT layer on the PVA/PET substrate. The changes in the CNT connections that occurred as a result of the presence of the substrate on a hot plate were possible because of the softness

*Corresponding author: jbyoo@skku.edu, zium98@skku.edu

of the PVA.

The transparent conductive CNT film was characterized by field emission scanning electron microscopy (FESEM: JEOL, JSM-6700). The sheet resistance (R_s) and optical transmission properties (% T) of the transparent conductive film were measured using a four-point probe (CMT-SR100N) and UV-visible spectrometry (SCINCO, UV S-2100), respectively. In addition, the thickness of each PVA layer was measured according to different contents and coating methods using atomic force microscopy (AFM: THERO-MICROSCOPES, USA).

3. RESULTS AND DISCUSSION

3.1. Analysis of Surface Properties

Two advantages can be expected from the hydroxyl group of PVA. The first is the changing of substrate surface properties for the dispersion of acid-treated CNTs on the substrate. The second is improved adhesion properties of the acid-treated CNTs to the plastic substrates. The wet angle to deionized (DI) water on the plastic substrate surface was measured. The wettability of DI water on the plastic film surface increased after coating the PET surface with PVA. The contact angle of the uncoated PET substrates was approximately 56.6° . On the other hand, the contact angle of the PVA-coated PET films was approximately 20.8° .

Figure 1 shows the characteristics of the CNT layer formed on the plastic substrates. The same volume of CNT-IPA was sprayed onto each substrate. The CNT (0.03 wt.%)–IPA sprayed on the PVA-coated (9 wt.%) PET films was more uniform than the CNTs sprayed on the bare PET film. Figure 1(A) shows the dispersed CNTs on the bare PET film, and Figs. 1(B) and (C) show the CNTs dispersed on PVA-coated PET films by the bar-coating and spin-coating methods, respectively.

The CNTs on the bare PET films showed slight aggregation with many vacancies within the films. The CNTs on the PVA-coated PET films appeared to be well dispersed compared with those on the bare PET films. Under the same conditions, the PVA coating thickness on PET films could be

controlled through the coating method, such as bar-coating or spin coating. The thickness of the bar-coated PVA on the PET substrates was several hundreds of μm , whereas the thickness of the spin-coated PVA on the PET substrates was approximately $1\ \mu\text{m}$.

As shown in Figs. 1(B) and (C), the PVA layer bonds strongly to the sprayed CNTs, but an excessive polymer bonding force can interrupt the adsorption of CNTs to the PVA layer. More abundantly packed CNTs can be seen on the thinner PVA layer coated by spin-coating than on the PVA layer coated by bar-coating. The R_s of Figs. 1(A), (B) and (C) were $1.79\ (\text{M}\Omega/\text{sq.})$, $148\ (\text{M}\Omega/\text{sq.})$ and $0.12\ (\text{M}\Omega/\text{sq.})$, respectively. In order to improve the electrical properties of the transparent conductive CNT film, the CNT content must be increased and the PVA thickness must be decreased.

3.2. Optical and Electrical Properties of TCF

Figure 2 shows the CNT films formed on the 9 wt.% (A) and 1 wt.% (B) PVA spin coated PET films. PVA was coated using the same processing on the PET films, and the thickness was approximately $30\ \text{nm}$ by changing the contents from 9 wt.% to 1 wt.%. The sprayed CNTs used for forming a film of one layer on the PVA/PET substrate had a concentration of 0.05 wt.% in 6 ml of solvent. The R_s and % T at $600\ \text{nm}$ of the CNT (0.05 wt.%) film formed on the 9 wt.% PVA were approximately $10.9\ (\text{k}\Omega/\text{sq.})$ and 60.3%, respectively, as shown in Fig. 2(A). The R_s and % T at $600\ \text{nm}$ of the CNT (0.05 wt.%) film formed on the 1 wt.% PVA were approximately $2.87\ (\text{M}\Omega/\text{sq.})$ and 67.7%, respectively, as shown in Fig. 2(B). The effect of the PVA layer on % T was analyzed. Although there was a subtle increase of approximately 1% T with the PVA coating of the PET substrates independently of PVA contents, no significant difference was produced.

A comparison of Fig. 1(C) with Fig. 2(A) shows increasing electrical conductivity with increasing quantity of CNTs sprayed. On the 9 wt.% PVA layer, the as-sprayed CNTs content was changed from 0.03 wt.% to 0.05 wt.%. The corresponding R_s decreased from $120\ (\text{k}\Omega/\text{sq.})$ to $11\ (\text{k}\Omega/\text{sq.})$.

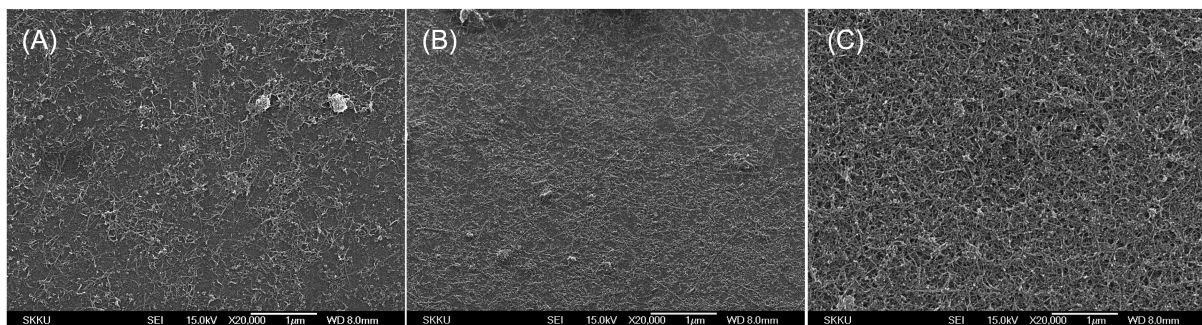


Fig. 1. The dispersed morphology (FE-SEM images) of the sprayed CNTs (0.03 wt.%) on (A) bare PET film, PVA coated PET film using the bar-coating method (B) and using the spin-coating method (C).

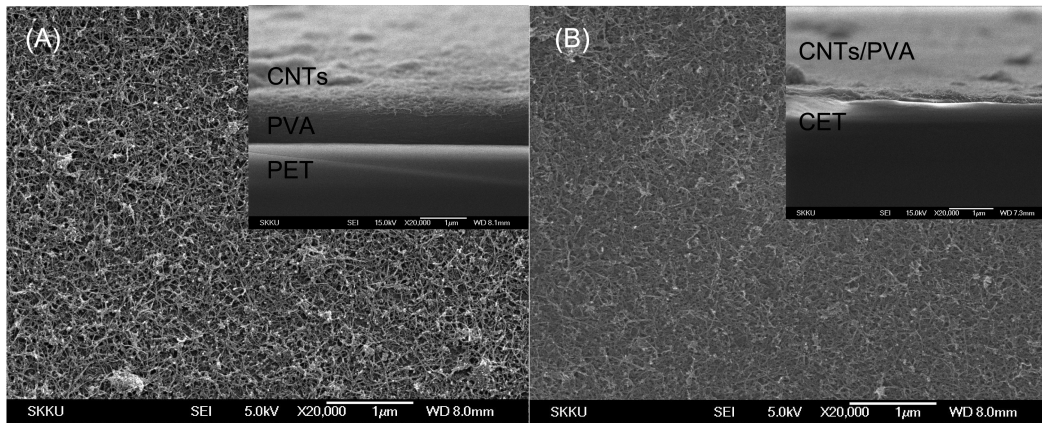


Fig. 2. Top and cross-sectional (inserted at each top image) view FE-SEM images of the CNTs film formed on the (A) 9 wt.% and (B) 1 wt.% PVA spin-coated PET films.

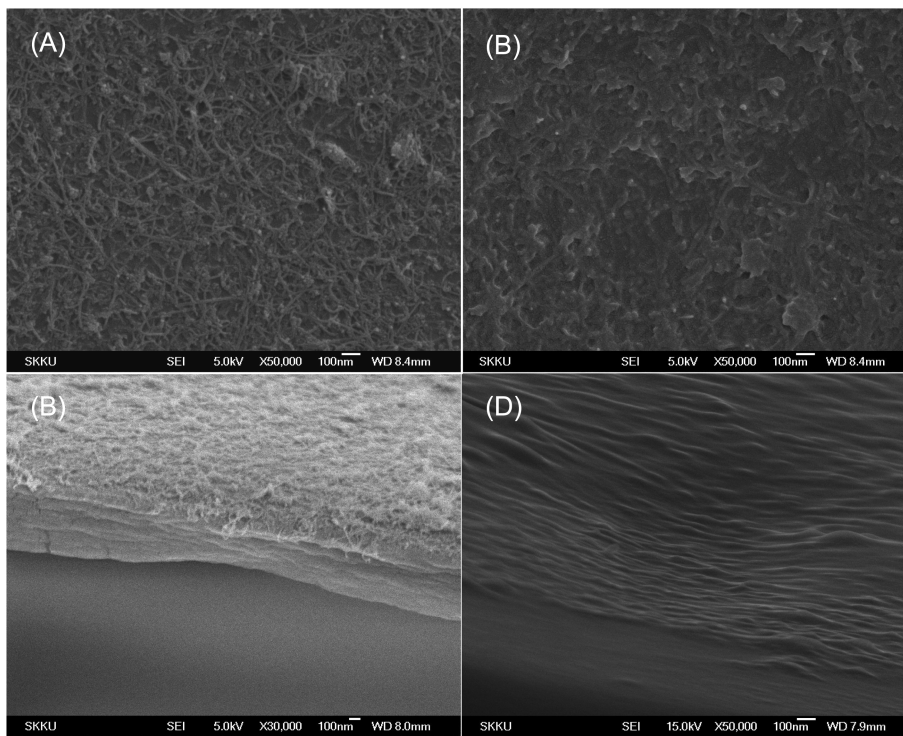


Fig. 3. The top and tilted FE-SEM images after the soft thermal aging process of the CNTs film formed on the PVA coated PET substrates: (A) and (B) are on PVA of 9 wt.% and (C) and (D) are on PVA of 1 wt.%.

Soft thermal aging was attempted in order to increase the electrical conductivity of the CNT film. The dispersed CNTs morphology can be changed according to the physical phase transition of the PVA layer. Figure 3 shows these phenomena. After soft thermal aging at 90°C for 1 hr, the clear CNTs on the PVA layer became blurred. However, there was no difference in transparency between before and after soft thermal aging. Figures 3(A) and (B) indicate that the CNTs tend to tangle with each other. On the other hand, Figs. 3(C) and (D) show the CNTs tangling with the PVA. The CNT film formed on the 9 wt.% PVA coated PET substrates showed an

almost 39% improvement in R_s after thermal aging. The R_s of 10.9 ($k\Omega/sq.$) decreased to 6.6 ($k\Omega/sq.$) through thermal aging. In contrast, the CNT film formed on the 1 wt.% PVA-coated PET substrates did not show large changes in R_s , from 2.87 ($M\Omega/sq.$) to 3.80 ($M\Omega/sq.$). Suitable CNT aggregation with good junctions may be more effective for improving electrical conductivity than CNT film with well-dispersed CNTs but poor junctions between the CNTs.

Therefore, an attempt was made to increase the junction of sprayed CNTs at the same time as spray-working. The CNT-IPA solution was sprayed over the PVA-coated PET films on

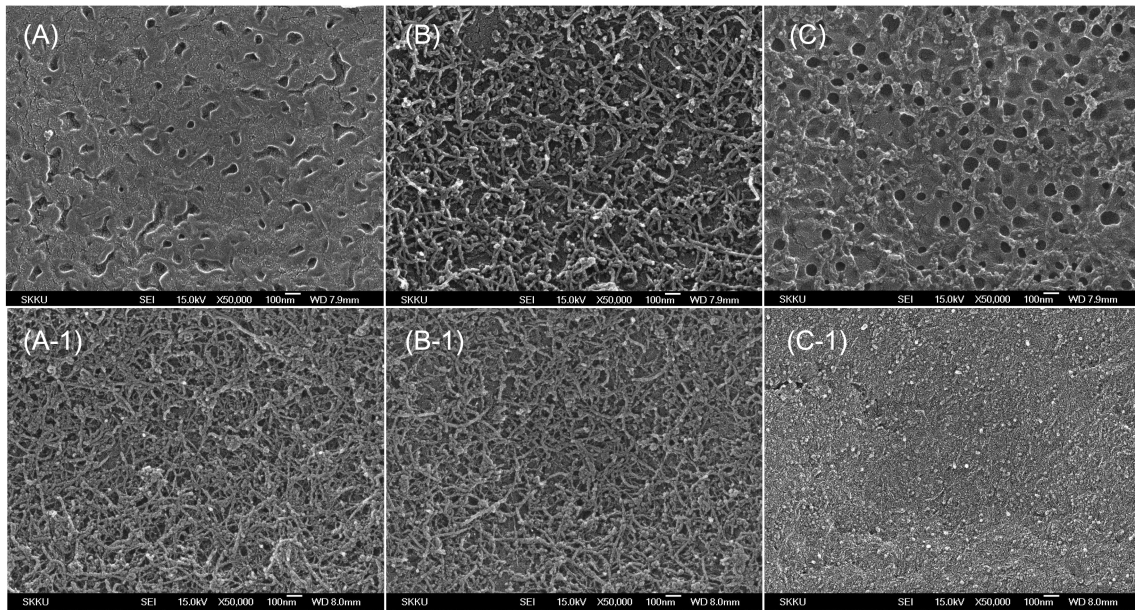


Fig. 4. FE-SEM images before: (A, B and C) and after: (A-1, B-1 and C-1) the soft thermal aging process of the CNTs film formed on the PVA coated PET films heated to 30°C on a hot plate: (A) and (A-1) 9 wt.%, (B) and (B-1) 3 wt.%, (C) and (C-1) 1 wt.% PVA coated PET substrates that were soft baked and then sprayed with the CNTs on the heated hot plate.

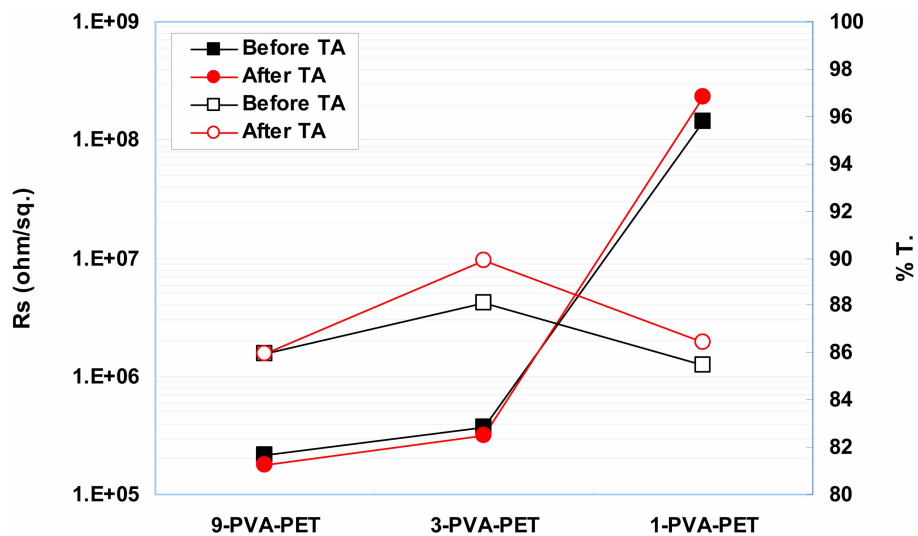


Fig. 5. Graphs of the sheet resistance (R_s) and transparency (% T) of the CNTs films shown in Fig. 4. (The closed square and circle symbols represent the R_s . The open square and circle symbols represent the % T .)

a plate heated to approximately 30°C. In addition, the wt.% change in PVA to the sprayed CNTs distribution under the same volume of CNTs was considered. Figure 4 shows the unique morphology of the sprayed CNTs under the above-mentioned process. No CNTs were observed on the 9 wt.% PVA/PET films, and it appears that the CNTs were buried below the PVA layer (see Fig. 4(A)). In the case of the 3 wt.% and 1 wt.% PVA, the CNT film exhibited different characteristics. In Fig. 4(B) with the 3 wt.% PVA layer, the CNTs appeared similar to those shown in Fig. 3(A), i.e., the CNTs were tangled with the PVA. Figure 4(C) shows more

tangled CNTs with 1 wt.% PVA than can be observed in Fig. 4(B). Baking for 1 hr at 90°C was performed to determine if there was any soft thermal aging effect. As shown in Figs. 4(A-1) and (B-1), more CNTs appeared on the surface after thermal aging. Figure 4(C-1) indicates that after thermal aging, the surface was covered with PVA rather than CNTs.

The R_s and % T of CNT films shown in Fig. 4 were analyzed. Figure 5 shows the characteristics. The % T excluding the substrates at 600 nm ranged from 85.5% to 88.1%. After thermal aging, the % T showed a subtle increase of approximately 2%. The R_s on the 9, 3, and 1 wt.% PVA

coated substrates before and after thermal aging were approximately 211 to 177 ($k\Omega/sq.$), 366 to 314 ($k\Omega/sq.$) and 143 to 234 ($M\Omega/sq.$), respectively.

A comparison of Figs. 2(A) and (B) with Figs. 4(A) and (C) shows that heating the PVA/PET films does not increase the number of junctions of sprayed CNTs simultaneously with spray-working. The R_s values of Figs. 2(A) and (B) were better than those of Figs. 4(A) and (C). However, thermal aging can increase the number of junctions between the dispersed CNTs on 9 wt.% and 3 wt.% PVA layers.

4. CONCLUSIONS

A new method for CNT dispersion was introduced using a PVA layer on a flexible plastic substrate. The transparent conductive CNT film formed had a sheet resistance of 6.6 ($k\Omega/sq.$) and a transparency of 60.3%. In an effort to increase the junction of sprayed CNTs, a CNT-IPA solution was sprayed over PVA-coated PET films heated to approximately 30°C. Soft thermal aging of the PVA was also attempted to determine if there were any changes in physical configuration and improvements in the electrical properties of the CNTs dispersed on the PVA-coated PET. Transparent conductive CNT film with a sheet resistance of 177 ($k\Omega/sq.$) and a transparency of 86% was formed. The CNT films formed on the 9 wt.% PVA-coated PET substrates were

comprised of a well-dispersed CNT layer. Through soft thermal aging of the PVA, the CNT layer that exhibited a distorted physical configuration showed an improvement in sheet resistance.

ACKNOWLEDGEMENTS

This study was supported by the Samsung Advanced Institute of technology (SAIT) through Sungkyunkwan Advanced Institute of Nano Technology (SAINT) and the Korean Science and Engineering Foundation (KOSEF) through the Center for Nanotubes and Nanostructured Composites (CNNC) at Sungkyunkwan University.

REFERENCES

1. D. Tasis, N. Tagmatarchis, A. Bianco, and M. Prato. *Chem. Rev.* **106**, 1105 (2006).
2. A. G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C. B. Huffman, F. J. Rodríguez-Macías, P. J. Boul, A. H. Lu, D. Heymann, D. T. Colbert, R. S. Lee, J. E. Fischer, A. M. Rao, P. C. Eklund, and R. E. Smalley, *Appl. Phys. A* **67**, 29 (1998).
3. J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, and R. E. Smalley, *Science* **280**, 1253 (1998).
4. J. S. Moon, J. H. Park, T. Y. Lee, Y. W. Kim, J. B. Yoo, C. Y. Park, J. M. Kim, and K. W. Jin, *Diamond & Related Materials* **14**, 1882 (2005).