

# EFFECT OF SURFACE TREATMENT OF CNTs ON THE ELECTRICAL CONDUCTIVITY AND HYDROPHILICITY OF PANI COATED CNTs/EPOXY COMPOSITES

**Ok-Kyung Park<sup>1,2</sup>, Sambhu Bhadra<sup>2</sup>, Nam Hoon Kim<sup>1</sup>, Joong-Hee Lee<sup>1,3\*</sup>**

<sup>1</sup>Department of Hydrogen and Fuel Cell Engineering, Chonbuk National University

<sup>2</sup>Core Technology Research Center for Fuel Cell, Gu-doon ri 587-4, Bong-dong eup, Jeonju, Jeonbuk 565-902,

<sup>3</sup>Bin Fusion Research Team, Dept Polymer and Nano Engineering, Chonbuk National University,

Jeonju, Jeonbuk, 561-756, Republic of Korea (\*Corresponding to Joong Hee Lee (jhl@chonbuk.ac.kr))

## Introduction

The most common material for non-metal bipolar plates is graphite. The manufacturing of bipolar plate using pristine graphite is complicated because it is brittle in nature. Recent trend of the study is the preparation of moldable composite bipolar plates comprised of high content of graphite and additional conductive fillers in a polymer matrix (binder). The additional conductive fillers are incorporated to enhance the electrical conductivity and physical properties of such composites. Carbon nanotubes (CNTs) are attractive conductive filler for improving both the electrical conductivity and physical properties of composites. However, CNTs tend to aggregate into ropes or entangle into bundles and thus cause poor dispersion in the matrix. CNTs also have a very weak interfacial bonding with polymer matrix. Several surface treatment procedures have been demonstrated to disperse efficiently individual CNTs in a polymer matrix. However, this surface treatment also has a detrimental effect on the conductivity of the composites. The polymer composite which is applicable for the bipolar plate of fuel cell should also be hydrophilic at the cathode side in order to manage the water generated during the electrochemical reactions inside the fuel cell [1]. Polyaniline (PANI) is a hydrophilic conducting polymer. In order to obtain both good conductivity and hydrophilicity of the composites, the PANI coated CNTs was prepared and added as conducting filler to the epoxy matrix (binder). The present study investigates the effect of surface treatment of CNTs on the electrical conductivity and the hydrophilicity of PANI coated CNTs (PANI-c-CNTs)/epoxy (EP) composites.

## Experimental

The preparation of O-CNTs is as follows: Raw CNTs (Hanwha-nanotech, Korea) were immersed in

acid mixtures ( $\text{HNO}_3:\text{H}_2\text{SO}_4$ ; 1:3), sonicated for 30min and then refluxed at  $110^\circ\text{C}$  for 1hr. The O-CNT thus obtained was filtered, washed and then dried at  $60^\circ\text{C}$  for 24.

The Preparation of K-CNT and S-CNT are as follows: The raw CNTs were immersed in potassium persulfate (KPS) / sodium dodecyl sulfate (SDS) (0.1M), sonicated for 30min and then stirred for 24 hrs. After that the K-CNTs/S-CNTs were filtered, washed and then dried at  $60^\circ\text{C}$  for 48 hrs. The O-CNTs were used to prepare K-OCNTs/S-OCNTs with similar experimental procedure.

The surface treated CNTs were dispersed in 0.1M Dodecyl benzene sulfuric acid (DBSA) for 1hr. Then aniline monomer was added into it and sonicated for 30min. To polymerize the adsorbed aniline on the CNTs surface, aqueous solution of ammonium persulfate (APS) was added drop wise to the above suspension with constant stirring. The polymerization was continued for 6hrs at room temperature with constant stirring. The precipitated PANI-CNT composite was then washed with DI water and dried at  $60^\circ\text{C}$  for 24 hr.

The preparation of PANI coated CNT/Epoxy (EP) composites are as follows: EP (YSLV-80XY) and hardener (TAMANOL758) were mixed by the weight ratio of 1:0.5 and 1 wt % accelerator (TPP) was added and mixed again. Each PANI coated CNTs (PANI-c-CNTs) and EP resin were taken by the volume ratio of 3:1 and mixed. Each mixture was hot pressed at  $130^\circ\text{C}$  for 1 hr under a pressure of 45MPa and finally cooled to room temperature.

FE-TEM observation was carried out with a JEM 2200 FS. The electrical conductivity was measured by a programmable DC voltage/current detector. The water contact angle was measured using a Phoenix-300(Search engine optimization, Korea).

## Results and Discussion

Table 1 presents the electrical conductivity of PANi-c-CNTs/EP composites. The electrical conductivity of PANi-K-OCNT/EP, PANi-S-OCNT/EP and PANi-O-CNT/EP composites are lower than PANi-K-CNT/EP and PANi-S-CNT/EP composites. Amine groups of PANi in PANi-c-CNTs are covalently bonded with the epoxy end-groups leading to the wrapping of CNTs by epoxy after curing. The wrapped epoxy acts as barrier between the PANi of PANi-c-CNT and c-CNT wall, which reduces the electron tunneling effect of composite [2]. The electrical conductivity of the PANi coated CNTs is reflected in the conductivity of their epoxy composites. The electrical conductivity of PANi-K-OCNT/EP and PANi-S-OCNT/EP are less than PANi-O-CNT/EP composite. This is due to the formation of an electrically insulating surface layer over the CNTs by the SDS and KPS treatment. It is clearly observed from the FE-TEM images (Fig.1). The O-CNTs does not produce any chemical layer on the surface of CNTs (Fig1 (a)). However, after SDS and KPS treatment, a amorphous chemical layer is formed on the surface of CNTs (Fig 1(c,d,e)). Introduction of chemical layer over the surface of CNTs strongly influences the electrical conductivity of the CNTs and their composites

Table 1. The electrical conductivity of PANi coated c-CNTs /Epoxy (PANi-c-CNTs/EP) and Raw CNTs/Epoxy (Raw CNTs/EP) composites.

Samples	Electrical conductivity(s/cm)
Raw CNTs/EP	0.3931
PAni (DBSA) /EP	0
PAni -O-CNTs/EP	0.0813
PAni-K-CNTs/ EP	0.3383
PAni-K-OCNTs/EP	0.0648
PAni-S-CNT/ EP	0.3856
PAni-S-OCNT /EP	0.0747

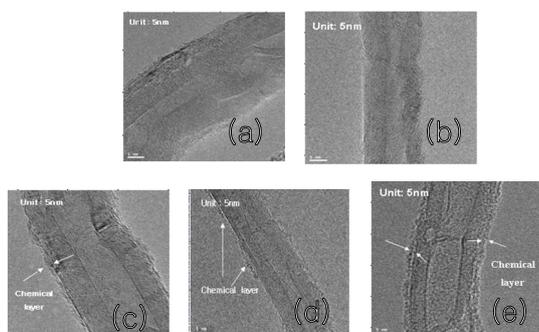


Fig. 1. FE-TEM images of (a) O-CNTs, (b) K-CNTs, (c) K-OCNTs, (d) S-CNTs and (e) S-OCNTs

Fig.2 shows the water contact angle values of PANi-c-CNTs/EP and Raw CNT/EP composites. The decrease in water contact angle implies an increase in water wettability or hydrophilicity. From the contact angle data it is clear that after the coating of PANi on the O-CNT, K-OCNTs, and S-OCNTs, the hydrophilic behavior of these composites is increased to a large extent.

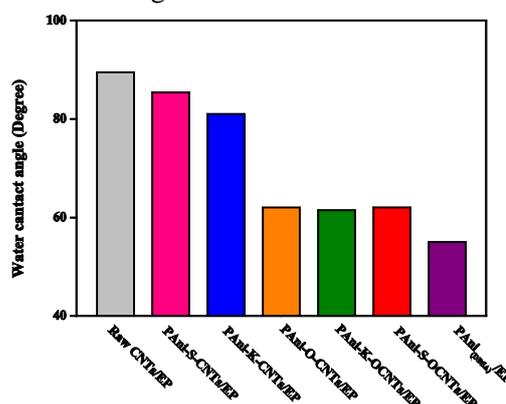


Fig. 2. The water contact angle of PANi-c-CNTs/EP, Raw CNT/EP and PANi (DBSA)/EP composites

## Conclusion

The surface treatment of CNTs has strong influence on the electrical conductivity and hydrophilicity of its composites. The hydrophilicity of the composites was improved after the coating of treated CNTs with PANi; however electrical conductivity was decreased due to this coating. The PANi-c-CNT/EP composites may provide additional advantage for the water management due to their hydrophilic characteristic.

## Acknowledgements

This research work was supported by the Core Technology Research Center for Fuel Cell funded by the Ministry of Knowledge and Economy(MKE), and the National Space Laboratory (NSL) Program (S108A01003210), funded by the Ministry of Education, Science and Technology of Korea

## References

1. Le AD, Zhou B. *Electrochimica Acta* 54 (2009)2137.
2. Ramesh P, Bhagyalakshmi S, Sampath S. J *colloid interface Sci* 274(2007)95.