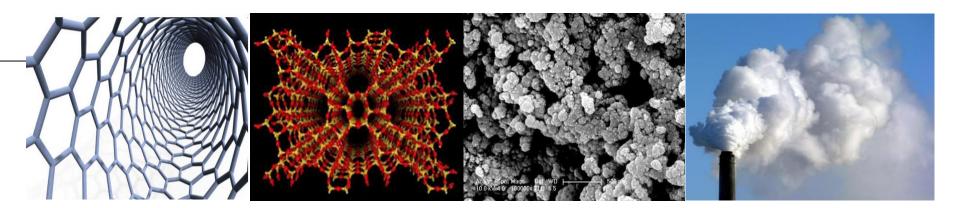
## Functional carbon nanotube reinforced cementitious composites

H.K. Lee and G.M. Kim

**Department of Civil & Environmental Engineering** 

Korea Advanced Institute of Science and Technology

October 6, 2016

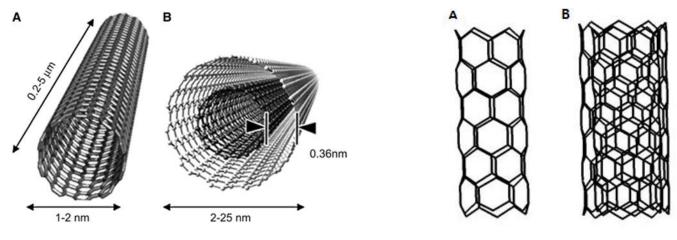


- I. Introduction
- II. Electromagnetic wave shielding CNT/cement or epoxy composites
- III. Piezoresistive and piezoelectric CNT/epoxy composites
- IV. Self-heating CNT/cement composites
- V. Future works

## Introduction

#### **Outstanding properties of CNT**

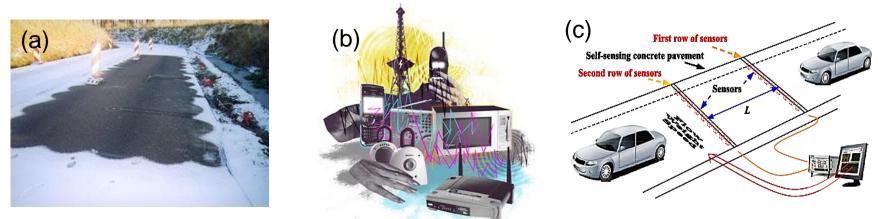
- CNT has been used in a variety of fields due to its remarkable physical properties since late 20<sup>th</sup> century.
- Yield strength of CNT can be up to 120 times greater than that of steel, and CNT exhibits an electrical conductivity more than 1,000 times greater than copper wire<sup>[1,2]</sup>.
- ➢CNT can replace metals due to its low cost, good durability, easy fabrication and no corrosion issues<sup>[5]</sup>.



(a) Single wall (b) multi-wall nanotubes<sup>[3,4]</sup>

#### **CNT composites as a construction material**

- CNT can be embedded in various types of organic (e.g., epoxy, polystyrene (PS), poly methylmethacrylate (PMMA)) and inorganic (e.g., cement) matrices<sup>[5]</sup>.
- Effective dispersion of CNT into the matrices is crucial to assure the desired performance of target functional materials.
- CNT-incorporated new materials in construction can be used for self-sensing, self-heating, electromagnetic wave shielding/absorbing, etc.



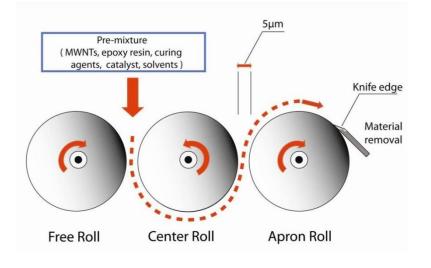
(a) self-heating<sup>[6]</sup>, (b) EMI wave distruption<sup>[7]</sup>, and (c) self-sensing pavement sensor for traffic flow detection<sup>[8]</sup>

## Electromagnetic wave shielding CNT/cement or epoxy composites

#### Fabrication of CNT/epoxy film

>Epoxy and CNT were mixed and fabricated as thin films.

- A three-roll milling machine was used to well disperse CNT in the epoxy resin<sup>[9]</sup>.
- Electromagnetic (EMI) wave shielding effectiveness of CNTembedded epoxy composites was investigated via free space or coaxial methods.

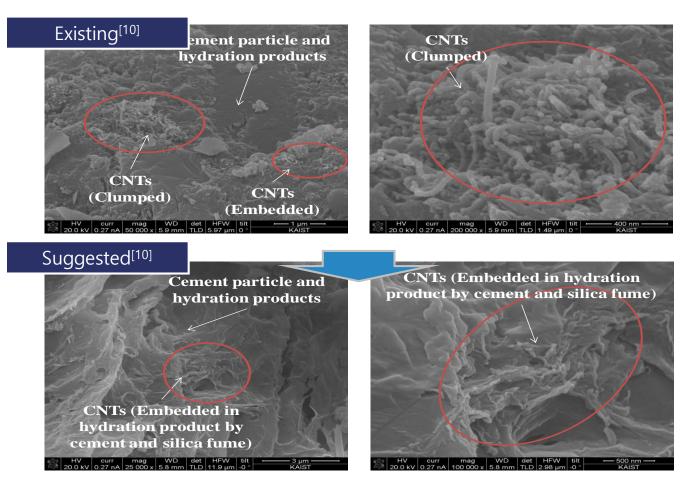




#### Three-roll milling machine<sup>[9]</sup>

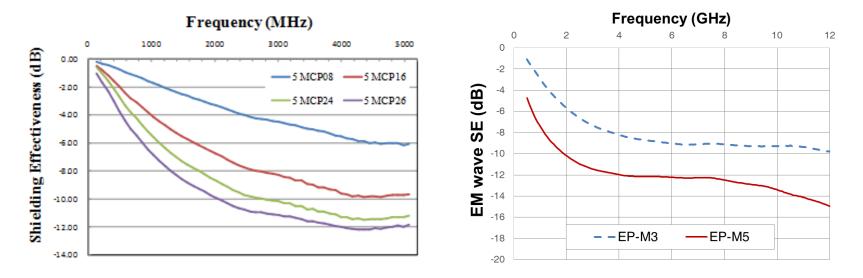
#### **Fabrication of CNT/cement composites**

Problems of CNT/cement composites were agglomerations of CNT, resulting in CNT clumps and poor dispersion of CNT into the matrix. Micro silica (e.g., silica fume) was newly added to effectively disperse the CNT.



#### EM shielding effectiveness of CNT/epoxy film

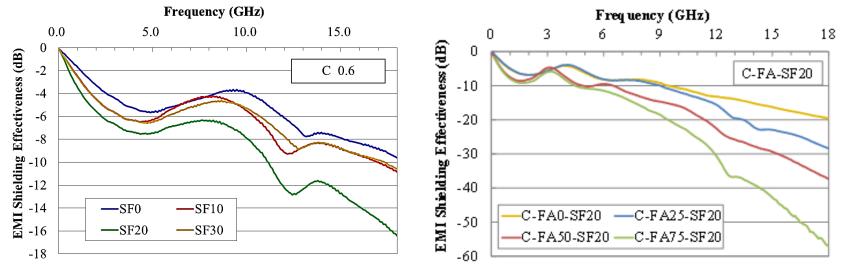
- >5MCP26 was able to shield the EM wave 7 ~ 12 dB (80 ~94 %) at frequencies1 ~ 5 GHz.
- ➢EP-M5 was able to shield the EM wave over -10 dB (90 %) from a low frequency bound 2.0 GHz.
- The EM wave which generated from GPS, PCS, WLANs, and microwave ovens can be blocked using the EP-M5 (2.67 mm in thickness) with -10 dB (90 %) shielding<sup>[9]</sup>.



#### **EM SE of CNT/cement composites**

Specimen adopting new dispersion method was able to shield the EM wave 3.5 ~ 16.52 dB (55 ~98 %) at frequencies1 ~ 18 GHz.

Specimen having CNT and Fe<sub>2</sub>O<sub>3</sub> was able to shield the EM wave 8 ~ 57 dB (84 ~99.9 %) at frequencies1 ~ 18 GHz.

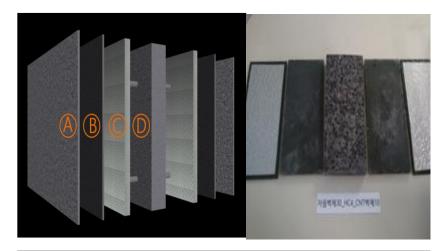


**CNT/cement composite block**<sup>[10]</sup>

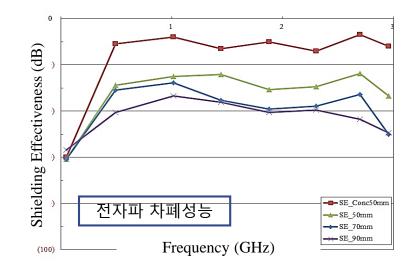
CNT/Fe<sub>2</sub>O<sub>3</sub>/cement composite block<sup>[10]</sup>

#### EM shielding sandwich composite panel I

- Composite panel consisting of CNT/cement mortar, honeycomb plate, lightweight porous block was fabricated as an interior or exterior EM shielding system panel.
- EM shielding effectiveness of the panel was measured at the electromagnetic anechoic chamber.



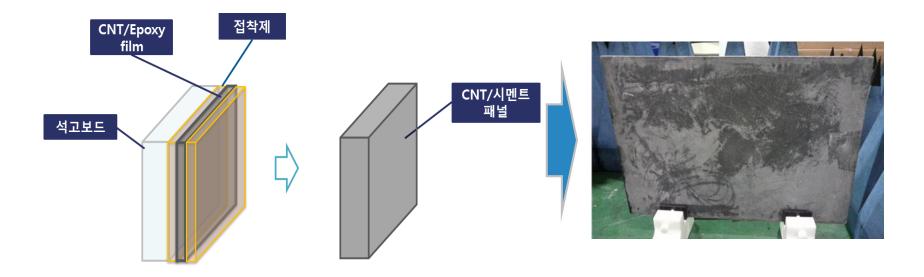
Panel configuration: (A) Finishing material (B) EM shielding/absorbing CNT/cement mortar (C) Honeycomb plate (D) lightweight porous block<sup>[16]</sup>



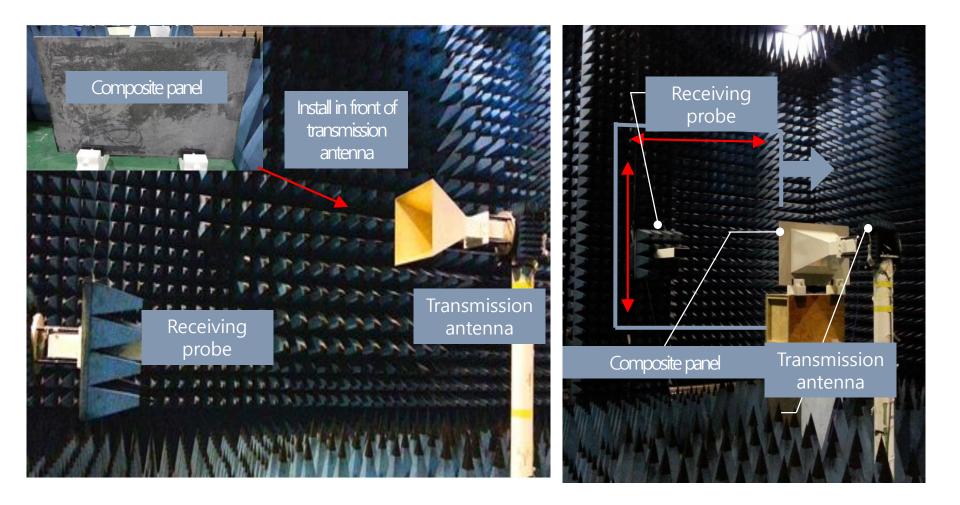
EM SE of 50 mm panel: 20dB(99.9%)<sup>[11]</sup>

#### EM shielding sandwich composite panel II

- Composite panel consisting of CNT/epoxy film and gypsum board was fabricated as an interior or exterior EM shielding system panel.
- EM shielding effectiveness of the panel was measured at the electromagnetic anechoic room.

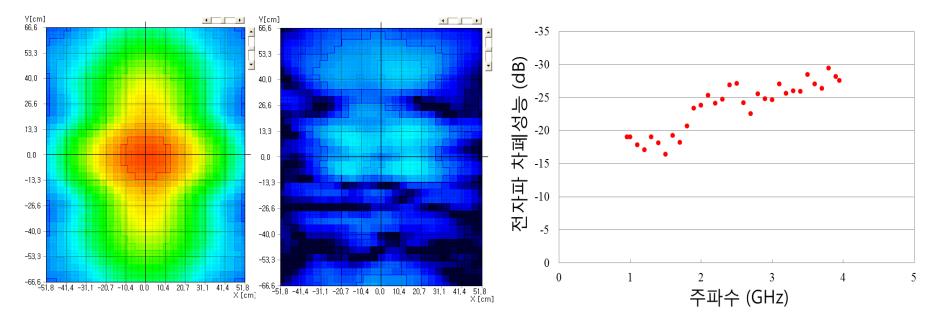


#### Mock up test of sandwich composite panel II



#### Mock up test results of composite panel II

- Composite panel consisting of CNT/epoxy film and gypsum board was able to shield the EM wave 16 ~ 29 dB (97.5 ~ 99.99 %) at frequencies1 ~ 4 GHz.
- EM shielding effectiveness increases with frequency.



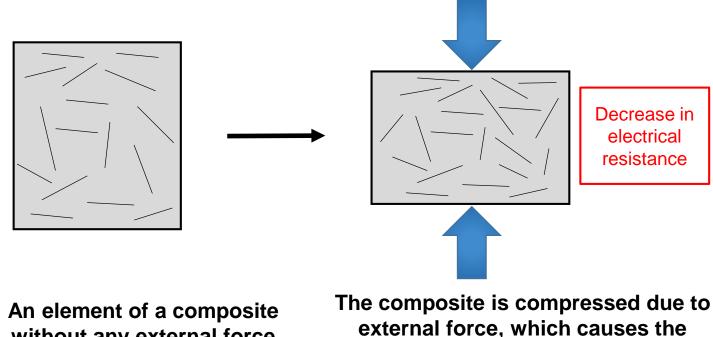
Received EM wave at 2.7 GHz: with (left) and without (right) the CNT/epoxy film<sup>[11]</sup>

EM Shielding effectiveness<sup>[11]</sup>

## Piezoresistive and piezoelectric CNT/epoxy composites

#### **Piezoresistivity of CNT composites**

- Piezoresistivity is the change in electrical resistivity due to applied mechanical stress<sup>[12]</sup>.
- Electrical resistance decreases when compressive stress is applied since conductive networks newly form or change by geometrical deformation<sup>[14]</sup>.



#### Field test of CNT composite sensors

- Piezoresistive (CNT/PU composite) sensors were manufactured and attached on cement mortar blocks to be embedded in the pavement.
- A field test was conducted to detect movements of vehicles by the piezoresistive (CNT/PU composite) sensor which is embedded in the pavement.
- Electrical resistivity was changed when external force was applied by vehicles.



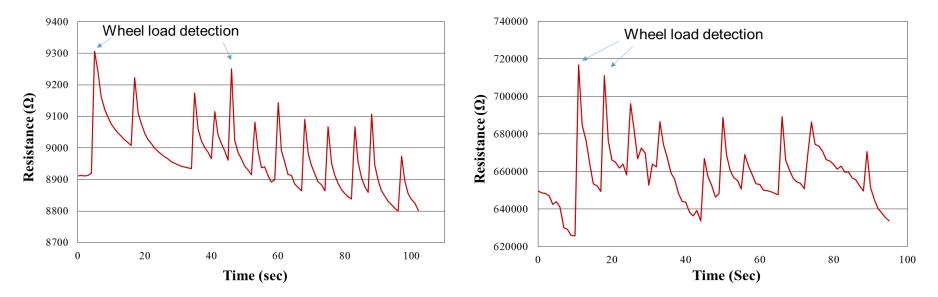
A mold used to fabricate piezoresistive sensors<sup>[13]</sup>

Experimental setup of field test with measurement devices<sup>[13]</sup>

#### Field test results of CNT composite sensors

Piezoresistive CNT sensors were able to detect every movement of the vehicle in the field test.

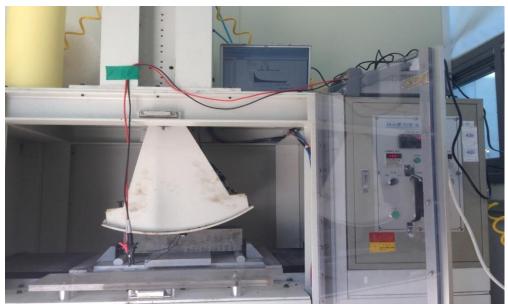
The change in resistance was in the form of increment due to the impact damage or micro-cracks made by the vehicle<sup>[13]</sup>.



Resistance vs. time of 6 wt.% MWNT/PU composite obtained from the field test<sup>[13]</sup> Resistance vs. time of 5 wt.% MWNT/PU composite obtained from the field test<sup>[13]</sup>

#### **Durability of CNT composite sensors**

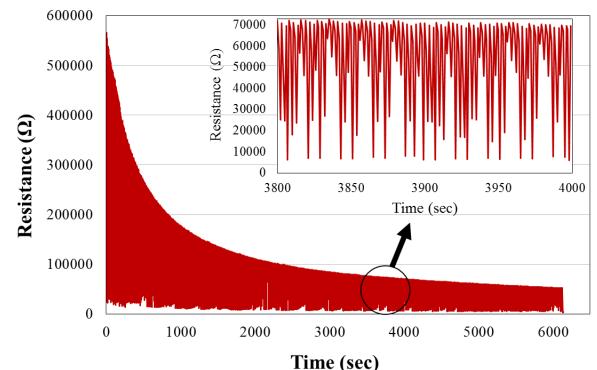
- Durability of piezoresistive CNT sensors was studied by the wheel load test.
- ➢Number of cycles were set at 2000, and the magnitude of the compressive load was set at 400 Kg.
- Change in the electrical resistance was measured during the wheel load test.



Wheel load test experimental set-up for 5 wt.% MWNT/PU composite (KCL institute)

#### **Durability of CNT composite sensors**

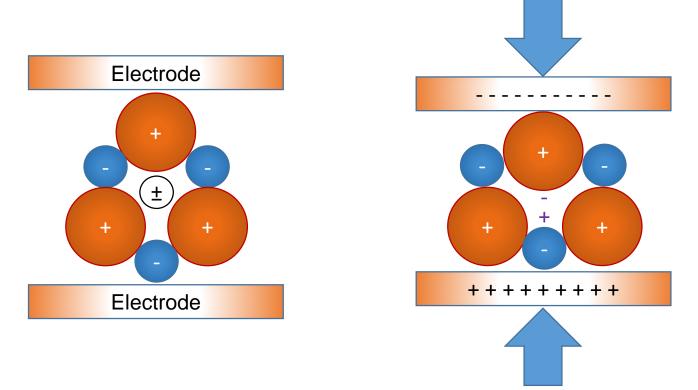
- The piezoresistive sensor was able to detect every single trial during wheel load test.
- Electrical resistance decreased continuously due to the formation of conductive networks under long-term periodic compressive load condition.



Experimental results of wheel load test for 5 wt.% MWNT/PU composite (KCL institute) 20

#### **Piezoelectricity of CNT/ZnO/PU composites**

- Piezoelectricity is the ability of specific type of materials to generate voltage when mechanical stress is applied<sup>[14]</sup>.
- Piezoelectric materials have a specific electrical crystalline structure.



Without any external force

Generation of electrical voltage due to the external forces by piezoelectricity

#### **Piezoelectric CNT/ZnO/PU generators**

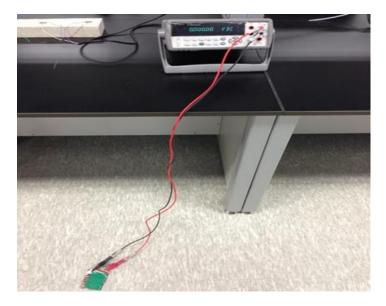
- MWNT and Zinc Oxide (ZnO) nanoparticles were dispersed in the polyurethane (PU) matrix.
- Piezoelectric properties of both MWNT and ZnO were studied to better understand the change in electrical voltage when mechanical strain is applied to the materials<sup>[15,16]</sup>.
- Piezoelectric CNT composite materials can act as a voltage generator when external force is applied to the composites.

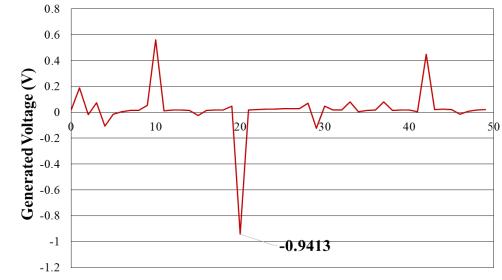


MWNT/ZnO based piezoelectric generator (CNT/ZnO/PU composites, 5×7×0.7 cm<sup>3</sup>)

#### **Performance of CNT/ZnO/PU generators**

- The composite generator was stamped by foot of a person (80 Kg) and the peak voltages generated from the composite were measured.
- The obtained voltages were 60mV, and the maximum value of obtained voltages was nearly 1V.





Time (sec)

Experimental set-up of CNT/ZnO/PU voltage generator<sup>[15]</sup>

Generated voltage under applied foot step vs. time<sup>[15]</sup>

#### Field test of CNT/ZnO/PU generators

- The piezoelectric CNT/ZnO/PU generators were manufactured and attached on cement mortar blocks to be embedded in the pavement.
- ➤A field test was conducted to observe the piezoelectric performance of the CNT/ZnO/PU generator. The generated voltages with the manufactured generator by movement of vehicles were monitored.

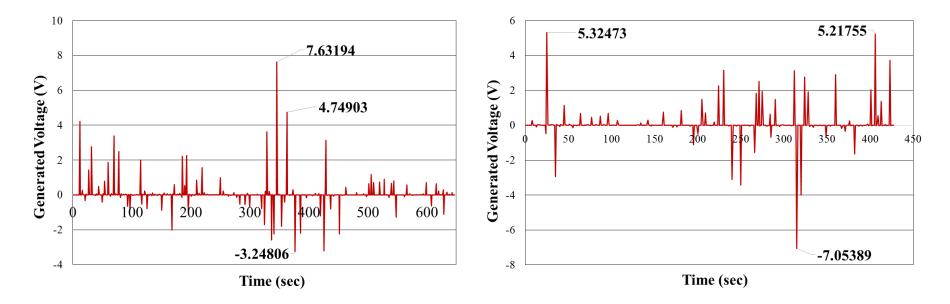


Experimental setup of field test with measurement devices Applied pressure by vehicle

#### Field test results of CNT/ZnO/PU generators

The piezoelectric CNT/ZnO/PU generator was able to generate voltages by movement of the vehicle in the test.

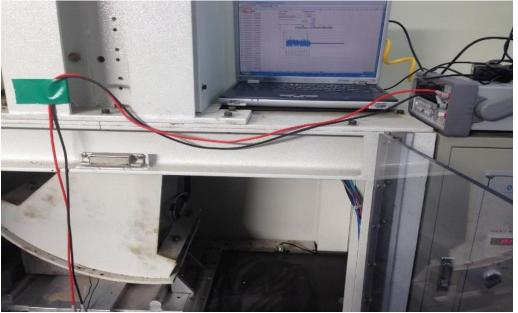
The deviation between obtained voltages was very large, and average obtained voltages were nearly 1.4V.



Generated voltage under applied load vs. time for piezoelectric generator with high ZnO ratio<sup>[15]</sup> Generated voltage under applied load vs. time for piezoelectric generator with low ZnO ratio<sup>[15]</sup>

#### **Durability of CNT/ZnO/PU generators**

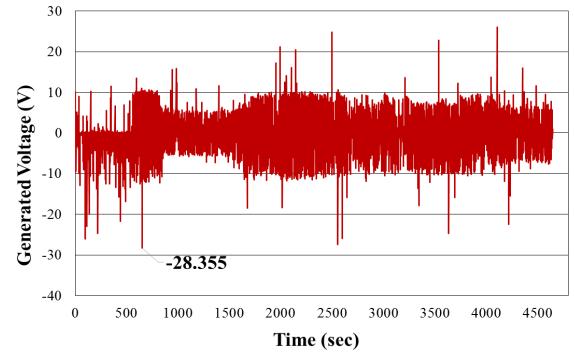
- Durability of piezoelectric CNT/ZnO/PU generator was studied by the wheel load test.
- ➤The number of cycles were set at 2000, and the magnitude of compressive load was set at 400 Kg.
- The generated voltages were measured during the wheel load test.



Wheel load test experimental set-up for MWNT/ZnO/PU generator (KCL institute)

#### **Durability of CNT/ZnO/PU generators**

- The piezoelectric CNT/ZnO/PU generator was able to generate voltages during wheel load test.
- >The average obtained voltages were close to  $\pm 10V$ .
- Comparatively lower numbers of peak values were more than ±20V.

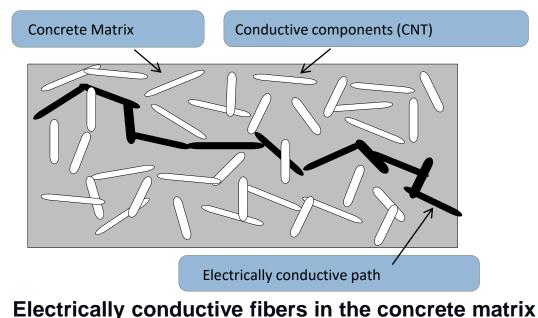


Experimental results of wheel load test for MWNT/ZnO/PU generator (KCL institute)

# Self-heating CNT/cement composites

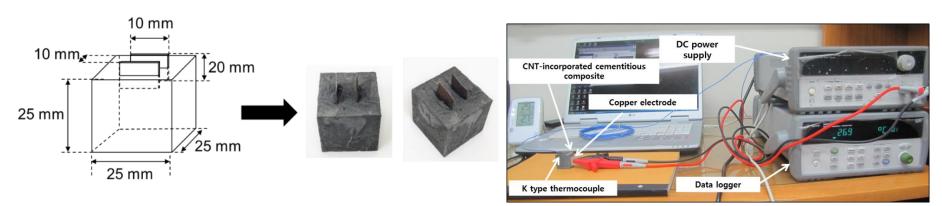
#### **Electrically conductive concrete**

- Electrically conductive concrete is a cementitious composite that contains electrically conductive components (e.g., CNT) in the concrete matrix to ensure low electrical resistivity<sup>[17]</sup>.
- Electrically conductive concrete works on the principle of resistive heating<sup>[18]</sup>.
- Resistive heating produces heat when electric current passes through electrical conductor<sup>[17]</sup>.



#### **Percolation threshold fiber ratio**

- The CNT-incorporated cementitious composites block were composed of Portland cement, silica fume, CNT, superplasticizer, and water.
- Poly-carboxylic acid based superplasticizer and silica fume were used as dispersion agents.
- The amount of CNT added to the composites and the input voltages were varied from 0.1 wt% to 2.0 wt% and from 3 V to 20 V, respectively.



Geometry of the CNT-incorporated cementitious composite<sup>[17]</sup>

Experimental set up<sup>[17]</sup>

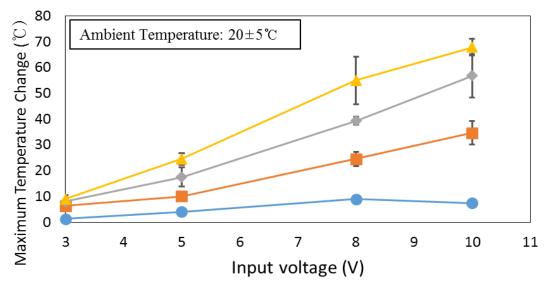
#### Self heating performance of the composites

The composite with higher CNT ratio indicated higher maximum temperature during heating.

>Maximum temperature increases as input voltage increases.

The maximum temperature change was over 60°C in the case of CNT 2.0% with the input voltage of 10V.

-CNT 0.3 ----CNT 0.6 ---CNT 1.0 ----CNT 2.0

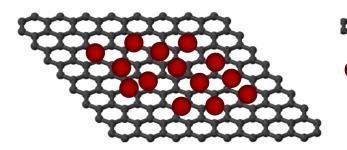


Maximum temperature change of CNTs/cement composites vs. input voltage

### Future works

#### **Graphene-TiO<sub>2</sub> synthesis (future works)**

- Pollutants (e.g., NOx, CO<sub>2</sub>) removal using synthesized graphene-TiO<sub>2</sub>
  - Graphene has exceptional mechanical, electrical and photochemical properties due to the existence of 2dimensional layers of carbon atoms present in graphene<sup>[19]</sup>.
  - Titanium dioxide (TiO<sub>2</sub>) is regarded as excellent photocatalyst since the discovery of Honda-Fujishima effect in 1972<sup>[20]</sup>.
  - Hybrids of 2-d graphene sheets and TiO<sub>2</sub> nanoparticles have shown exceptional properties for energy and environmental applications among others<sup>[21,22]</sup>.

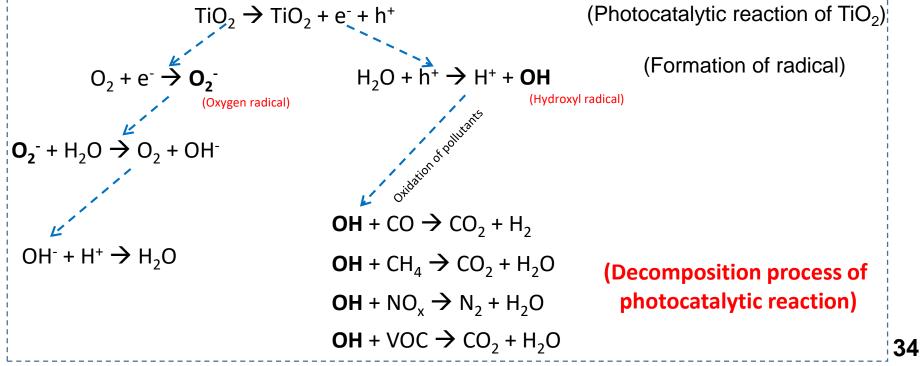


- Graphitic Carbon sheets in graphene
  - TiO<sub>2</sub> nanoparticles

#### **Graphene-TiO<sub>2</sub> synthesis (future works)**

#### Application to concrete structures

- Our research work will focus on the synthesis of graphene-TiO<sub>2</sub> hybrids and their applications in construction materials to remove pollutants through synergistic photocatalytic effects of graphene and TiO<sub>2</sub>.
- Advanced sol-gel incorporated in-situ fabrication techniques will be researched.
- Establishment of experimental setup for recording the removal of CO<sub>2</sub>
  --- and NOx-is-in-process.



#### References

- 1. http://www.wamgroup.com/en-GB/corporate/SDetail/S569/SOL\_CON/Concrete-Production-Plant-Equipment
- 2. http://www.tececo.com/files/newsletters/Newsletter52.htmPage CL, Treadaway KWJ. Aspects of the electrochemistry of steel in concrete.
- 3. https://www.iea.org/publications/freepublications/publication/etp2010.pdf
- 4. http://www.netl.doe.gov/technologies/carbon\_seq/corerd/co2utilization.html
- 5. http://socalcarb.org/storage.html
- 6. http://www.captage-stockage-valorisation-co2.fr/en/deep-saline-aquifers
- 7. http://www2.technologyreview.com/article/418542/tr10-green-concrete/
- You, K. S., Lee, S. H., Hwang, S. H., Kim, H. S., & Ahn, J. W. (2011). "CO<sub>2</sub> Sequestration via a Surface-Modified Ground Granulated Blast Furnace Slag Using NaOH Solution", Materials Transactions, Vol. 52(10), pp. 1972-1976
- 9. Nam, I.W., Lee, H.K. and Jang, J.H. (2011). "Electromagnetic interference shielding/absorbing characteristics of CNT-embedded epoxy composites," Composites Part A: Applied Science & Manufacturing, Vol. 42, No. 9, pp. 1110-1118.
- 10. Nam, I.W., Kim, H.K. and Lee, H.K. (2012). "Influence of silica fume additions on electromagnetic interference shielding effectiveness of multi-walled carbon nanotube/cement composites," Construction & Building Materials, Vol. 30, pp. 480-487.
- 11. Nam, I.W., Lee, H.K., Sim, J.B. and Choi, S.M. (2012). "Electromagnetic characteristics of cement matrix materials with carbon nanotubes," ACI Materials Journal, Vol. 109, No. 3, pp. 363-370.
- 12. Kim, H.K., Park, I.S. and Lee, H.K. (2014). "Improved piezoresistive sensitivity and stability of CNT/cement mortar composites with low water-binder ratio," Composite Structures, Vol. 116, pp. 713-719.
- 13. Souri, H., Nam, I.W., Lee, H.K. (2015). "Electrical properties and piezoresistive evaluation of polyurethane-based composites with carbon nano-materials," Composites Science and Technology, Vol. 121, pp. 41-48.
- 14. Priya, S., & Inman, D. J. (Eds.). (2009). Energy harvesting technologies (Vol. 21). New York: Springer.
- 15. Lee, J. H., Lee, K. Y., Gupta, M. K., Kim, T. Y., Lee, D. Y., Oh, J., ... & Yoo, J. B. (2014). Highly stretchable piezoelectric-pyroelectric hybrid nanogenerator. Advanced Materials, 26(5), 765-769.
- 16. Souri, H., Nam, I.W., and Lee, H.K. (2015). "A zinc oxide/polyurethane-based generator composite as a self-powered sensor for traffic flow monitoring," Composite Structures, Vol. 134, No. 15, pp. 579-586.
- 17. Kim, G.M., Naeem, F., Kim, H.K., and Lee, H.K. (2016). "Heating and heat-dependent mechanical characteristics of CNT-embedded cementitious composites," Composite Structures, Vol. 136, pp. 162-170.
- 18. Kim, G.M, Yang, B.J., Ryu, G.U. and Lee, H.K. (2016). "The electrically conductive carbon nanotube (CNT)/cement composites for accelerated curing and thermal cracking reduction," Composite Structures, accepted.
- 19. Allen, Matthew J., Vincent C. Tung, and Richard B. Kaner. (2009). "Honeycomb carbon: a review of graphene." Chemical reviews, Vol. 110.1 pp. 132-145.
- 20. Pelaez, M., Nolan, N. T., Pillai, S. C., Seery, M. K., Falaras, P., Kontos, A. G., ... & Entezari, M. H (2012). "A review on the visible light active titanium dioxide photocatalysts for environmental applications." Applied Catalysis B: Environmental. Vol. 125 pp. 331-349.
- 21. Kim, J. H., Choi, W., Jung, H. G., Oh, S. H., Chung, K. Y., Cho, W. I., ... & Nah, I. W. (2017). Anatase TiO 2-reduced graphene oxide nanostructures with high-rate sodium storage performance. Journal of Alloys and Compounds, Vol. 690, pp. 390-396.
- 22. Bhatia, V., Malekshoar, G., Dhir, A., & Ray, A. K. (2017). Enhanced photocatalytic degradation of atenolol using graphene TiO 2 composite. Journal of Photochemistry and Photobiology A: Chemistry, Vol. 332, pp. 182-187.

## Thank you for your attention