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Smart Structural Health Monitoring Using Carbon Nanotube Polymer Composites

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ABSTRACT

This paper presents an experimental study on the piezoresistive behavior of nanocomposite strain sensors subjected to various loading modes and their capability to detect structural deformations and damages. The electrically conductive nanocomposites were fabricated in the form of a film using various types of thermoplastic polymers and multi-walled carbon nanotubes (MWNTs) at various loadings. In this study, the nanocomposite strain sensors were bonded to a substrate and subjected to tension, flexure, or compression. In tension and flexure, the resistivity change showed dependence on measurement direction, indicating that the sensors can be used for multi-directional strain sensing. In addition, the sensors exhibited a decreasing behavior in resistivity as the compressive load was applied, suggesting that they can be used for pressure sensing. This study demonstrates that the nanocomposite strain sensors can provide a pathway to affordable, effective, and versatile structural health monitoring.

초 록

탄소나노튜브 고분자 복합체는, 외력에 의한 변형에 따라 전기적 저항이 변화하는 피에조저항(piezoresistivity) 거동을 나타낸다. 피에조저항은 고분자 모재 내에서 탄소나노튜브가 형성하는 전기전도망(conductive network)의 변화에 의해서 발현된다. 피에조저항 낮은 탄소나노튜브 함유량에서 더 현저하게 나타난다. 탄소섬유, 카본블랙 등 타 탄소기반 소재에 비해 전기전도도와 길이 대 직경비(aspect ratio)가 월등히 우수하기 때문에, 낮은 탄소나노튜브의 함유량에서도 스트레인 센싱시스템을 구현할 수 있다. 본 연구에서는, 구조물에 부착 또는 임베드 시켜서 구조물의 건전성을 실시간을 진단할 수 있는 탄소나노튜브 고분자 복합체 기반 센싱시스템을 개발하였다. 센서는 열가소성 수지와 다중벽 탄소나노튜브를 사용하여 필름 형태로 제조되었으며, 센싱 성능은 나노복합체를 구조물에 부착한 후 인장, 굽힘, 압축 등의 다양한 형태의 하중을 가하면서 평가하였다.

Key Words : 열가소성 수지 나노복합체(thermoplastic nanocomposites), 탄소나노튜브(carbon nanotubes), 피에조저항(piezoresistivity), 스트레인 센싱(strain sensing), 구조건전성 진단(structural health monitoring)

1. Introduction

Among a number of interesting unique electrical behaviors,

such as electromagnetic interference shielding and radiation absorption [1,2], polymer/carbon nanotube nanocomposites have been shown to exhibit piezoresistive behavior, i.e., their

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resistivity (conductivity) changes when subjected to mechanical strains [3,4]. The piezoresistive property evidently arises from: 1) changes in intrinsic conductive properties of the carbon nanotubes (CNTs) subjected to strains [5-8], and 2) changes in the microstructure of the conductive network within the composites. In the latter, strain-induced translation and rotation of the CNTs disrupt or rearrange the conductive paths of mutually contacting CNTs, thereby altering the network conductivity, a phenomena that have been noted in previous research on other heterogeneous conductive polymers, e.g., carbon black and carbon fiber-based composites [9-13]. Additionally, applied strain could affect the nature of CNTs' inter-connectivity (contact), which is highly influential to the electrical conduction of CNT network within the composites. It has been demonstrated, for example, that the contact resistance between CNTs depends strongly on the contact region [14,15]. The resistive values can vary over one order of magnitude, depending on factors such as the extent of interfacial surface and the alignment of molecules across the interface. Furthermore, inter-CNT resistance is dramatically elevated when a separation exists between the CNTs. Here, conductance is possible by means of tunneling mechanism [16,17], and the magnitude of the tunneling resistance is exponentially proportional to separating gap.

Moreover, piezoresistivity has been shown to be more pronounced in nanocomposites with lower CNT concentration [3,4], a reflection of factor 2) mentioned above. This would permit fabrication of strain-sensing material with tunable piezoresistivity or gage factor. Unlike other heterogeneous conductive polymers, e.g., carbon black and carbon fiber-based composites, the small size and high aspect ratio of the CNT allow desirable range of conductivity with low concentration of fillers, thereby minimizing degradation of inherent polymeric properties [18,19]. Fabrication of CNT composites is possible using a variety of traditional thermoplastic and thermosetting polymers. The nanocomposites are also sensitive to small strain and the piezoresistive behavior is fairly reversible within certain strain ranges [3]. Such attributes indicate the potential for an inexpensive and versatile sensing device that could conveniently be integrated into structures for monitoring strains, loading conditions, or damages, collectively known as health monitoring.

This study investigates CNT nanocomposites as sensing material by monitoring electrical resistance of the sensors under various loading modes. The use of electrical resistance has been explored, e.g., for strain and damage sensing in carbon fiber composite structures [20,21] or for damage

detection in CNT composite parts [22-26] with promising results. This work focuses on CNT nanocomposite sensors as stand-alone devices that can be affixed, imbedded or otherwise integrated into existing structures. The sensors were fabricated in the form of a film using thermoplastic polymers and multi-walled carbon nanotubes (MWNTs). The sensing performance was studied by bonding the film-type nanocomposite sensor to a substrate and subjecting it to tension, flexure, or compression.

2. Experimental

2.1 Materials and Sample Preparation

MWNTs having a purity rating of 95% were obtained from Aldrich (St. Louis, MO). The MWNTs were 0.5-500 μ m in length, 5-10 nm in ID, and 60-100 nm in OD. The polymers used to fabricate the nanocomposites films include molding-grade PMMA compound (Acrylite S10/8N) from Cyro (Rockaway, NJ) and polycarbonate (Lexan 103) purchased from GE Plastics (Pittsfield, MA).

Polymer pellets were dissolved in chloroform, at volume ratio of approximately 1/40, using a mechanical stirrer for 30-45 minutes. Weighted amounts of MWNTs were added to the solution and sonicated for 2 hours. Solvent was subsequently removed by air-dry, then by vacuum oven at 60°C (PMMA/MWNT) and 125°C (PC/MWNT) for 3 hours to produce polymer/MWNT composites with 10 wt.% of MWNT. Sample films were fabricated by hot pressing the solution cast nanocomposite mixture in a 10-ton hydraulic Carver press (Wabash, IN). Steel shim stock was used to produce films with a constant thickness of approximately 0.127 mm (0.005 in).

To assess the strain-sensing capability of the polymer/MWNT films in structures subjected to tensile and flexural loads, a set of test specimens was fabricated as shown schematically in Fig. 1. The specimens were constructed from acrylic or Lexan panels for use with PMMA/MWNT or PC/MWNT sensors, respectively. Tensile samples, designated as I and II, and three-point bending samples III and IV measured approximately 140 mm X 20 mm X 2.3 mm. The polymer/PMMA sensors, 20 mm X 20 mm in dimensions, were thermally bonded to the specimens without any use of adhesive. Electrical probes, approximately 10-15 mm apart, were attached to the films surface using epoxy-based conductive adhesive to record electrical resistance.

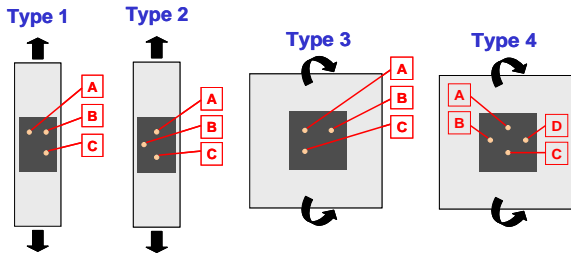


Fig. 1 Sample configurations for strain sensing under tensile and flexural loading.

Compressive samples were constructed by sandwiching a circular composite film (5.5 mm in diameter) between two circular copper foils which function as the electrodes (Fig. 2). Two sets of samples were prepared. In one set, thermal curable 3M Z-axis conductive adhesive is used to bond the copper foil electrodes with the composite sensors. In the other set, the sensors were placed between the copper foils. The sandwich structure was then lightly pressed under elevated temperature close to the heat deflection temperature of the polymers to achieve more uniform contact between the sensors and the electrodes. No adhesive was used in the second set.

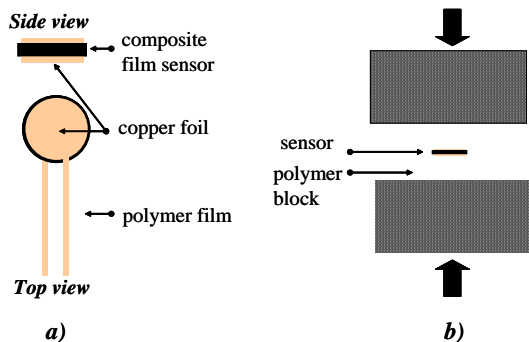


Fig. 2 Schematics of compressive sensor construction (a) and compressive load sensing experimental setup (b).

2.2 Strain and Pressure Sensing Experiments

A table-top Shimadzu AutoGraph (Kyoto, Japan) micro tensile tester having a 5 kN load cell was used to apply tensile, flexural, or compressive load. Electrical resistance was recorded using a Keithley 2000 (Cleveland, OH) multimeter using two-probe method. For strain and damage sensing samples, resistance was measured between alternating pairs of electrodes, i.e., AB, AC, and BC, while the specimens was subjected to tensile load or three-point bending. Refer to Fig.

1 for a more detailed description of the specimen and the electrical probes arrangement. For sensing of compressive loads, the sensor was placed between two PMMA blocks (or PC blocks, for PC-based sensors), which helped provide more uniformly distributed pressure on the sensors and insulate the sensor from the steel fixture of the tensile machine (Fig. 2). Force-controlled, compressive cyclic loading between 0.5 and 4.5 kN was applied on the assembly while resistance was recorded.

3. Results and Discussions

3.1 Strain Sensing Experiments

To explore the capability of the films as strain gages, resistance was measured as the specimens were subjected to tensile or flexural (3-point bending) loading. The results were normalized and are shown in Figs. 3 and 4 for PMMA/MWNT specimens. Considering Sample I, the results (Fig. 3(a)) illustrate again the positive correlation between resistance and tensile strain. Note that the strain values shown in the chart were calculated for the principal (loading) direction. It can be seen that the curves representing resistance measured between BC, AC, and AB have different slopes. This reflects the fact that at any given time, the (tensile) strain in direction BC is greater than that of AC, and strain in direction AC is greater than that of AB. It is also interesting to note that although there is no tensile strain (only compressive strain) in AB direction, the measured resistance between AB still increased. This is because the conductive network that spans AB is three-dimensional. It is therefore susceptible to disruption caused by tensile strain in directions other than AB. Clearly the extent of disruption, reflected by the magnitude of change in resistance, is most pronounced in the direction of the applied (tensile) strain, and progressively less in directions diverting from this principal (tensile) direction, as evidenced in Fig. 3(a).

The results obtained from Samples II, III, and IV, shown Fig. 3(b) and Fig. 4, reaffirm the trends observed in Sample I. Several tantalizing implications can be inferred from these results, in light of utilizing polymer/CNT films as strain sensor. First, the film offers the possibility of measuring, or at least monitoring, the relative (tensile) strain within a part in any desired direction. Second, using a single film, and properly measuring and calibrating resistance data from multiple selected directions, the direction and magnitude of the principal (tensile) strain within the part can be estimated.

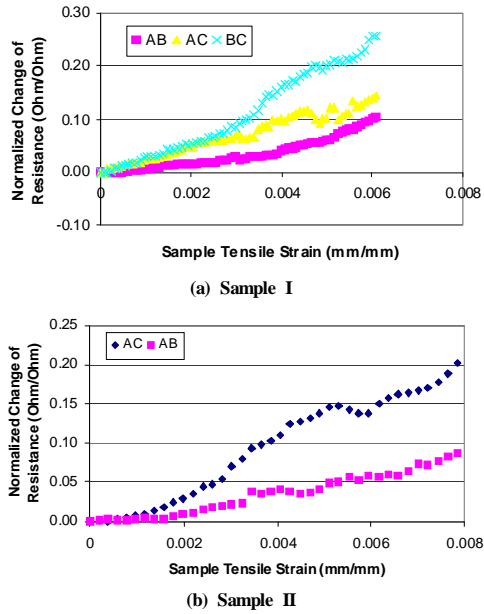


Fig. 3 Normalized change in resistance in various measuring directions - PMMA/MWNT specimens subjected to tensile loading.

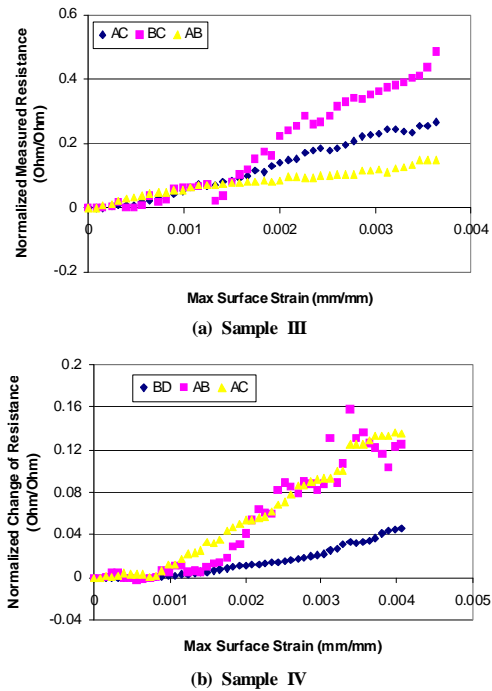


Fig. 4 Normalized change in resistance in various measuring directions - PMMA/MWNT specimens subjected to flexural loading.

3.2 Compressive Load Sensing Experiments

Compressive cyclic loads between 0.5 and 4.5 kN were applied to the sensor assembly (Fig. 2), and resistance data was recorded to assess the pressure sensing performance of the device. Figures 5 and 6 show the responses of PMMA/MWNT and PC/MWNT sensors whose constructions used conductive adhesive. In both cases, sensor resistance gradually dropped with increasing compressive load. The transient resistance lagged somewhat in response to compressive loading. Overall, however, after some fluctuation in response in the first few cycles, sensing performance was repeatable. Assuming the sensors bore the full load, compressive strains in the sensors would be roughly 5.8% and 8% at 4.5 kN load, which translate to compressive gage factors of about 4.2 and 5.5 for the PMMA/MWNT and PC/MWNT sensors, respectively. (Gage factors were obtained from dividing the change in resistance by the original resistance and the applied strain [1].) These numbers are higher than anticipated for composites at 10 wt.% [1], perhaps due to the presence of the thin layer of the conductive adhesive in the sensors.

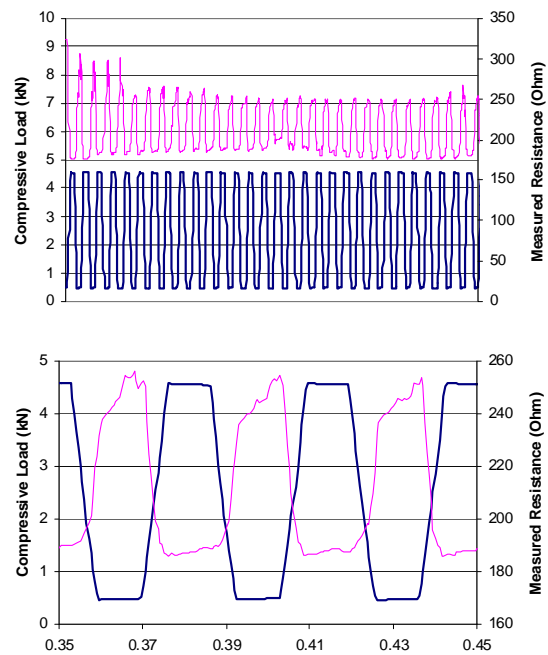


Fig. 5 Sensor (PMMA/MWNT (10 wt.% MWNT)) response to compressive cyclic loads. The sensors were constructed with conductive adhesive between copper foils and composite sensing element. Blue line represents the applied load and the pink the resulting resistance.

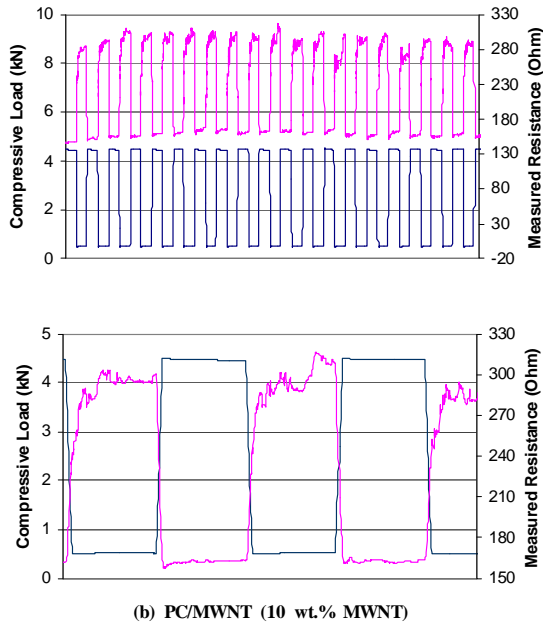


Fig. 6 Sensor (PC/MWNT (10 wt.% MWNT)) response to compressive cyclic loads.

Overall, the results from compressive load sensing experiments confirm the sensing capability of the nanocomposites sensors, whose degree of sensitivity varies depending on the CNT concentration. This conclusion carries an exciting implication. That is, given that the nanocomposites can be fabricated at different CNT concentration, using different polymers having different strength and stiffness, the sensors could be tailored to accommodate broad ranges of pressure. In this study, for example, the sensors apparently can sense pressures up to around 25,000 psi (~ 180 MPa).

4. Conclusions

This study explores the use of polymer/MWNT films as strain and damage sensing element for structures subjected to various loading modes. In tension and flexure, the resistivity change showed dependence on measurement direction, indicating that the sensors can be used for multi-directional strain sensing. In addition, the sensors exhibited excellent potential for pressure sensing, suggesting a possibility for tailoring to meet pressure range and sensitivity requirements. Overall, the study shows that the nanocomposite strain sensors can provide a pathway to affordable, effective, and

versatile health monitoring technology. Research is in progress to systematically characterize and model the sensing behavior of polymer/CNT nanocomposites and to explore applications beyond conventional strain gages' capabilities, e.g., strain sensing on irregular surfaces, such as curves or corners, etc.

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참고문헌

- 1) 이상의, 박기연, 이원준, 김천곤, 한재홍, “다중벽 탄소나노튜브가 첨가된 평직 유리섬유/에폭시 복합재료의 미세구조 및 전자기적 특성,” 한국복합재료학회지, Vol. 19, No. 1, 2006, pp. 36-42.
- 2) 김진봉, 이상관, 김천곤, “전자파 흡수체를 위한 전도성 소재로서의 탄소나노소재의 특성에 대한 연구,” 한국복합재료학회지, Vol. 19, No. 5, 2006, pp. 28-33.
- 3) Pham G.T., Park Y.-B., Liang Z., Zhang C., and Wang B., “Processing and Modeling of Conductive Thermoplastic/Carbon Nanotube Films for Strain Sensing,” *Composites Part B*, Vol. 39, 2008, pp. 209-216.
- 4) Kang I., et al., “Introduction to Carbon Nanotube and Nanofiber Smart Materials,” *Composites Part B*, Vol. 37, 2006, pp. 382-394.
- 5) Yang L. and Han H., “Electronic Structure of Deformed Carbon Nanotubes,” *Phys. Rev. Lett.*, Vol. 85, 2000, pp. 154-157.
- 6) Paulson S, Falvo M.R., Snider N., Helsen A., Hudson T., Seeger A., Taylor R.M., Superfine R. and Washburn S., “In situ Resistance Measurements of Strained Carbon Nanotubes,” *Appl. Phys. Lett.*, Vol. 75, 1999, pp. 2936-2938.
- 7) Kuzumakia T. and Mitsuda Y., “Dynamic Measurement of Electrical Conductivity of Carbon Nanotubes during Mechanical Deformation by Nanoprobe Manipulation in Transmission Electron Microscopy,” *Appl. Phys. Lett.*, Vol. 85, No. 7, 2004, pp. 1250-1252.
- 8) Dharap P., Li Z., Nagarajaiah S. and Barrera E., “Nanotube Film Based on SWNT for Macrostrain Sensing,” *Nanotechnology Journal*, Vol. 15, No. 3, 2004, pp. 379-382.
- 9) Aneli N., Zaikov G.E., and Khananashvili L.M., “Effects of

- Mechanical Deformations on the Structurization and Electrical Conductivity of Electric Conducting Polymer Composites," *J. of Appl. Polym. Sci.*, Vol. 74, 1999, pp. 601-621.
- 10) Flandin L., Chang A., Nazarenko S., Hiltner A., and BaerE., "Effect of Strain on the Properties of an Ethylene-Octene Elastomer with Conductive Carbon Fillers," *J. of Appl. Polym. Sci.*, Vol. 76, 2000, pp. 894-905.
 - 11) Das N.C., Chaki T.K., and Khastgir D., "Effect of Axial Stretching on Electrical Resistivity of Short Carbon Fibre and Carbon Black Filled Conductive Rubber Composites," *Polymer International*, Vol. 51, 2002, pp. 156-163.
 - 12) Wang X. and Chung D.D.L., "Self-Monitoring of Fatigue Damage and Dynamic Strain in Carbon Fiber Polymer-Matrix Composite," *Composites Part B*, Vol. 29, 1998, pp. 63-73.
 - 13) Gordon A.D., Wang S., and Chung D.D.L., "Piezoresistivity in Unidirectional Continuous Carbon Fiber Polymer-Matrix Composites: Single-Lamina Composite versus Two-Lamina Composite," *Composite Interfaces*, Vol. 11, 2004, pp. 95-103.
 - 14) Buldum A. and Lu J.P., "Contact Resistance between Carbon Nanotubes," *Phys. Rev. B*, Vol. 63, 2001, 161403.
 - 15) Buia C., Buldum A., and Lu J.P., "Quantum Interference Effects in Electronic Transport through Nanotube Contacts," *Phys. Rev. B*, Vol. 67, 2003, 113409.
 - 16) Simmons G.J., "Generalized Formula for Electric Tunnel Effect between Similar Electrodes Separated by a Thin Insulating Film," *J. Appl. Phys.*, Vol. 34, 1963, pp. 1793-1803.
 - 17) Sheng P., Sichel E.K., and Gittleman J.L., "Fluctuation-Induced Tunneling Conduction in Carbon Polyvinylchloride Composites," *Phys. Rev. Lett.*, Vol. 40, No. 18, 1978, pp. 1197-1200.
 - 18) Baughman R.H., Zakhidov A.A., de Heer W.A., "Carbon Nanotubes - the Route toward Applications," *Science*, Vol. 297, 2002, pp. 787-792.
 - 19) Breuer O. and Sundararaj U., "Big Returns from Small Fibers: a Review of Polymer/Carbon Nanotube Composites," *Polymer Composites*, Vol. 25, No. 6, 2004, pp. 31-37.
 - 20) Wang S. and Chung D.D.L., "Self-Sensing of Flexural Strain and Damage in Carbon Fiber Polymer-Matrix Composite by Electrical Resistance Measurement," *Carbon*, Vol. 44, 2006, pp. 2739-2751.
 - 21) Wang D. and Chung D.D.L., "Comparative Evaluation of the Electrical Configurations for the Two-Dimensional Electric Potential Method of Damage Monitoring in Carbon Fiber Polymer-Matrix Composite," *Smart Materials and Structures*, Vol. 15, 2006, pp. 1332-1344.
 - 22) Park J.M., Kim D.S., Lee J.R., and Kim T.W., "Nondestructive Damage Sensitivity and Reinforcing Effect of Carbon Nanotube/Epoxy Composites Using Electro-Micromechanical Technique," *Material Science and Engineering*, Vol. 23(C), 2003, pp. 971-975.
 - 23) Thostenson E.T. and Chou T.-W., "Carbon Nanotube Networks: Sensing of Distributed Strain and Damage for Life Prediction and Self-Healing," *Adv. Mater.*, Vol. 18, 2006, pp. 2837-2841.
 - 24) Thostenson E.T. and Chou T.-W., "Real-Time in situ Sensing of Damage Evolution in Advanced Fiber Composites Using Carbon Nanotube Networks," *Nanotechnology*, Vol. 19, 2008, 215713.
 - 25) Gao L., Thostenson E.T., Zhang Z., Chou T.-W., "Sensing of Damage Mechanisms in Fiber-Reinforced Composites under Cyclic Loading using Carbon Nanotubes," *Adv. Func. Mater.*, Vol. 29, 2009, pp. 123-130.
 - 26) 왕작가, 공조엘, 박종만, 이우일, 박종규, "미세역학적 실험법과 젖음성을 이용한 CNT-에폭시 나노복합재료 경사면 시편의 계면특성," *한국복합재료학회지*, Vol. 22, No. 5, 2009, pp. 8-14.