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Percolation threshold and piezoresistive response of multi-wall carbon nanotube/cement composites

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Abstract. The present work aims to develop piezoresistive sensors of excellent piezoresistive response attributable to change in nanoscale structures of multi-wall carbon nanotube (MWNT) embedded in cement. MWNT was distributed in a cement matrix by means of polymer wrapping method in tandem with the ultrasonication process. DC conductivity of the prepared samples exhibited the electrical percolation behavior and therefore the dispersion method adopted in this study was deemed effective. The integrity of piezoresistive response of the sensors was assessed in terms of stability, the maximum electrical resistance change rate, and sensitivity. A composite sensor with MWNT 0.2 wt.% showed the lowest stability and sensitivity, while the maximum electrical resistance change rate exhibited by this sample was the highest (96 %) among others and even higher than those found in the literature. This observation was presumably attributed by the percolation threshold and the tunneling effect. As a result of the MWNT content (0.2 wt.%) of the sensor being near the percolation threshold (0.25 wt.%), MWNTs were close to each other to trigger tunneling in response of external loading. The sensor with MWNT 0.2 wt.% was able to maintain the repeatable sensing capability while sustaining a vehicular loading on road, demonstrating the feasibility in traffic flow sensing application.

Keywords: piezoresistive sensor; multi-wall carbon nanotube; cement composite; percolation threshold; sensitivity and stability

1. Introduction

Piezoresistive sensors are stress/strain detection devices of which the electrical resistance varies in response to an applied load (Chung 2012, Kang *et al*. 2006). Piezoresistive sensors perceive stress or strain according to the electrical resistance change stemming from the load-induced deformation of the sensors in the direction of electrical conductive paths (Chung 2012, Kang *et al*.

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2006). These sensors are used for vibration control purposes in civil structures, vehicle loading monitoring applications, and structural health monitoring applications (Wen and Chung 2001).

During the last few decades, composite sensors incorporated with carbon nanotube (CNT) have received a great deal of attention due to the outstanding physical properties of CNT (Azhari and Banthia 2012, Han *et al*. 2009, Han *et al*. 2010, Hu *et al.* 2008, Kim *et al*. 2014b, Li and Chou 2008, Li *et al*. 2007, Luo *et al*. 2011, Park *et al*. 2008, Yu and Kwon 2009). Excellent electrical conductivity attributed to high aspect ratios and a tunneling effect associated with the electron emission characteristics of the CNT meant that CNT-incorporated composites were a promising piezoresistive sensor (Hu *et al*. 2008, Yu and Kwon 2009).

Extensive studies of CNT/polymer piezoresistive sensors have been carried out since the early 2000s, revealing noteworthy sensitivity with respect to strain (Souri *et al*. 2015). From the mid-2000s, the piezoresistive response of CNT/cement sensors has been studied in an effort to apply these sensors to buildings and other forms of infrastructure (Wood *et al*. 2000, Zhao *et al.* 2001). The high durability, low chemical reactivity, and good cost effectiveness of CNT/cement sensors make them more feasible in civil structures as compared to CNT/polymer sensors. Li *et al.* (2007) reported the pressure-sensitive characteristics and mechanical properties of CNT/cement composites. They utilized an ultrasonication method as the CNT dispersion process and obtained a change in the electrical resistance of 11 % with respect to an applied stress of 1.5 MPa (Li *et al*. 2007). Yu and Kwon (2009) studied the effects of the CNT dispersion method and its content ratio on changes in the electrical resistance of CNT/cement composites when they were subject to compressive stress. The authors found that an acid treatment when used with an ultrasonication method can improve the electrical resistance change rate and reduce noise signals in the piezoresistive response of composites (Yu and Kwon 2009).

Han *et al.* (2009) assessed the piezoresistive response of CNT/cement composites subject to vehicle loading. A surfactant wrapping of CNT was chosen as the dispersion method, and stable electrical resistance changes at a maximum 0.4 % were detected on passes with vehicle loadings (Han *et al*. 2009). Han *et al*. (2010) reported the influence of the moisture content in CNT/cement composites on their piezoresistive sensing ability. They found that changes in the electrical resistance rate tended to decrease as the moisture content increased (Han *et al*. 2010). Luo *et al*. (2011) and Azhari and Banthia (2012) studied the piezoresistive responses of carbon fiber/CNT-incorporated cement sensors. Azhari and Banthia (2012) found they demonstrated more stable repeatability of the electrical resistance change rate under randomly applied loads than a carbon fiber/cement sensor. Jeon (2012) and Kim *et al*. (2014b) reported the piezoresistive sensing ability of CNT/cement sensors fabricated with an addition of silica fume in an effort to enhance the CNT dispersion, and Kim *et al.* (2014b) revealed that oven dried-sensors tended to show more sensitive and stable piezoresistive responses as water-to-binder ratio increased. It can be said that from the literature review, repeatable piezoresistive sensing responses of CNT/cement composites fabricated by various approaches were attained.

However, a parametric study for the determination of the CNT content percolation threshold leading to the formation of a wide-ranging network without disconnections has not been carried out. Given that change in the electrical resistance rate of CNT/cement sensors reach a peak when the CNT content is close to the percolation threshold, the identification of the percolation threshold is significant (Hu *et al*. 2008). In the present work, the electrical conductivity of CNT/cement composites fabricated by the polymer wrapping method with ultrasonication was examined with different CNT content ratios. In addition, the compressive strength of these composites was measured in an effort to understand their basic mechanical properties. The piezoresistive response

of the composites was also evaluated. Specifically, the piezoresistive response was assessed in terms of the stability, the maximum change in the electrical resistance rate, and the sensitivity level, as proposed by Kim *et al*. (2014b). A vehicle loading test was additionally carried out to demonstrate the repeatable sensing ability of the MWNT/cement composite sensors.

2. Sample preparation

MWNT, PSS (Polysodium4-styrenesulfonate) as a polymeric dispersant, tap water, ordinary Portland cement (OPC), a super-plasticizer (SP), and nylon fiber were used in the present work. Specifications of all materials used in the present work can be found in the Nam *et al*. (2012) except for MWNT. MWNT was a proprietary product of Hyosung Co. (M1111) and was produced by a chemical vapor deposition process. The diameter and purity of MWNT were 12.29 ± 2.18 nm and 96.2 %, respectively.

The procedure for the dispersion of MWNT in water was based on that described in Nam et al. (2012). A mass ratio of 1:1 was chosen for the MWNT and the PSS, and the amount of water was determined by a water-to-cement ratio of 0.4 (Nam *et al*. 2012). The mixtures of MWNT and PSS in water were sonicated in a bath-type ultrasonicator for 30 min and in a tip-type ultrasonicator for 1 hour, consecutively (Nam *et al*. 2012). In particular, the tip-type ultrasonicator paused for eleven seconds after every nine seconds of sonication in an effort to prevent an undesirable increase in the temperature of the mixtures. Accordingly, the entire duration of the operation of the tip-type sonicator was approximately two hours. All experiments were conducted at room temperature. The sonication process resulted in the exfoliation of bundled MWNTs and the isolation of MWNTs with PSS wrapping.

Type 1 Portland cement, SP, and nylon fiber at a ratio of 100:1.6:0.2 were used and mixed with the MWNT-dispersed water. The weight ratios of the MWNT corresponded to 0, 0.2, 0.3, 0.4, 0.5, 0.6, and 1.0 wt.% by cement weight. The MWNT/cement composites were designated depending on their MWNT content ratio, e.g., PSS-M0.3, PSS-M0.4, and so on. The MWNT content ratio was determined by the weight of the MWNT as compared to that of the cement.

The specimens were fabricated by the following steps. First, the MWNT-dispersed water, SP, nylon fiber, and cement were poured into a steel bowl and were mixed by an electric hand mixer for three minutes. Second, the prepared mixtures were decanted into molds. Third, the molds were placed at room temperature (18-20℃) under a humid condition for 24 to 48 hours in order to cure the specimens. Afterwards, the specimens were removed from the molds. The hardened specimens manufactured for the purpose of measuring the piezoresistive properties were cured for four days in sealed vinyl, whereas the specimens for the measurement of the electrical conductivity were cured in water for five days. Finally, the specimens for both the piezoresistivity and the electrical conductivity tests were dried in an oven for three days at a temperature of 55 ± 5℃.

3. Test methods

3.1 Electrical conductivity and piezoresistivity response

The preparation procedures of samples for DC conductivity measurement was carried out as follows. The constituent materials were weighed according to mixing proportions and mixed by

the electric hand mixer, as described in Section 2. The produced mixture was poured into plastic molds that were designed in accordance with the sample size. The sample size was $25 \times 25 \times 25$ mm^3 for the DC conductivity measurement, as shown in Fig. 1(a). A pair of copper electrodes were prepared with size of $10 \times 35 \times 0.5$ mm^3 and they were embedded with a spacing of 8 mm in the composite samples, as shown in the Fig. 1(a), while the mixture was still fresh. The curing conditions for the first day followed the conditions described in Section 2 and then samples were detached from the molds. To prevent unexpected fracture of the samples, they were soaked in tap water for a minimum of five days in an effort to develop mechanical strength. As a last procedure of the sample preparation, silver paste was coated on both sides of the fabricated samples in an effort to set up another pair of electrodes as illustrated in the Fig. 1(a).

The DC conductivity measurement method in the present work was conducted on the basis of SEMI MF43 (SEMI, 2005). DC current was supplied by a power supply (Agilent E3642A), with current passing through the silver paste electrodes, and the resultant voltage change was measured by a digital multi-meter (Agilent 34410A) connected to the copper electrodes. The measurement system is illustrated in Fig. 1(b). The power supply limited voltage to 20 V and current to 0.2 A. All the measurements were conducted at room temperature.

The resistance of the composite sample was determined by Ohm's law and the DC conductivity σ (S/m) was calculated by plugging the resistance value into a following equation

$$\sigma = \frac{1}{\rho} = \frac{1}{R}\frac{L}{A} \tag{1}$$

where ρ (ohm·m), *R*, *L*, and *A* indicate the DC resistivity, DC resistance, spacing between the electrodes, and the electrode's cross sectional area that contacts the composite samples, respectively (Park *et al.* 2008, Xie *et al*. 1996).

The piezoresistive properties of the composites were determined by the change in the electrical resistance originating from the cyclic compressive loading. In the present study, a cyclic compressive load with a maximum magnitude of 25 kN and a displacement rate of 0.6 mm/min was applied using a universal testing machine (UTM). Details of the test method can be found in Kim *et al.* (2014b), and the change in the electrical resistance rate of the specimens was evaluated by Eq. (1), as in Kim *et al*. (2014b).

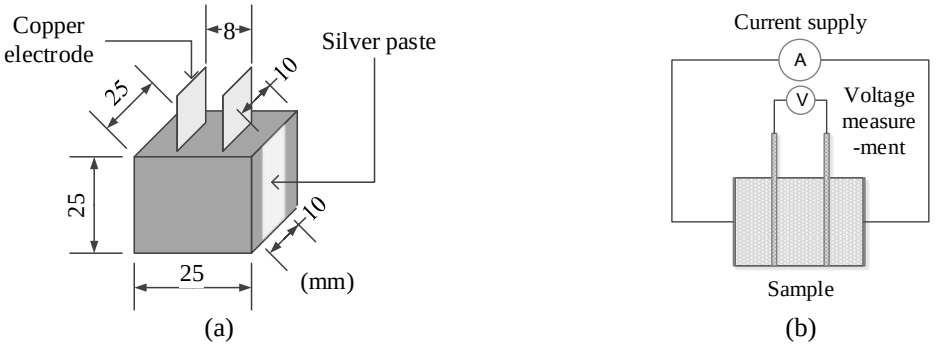


Fig. 1 (a) The dimensions of the samples for the DC conductivity measurement and (b) schematic illustrations of the DC conductivity measurement for the composites.

3.2 Compressive strength and porosity

The compressive strength of the composites was measured after 28 days of curing in compliance with the ASTM C 109 test methods using 50-mm cubic specimens (ASTM, 2012). The compressive strength measurements were conducted using a UTM with a capacity of 300 t with displacement control at a constant head-loading rate of 0.02 mm/s.

The porosity of the specimens with different MWNT ratios was assessed in accordance with ASTM C 642 (ASTM, 2013). The porosity, referring to the volume of the permeable space (voids) in the specimens, was determined by the following equation (ASTM, 2013).

$$\text{Porosity (vol.\%)} = \frac{C - A}{C - B} \times 100 \tag{2}$$

Here, A is the mass of the oven-dried specimen in air, B denotes the apparent mass of the specimen in water after it is immersed and boiled in water, and C is the mass of the surface-dried specimen in air after immersion and boiling (ASTM, 2013).

4. Test results and discussion

4.1 Electrical conductivity

Figure 2 shows the electrical conductivity of the MWNT-incorporated cement composites as the MWNT content in the composites increases from 0 to 1.0 wt.%. As found in cement or polymer-based composites fabricated with an addition of various types of conductive fillers in literature, the Fig. 2 also shows an S-curve, which indicates the percolation phenomena (Kim *et al*. 2005, Xie *et al*. 1996). The percolation phenomena refer to the formation of wide-ranging conductive networks constructed by the conductive fillers without disconnections in the matrix materials (e.g., the polymers, the cement, etc.) (Xie *et al*. 1996). A dramatic increase in the electrical conductivity was exhibited at a MWNT content range of 0.2 to 0.3 wt.% in the present work. Accordingly, it can be said that the percolation threshold of the composite is 0.25 wt.% (0.26 vol.%) when determined as a mean value of the MWNT content range, demonstrating a dramatic increase in the electrical conductivity. This percolation threshold value is much lower than that obtained with carbon black-incorporated cement composites (Li *et al*. 2006). However, this percolation threshold is greater than that obtained with MWNT-incorporated polymer-based composites (Kim *et al*. 2005). This is likely due to the following two reasons. First, the comparatively high percolation threshold could stem from an increase in the contact resistance among the MWNTs due to the PSS polymer (Li and Chou 2008).

The insulating PSS polymer wrapped the surfaces of MWNTs and could therefore increase the contact resistance between MWNTs neighboring one another. Second, the deterioration of the intrinsic electrical properties of the MWNT due to the sonication process could lead to increased resistance of the composites, resulting in a high percolation threshold (Lu *et al*. 1996). Lu *et al*. (1996) reported that the electrical conductivity of MWNT itself can deteriorate due to the sonication process, causing damage to the surfaces of the MWNTs.

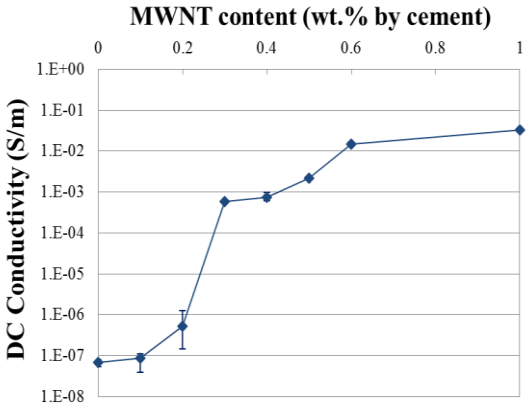
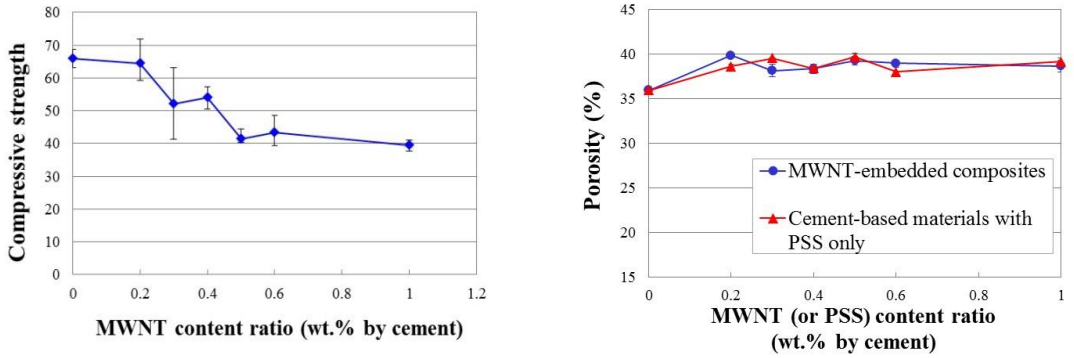


Fig. 2 Logarithmic plot of the electrical conductivity of MWNT/cement composites fabricated as a function of the MWNT content



(a) (b)

Fig. 3 Compressive strength (a) and porosity (b) of MWNT/cement composites as the amount of MWNT is increased

4.2 Compressive strength

The compressive strength of the composites steadily decreased as the MWNT content increased as shown in Fig. 3(a). Deterioration of the compressive strength was not ascribed to the poor MWNT distribution, as the electrical conductivity result of the composites demonstrated the percolation phenomena, which indicates that MWNT was satisfactorily distributed in the cement matrix. If the MWNT distribution was poor in the cement matrix, numerous MWNT clumps, i.e., excessively entangled MWNT, can exist in the cement matrix. The MWNT clumps can, consequently, cause the deterioration of the compressive strength, as they tend to retain pores inside them (Kim *et al*. 2014a, Sanches and Ince 2009).

The decrease of compressive strength was likely due to the addition of the PSS polymer, which is an anionic surfactant and tends to generate voids in the composites. To investigate the effect of

PSS, samples of the MWNT/cement composites and cement-based materials fabricated with PSS only were prepared and their porosity was evaluated. Fig. 3(b) shows the porosity of the MWNT/cement composites increased with increments from 2.2 to 3.9 %, compared to the control sample. Fig. 3(b) also revealed that the porosity of the cement-based materials with PSS was greater than that of the control sample with increments from 2.1 to 3.7 %. The increase of porosity in the MWNT/cement composites thus is believed to be related to the increase of porosity in the PSS-added cement materials.

Based on the porosity evaluation, the decrease of compressive strength appears to be closely related to the incorporation of PSS. However, an investigation of the porosity may be insufficient to fully understand the decrease of the mechanical properties of the composites since complex factors such as MWNT agglomeration, water absorption in MWNTs, effects of PSS on the micro structure of the composites, etc. should be considered.

The evaluation on compressive strength and porosity also indicated that considerable decrease (40.1%) in the compressive strength was obtained despite of only 2.7% increase of porosity in the MWNT content ranged from 0 to 1%. It is also likely due to the complex factors such as MWNT agglomerations, effect of PSS in micro structure of the composite etc. In addition to these factors, the decrease in strength might stem from increase in maximum pore length, which revealed a close correlation with strength reduction (Kendall *et al*. 1983). The addition of MWNT and PSS would increase the MWNT agglomeration or decrease air entraining effect of SP, and these might result in increase of maximum pore length.

4.3 Piezoresistive response

The samples of the MWNT/cement composites were prepared for the piezoresistive sensing test. Three replicated samples were fabricated for each sample type, and the piezoresistive sensing test was conducted according to the descriptions in Section 3.1. All of the composites showed variations in the electrical resistance in response to the applied cyclic stress.

Kim *et al*. (2014b) suggested three factors to assess the integrity of piezoresistive sensors. The first factor is the stability of the piezoresistive response during loading and unloading cycles (Kim *et al.* (2014b). This value represents the consistency of changes in the rates of electrical resistance of the composites in response to repeated loading and unloading processes. Fig. 4 shows the electrical resistance change rate versus the applied stress obtained from composites with MWNT contents of 0, 0.2, 0.3, 0.4, 0.5, 0.6, and 1.0 wt.%. The data were obtained from a sample of which the electrical resistance rate was median among the three replicated samples and minimum five cycles for each sample type were plotted in the figure. If the width of the electrical resistance change loop is large, the stability of the composite is considered to decrease according to a concept suggested by Kim *et al*. (2014b). The loop curves of the PSS-M0.4, PSS-M0.5, and PSS-M1.0 composites exhibit similar widths, but the width of the curve of the PSS-M0.2 composite is wider. Thus, the PSS-M0.2 composite reveals the least consistent values with regard to changes in the resistance in response to cyclic loading and unloading processes.

The second factor suggested by Kim *et al*. (2014b) is the maximum electrical resistance change rate. To compare the mean values of the maximum electrical resistance change rate in the composite types, the maximum electrical resistance change rates of the three replicated samples were averaged in each sample type. These values were then plotted, as shown in Fig. 5. The maximum electrical resistance change rate was 96 % at PSS-M0.2, and it decreased to 50 % when PSS-M0.4 was assessed. It continually decreased to 37 % for PSS-M0.5 but increased to 54 % at

PSS-M1.0. The variation in the maximum electrical resistance change rates can be explained by the percolation threshold and the tunneling effect (Hu *et al*. 2008).

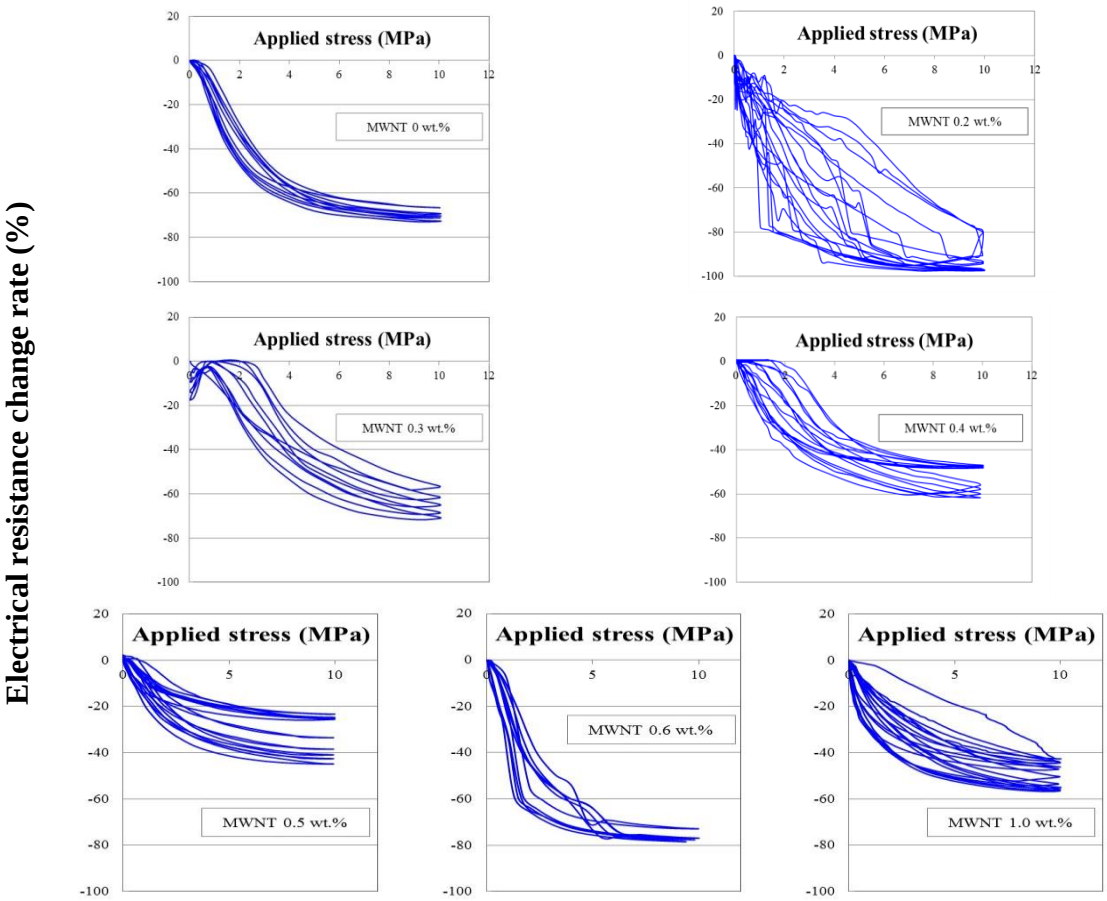


Fig. 4 Stability of the piezoresistive response under loading and unloading cycles

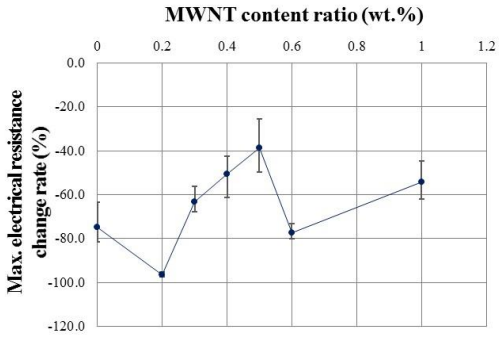


Fig. 5 The maximum electrical resistance change rate with an increase in the MWNT content

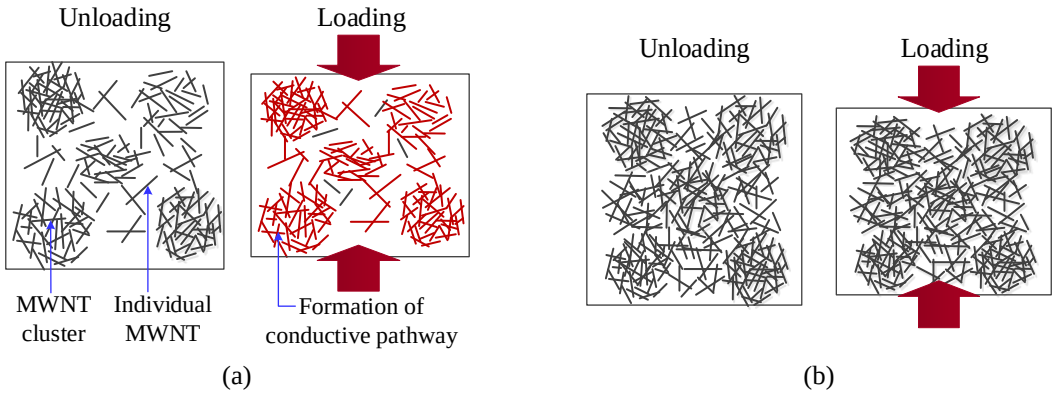


Fig. 6 Change in the electrical conductive paths formed by MWNT in cement matrix according to application of load when the MWNT content is close to the percolation threshold (a), and the MWNT content exceeded the percolation threshold (b)

The tunneling effect refers to the transfer of electrons at the gap which exists between the MWNTs, attributed to the decrease in the distance between the MWNTs under loading (Han *et al*. 2010, Li and Chou 2008). Hu *et al.* (2008) reported that the tunneling effect manifested in the larger number of gaps formed between the MWNTs as the MWNT content increased and thus approached the percolation threshold. On the basis of the findings in Hu *et al.* (2008), PSS-M0.2 could induce a great deal of tunneling, meaning a considerable change in the electrical resistance in response to the applied load, as the MWNT content of 0.2 wt.% is close to the percolation threshold (0.25 wt.%), as shown in the Fig. 2. On the other hand, other composite samples with higher MWNT contents showed lower changes in their maximum electrical resistance rates compared to PSS-M0.2, as the MWNT content exceeded the percolation threshold.

To explain this correlation between the degree of tunneling and the MWNT content, Fig. 6 illustrates the change in the electrical conductive paths formed by MWNTs (or MWNT clusters) in a cement matrix with respect to the applied load. Fig. 6(a) shows a MWNT/cement composite with the MWNT content under the percolation threshold. Prior to loading the composites, the MWNTs (or MWNT clusters) were not close enough for tunneling to take place, but the MWNTs (or MWNT clusters) became connected to one another or close enough to induce tunneling after loading.

The tunneling effect requires distance of the gap to be as close as nanometer level between MWNTs (Lutwyche and Wada 1995). Although the samples are subjected to stress inducing mirco-level displacement, the tunneling effect manifests attributable to reduction of the gap distance between MWNTs (or MWNT clusters) from mirco level to nano level or due to electrical connection of MWNTs (Fig. 6(a)). The phase of MWNT distribution shown in Fig. 6(a) possesses great potential to induce the tunneling or the electrical connection of MWNTs (MWNT clusters), which means noticeable electrical resistance change. The case of Fig. 6(a) corresponds to the microstructures in PSS-M0.2. Fig. 6(b) shows a case in which the MWNT content exceeds the percolation threshold. Numerous MWNTs were already connected or close enough for tunneling prior to loading so the generation of interconnections or the tunneling were minor under loading in

terms of their contribution to the overall electrical conductivity. This case corresponds to the microstructures in PSS-M0.4, PSS-M0.5, and PSS-M1.0.

The maximum electrical resistance change rate of PSS-M0.2 was compared to those found in the literature. The change in the maximum electrical resistance rate obtained in the present work was greater than the results in the literature, as shown in Fig. 7 (Azhari and Banthia 2012, Han *et al*. 2010, Kim *et al*. 2014b, Li *et al*. 2004, Yu and Kwon 2009). There are three possible explanations of this. First, a high electrical resistance change was achieved since the optimum MWNT content was identified in consideration of the percolation threshold of the MWNT network in the present work. The optimum MWNT content did not exceed the percolation threshold since greater tunneling can take place with MWNT contents near the percolation threshold (Hu *et al*. 2008). MWNT/cement piezoresistive sensors fabricated with the identification of the optimum MWNT content below the percolation threshold of MWNTs were not found in the literature. Secondly, this relatively great change is attributable to lower compressive strength of the piezoresistive sensing composites in the present work due to the short curing period and the micro cracks induced by shrinkage in the dry oven. Li *et al*. (2004) and Kim *et al.* (2014b) reported higher electrical resistance change rates obtained in composites with lower compressive strengths. Lastly, it can be attributed to the dryness of the composites since a high moisture content could impede the piezoresistive sensing capability (Han *et al*. 2010, Kim *et al*. 2014b).

In addition, nylon fibers, which were incorporated in the present work, may have affected piezoresistive performance of the composites. Yap *et al*. (2013) reported that nylon fiber addition in concrete resulted in a reduction in the modulus of elasticity (MOE) and larger strain, which potentially increased the electrical resistance change rate. It was also reported that synthetic fibers such as nylon fiber, polypropylene fiber, etc. tended to enhance the compressive and flexural strength of concrete but the electrical resistivity was not significantly altered at about 0.16% of fiber volume fraction (Kakooei *et al*. 2012, Yap *et al*. 2013).

The last factor which indicates the integrity of piezoresistive sensors is the time-based sensitivity (Kim *et al*. 2014b). As shown in a following equation, the sensitivity was defined in terms of a ratio of time delay between stress peak and resistance peak (Δt) to time of resistance peak (t_p). Details of the sensitivity and its all characteristics can be found in Kim *et al*. (2014b).

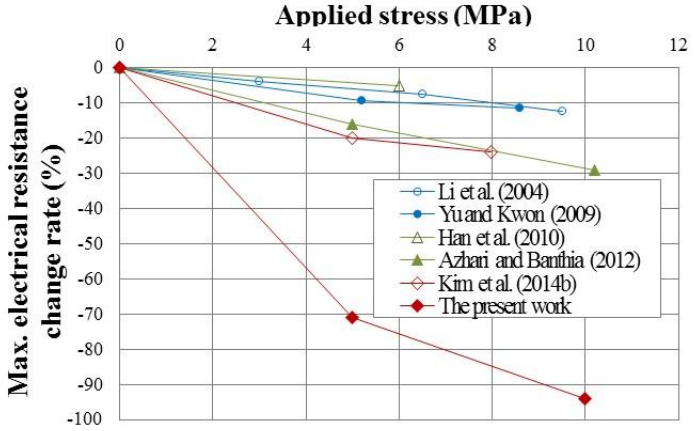


Fig. 7 The maximum electrical resistance change rate of PSS-M02 compared to results in the literature

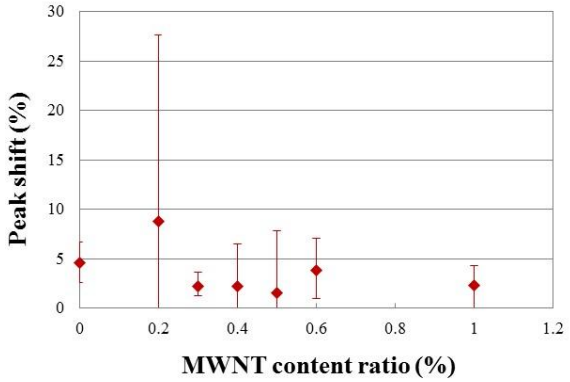


Fig. 8 Variation in the sensitivity expressed as the peak shift of the composites

$$\text{Sensitivity} = \frac{\Delta t}{t_p} \times 100 \tag{3}$$

Fig. 8 shows the sensitivity (peak shift) versus the MWNT content of the composites. The peak shift tended to decrease as the MWNT content increased. PSS-M0.2 exhibited the greatest peak shift as well as large deviations from the maximum and minimum values. It is important to note that the large deviations in PSS-M0.2 are related to the large width in the stability curve of the Fig. 4. In other words, the high peak shift and the large deviations account for the lower level of stability. As shown in the Figs. 5 and 8, the peak shift tended to increase as the maximum electrical resistance change rate increased. This indicates that composites with a high electrical resistance change rate can show low sensitivity.

5. Vehicle loading test

The piezoresistive response test by means of UTM was carried out with maximum loading of 10 MPa in the previous section but the loading value was different with actual vehicle loading values (approximately 1~2 MPa). Accordingly, a piezoresistive response test by means of vehicle wheel loads was additionally conducted in the present work. For the vehicle loading test, the composite with the optimum MWNT content ratio (0.2 wt.%) determined by the electrical conductivity and piezoresistivity tests was newly prepared with an enlarged size. The composite mixture was prepared and mixed according to Section 2 but the size of the composite sensor was prepared as $100 \times 100 \times 370\,(\text{mm}^3)$. Due to the enlarged sensor size, a steel mold was prepared according to the size prior to the fabrication of sensor. A pair of copper plates was embedded as electrodes in the composite with a spacing of 10 mm and the size of the copper plates was $30 \times 400 \times 0.5\,(\text{mm}^3)$. The spacing of the electrodes was identical to that of 5 cm-cubic samples used in the UTM loading test for consistency of the spacing. The 10 mm spacing was small when the size of sample used in the vehicle loading test is considered. However, this was suggested in an

effort to detect slight differences within the spacing by means of the electrical resistance measurement.

The following procedure was adopted to install the sensor. First, a part of the road pavement was cut out with a depth of 12 ~ 13 cm, which is greater than the height of the sensor itself, to allow embedment of the sensor and also placement of rapid hardening mortar used to support the sensor. Second, the rapid hardening mortar was placed with thickness of 2 ~ 3 cm in a cavity prior to mounting the sensor in an effort to support the sensor firmly. One of the most critical characteristics of the rapid hardening mortar is its ability to flow in order to provide level supporting ground. Third, the sensor was mounted in the cavity prepared by cutting out the pavement and placing the rapid hardening mortar. Figs. 9(a) and 9(b) show the installed composite sensor in concrete pavement and a pass of the vehicle wheel load on the sensor, respectively.

Fig. 10 shows the change in the electrical resistance rate of the composite sensor on which a car weighing approximately 1.4 tons passed over four times at a speed of 20~25 km/h. The composite sensor detected every pass of the car, and the electrical resistance change rate ranged from 2 to 6.5%. A pass of the vehicle including the front and rear wheels produced one negative peak in the electrical resistance change rate due to the speed of the vehicle.

The electrical resistance showed an increasing tendency due to the electric polarization phenomena in the composite sensor. Electrical polarization refers to displacement of positive (or negative) charges towards the electrode sides with the opposite pole (Cao and Chung 2004). In the course of electrical polarization, the electric charges accumulate nearby the electrodes and this hinders electric current, resulting in the increase of electrical resistance (Banthia *et al*. 1992).

The polarization phenomena also affected the piezoresistive sensing test. The electrical resistance increased under loaded state as well as under unloaded state. An increase of electrical resistance at the 4th pass of the vehicle (Fig. 10) in comparison to that of the 2nd pass is associated with the polarization phenomena. Although the electrical resistance of sensor changed with a lapse of time, the pass of loading could be detected in terms of the electrical resistance change rate determined by a ratio $((R_i - R_{i-1})/R_{i-1})$ between the electrical resistance measured at a present point (R_i) and a previous point (R_{i-1}).

(a) (b)

Fig. 9 An installation of the composite sensor in the road pavement (a) and an application of the vehicle wheel load on the sensor (b)

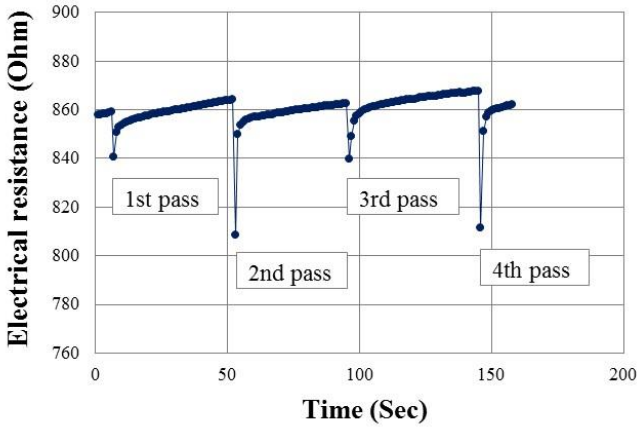


Fig. 10 The electrical resistance versus a time plot of the composite used in the vehicular loading test

6. Conclusions

MWNT/cement composites were fabricated by a polymer wrapping method in tandem with an ultrasonication method and the electrical conductivity levels, compressive strengths, and piezoresistive responses of the composites were examined in the present work. In particular, the piezoresistive response was assessed by the three factors of the stability, the maximum electrical resistance change rate, and the sensitivity. The conclusions of this study can be summarized below.

- A parametric study of the electrical conductivity versus the MWNT content showed that the percolation threshold of the MWNT/cement composites was 0.25 wt.% (0.26 vol.%).
- The compressive strength of the composites decreased as the MWNT content increased. This was likely due to the increased addition of the PSS polymer, which was incorporated with the same amount of MWNT, as PSS polymer is likely to produce voids as an anionic surfactant.
- PSS-M0.2 exhibited the highest electrical resistance change rate, but the stability and sensitivity of PSS-M0.2 showed the lowest values among the composite types.
- A higher electrical resistance change rate was obtained by PSS-M0.2 in comparison with the results found in the literature, as the MWNT content of 0.2 wt.% was close to the percolation threshold (Hu *et al*. 2008). In addition, a decrease in the compressive strength due to micro cracks and a decrease in the moisture content due to the oven drying procedure may have increased the electrical resistance change rate (Han *et al*. 2010, Kim *et al*. 2014b, Li *et al*. 2004).
- A vehicle loading test demonstrated the repeatable sensing capability of PSS-M0.2 with an electrical resistance change rate ranging from 2 to 6.5 %.

Although the piezoresistive responses in the lab and in the field show a possible application of the MWNT/cement composites to real structures, a future work is still needed to enhance the stability and sensitivity levels of the piezoresistive sensors.

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