Composites Science and Technology 121 (2015) 41–48

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Electrical properties and piezoresistive evaluation of polyurethane-based composites with carbon nano-materials

H. Souri [a], I.W. Nam [b], H.K. Lee [b,*]

[a] Carbon Convergence Materials Research Center, Institute of Advanced Composite Materials, Korea Institute of Science and Technology, San 101, Eunha-ri, Bongdoung-eup, Wanju-gun, Jeollabuk-do, 565-905, South Korea

[b] Department of Civil and Environmental Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon, 305-701, South Korea

ARTICLE INFO

Article history:
Received 2 August 2015
Received in revised form
30 October 2015
Accepted 2 November 2015
Available online 10 November 2015

Keywords:
Carbon nanotubes
Expanded graphite
Graphite nanoplatelet
Three-roll milling process
Electrical characteristics
Piezoresistivity
Polyurethane
Composite

ABSTRACT

The present study assesses the applicability of carbon materials-embedded polyurethane (PU) composites characterized by high piezoresistive capability, as a traffic loading sensor. PU composites incorporating multi-wall carbon nanotubes (MWNTs), expanded graphite (EG), and a hybrid of MWNTs and graphite nanoplatelets (GNPs) were fabricated and their electrical conductivities were measured in an effort to determine the most suitable filler type for the piezoresistive sensor and its optimum content ratio. The best electrical characteristics were achieved by the MWNT/PU composites as exhibiting the percolation threshold at 5 wt.% of MWNT and the maximum electrical conductivity of 0.33 S/m at 7 wt.%. Accordingly, the MWNT/PU composites were prepared as a piezoresistive sensor, and its sensing capabilities and durability were examined by three different tests, i.e., lab-scale loading, vehicular loading, and cyclic wheel loading tests. The composite with MWNT 5 wt.% showed the best sensing capability in terms of the electrical resistance change rate obtained from the lab-scale and vehicular loading tests. In addition, the cyclic wheel loading test demonstrated that the 5 wt.% MWNT-embedded PU composite was durable during 2000 cycles of the wheel loading.

1. Introduction

Fabrication of polymer-based composites is considered as a critical area of current nanotechnology and composite science due to their multi-functionalities and remarkable mechanical, electrical, and thermal properties as well as other useful attributes [1]. In particular, the use of polymer-based composites embedded with micro/nano-scaled carbonic materials has attracted the interest of researchers owing to their diverse applications in the automotive, aerospace, construction, and electronic industries [2,3]. In recent decades, the demands for lower percolation threshold of conductive composites have motivated researchers to employ highly conductive carbonic fillers [2]. In particular, the addition of CNTs to polymeric matrices not only provides composites with high electrical conductivity, but also alters the electrical resistance under applied load/strain, a phenomenon known as piezoresistivity [4,5].

In the past few years, the electrical conductivity of composites has been extensively researched and the percolation threshold obtained from less than 1.0 wt.% to over 10.0 wt.% of filler loading. For instance, Chen et al. (2001) prepared a EG/Polymethyl methacrylate (PMMA) composite by the *in-situ* polymerization method, which showed the percolation threshold at 3.5 wt.% of EG loading [6]. Jiang et al. (2005) reported maximum electrical conductivity of 10 S/m at 7.4 wt.% of multi-walled CNTs (MWNTs) and 0.3 wt.% as the percolation threshold for MWNT/polyimide (PI) composites prepared by an *in-situ* polymerization method [7]. Moreover, Yu and Li (2008) obtained the percolation threshold of a GNP/polyvinyl alcohol (PVA) composite made by solution casting method at 4 wt.% of GNP loading whereas the peak value of electrical conductivity was 10^{-5} S/m at 7 wt.% of GNP content [8]. McNally et al. (2005) fabricated a polyethylene (PE) matrix containing 10 wt.% of MWNTs using melt blending method which showed maximum conductivity as high as 10^{-3} S/m and the percolation threshold at 7.5 wt.% [9]. Furthermore, She et al. (2007) manufactured a PE composite incorporating modified EG which showed the percolation threshold at 5.7 wt.% of EG loading and the maximum electrical conductivity value of the composites was as high as 10^{-1} S/m at 8 wt.% [10].

* Corresponding author.
E-mail address: leeh@kaist.ac.kr (H.K. Lee).

http://dx.doi.org/10.1016/j.compscitech.2015.11.003
0266-3538/

Recently, CNT-embedded polymer composites have been frequently used as piezoresistive sensors since CNT exhibited promising merits such as low percolation threshold, notable piezoresistive characteristics, and so forth [11,12]. For instance, Kang et al. (2009) reported that 0.05 wt.% of single-wall CNTs (SWNTs) addition in a PI matrix showed a 2% electrical resistance change under tensile stress of 16 MPa, while the electrical resistance of a 10 wt.% MWNT/PI system changed up to 0.35% under the same loading conditions [13]. Also, Wichmann et al. (2009) studied the piezoresistive response of epoxy-based composites with MWNTs and CB under a tensile load and reported the electrical resistance change rate from 7 to 12% as the MWNT loading was increased from 0.1 to 0.5 wt.% [14].

However, few studies in the literature focused on comparison of electrical properties of composites incorporating various carbon fillers and determination of the percolation threshold of the composites to ascertain the optimum filler content leading to the maximum electrical resistance change rate of piezoresistive sensors [15]. There also exists a lack of research in the literature in which three-roll milling machine technique, which is fast, simple, and compatible with standard industrial techniques, was used to fabricate MWNT/PU composites as well as EG and hybrid of MWNT and GNP embedded PU composites. In addition, experimental studies to examine the piezoresistive response of MWNT/PU composites subjected to external loads and their applicability as traffic loading sensors were scarce.

In this study, the electrical properties and the percolation threshold of MWNTs, EG, and a hybrid of MWNT and GNP-embedded polyurethane (PU) composites fabricated with a three-roll milling process were investigated. Subsequently, the piezoresistive characteristic of the MWNT/PU composites, which showed a low percolation threshold, was studied through lab-scale loading tests. In the specimen fabrication, PU was adopted as the matrix material due to its excellent properties such as abrasion resistance, UV durability, high hardness and impact resistance, etc., which make this material an excellent choice to be used in a wide range of civil engineering applications such as coating on pipelines, roofs and floors, and suitable choices for fabricating sensors [16–18]. Subsequently, the piezoresistive characteristic of the MWNT/PU composites, which showed low percolation threshold, was studied through lab-scale loading tests.

2. Specimen preparation

In the present study, chemical vapor deposition (CVD) growth MWNTs were purchased of Hyosung Inc. (M1111). The purity and diameter of the MWNTs were 96.6% and 12.29 ± 2.18 nm, respectively. Acid washed graphite flakes were provided by Asbury Carbons Inc. (Item number 3772) as the source material to produce EG and GNPs. PU consisted of PF-359 and E-145 and was supplied from Kangnam Hwasung Chemical Co. Ltd. Toluene was used as a solvent for the two-component PU in an effort to make low viscous composite mixtures.

In order to produce EG, the acid-washed graphite flakes were heated to 1050 °C for 30 s with the aid of a furnace [19]. To obtain GNPs, EG was ultrasonicated in acetone using a high power bath-type sonicator for 8 h [19]. Subsequently, the GNPs were filtered by a filter paper and dried at room temperature. All experiments were conducted at room temperature.

A variety of conductive filler contents were employed in order to investigate the electrical conductivity behavior of various types of composites. The MWNT ratios ranged from 4 to 8 wt.% of the total amount of two components of PU whereas the EG ratios were from 3 to 7 wt.%. Moreover, in the case of the hybrid of MWNT and GNP embedded PU composites, the weight fraction of each filler ranged from 2 to 5 wt.% of the total PU. The ratio of toluene was approximately 5 wt.% of the total PU. On the other hand, MWNT loadings of 5, 6, and 7 wt.% of the total PU were chosen to fabricate the piezoresistive sensors (Table S1, Supplementary information).

The specimen preparation can be explained as follows: a specified amount of each component of PU was measured and poured into a steel bowl. Afterwards, the carbon nano-materials including MWNT, EG, and a hybrid of MWNT/GNP were measured according to the mix proportions in Table S1. These were thoroughly mixed with the mixture of the two components of PU for 2 min. In this stage, toluene was added to the mixture in order to reduce the viscosity of the mixture. It is noteworthy to say that the viscosity of the mixture has to be low so that it will be feasible to use a three-roll milling machine to manufacture the composites. After the mixture was pre-mixed, the three-roll milling machine (EXAKT80S, EXAKT Technologies Inc., Germany) was used to achieve a better dispersion quality of MWNT, EG, and hybrid of MWNT/GNP in the fabricated composites (Fig. S1 (a)) [20]. The mixture was poured into the three-roll milling machine where the parallel rollers rotated at a rate of 200 rpm [20]. Note that the gap size between the rollers was 5 μm for the MWNT/PU composites, but it was increased for other types of composites due to the size of carbon materials used. This mixing process was performed five times for each batch [20]. During this process, the fillers within premixed mixtures could be more dispersed with the aid of the shear force applied by the rotating rollers. A schematic illustration of this process is shown in Fig. S1 (b). In the middle of the process, toluene was mostly eliminated from the mixture. Afterwards, the final mixture was poured into a 2.5 × 2.5 × 2.5 cm^3 plastic mold to shape the cubic specimens.

Silver paste was applied to two surface sides facing each other in the specimen as electrodes when the DC conductivity of the composites was examined. Two copper electrodes coated with silver paste with a size of 1 cm in width, 3.5 cm in length, and 0.5 mm in depth were embedded with a spacing of 8 mm in the MWNT/PU composite specimens to evaluate their piezoresistivity (Fig. S2). Due to the use of fast curing PU, all specimens were removed from the mold after a day of curing at room temperature.

3. Test methods

3.1. Electrical conductivity

The direct contact method was chosen to measure the DC resistance of the composites. In this method, the two probes of a digital multi-meter (Agilent Technologies 34410A) were brought into contact with two opposite sides of the specimen, where each side was coated with silver paste in order to make better contact. All measurements were conducted at room temperature.

The DC conductivity σ (S/m) of the composites was calculated by Ohm's law by plugging the obtained resistance values into the following equation [21,22]:

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

where ρ (ohm·m), R, L, and A denote the DC resistivity, DC resistance, the distance of the two opposite sides of the specimen, and the cross sectional area of composite specimen, respectively [21,22].

3.2. Piezoresistivity

In the present study, the DC resistance change of the composite specimens under compressive loading was measured using a two-probe method that involves connecting two wires to respective electrodes embedded in the specimens and was assessed by means of a digital multi-meter (Agilent Technologies 34410A) [4]. A uniaxial compressive cyclic load for 5 cycles with a maximum value of 1.875 kN (3 MPa) was applied by a Universal Testing Machine (UTM: Instron 5583) at a displacement rate of 0.36 mm/min on the specimens perpendicular to the direction of the electrodes while the electrodes were connected to the DMM transmitting the data to a computer synchronously via wires. As a result, the DC resistance change under compression was recorded by the computer. Fig. 1 illustrates the experimental setup for measuring the piezoresistivity of the MWNT/PU composites. Note that non-conductive tape was attached to the top and bottom surfaces of UTM, which come in contact with the composites, to insulate the specimens from the surface of the UTM.

4. Test results and discussion

4.1. Electrical conductivity

The electrical characteristics of various types of composites fabricated in the present study were discussed in the following. Fig. 2 presents the electrical conductivity of the composites according to the loading levels of various conductive fillers at room temperature. As shown in Fig. 2, the electrical conductivity of the MWNT/PU composites dramatically increased in a range of 4–6 wt.% of MWNT loading. The electrical conductivity of the composites with MWNT ratios lower than 4 wt.% was not measurable due to the high level of resistivity for these composites. The curve in Fig. 2 indicates the percolation phenomena for the composites in which conductive networks without disconnections are formed by MWNTs. The percolation threshold of the MWNT/PU composites was obtained at approximately 5 wt.% of MWNT loading as a mean value of the aforementioned MWNT content range. Furthermore, the highest electrical conductivity value was 0.33 (S/m) at 7 wt.% of MWNTs. The electrical conductivity values leveled off with further addition of MWNTs.

The percolation threshold of the MWNT/PU composites was higher than that obtained in previous studies available in the literature. According to the review paper [19], the use of the three-roll milling machine technique, which is speedy and simple, and compatible with standard industrial techniques, to fabricate polymeric composites has shown high levels of percolation threshold value, while other techniques such as in-situ polymerization, solution compound, and combination of different techniques could lower the percolation threshold. For instance, the percolation threshold of MWNT/epoxy composites fabricated with a solution compounding method was detected at 0.072 wt.% of MWNT loading [23]. On the other hand, the obtained percolation threshold for MWNT/PU composites in this study was lower than that obtained by some composites manufactured with the melt blending method. The use of 7.5 wt.% of MWNTs was reported as the percolation value for MWNT/polyethylene composites prepared by a mini-twin screw extruder [9].

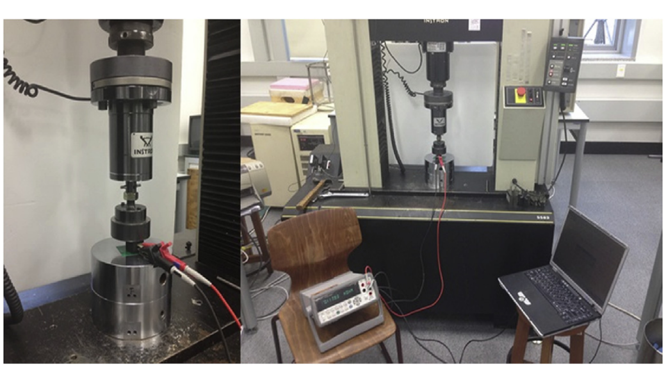

Fig. 1. Experimental setup for the piezoresistive sensing test using a UTM.

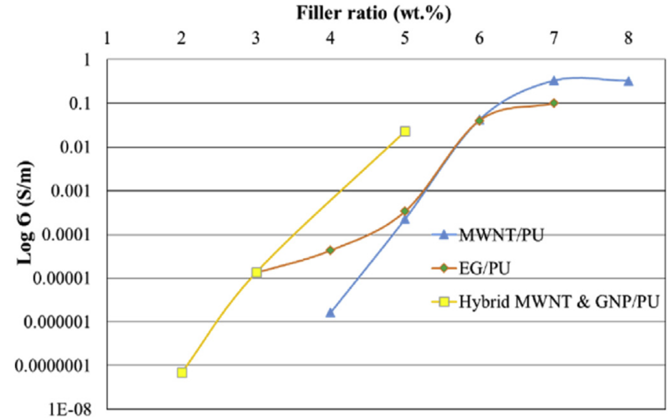

Fig. 2. Logarithmic plot of electrical conductivity of various types of composites as a function of the conductive filler content ratio.

Fig. 2 shows the DC electrical conductivity of EG/PU composites versus the EG loading curve at room temperature. As observed in the figure, the electrical conductivity values abruptly increased near the percolation threshold of the composites, which was acquired at approximately 5.5 wt.% of EG content. By further addition of EG, the electrical conductivity value slightly increased after 6 wt.% of the EG content and leveled off at 7 wt.%. The maximum electrical conductivity of the composites was 0.1 (S/m) at this ratio. The DC electrical conductivity of the hybrid of MWNT and GNP embedded PU composites versus each filler ratio is also shown in Fig. 2. As plotted in the figure, a very low level of DC conductivity with a maximum value of 0.022 (S/m) at 5 wt.% of each filler content was evaluated for this type of composite.

The lower level of electrical conductivity for the EG/PU and the hybrid of MWNT and GNP embedded PU systems compared to the conductivity of MWNT/PU composites was mainly due to the dispersion quality of the fillers within the matrix. A SEM image of the 6 wt.% MWNT-embedded PU composite is shown in Fig. 3. As shown, well-dispersed MWNTs in PU matrix confirmed that conductive networks were formed. On the contrary, agglomeration of EGs due to their tendency to aggregate [24] was observed within the PU matrix, as illustrated in Fig. S3. On the other hand, the SEM image of the hybrid of 3 wt.% of MWNT and GNP/PU composite showed a poor dispersion status due to the presence of agglomerated GNPs as well as MWNT clumps, which led to a lack of interconnected conductive networks in the PU matrix (Fig. S4). The amount of conductive filler was so low that the electrical conductivity of the composites was hardly measurable.

4.2. Piezoresistive response in lab scale tests

In the present study, the MWNT/PU composites outperformed other types of composites in terms of the DC conductivity. Consequently, the piezoresistivity of 5 (M-5.0), 6 (M-6.0), and 7 (M-7.0) wt.% MWNT-embedded PU composites was investigated following the descriptions in Section 3.2. The composites with MWNT loadings near the percolation threshold were chosen so that high electrical resistance change rates could be detected using the two-probe multi-meter with the equipment setup shown in Fig. 1 [15].

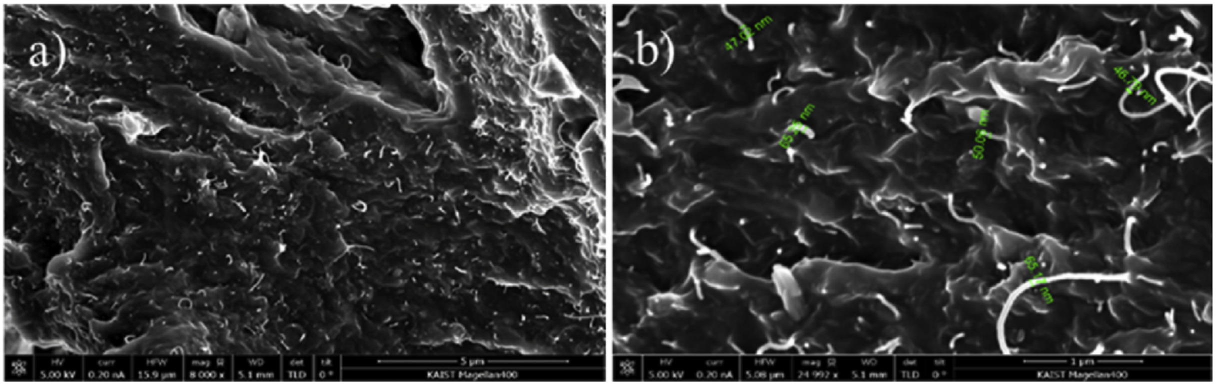

Fig. 3. SEM images of the fractured surface of MWNT/PU composites with the MWNT content of 6 wt.% at ×8000 (a) and ×25,000 (b).

The DC conductivity of the composites varied under the applied cyclic compressive stress.

The piezoresistive responses of M-5.0, M-6.0, and M-7.0 composites with regard to the applied compressive stress and time are shown in Fig. 4, respectively. As plotted, once the uniaxial compressive load was applied on the specimen, the electrical resistance drastically decreased until the compressive stress reached 3 MPa. The distance between neighboring MWNTs was minimized under compressive loads, mainly due to deformation of the matrix materials [25]. As a result, the tunneling resistance (R_{tunnel}) remarkably decreased in a nonlinear form as the compressive stress increased [25]. Accordingly, the total resistance of the composites nonlinearly decreased [25].

However, a decrease in the electrical resistance of the composites was examined for a short period after the compressive stress started to be removed. This behavior corresponds to the development of a new percolation network of the fillers caused by the macromolecular relocation of the matrix in a slow rate [26]. Subsequently, the composites showed a polymeric recovery with the materials returning to their initial shape prior to the applied compressive stress. At the same time, their electrical resistance gradually increased to the same level as at the starting point. This piezoresistive behavior was observed for all of the specimens of various types of composites during the test.

The maximum rate of electrical resistance change is an important factor to evaluate the performance of piezoresistive sensors [4]. The average value of the maximum electrical resistance change rate of the fabricated specimens for each type of composite was thus calculated. This value was 92.92% for the M-5.0 composites whereas it decreased for the M-6.0 and M-7.0 composites to 88.47 and 73.76%, respectively. This behavior can be explained by the percolation threshold of the MWNT/PU composites and the tunneling effect near the percolation threshold [15]. The tunneling effect can be defined as the electron transfer through the matrix material between neighboring MWNTs when their distance is less than the cut-off distance and greater than the diameter of the MWNTs [15]. Moreover, the distance between adjacent MWNTs within the PU matrix can be lowered under the applied compressive load. In accordance with the findings in Hu et al. [15], the tunneling effect can be considerably detected near the percolation threshold of the composites; however, this effect gradually vanished with further addition of conductive fillers. Accordingly, M-5.0 could potentially show a great deal of tunneling due to being close to the percolation threshold, which would account for the significant electrical resistance change as the external compressive load was applied. In contrast, in the case of M-6.0 and M-7.0 composites, the maximum electrical resistance change rates decreased since MWNTs were additionally embedded in the composites over the percolation threshold [15].

The maximum electrical resistance change rate of the M-5.0 composite was compared with the experimental results of other works found in the literature. It was found that the maximum electrical resistance change rate in this study was superior to the values reported in the literature [13,27,28]. This can be ascribed to the characterization of the percolation threshold and choosing MWNT content near the percolation threshold since greater tunneling occurs at ratios close to the percolation threshold [15].

Fig. S5 illustrates the status of MWNTs within the matrix in an effort to understand the correlation between the tunneling effect and the MWNT loading. When the compressive load is applied on the composites filled with MWNT content close to, but not exceeding the percolation threshold, the largest tunneling effect will manifest, among the various types of composites under compressive load (Fig. S5 (a)). However, when the MWNT ratio is much lower than the percolation threshold (Fig. S5 (b)), the number of conductive networks within the matrix is too low. After applying the compressive load, there exists a few connected fillers to form conductive networks, which led to a low level of piezoresistivity [29]. On the other hand, when the MWNT ratio surpasses the percolation threshold (Fig. S6), a large number of MWNTs become close to one another, which results in forming a highly conductive composite; the tunneling effect consequently has a minor influence on the electrical resistance change of the M-6.0 and M-7.0 composites [29]. It can be thus said that as the MWNT ratio increases after the percolation threshold, the electrical resistance change decreases due to the comparatively lower tunneling effect under the applied compressive load. Consequently, M-7 is expected to show a lower electrical resistance change than M-6.

As another important factor to assess the functionality of piezoresistive sensors, the stability of the sensors was examined during the loading and unloading process [4]. This factor indicates the reliability of the electrical resistance change rate under a cyclic load. The electrical resistance change rates versus the applied stress for the M-5.0, M-6.0, and M-7.0 composites are illustrated in Fig. S7. Four cycles per each type of composite are plotted in the figures. In accordance with the proposed concepts by Kim et al. (2014), the stability of the piezoresistivity of the composites under cyclic loading is thought to be lower when the gap between the hysteresis loops in Fig. S7 is wider and vice versa [4]. As can be observed in the figure, the widths of the curves corresponding to the M-6.0 and M-7.0 composites were greater than those of the M-5.0 composite. As a result, the M-5.0 type exhibited the highest consistency in terms of electrical resistance change under the applied cyclic loads.

The last factor that Kim et al. (2014) proposed to evaluate the

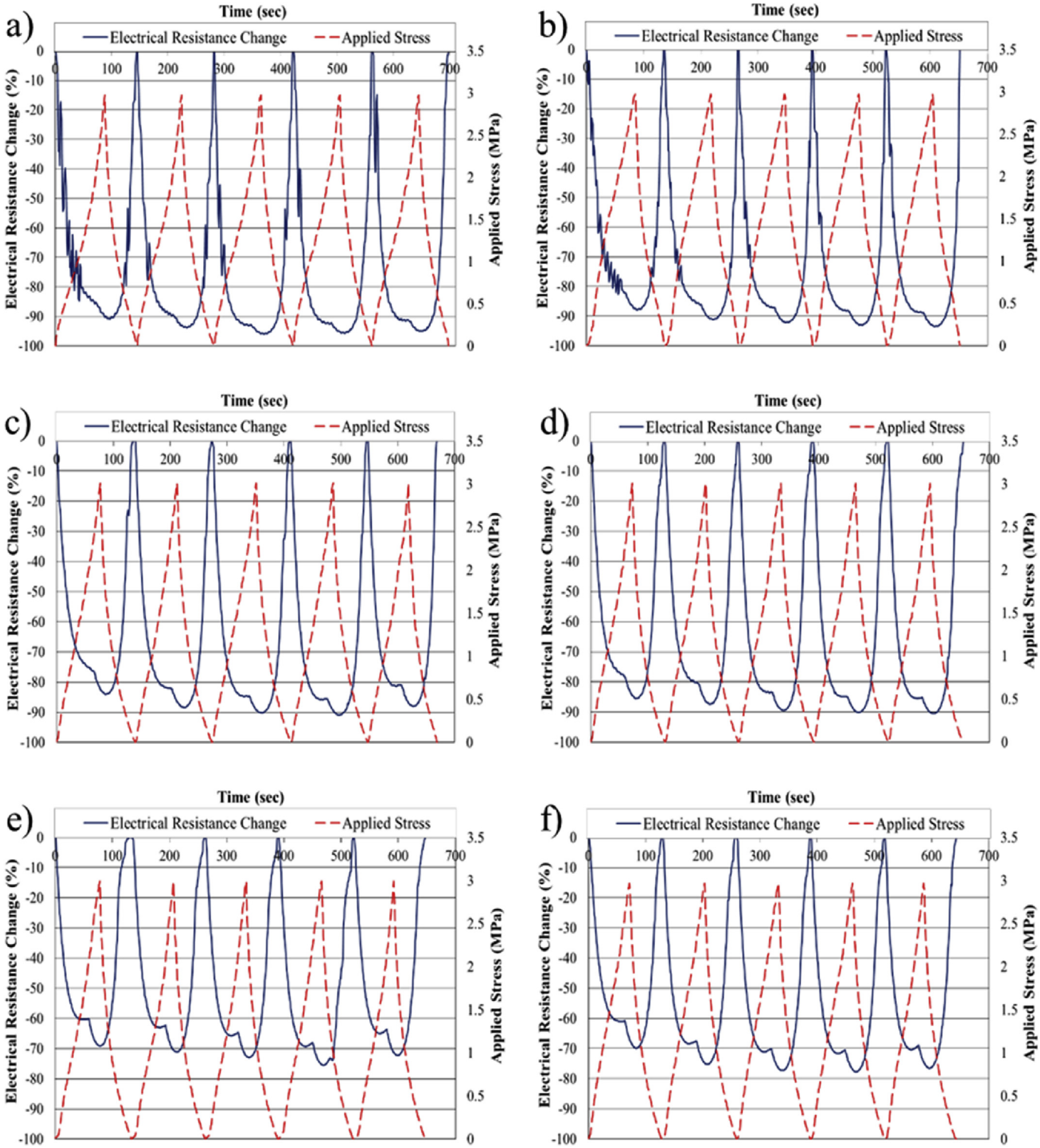

Fig. 4. Piezoresistivity of the M-5.0 composites for specimen 1 (a) and specimen 2 (b), M-6.0 composites for specimen 1 (c) and specimen 2 (d), and M-7.0 composites for specimen 1 (e) and specimen 2 (f).

integrity of piezoresistive sensors is the time-based sensitivity determined by Eq. (2) in their work [4]. In accordance with the obtained results, the average peak shift ranged from 4.78 to 6.43% as the MWNT content was varied (Fig. S8). The M-6.0 composite exhibited the greatest peak shift, resulting in a lower level of stability. In addition, the lowest peak shift value was obtained by composite type M-5.0. The lowest peak shift value is believed to be related to the experimental result that the M-5.0 composite showed the best performance in terms of stability.

5. Vehicle loading test

In the present work, actual vehicle loading was applied to the composites in order to evaluate their response in a field test. Prior to the test, a support specimen with a size of 10 × 10 × 20 cm^3 made by cement mortar was designed and composite sensors were mounted on the mortar support specimen, as illustrated in Fig. S9. A model of the sensor was made by foam and attached to the middle part of a steel mold. Afterwards, the mixture of cement mortar was poured into the steel mold and casted. After one day, the specimen was demolded and wrapped with poly-ethylene film in an effort to prevent loss of moisture. It was then placed in an oven for one day at a temperature of 50 °C to accelerate the curing.

In order to conduct the vehicle loading test in the field scale, one specimen from each M-5.0, M-6.0, and M-7.0 composite type was chosen. The specimens were the same as those utilized in the lab scale test. The process of installing the sensors was as follows: First, a proper amount (25 cm in length, 15 cm in width, and 10–11 cm in depth) of ground was dug to place the cement mortar support. After the cement mortar support specimen was placed in the correct position, the area around the cement mortar was filled with sand to prevent any movement of the cement mortar support specimen. Subsequently, the piezoresistive sensor was placed in its position. Afterwards, one end of the wires was connected to the electrode whereas the other end of the wires was plugged in the DMM to receive the resistance data of the sensors. The resistance data were simultaneously collected by a computer. The experimental setup for the field test is shown in Fig. S10.

Fig. 5 indicates the DC electrical resistance change versus time when the vehicle load (approximately 350 kg for a vehicular wheel) was applied at a low speed (less than 20 km/h). The piezoresistive sensors could effectively detect every movement of the vehicle's front wheel on the left side during the experiment. The resistance change caused by the passing of the vehicle on the sensors was in the form of an increase in resistance, and this confirmed detection of passing of the front wheel on the left side. The increase in resistance for this test resulted from the destruction of the conductive network within the composites due to the impact by the vehicle load. The increase of resistance can be enhanced as the instantaneous compressive load is increased [30,31]. The electrical resistance change rate ranged from 2.82 to 14.55% for M-5.0, 1.67–4.32% for M-6.0, and 2.17–8.83% for M-7.0. The M-5.0 type showed the greatest electrical resistance change rates whereas M-6.0 showed the lowest.

6. Cyclic wheel loading test

In order to assess the durability of piezoresistive sensors, the sensing performance of the best sensor in terms of the electrical resistance change rate and stability of piezoresistivity was examined under a cyclic compressive load exerted by a wheel with a weight of 400 Kg. The experimental setup for this test is shown in Fig. S11 and the M-5.0 composite was chosen for the test. According to the fabrication procedures in Section 5, a cement mortar support specimen with a size of 10 × 10 × 40 cm^3 was prepared and the sensor was placed in position during this test. Subsequently, the change in resistance of the piezoresistive sensor was measured by the DMM and then the data were simultaneously stored in a computer connected to the DMM, as illustrated in the Fig. S11. The wheel employed in this test provided repetitive compressive loading with a frequency of 0.33 Hz. The number of total cycles was set to 2000.

Fig. 6 presents the change in resistance versus time for the M-5.0 composite when the repetitive compressive load was applied by a wheel on the composite. As shown in the figure, the change in resistance of the composite lowered as the compressive load was applied. Moreover, the electrical resistance in the unloading state, decreased as the number of loading cycles increased. This phenomenon may be explained by the formation of more conductive paths inside the composite, due to the permanent deformation of

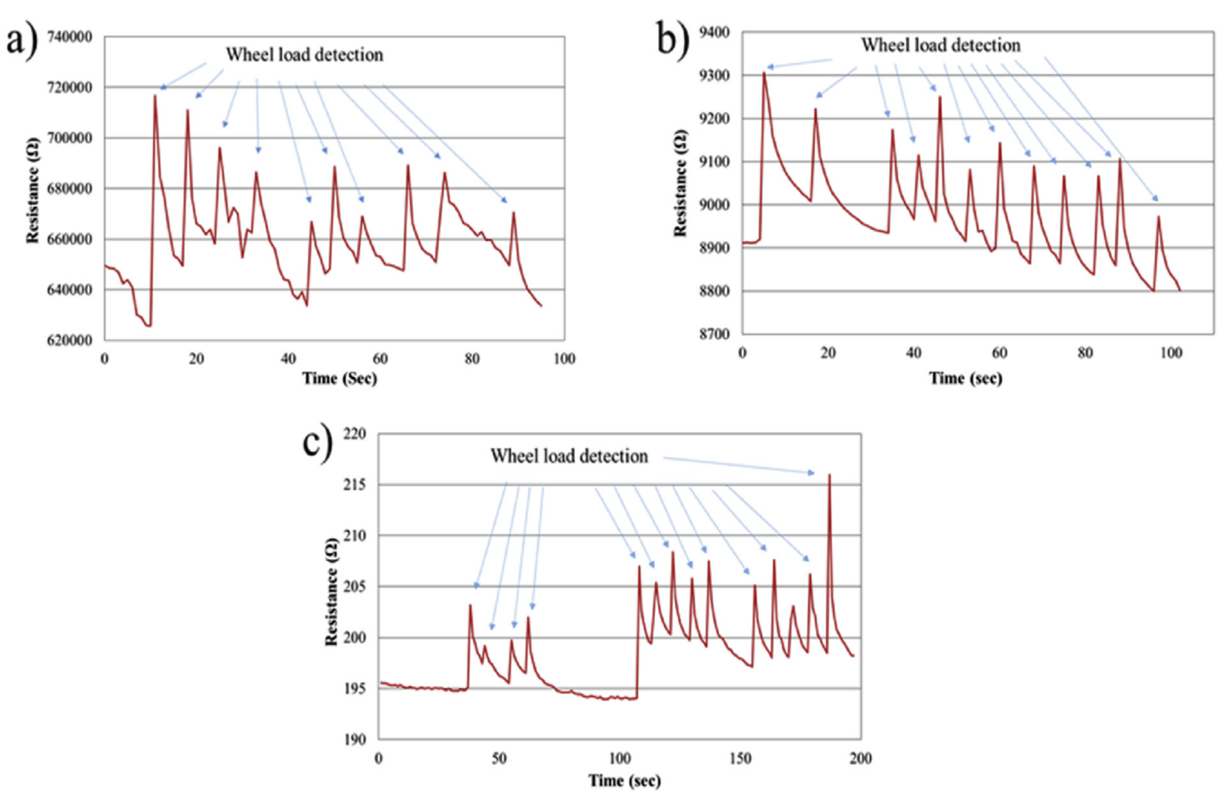

Fig. 5. Plots of electrical resistance versus time during field test for M-5.0 (a), M-6.0 (b), and M-7.0 (c).

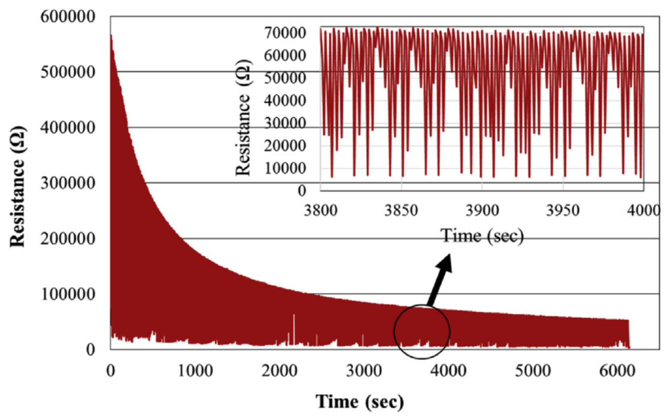

Fig. 6. Plot of electrical resistance versus time during the wheel loading test.

the polymeric composite under compression as the number of cycles increased. According to several studies in the literature [32–34], it has been shown that a cyclic loading-unloading process even with a low magnitude of compressive stress induced permanent strain in PU material due to the change in its structure caused by rupturing of some cell wall membranes and fracturing of some cells and edges [32–34]. The induced permanent strain may result in reduction of resistance, since the resultant resistance of the specimens is proportional to the thickness of the specimens. Moreover, the tunneling effect is another important reason for this behavior. As the number of cycles increased, MWNTs within the matrix become closer to each other due to the matrix deformation under the applied compressive load. The electrical resistance of the composite in the unloading state hence could be lowered.

The resistance change rate in the beginning of the test was as high as 86.24%, which was considerably higher than that obtained at the end of test, which was as low as 1.08%. It is noteworthy that the sensor was able to detect every single compressive load applied by the wheel, as shown in Fig. 6. Moreover, damage was not observed in the composite after 2000 cycles.

7. Concluding remarks

In the present work, the electrical characteristics of polymer (PU)-based composites including conductive micro/nano-sized fillers such as MWNTs, EG, and GNPs with different filler ratios were studied. The morphology of the composites was also examined in order to study the microstructure of the composites. Moreover, the piezoresistive behavior of MWNT-embedded PU composites with consideration of the percolation threshold was studied in an effort to develop new construction materials with a self-sensing function. Three different tests were employed to understand the piezoresistive behavior of the composites: (1) a UTM cyclic loading test, (2) a vehicular loading test, and (3) a wheel cyclic loading test. The findings of the experimental study can be summarized as follows:

(1) The maximum electrical conductivity of the MWNT-embedded PU composites was found to be 0.33 (S/m) at 7 wt.% of MWNT content. In addition, the percolation threshold of the composites was 5 wt.% of MWNTs. The 7 wt.% EG/PU composite showed a maximum value of electrical conductivity as high as 0.1 (S/m). Moreover, the percolation threshold of the composite was obtained at 5.5 wt.% of EG loading. In the case of the hybrid of GNP and MWNT/PU composites, the peak value of electrical conductivity was 0.022 (S/m), which was significantly lower than that obtained with the other types of composites. This was ascribed to the agglomeration of GNPs as well as presence of MWNT clumps within the matrix material.

(2) The use of 5, 6, and 7 wt.% of MWNTs in the PU matrix led to remarkable resistance changes of the composites under a cyclic load of 3 MPa applied by the UTM. The electrical resistance change rate was 92.92, 88.47, and 73.76% for the M-5.0, M-6.0, and M-7.0 composites, respectively. The M-5.0 composites exhibited the highest electrical resistance change rate, which was comparatively higher than the results found in the literature. This was attributable to the addition of MWNTs with an optimum content ratio determined near the percolation threshold.

(3) During the field test, vehicular loading was applied on the M-5.0, M-6.0, and M-7.0 types of sensors. The piezoresistive sensors were able to effectively detect the vehicle's movements and the resultant electrical resistance change ranged from 2.82 to 14.55% for M-5.0, 1.67–4.32% for M-6.0, and 2.17–8.83% for M-7.0.

(4) The durability of the piezoresistive sensor M-5.0 was studied through cyclic loading applied by a wheel 2000 times with a magnitude of 400 Kg. The obtained results revealed that the sensor can effectively detect every wheel load during the test. The electrical resistance change rate of the composite decreased from 86.24% in the beginning cycles to 1.08% in the last cycle.

These experimental findings demonstrated the potential of using MWNT/PU composites as piezoresistive sensors for civil structures such as roadways and bridges. Future work can be focused on combining fabrication methods in an effort to lower the percolation threshold of these composites, which can eventually lead to more economical piezoresistive sensors.

Acknowledgment

This research was supported by the KUSTAR-KAIST Institute, KAIST, Korea. The authors also would like to thank KAIST for permitting us to conduct a field scale test with piezoresistive sensors and appreciate Asbury Carbons Inc. for providing the materials.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.compscitech.2015.11.003.

References

[1] B. Li, W.H. Zhong, Review on polymer/graphite nanoplatelet nanocomposites, J. Mater. Sci. 46 (No. 17) (2011) 5595–5614.
[2] T. Kuilla, S. Bhadra, D. Yao, N.H. Kim, S. Bose, J.H. Lee, Recent advances in graphene based polymer composites, Prog. Polym. Sci. 35 (No. 11) (2010) 1350–1375.
[3] B.J. Yang, H. Souri, S. Kim, S. Ryu, H.K. Lee, An analytical model to predict curvature effects of the carbon nanotube on the overall behavior of nanocomposites, J. Appl. Phys. 116 (No. 3) (2014) 033511.
[4] H.K. Kim, I.S. Park, H.K. Lee, Improved piezoresistive sensitivity and stability of CNT/cement mortar composites with low water–binder ratio, Compos. Struct. 116 (2014) 713–719.
[5] M. Amjadi, A. Pichitpajongkit, S. Lee, S. Ryu, I. Park, Highly stretchable and sensitive strain sensor based on silver nanowire–elastomer nanocomposite, ACS Nano 8 (No. 5) (2014) 5154–5163.
[6] G.H. Chen, D.J. Wu, W.G. Weng, W.L. Yan, Preparation of polymer/graphite conducting nanocomposite by intercalation polymerization, J. Appl. Polym. Sci. 82 (No. 10) (2001) 2506–2513.
[7] X. Jiang, Y. Bin, M. Matsuo, Electrical and mechanical properties of polyimide–carbon nanotubes composites fabricated by in situ polymerization, Polymer 46 (No. 18) (2005) 7418–7424.
[8] C. Yu, B. Li, Preparation and characterization of carboxymethyl polyvinyl

alcohol–graphite nanosheet composites, Polym. Compos. 29 (No. 9) (2008) 998–1005.
[9] T. McNally, P. Pötschke, P. Halley, M. Murphy, D. Martin, S.E. Bell, J.P. Quinn, Polyethylene multiwalled carbon nanotube composites, Polymer 46 (No. 19) (2005) 8222–8232.
[10] Y. She, G. Chen, D. Wu, Fabrication of polyethylene/graphite nanocomposite from modified expanded graphite, Polym. Int. 56 (No. 5) (2007) 679–685.
[11] A.I. Oliva-Avilés, F. Avilés, V. Sosa, Electrical and piezoresistive properties of multi-walled carbon nanotube/polymer composite films aligned by an electric field, Carbon 49 (No. 9) (2011) 2989–2997.
[12] J. Hwang, J. Jang, K. Hong, K.N. Kim, J.H. Han, K. Shin, C.E. Park, Poly (3-hexylthiophene) wrapped carbon nanotube/poly (dimethylsiloxane) composites for use in finger-sensing piezoresistive pressure sensors, Carbon 49 (No. 1) (2011) 106–110.
[13] J.H. Kang, C. Park, J.A. Scholl, A.H. Brazin, N.M. Holloway, J.W. High, J.S. Harrison, Piezoresistive characteristics of single wall carbon nanotube/polyimide nanocomposites, J. Polym. Sci. Part B Polym. Phys. 47 (No. 10) (2009) 994–1003.
[14] M.H. Wichmann, S.T. Buschhorn, J. Gehrmann, K. Schulte, Piezoresistive response of epoxy composites with carbon nanoparticles under tensile load, Phys. Rev. B 80 (No. 24) (2009) 245437.
[15] N. Hu, Y. Karube, C. Yan, Z. Masuda, H. Fukunaga, Tunneling effect in a polymer/carbon nanotube nanocomposite strain sensor, Acta Mater. 56 (No. 13) (2008) 2929–2936.
[16] D.E. Fiori, Two-component water reducible polyurethane coatings, Prog. Org. Coat. 32 (No. 1) (1997) 65–71.
[17] A. Samimi, S. Zarinabadi, Application polyurethane as coating in oil and gas pipelines, Int. J. Sci. Invest. France (2012) 43–45.
[18] H. Souri, I.W. Nam, H.K. Lee, A zinc oxide/polyurethane-based generator composite as a self-powered sensor for traffic flow monitoring, Compos. Struct. 134 (2015) 579–586.
[19] R. Sengupta, M. Bhattacharya, S. Bandyopadhyay, A.K. Bhowmick, A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites, Prog. Polym. Sci. 36 (No. 5) (2011) 638–670.
[20] I.W. Nam, H.K. Lee, J.H. Jang, Electromagnetic interference shielding/absorbing characteristics of CNT-embedded epoxy composites, Compos. Part A Appl. Sci. Manuf. 42 (No. 9) (2011) 1110–1118.
[21] P. Xie, P. Gu, J.J. Beaudoin, Electrical percolation phenomena in cement composites containing conductive fibres, J. Mater. Sci. 31 (1996) 4093–4097.
[22] J.M. Park, P.G. Kim, J.H. Jang, Z. Wang, J.W. Kim, W.I. Lee, J.G. Park, K.L. DeVries, Self-sensing and dispersive evaluation of single carbon fiber/carbon nanotube (CNT)-epoxy composites using electro-micromechanical technique and nondestructive acoustic emission, Compos. Part B Eng. 39 (2008) 1170–1182.
[23] S. Cui, R. Canet, A. Derre, M. Couzi, P. Delhaes, Characterization of multiwall carbon nanotubes and influence of surfactant in the nanocomposite processing, Carbon 41 (No. 4) (2003) 797–809.
[24] J.J. George, A.K. Bhowmick, Ethylene vinyl acetate/expanded graphite nanocomposites by solution intercalation: preparation, characterization and properties, J. Mater. Sci. 43 (No. 2) (2008) 702–708.
[25] N. Hu, H. Fukunaga, S. Atobe, Y. Liu, J. Li, Piezoresistive strain sensors made from carbon nanotubes based polymer nanocomposites, Sensors 11 (No. 11) (2011) 10691–10723.
[26] Q. Zheng, J.F. Zhou, Y.H. Song, Time-dependent uniaxial piezoresistive behavior of high-density polyethylene/short carbon fiber conductive composites, J. Mater. Res. 19 (No. 09) (2004) 2625–2634.
[27] A. Baltopoulos, N. Athanasopoulos, I. Fotiou, A. Vavouliotis, V. Kostopoulos, Sensing strain and damage in polyurethane-MWCNT nano-composite foams using electrical measurements, Express Polym. Lett. 7 (No. 1) (2013).
[28] S. Qu, S.C. Wong, Piezoresistive behavior of polymer reinforced by expanded graphite, Compos. Sci. Technol. 67 (No. 2) (2007) 231–237.
[29] I.W. Nam, H. Souri, H.K. Lee, Percolation threshold and piezoresistive response of multi-wall carbon nanotube/cement composites, Smart Struct. Syst. (2015) in review.
[30] L. Wang, F. Ma, Q. Shi, H. Liu, X. Wang, Study on compressive resistance creep and recovery of flexible pressure sensitive material based on carbon black filled silicone rubber composite, Sensors Actuators A Phys. 165 (No. 2) (2011) 207–215.
[31] L. Wang, T. Ding, P. Wang, Effects of instantaneous compression pressure on electrical resistance of carbon black filled silicone rubber composite during compressive stress relaxation, Compos. Sci. Technol. 68 (No. 15) (2008) 3448–3450.
[32] H.J. Qi, M.C. Boyce, Stress–strain behavior of thermoplastic polyurethanes, Mech. Mater. 37 (No. 8) (2005) 817–839.
[33] Y. Shen, F. Golnaraghi, A. Plumtree, Modelling compressive cyclic stress–-strain behaviour of structural foam, Int. J. Fatigue 23 (No. 6) (2001) 491–497.
[34] A. Bezazi, F. Scarpa, Tensile fatigue of conventional and negative Poisson's ratio open cell PU foams, Int. J. Fatigue 31 (No.3) (2009) 488–494.