A zinc oxide/polyurethane-based generator composite as a self-powered sensor for traffic flow monitoring

H. Souria, I.W. Nam, H.K. Lee

Abstract
A zinc oxide (ZnO)/polyurethane (PU)-based generator composite was fabricated and its piezoelectric performances were examined in the present work. In addition, the influence of multi-wall carbon nanotubes (MWNTs) and copper powder incorporation on the piezoelectric performance of composites was also studied. The performance level of the composites with various ratios of the constituents was compared in terms of piezoelectric responses obtained from three different tests, i.e., foot stamping, vehicle loading, and cyclic wheel loading tests. The foot stamping and vehicle loading tests revealed that the generator composite solely embedded with ZnO nano materials exhibited the best performance among the others, while the influence of MWNT and copper powder addition on the performance was minor. The cyclic wheel loading test (durability test) demonstrated that the generator composite sustained 2000 cycles of 400 kg-weighed wheel loading and a prominent output voltage peak produced was as high as 40.45 V.

1. Introduction
Currently, global energy consumption has dramatically increased due to the growth of the population and advances in industrialization, while the depletion of energy resources and global warming due to carbon dioxide emissions are considered as the main problems faced by the global society over the past few decades [1,2]. In particular, research on the depletion of energy resources revealed that the use of fossil fuels, considering the rate of world consumption, may end in next 40–50 years for petroleum, 50–60 years for natural gas, and 200–220 years for coal [3].

To overcome these problems, many refer to the use of renewable energy resources, which are available at most places [1,2]. In the recent years, sources of reproducible energy have been solar [4], wind [5], hydro power [6], biomass [7], tidal [8], piezoelectric energy [9] and other types of energy. Among these methods, employing piezoelectric generator composites which convert vibrational and mechanical energy sources from human activities such as pressure, bending, and stretching motions into electrical energy, has shown promise.
Furthermore, BaTiO$_3$, which is frequently adopted as a piezoelectric material, has been assessed by several researchers. For instance, Park et al. [17] fabricated BaTiO$_3$-based generator composites on polymer substrates. When these were periodically deformed by bending with the fingers, the output voltage was as high as 1 V [17]. Lin et al. [18] fabricated BaTiO$_3$ nanotube-based generator composites that were not only flexible but also transparent. The open-circuit voltage peak reached 5.5 V under compressive stress of 1 MPa [18]. Park et al. [19] fabricated lead-free BaTiO$_3$ nanowire-based flexible generator composites using PDMS as the matrix material. The maximum generated voltage reported in their work was approximately 7 V in bending/unbending states [19]. Another outstanding and novel study was conducted by Park et al. [11], in which flexible generator composites were fabricated using BaTiO$_3$ nano-particles and graphitic carbons. In this work, carbon nanotubes (CNTs) were used to enhance the output voltage of the generator composite and the reported value for the maximum output voltage under bending/unbending cyclic loading was 3.2 V [11].

Furthermore, ZnO nano-particles (NPs) have attracted a considerable amount of attention due to their outstanding piezoelectric properties compared to other piezoelectric materials. Kandpal et al. [20] fabricated generator composites with a ZnO nanoparticle-embedded polymer (SU-8), which showed piezoelectric coefficients peak ranging from 15 to 23 pm/V, the highest value for this material thus far. Yang et al. [21] fabricated a spring-connected generator composite composed of a mixture of ZnO nano-particles and multi-wall CNTs (MWNTs). Their test demonstrated that the voltage and power could reach 9 V and 27 $\mu$W per cycle, respectively [21]. Sun et al. [12] fabricated a novel flexible generator composite consisting of ZnO nano-particles and MWNTs in PDMS. According to their experimental results, the generator composite showed peak voltage values of 0.4 V, 7.5 V, and 30 V as a consequence of a finger gesture, cyclic hammer knocking, and foot stamping, respectively [12]. However, there is a lack of research corresponding to applications in traffic flow monitoring and energy harvesting with the aid of generator composites on roads.

In the present study, ZnO nano-powder was used due to its superior piezoelectric property in comparison with other types of nano-sized piezoelectric materials to fabricate a generator composite to be applied to monitor traffic flows and to serve as a power generator. A foot stamping test, a field test, and a durability test, which involved repetitive wheel loading were conducted on different types of generator composites to assess their performances.

2. Specimen preparation

In preparation of the generator composites, ZnO nano-powder was utilized as a piezoelectric material, as they have a greater surface-to-volume ratio and their shape effect improves the piezoelectric properties [12]. The nominal size of these nano-powders was less than 100 nm. The material was a proprietary product of Sigma–Aldrich Co. (Item number: 544906). As received MWNT, two components of polyurethane (PU), toluene, and copper powder were also used. The MWNT was a proprietary product of Hysong Inc. (M1111) produced by the chemical vapor deposition (CVD) growth method. Their diameter and purity were 12.29 ± 2.18 nm and 99.6%, respectively. The PU material included the two components of PF-359 and E-145, which are proprietary products of Kangnam Hwasung Chemical Co. Ltd. As another type of conductive filler, copper powder was used. The nominal size and purity of these spherical copper powders were 14–25 $\mu$m and 99%, respectively. The copper powder was a proprietary product of Sigma–Aldrich Co. (Item number: 326453).

As shown in Table 1, various types of generator composites based on different filler ratios were manufactured. The MWNT ratio was held constant, whereas the ZnO nano-powder content ratio varied from 5.7 to 20 times with regard to MWNT. The copper powder content ratio ranged from 0 to 20 times with regard to MWNT. The amount of toluene used for each type was approximately 5 wt.% by weight of total PU.

The preparation method of the generator composite specimens proceeded as explained below. The proper amounts of two components of PU were poured into a plate for mixing with measured amounts of the other constituent materials, in this case MWNT, ZnO nano-powder, copper powder, and toluene. The mixtures were completely pre-mixed for 2 min. Toluene was used to lower the viscosity of the mixture so that it could be poured into a three-roll milling machine. After the pre-mixing process, a three-roll milling machine (EXAKT80S, EXAKT Technologies Inc., Germany) was employed to enhance the dispersion quality of the generator composites [22]. The gap size and speed of the rollers were set to 5 $\mu$m and 200 rpm, respectively [22]. This mixing process was performed five times for each batch [22]. During this process, the toluene mostly evaporated from the mixture.

After the mixing process by the three-roll milling machine, the mixture was cast in 5 $\times$ 7 $\times$ 0.7 cm$^3$ molds. After the specimens were molded, the surfaces on the bottom and top were ground in order to create smooth surfaces. In an effort to make the contact more effective, silver paste was coated onto both the bottom and top surfaces of the composites. Afterwards, copper conductive tape was attached on the both the top and the bottom sides to act as electrodes to effectively transfer the electric charges created by the ZnO nano-powders. In order to insulate the electrodes, non-conductive tape was utilized to cover the top surface of the electrodes. Fig. 1 shows a prepared piezoelectric sensor of the type used in both lab and field-scale tests. Scanning electron microscope (SEM) images were taken of the ZnO-based piezoelectric sensor, where the amount of ZnO nano-powder was 5.7 times greater than that of MWNT. As shown in Fig. 2, both the MWNT and ZnO nano-powder were well dispersed within the matrix.

3. Test methods

Generator composites fabricated with a variety of filler ratios were stamped by the foot of a person with a mass of approximately 80 kg and the peaks of the output voltage from the specimens were measured. Fig. 3 shows the experimental setup during the foot step test. The copper tape, which served as electrodes, was connected to the wires of a digital multi-meter (DMM) such that the generated voltages could be measured. At the same time, the obtained data were recorded on a computer which was connected to the DMM. Efforts were made to ensure that every foot stamp was similar in terms of the magnitude of the applied load and the timing when applying the load.

4. Test results and discussion

The use of conductive fillers, especially nano-sized materials such as CNTs, has been shown to have an effect on the magnitude of the voltage generated by generator composites [11,12]. In accordance with findings in Park et al. [11] and Sun et al. [12], MWNTs can play a key role as a “nano-electrical bridge” between different piezoelectric material to transmit energy to electrodes. In addition, MWNTs can effectively improve the dispersion of the particles of piezoelectric material [11,12]. Another role of MWNTs is to increase the mechanical properties of the composite [23,24]. Consequently, the use of MWNTs and copper powder in the composites was examined in this study in an effort to evaluate the
Table 1
The constituent materials and their mix proportions for the fabricated composites for piezoelectric sensors.

<table>
<thead>
<tr>
<th>Specimen type</th>
<th>Composite type</th>
<th>PU (Part A) (g)</th>
<th>PU (Part B) (g)</th>
<th>MWNT (g)</th>
<th>Copper powder (g)</th>
<th>Piezoelectric material (ZnO) (g)</th>
<th>MWNT: ZnO: Copper powder</th>
<th>Toluene (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PU</td>
<td>19.87</td>
<td>19.87</td>
<td>0</td>
<td>0</td>
<td>33.85</td>
<td>0:12:0</td>
<td>3–4</td>
</tr>
<tr>
<td>2</td>
<td>7 wt% MWNT/PU</td>
<td>20</td>
<td>20</td>
<td>2.8</td>
<td>0</td>
<td>16</td>
<td>1:5:7:0</td>
<td>4–5</td>
</tr>
<tr>
<td>3</td>
<td>7 wt% MWNT/PU</td>
<td>20</td>
<td>20</td>
<td>2.8</td>
<td>0</td>
<td>34</td>
<td>1:12:0</td>
<td>4–5</td>
</tr>
<tr>
<td>4</td>
<td>7 wt% MWNT/PU</td>
<td>15</td>
<td>15</td>
<td>2.08</td>
<td>2.08</td>
<td>25</td>
<td>1:12:1</td>
<td>4–5</td>
</tr>
<tr>
<td>5</td>
<td>7 wt% MWNT/PU</td>
<td>15</td>
<td>15</td>
<td>2.08</td>
<td>25</td>
<td>25</td>
<td>1:12:12</td>
<td>4–5</td>
</tr>
<tr>
<td>6</td>
<td>7 wt% MWNT/PU</td>
<td>15</td>
<td>15</td>
<td>2.1</td>
<td>42</td>
<td>42</td>
<td>1:20:20</td>
<td>5–6</td>
</tr>
</tbody>
</table>

Fig. 1. The prepared piezoelectric sensor based on ZnO nanopowder.

Fig. 2. SEM image of generator composite Type 2.

Fig. 3. Experimental setup for the foot stamping test.
effects of these conductive materials on the output voltage of the generator composites.

The results of the foot stamping test on the six types of generator composites in total are discussed here. As shown in Fig. 4(a), piezoelectric sensor Type 1 showed a peak value of 1.16 V for the output voltage during the foot stamping test. For generator composite Type 2, in which the MWNT:ZnO nano-powder ratio was 1:5.7, the maximum output value for the generated voltage was 0.74 V (Fig. 4(b)). The Type 3 generator composite included more ZnO nano-powder. In this case, the ratio of MWNT to the ZnO nano-powder was set to 1:12. The output voltage versus the time for this composite is depicted in Fig. 4(c). The obtained peak voltage value was 0.94 V. The reason for changing the sign of this value can be explained as follows. Because the ZnO nano-powders were randomly been dispersed in the PU matrix, the resulting charges released by the ZnO nano-powders can differ upon any foot stamp. In other words, the dipole layer accumulated near either of the electrodes may have a different sign at every attempt due to the unaligned ZnO nano-powders within the composite, resulting in an irregular pattern of the output voltages [18]. Consequently, the measured voltage value between the electrodes may differ in terms of the value and sign for each attempt. It should be noted that the absolute value of the maximum generated voltage for this type of composite was higher than that of Type 2.

In the three types of generator composites, from Type 1 to Type 3, copper powder was not used since the effect of the variation of the ZnO nano-powder ratios on the piezoelectricity was studied. In the present work, three types of generator composites were also fabricated with the presence of copper powder considering the fact that it can enhance the electrical conductivity of the composites. The MWNT:ZnO nano-powder:Copper powder ratios were set to 1:12:1, 1:12:12, and 1:20:20. Fig. 4(d)–(f) demonstrate the performance of the fourth, fifth and sixth types of generator composites, respectively. A maximum voltage of 0.946 V was generated by

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**Fig. 4.** Generated voltage under applied foot stamping over time for piezoelectric sensor Types 1 (a), 2 (b), 3 (c), 4 (d), 5 (e), and 6 (f).
Type 4, as shown in Fig. 4(d), while Type 5 showed a relatively high value, with its maximum output voltage of 1.121 V, as plotted in Fig. 4(e). In this type of composite, a similar weight fraction of the ZnO nano-powder was incorporated for copper powder. The results showed that the maximum value of the output voltage for Type 5 was higher than that of Type 4. Finally, a further addition of both ZnO nano-powder and copper powder resulted in a lower peak value of the output voltage for generator composite Type 6, which exhibited a maximum output voltage value of 0.25 V (Fig. 4(f)).

Although it was noted in Park et al. [11] and Sun et al. [12] that a further addition of a conductive filler could effectively increase the output voltage, the results obtained in this study showed a different trend. The maximum peak value of output voltage was obtained for Type 1, where only ZnO nano-powder was used as a filler, while the lowest one was acquired when the combination of MWNT:ZnO nano-powder:Copper Powder was 1:20:20. In this study, the average peak voltages in the form of the absolute value for nearly 40 foot stamping trials was calculated, as illustrated in Fig. 5. As shown in the figure, the Type 1 generator composite showed the best performance in terms of the average absolute peak voltage values, at 0.068 V. Moreover, the generator composites of Types 4, 3, and 2 showed nearly identical performances. However, a comparatively large gap occurred for Type 5 and Type 6; their average absolute peak voltages were 0.04 and 0.03 V, respectively.

This behavior can be explained in terms of the changes in the stiffness of the generator composite due to the further addition of the filler. MWNT and copper powder not only enhanced the electrical conductivity of the composites but also increased the mechanical properties [24]. In order to obtain higher output voltages, generator composites should be relatively flexible. However, the addition of the MWNT and copper powder led to less deformation for the generator composites under the same load caused by the foot stamping. Taking this fact into account, it can be noted that the more flexible generator composite, Type 1 in this case, had the greatest amount of deformation and thus generated more voltage. In the case of Type 4, it can be said that the presence of a small amount of copper powder in the composite had a minor effect on the overall performance. In addition, Type 3 outperformed Type 2 in terms of the average absolute peak voltage value due to the existence of more ZnO nano-powder. On the other hand, a further addition of copper powder did not improve the voltage generated by the Type 5 and Type 6 composites due to the enhancement of the stiffness of these composites.

**Fig. 5.** The average absolute peak values of voltages for various types of piezoelectric sensors in the foot stamping test.

![Graph showing average absolute peak values of voltages](image)

**Fig. 6.** An experimental setup for the piezoelectric property measurement via a field test.

(a) The field test experimental setup

(b) The moment the vehicle passes the sensor
5. Vehicle load test

In the present work, an actual vehicle load was applied to the specimens, which were 5 × 7 × 0.7 cm³ in size. However, a support specimen on which to place the generator composites consisting of cement mortar was also manufactured. The size of this support specimen was 10 × 10 × 20 cm³. Prior to this test, the support specimen was firmly put into the ground. Subsequently, the generator composites were placed in their position and the electrodes of the specimens were connected to two wires connected to a DMM. Moreover, the DMM was linked to a computer such that the data could be stored. The experimental setup is shown in Fig. 6.

Fig. 7(a) shows the output voltage of the Type 1 generator composite over time during the field test. As illustrated in the figure, the maximum peak value of the output voltage was found to be −8.78 V, which was considerably greater than those obtained during the foot stamping test. The other high peak value was 7.48 V during the test. For the Type 2 generator shown in Fig. 7(b), the maximum peak value of the output voltage was −7.05 V. The next highest value of the positive peak voltage was approximately 5.32 V. Fig. 7(c) shows the detection of the vehicle's movement for generator composite Type 3. The addition of ZnO nanopowder slightly increased the peak value of the output voltage to 7.63 V. For this generator, the absolute value of the maximum generated voltage was observed to be greater than that of Type 2 but less than that of Type 1. In Fig. 7(d)–(f), the output voltage of generator composite Types 4, 5, and 6 are shown, respectively. The absolute values of peak voltages were found to be 9.85, 5.41, and 4.01 V for Types 4, 5, and 6, respectively.

Fig. 7. Generated voltage under an applied vehicle load over time during the field test of piezoelectric sensor Types 1 (a), 2 (b), 3 (c), 4 (d), 5 (e), and 6 (f).
It is important to note that all of the vehicle's movements on the generator composites could be effectively detected, though some of the peaks were comparatively low, as shown in Fig. 7. The speed of the vehicle was approximately 20 km/h during the test.

As a unique parameter for comparing the behavior of generator composites in terms of the output voltage, the average value of the absolute peak of the generated voltage values under a vehicle load was calculated. The calculated values for various types of composites are shown in Fig. 8. The trend in these values was found to be similar to that obtained during the foot stamping test.

As illustrated in Fig. 8, generator composite Type 1 clearly showed the best performance in terms of the average of the absolute peak values, with a major difference compared to the other types of composites. Its value was 2.65 V. On the other hand, Types 4, 3, and 2 exhibited similar average absolute peak values. Thus, the further addition of ZnO nano-powder in Type 3 resulted in a comparatively greater output voltage than that of Type 2, which is reasonable. The use of copper powder at the same weight fraction as the MWNTs in sensor Type 4 could also slightly increase the generated voltage. On the other hand, the further addition of copper powder deteriorated the averaged peak values of Types 5 and 6, as illustrated in Fig. 8. The generator composite Type 6 showed the lowest value of the average absolute peak voltage, despite the fact that the amounts of copper powder and ZnO nano-powder were highest. The reason for this behavior can be attributed to the stiffness of the composites, as explained earlier. On the other hand, composite Type 1 was more flexible such so that the average value of the absolute generated voltage was highest among all types of generator composites.

Consequently, it can be said that the influence of the addition of conductive materials on the overall generation of voltage of the composites was minor. The similar behavior in the foot stamping test also confirmed that the Type 1 generator can be considered as the best generator composite among all types tested here in terms of the average absolute peak voltage value. Taking this fact into account, a durability test involving wheel loading was carried out on composites Types 1 and 3. These results will be discussed in the next section.

6. Cyclic wheel load test

The durability of the generator composites Type 1 and 3 was examined and their output voltage by lapse of time was evaluated. A cyclic compressive wheel load with the magnitude of 400 kg and frequency of 0.4 Hz for 2000 cycles was applied on the generator composites. The experimental set-up for this test is shown in Fig. 9. During this test, a cement mortar specimen with the size of $10 \times 10 \times 40 \text{ cm}^3$ was employed to serve its purpose as a support on which the generator composites were placed during the test as to mimic the field condition where the composites were mounted on the mortar support. A pair of wires from the DMM was attached to the electrodes of the specimens and the data were collected by using a computer.

The output voltages of the composite Type 1 are plotted in Fig. 10(a). The amplitude of generated voltages was mostly ±10 V and outperformed the generated voltages of composite Type 3 shown in Fig. 10(b). It is evident that the initially observed behavior of the sensor was almost consistent until the last cycle. The behavior of composite Type 1 was more stable in comparison with that of Type 3. Moreover, the number of peak values above ±20 V for composite Type 1 was considerably higher than that of...
composite Type 3. In addition, the highest peak value for composite Type 1 was found to be 40.45 V, which accounts for a considerable amount of output voltage. The peak voltage values generated by Type 3 were mostly found to be around ±10 V, however the value at certain points changed to approximately ±6 V. The maximum absolute generated voltage for Type 3 was 28.35 V.

This test validated the durability of the generator composites under the aforementioned condition for about 2000 cycles. Further works are required to validate the durability of the generator composites subjected to compressive cyclic loading over 2000 cycles.

7. Concluding remarks

In this study, the piezoelectric property of various types of generator composites with regard to the various filler ratios was examined. ZnO nano-powders as piezo-materials, and MWNT and copper powder as conductive fillers were incorporated in the generator composites. The results of three different types of tests such as foot stamp, field test by a vehicular loading, and cyclic wheel load test can be summarized as follows.

1. The foot stamping test was carried out on the generator composites. In order to make a unique parameter to compare the performance of generator composites, the average of absolute peak voltage values were calculated. With respect to these values, Type 1 composite showed the most outstanding performance while Type 6 presented the lowest performance.

2. The results of the field test by a vehicular loading also showed the similar trend to the foot stamp test in which Type 1 composite revealed the highest value of the averaged absolute peak values whereas the lowest one was obtained by Type 6. It is worth mentioning that the composites were able to detect all of the vehicular movements.

3. In order to check the response of the generator composites in the repetitive loadings, the durability test was carried out using a cyclic wheel loading with a magnitude of 400 kg for 2000 cycles for composite Type 1 and 3. The results showed that Type 1 outperformed Type 3 with the relatively higher output voltage. Moreover, the greatest peak voltage value as high as 40.45 V was obtained for the composite Type 1 in this test.

4. The results of this research suggested that the generator composites fabricated by ZnO nano-powder and PU can be effectively used not only to monitor the traffic flow but also to generate power by deformation induced by vehicles on the roads as well as foot stampings.

The present work demonstrated that the utilization of generator composites based on ZnO nano-powders is feasible to bring out a number of applications to harvest energy in the real structures such as vehicle roads, joints in bridge, pedestrian roads, and stairways. Future works will focus on enhancing durability of the generator composites in an effort to make commercialization of these composites more feasible.

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References


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