



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



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## 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-weighted wheel loading and a prominent output voltage peak produced was as high as 40.45 V.

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## 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.

Recently, different types of nano-sized piezoelectric materials such as ZnO nanowires [10], BaTiO<sub>3</sub> nanoparticles [11], and ZnO nanoparticles [12] have been used to develop generator composite technologies. For instance, Wang and Song [13] reported that mechanical energy was converted into electrical energy by means of piezoelectric zinc oxide nanowire arrays at an approximate efficiency rate of 17–30%. This experimental work opened up a new trend in research to convert mechanical, vibrational, and hydraulic energy into electricity to generate power for nano-devices [13]. In a work of Xu et al. [14], a self-powered nanowire device was fabricated and the response of the device under different frequencies and compressive stress levels (from 0 to 6.25 MPa) was examined. The output voltage was increased as the compressive load increased, and the maximum generated voltage was around 50 mV under compressive stress of 6.25 MPa [14]. Zhu et al. [15] demonstrated a new type of nanogenerator incorporating ZnO nanowires. The peak open-circuit voltage reached 58 V under the impact of a human palm [15]. Lin et al. [16] fabricated a transparent flexible nanogenerator as a self-powered sensor using ZnO nanowires grown on PDMS substrates. The fabricated sensors were used as a traffic sensor and were examined at a range of speeds to monitor traffic [16]. It was also demonstrated that a heavier vehicle could generate higher output voltage [16].

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Furthermore, BaTiO<sub>3</sub>, which is frequently adopted as a piezoelectric material, has been assessed by several researchers. For instance, Park et al. [17] fabricated BaTiO<sub>3</sub>-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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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 Hyosung Inc. (M1111) produced by the chemical vapor deposition (CVD) growth method. Their diameter and purity were  $12.29 \pm 2.18$  nm and 96.6%, 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 spheroidal 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<sup>3</sup> molds. After the specimens were demolded, 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

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