NANO-ENHANCED TRIBOELECTRIC GENERATORS: INVESTIGATING ADDITIVE EFFECTS ON OUTPUT VOLTAGE

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ABSTRACT
Recent years have witnessed an increasing amount of attention coming to triboelectric generators (TEGs) as a means of harvesting energy from various sources, such as mechanical vibrations, wind, and even human motion. The ability to automatically convert mechanical energy into electrical energy without requiring external power sources, which makes them easily applied. Due to this quality, TEGs have many applications, like self-powered devices, wireless sensors, and renewable energy systems. In TEGs, a triboelectric material gives off electrical charges upon contact with another material. Such material features as electrical conductivity and dielectric constant play a decisive role in TEG efficiency. Among the research projects on increasing triboelectric properties, the use of nano-additives is one of the techniques extensively studied. In this research, the triboelectric characteristics of the polymer nanocomposites that are reinforced with multi-walled carbon nanotubes (MWCNT), silica (SiO₂), alumina (Al₂O₃), or a blend of them are studied when they are used as tribo-materials. The above dielectric nanoparticles can be added to modify the dielectric constant of the composite, which influences the triboelectric effect. Reinforcement concentration and rubbing time are adjusted in different ways and impact the output voltage. This study aims to uncover the possibility of using nano-reinforced polymers in TEG and other devices based on material triboelectricity.

KEYWORDS
TEG, MWCNT, SiO₂, Al₂O₃, Output voltage, Rubbing time, Energy harvesting.

INTRODUCTION
The search for sustainable energy solutions has erupted into the investigation of utilizing ambient mechanical energy by triboelectric nanogenerators (TENGs) as a great pathway, [1–3]. TENGs employ the triboelectric effect and electro-static induction to transform mechanical energy into electrical power, which can find application in wearable electronics, autonomous sensors, and environmental monitoring systems. One of the main elements in improving TENG efficiency is to explore the key aspects that determine the threshold for its energy harvesting capacity.
An important factor in this regard is the period of contact mechanical action, which is normally referred to as the rubbing time. Even though the TENG researcher does a comprehensive study on different parts of the TENG working mechanism, like the selection of material, design, and configuration, it has not been investigated in detail how rubbing time affects the performance of TENG up until now [4-6]. Among the different ways of mechanical energy harvesting, triboelectric nanogenerators (TENGs) seem to be a particularly promising method, thanks to the fact that mechanical energy is all around us, [7–14]. TENGs have several benefits as compared to usual energy harvesting devices, like their advent of the fabrication process, being light in weight, numerous material options, and their high energy conversion efficiency, [15–17]. Though TENGs use contact electrification and electrostatic induction for their function accordingly, the friction is certain between the surfaces of the two layers, which in turn results in the abrasion at the vicinity of those contact points and the drifting off the power output over time, [18–20]. Such fundamental shortcomings as energy output insufficiency and unsuitability for long-term use are the key factors that undermine the viability of the TENG technology, [21].

The working areas of TENGs are usually filled with more dust, moisture, and heat, which can worsen mechanical faults, [22–28]. As a result, there is a pressing demand for TENGs that exhibit high levels of reliability and durability when subjected to repeated mechanical stimuli. In addition, titanium electrode nanogenerators (TENG) gradually gained diverse applications on structures with varied shapes of surface thanks to innovative contact electrification facilitated by critical factors such as material systems, [26]. The latest gain in improving the robustness and reliability of TENG is accomplished by means of several approaches, like touch mode, [29, 30], rolling pattern, [31, 32], solid-liquid contacts, [33, 34], self-recovery, [20, 35], and encapsulation, [36, 37]. The other way is to make the device robust.

Polished parts have been replaced in several end-effectors using brushes, which offer a high ratio of static friction under elastic loading, [38]. In a recent study, there were sub-millimeter-long fur brushes that were highly lightweight, soft, and low-wear and excellent triboelectric materials that could be used in unimaginable TENG applications. Yang, Y. et al., [39] reported the first DC-TEG, which utilizes negative and positive geometric triboelectric materials encapsulated inside the tube to form rotating wheels and a belt and generates electricity under rotation. It attains the open-circuit voltage (+) 3200 V and illuminates up to the (thousand LED) array. There is a real possibility of having energy stored in a capacitor. It is a significant reason for the growth of autonomic electronics. Kim et al., [40] design an ecologically sensitive silk nanofiber networked bio-triboelectric generator based on silk biomaterial that comprises strong hydrogen bonding. Such a device of electrospinning is characterized by its long-lasting energy harvesting functionality, which provides it with a large surface-to-volume ratio, highly resilient silk fibers, and fracture-resistant nanofiber networks. Tran et al., [41] proposed the idea of a MN TEG, which shows a high electrical power with a maximum open-circuit voltage of one hundred volts and about fifteen μA, respectively.
The MN-TEG, produced at very low cost through laser ablation and molding processes, features an innovative energy harvesting mechanism that charges a 0.1 µF capacitor up to two volts within about 0.56 s and powers about fifteen series-connected LEDs through tapping. Fan et al., [42] offered a new approach by which the friction-induced charging mechanism of a triboelectric generator that is made of stacked polymer sheets and metal films, which can convert mechanical energy into electric power, is used. This cheap and flexible TEG generates a voltage can exceed three volt and a power density of 10 mW/cm3, which means it can be used in harvesting energy from different resources like human action, tire rotation, and mechanical vibration for various applications such as self-powered systems. Guo et al., [43] proposed a triboelectric generator operating on the principle of interdigital electrodes and a sandwich-like PET thin film, which was integrated into the helmet to convert motion power into electric power. The TEGC delivers an energy density of about two W/m2 and can charge a capacitor to 5 V in 35 seconds.

Real-time applications include gathering energy from mouse operations to power LED lights, offering high flexibility, light weight, durability, convenience, and portability. Valentini, L. et al., [44] discuss the PHB biopolymer in a triboelectric generator that can convert mechanical energy into electricity by using a PHB film between indium tin oxide-coated polyethylene terephthalate sheets. The TEG operates as a functional pressure sensor and may thus be utilized in touch screens and areas where continuous mechanical vibration occurs. This implies the possibility of self-powered sensors and potentially compostable electronics, enabling the reduction of electronic waste. This study aims to highlight the effect of nano-additives on the level of concentration and the rubbing time to determine the electrical conductivity of the composite material and its application in triboelectric generators. Data from the process have been scrutinized to recognize the relationship between nano-additive percentage, friction time, and output voltage.

MATERIALS AND METHODS
The study investigates the triboelectric properties of the polymer nanocomposites on the output voltage during the rubbing process of the composite against the solid electrode (an aluminum electrode), which produces electricity by friction energy released at the interface of the charged layers between electrodes. This type is commended for its adaptability and efficiency in harnessing energy from different sources without the need for extra electrodes. The materials used in this study included cellulose paper, aluminum strips, a polymer matrix (polyester), and nano-additives such as carbon nanotubes (CNTs), silica (SiO2), and alumina (Al2O3) with varied concentrations.

Nanofillers were chosen because of their high surface area. This leads to an increase in the energy harvested due to the high contact points between the material and the electrode. Different concentrations and types of nanofillers were mixed within resin using a high-speed mixer to ensure homogeneity, and then five categories of triboelectric layers were produced: neat PES, PES/MWCNTs, PES/SiO2, PES/Al2O3, and PES/Hybrid. The nanocomposites layers were fabricated through
compression molding. Two aluminum strips measuring 12cm by 5cm (as electrodes) were cut using a cutting knife and then fixed to cellulose paper. Next, rectangular layers of composite materials are made, each of which is designed with dimensions of 30 mm length, 30 mm width, and 2.5 mm thickness. These layers are rubbed against the aluminum electrode foil responsible for collecting and transferring electrons generated by rubbing the triboelectric polymer composite. A separation distance of 2 mm between Al layers is maintained to facilitate the transfer of electrons generated by the rubbing action.

Figure 1 shows the SEM of different nanofillers used in the fabrication process of polyester composites. The aluminum strips fixed to cellulose paper were connected to the digital multimeter to record the output voltage. The resulting composites were then rubbed against the other face of the cellulose paper for varying times. The output voltage was measured using an electric circuit and a digital multimeter. The experiment was performed under controlled conditions such as room temperature, maintaining a constant reciprocating speed of 1 mm/sec and a contact pressure of 2 N/mm² for a duration of 60 seconds. Figure 2 shows the experiment setup. The results of this study will provide insight into the effect of nano-additives concentration and rubbing time on the electrical conductivity of the composite materials and their potential applications in triboelectric generators. Data obtained from this study were analyzed to understand the relationship between nano-additives concentration and rubbing time with the output voltage.

Fig. 1 SEM of nanoparticles reinforcements a) MWCNTs b) SiO2 c) Al₂O₃.
RESULTS AND DISCUSSION
Influence of Polyester/MWCNTs on the Output Voltage

Fig. 3 demonstrates the experimental data, which shows the effect of rubbing time on the amount of voltage generated by the triboelectric nanogenerator (TENG) device using polymer nanocomposites ranging from 0% additives to 0.8% multi-walled carbon nanotubes (MWCNTs). For the sample consisting of 0% additives, when the rubbing time rises to 60 seconds, an observed increment in the output voltage is seen. This fact is proof that strengthened rubbing can improve the triboelectric effect in the polymer nanocomposite, causing larger charge accumulation at the tank between the polymer nanocomposite and electrode.
The recorded increase in output voltage with rubbing time indicates better energy extraction efficiency as the operational duration gets longer. Involved in the same investigation is the range of 0.2% to 0.8%, which has the same kind of trends, albeit with higher output voltages throughout all rubbing time intervals and remarkable higher values when compared to the 0% additive.

The results of the output voltage observed of samples with 0.6% and 0.8% are very close. This implies that there might be an optimum MWCNT level of content suitable for the maximum triboelectric effect; higher concentrations above this optimum do not improve perceived performance anymore. Hence, well-planned MWCNT usage is necessary to attain the desired level of triboelectric properties, but from the perspective of the respective material's cost-effectiveness.

Influence of Polyester/SiO\(_2\) on the Output Voltage

Fig. 4 demonstrates the experimental data of the output voltage produced by the triboelectric nanogenerator (TENG) using polymer/SiO\(_2\) with 0.5% and 1% SiO\(_2\). The outcomes shed light on the relationship of SiO\(_2\) percent with the triboelectric performance of the nanocomposites, which allows comparison of these outcomes with experiments conducted with materials containing different SiO\(_2\) and other additives, e.g., MWCNTs. In contrast with the examples of the SiO\(_2\) content being 0.5%, the output voltage shows a progressive development, which is consistent with the rubbing time. The maximum output voltage of the circuit was 2.25 volts. Furthermore, in another sample with 1% SiO\(_2\), the signal intensity showed a similar rising trend according to the duration of rubbing; the readings reached 2.27 volts. These results confirm that the combination of SiO\(_2\) nanofillers with a polymeric matrix leads to an improvement in the nanocomposite's triboelectric performance.

The SiO\(_2\) nanoparticles can be attributed to enhanced charge production as well as charge accumulation during friction. Such enhancements are possible because of
three specific mechanisms, including surface roughness increase, provision of additional contact area, and alteration of surface chemistry due to the introduction of SiO$_2$ nanoparticles. The data gathered through samples rubbed with 0.5% and 1% SiO$_2$ shows that the increased SiO$_2$ concentration from 0.5% to 1% does not have an essential impact on the triboelectric output voltage values. This implies that there may be an optimal SiO$_2$ concentration, and using a greater quantity of SiO$_2$ leads to a small effect.

Influence of Polyester/ Al$_2$O$_3$ on the Output Voltage

Figure 5 shows the electrostatic potential given by the triboelectric nanogenerator (TNG) for different compositions based on adding 0.5% and 1% aluminum oxide (Al$_2$O$_3$). Thus, these outcomes provide clues about the effect of Al$_2$O$_3$ percentage on the process of triboelectric and can easily be compared to the results of the triboelectric effect and those of other possibilities like the addition of SiO$_2$ and MWCNTs within the nanocomposites. By rubbing, the voltage is gradually increased with rubbing time, reaching a peak value of 2.37V for the sample containing 0.5%. Moreover, the sample, whose concentration was 1% of Al$_2$O$_3$, also displayed a similar curve of increasing voltage as the rubbing time, and the peak value reached 2.59 volts.

These results thus give information on the effect of nano-Al$_2$O$_3$ particles' addition to the polymer matrix on the triboelectric performance of the nanocomposites. Nanocomposite probably benefits charge generation and charge accumulation at the interface between nanocomposite and electrode. This development might be attributed to the widening of the surface roughness, the increased enhanced contact area, and the surface chemistry alterations produced by Al$_2$O$_3$ nanoparticle incorporation. Evaluation shows that a higher output voltage is yielded for the 1% Al$_2$O$_3$ sample through all values of rubbing time compared to the 0.5% Al$_2$O$_3$ sample. By raising the percent of Al$_2$O$_3$, the triboelectric performance is enhanced. The consideration of the change of the output voltage to the increasing amount of Al$_2$O$_3$ offers the possibility of getting better energy harvesting values with the appropriate adjustment of the added content.

Influence of Polyester/ hybrid nanofillers on the Output Voltage

The output voltage produced by the TENG device for a polymer nanocomposite filled with a concentration mix of 0.6% MWCNTs, 0.5% SiO$_2$, and 1% Al$_2$O$_3$ is shown in
Fig. 6, where the change in rubbing time is depicted. This composite is a multifunctional formulation that taps on the benefits of various nano-additives to optimize the electric output. The results show a clear boost in produced voltage associated with rubbing time for the composite material. Test conditions indicate an output voltage of 5.12 volts (maximum). This significant upshot of using MWCNTs, SiO$_2$, and Al$_2$O$_3$ nanoparticles reveals that the nanocomposite layer indeed enhances charge generation and accumulation at the interface between the nanocomposite and the electrode.

![Graph showing output voltage vs rubbing time]

Fig. 6 Output Voltage for Composite with Multiple Nano Additives.

![3D bar graph comparing voltage of different polyester/reinforcements]

Fig. 7 Comparison of Voltage of different Polyester/reinforcements.
Synergistic effects amongst the individual nano-additives may be combined to explain the improved triboelectric performance. The outstanding electric current conductivity, combined with the high ratio of length to diameter possessed by the MWCNTs, provides an easy charge transfer and accumulation phenomenon during rubbing. While SiO2 and Al2O3 nanoparticles simultaneously enhance surface roughness, increase the interfacial contact area, and modify the surface chemistry, charge separation and generation are due to these nanoparticles. Such comparisons of these results with those of the samples containing individual nano-additives or binary blends presented in Fig. 7 demonstrate a remarkable improvement in triboelectric performance by adding all three of the additives. The multiple composite formulation also shows higher output voltages across all rubbing time intervals, indicating the exponential impact of the MWCNTs, SiO2, and Al2O3 on power generation efficiency.

CONCLUSIONS
Within the domain of energy harvesting, investigations have delved into the triboelectric attributes of polymer nanocomposites fortified with a range of nanofillers. Through analysis of experimental data, the following outcomes have been observed:

• Incorporation of silica nanoparticles boosts triboelectric production and demonstrates an ascending voltage generation. Interestingly, further increases in SiO2 concentration do not significantly impact the output voltage. This suggests the existence of an optimal concentration level for achieving maximum triboelectric effect.

• The dispersion of aluminum (Al2O3) nanoparticles has enhanced the power harvesting voltage; during friction, the power collected increased gradually. A higher concentration of Al2O3 resulted in a higher output voltage.

• Hybrid nanocomposites consisting of MWCNTs, SiO2, and Al2O3 nanoparticles exhibit synergy that yields a substantial rise in output voltage in comparison with individual or binary combinations of additives.

REFERENCES