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The Effects of SnO_2 Filler towards PVDF/SnO_2 Flexible Piezoelectric Nanogenerator Performance

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***Abstract*— The growing dependence on conventional electrical energy sources has resulted in significant degradation of the environment and increased costs. Renewable energy sources provide a promising option, but their actual implementation is hindered by several constraints. Alternative energy harvesting systems propose an innovative approach that involves real-time energy collecting from the surrounding, allowing for instantaneous use with temporary storage. This study utilized the Polyvinylidene Fluoride (PVDF) as an alternative energy harvester and the effect of SnO_2 filler loading (1 wt%, 3 wt%, 5 wt%, 7 wt%, and 9 wt%) on the performance of PVDF flexible piezoelectric nanogenerators was investigated. The results obtained proved that the 5 wt% is the optimum filler loading percentage of SnO_2 in PVDF matrix which enhanced the electroactive β-crystal nucleation as well as the piezoelectric response.**

***Index Terms*—Energy Harvester, Piezoelectric, PVDF/SnO_2, SnO_2 filler, β-phase Crystal.**

I. INTRODUCTION

Conventional or non-renewable energy sources, such as coal, gas, and oil, are those energy sources that do not replenish themselves within a certain period. These energy sources have been heavily utilized for a long time to meet energy demands. However, conventional energy is responsible for serious issues like ozone depletion, global warming, acid rain, a broad variety of diseases, and high costs [1].

Renewable energy is an effective way to address these issues where this energy generated from constantly replenished sources such as solar energy, wind energy, hydroelectric energy, geothermal energy, and biomass energy [2]. Nevertheless, renewable energy sources cannot be relied on indefinitely due to climate change and large storage systems are required for storing enough electricity when renewable energy production drops.

Another approach to addressing these issues and to support renewable energy is alternative energy, in which the devices harvest energy from their surroundings in real time and use it immediately, requiring only temporary storage [3]. Energy harvesting is the process of harvesting energy from mechanical strain and motion to power low-power electronic components using unconventional methods such as ferroelectricity (electric field-dependent polarisation), pyroelectricity (temperature-dependent polarisation), and piezoelectricity (stress/strain-dependent polarization [4], [5], [6].

Piezoelectricity is found in non-centrosymmetric crystalline materials. This effect causes an electric polarization proportional to applied mechanical stress. Improved 'ferro' and 'piezo' electric properties is the best way to develop a human-motion-based flexible piezoelectric nanogenerator (NG). Piezoelectric materials are not won't be affected by internal electric fields that are applied or temperature changes [7].

The most used piezoelectric materials are barium titanate ($BaTiO_2$) and lead zirconate titanate (PZT), which have high piezoelectric constants and high energy conversion efficiency. However, these materials have drawbacks such as their high cost, toxicity, brittleness, and lack of environmental friendliness [8]. To counter this issue, organic piezoelectric polymers, such as poly (vinylidene fluoride) (PVDF) and its copolymer poly (vinylidene fluoride-trifluoroethylene) (PVDF-TrFE), which are flexible for conformation and large deformation, are used [9]. Furthermore, in order to increase the electroactive β phase fraction (piezoelectric properties), the filler is added to polymer solutions to increase the electroactive β phase fraction. The filler particles can act as nucleation sites for the formation of the desired phase, leading to an increase in the overall fraction of the desired phase.

Therefore, in this study, the SnO_2 powder is utilized as the filler for the PVDF solution. The effects of SnO_2 filler loading towards the PVDF flexible nanogenerator performance are investigated. The piezoelectric and morphological properties of deposited PVDF/SnO_2 flexible piezoelectric nanogenerator films were investigated.

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II. METHODOLOGY

Fig. 1 shows the overall deposition process and characterization of PVDF/SnO_2 flexible nanogenerator films. The process starts with the PVDF/SnO_2 solution preparation and followed by the immersion process. The prepared solution was then undergoing stirring and aging process. The film was then deposited using drop casting method before anneal in the vacuum furnace. Finally, the deposited films were characterized to observe the morphology and piezoelectric properties of the deposited PVDF/SnO_2 flexible nanogenerator films.

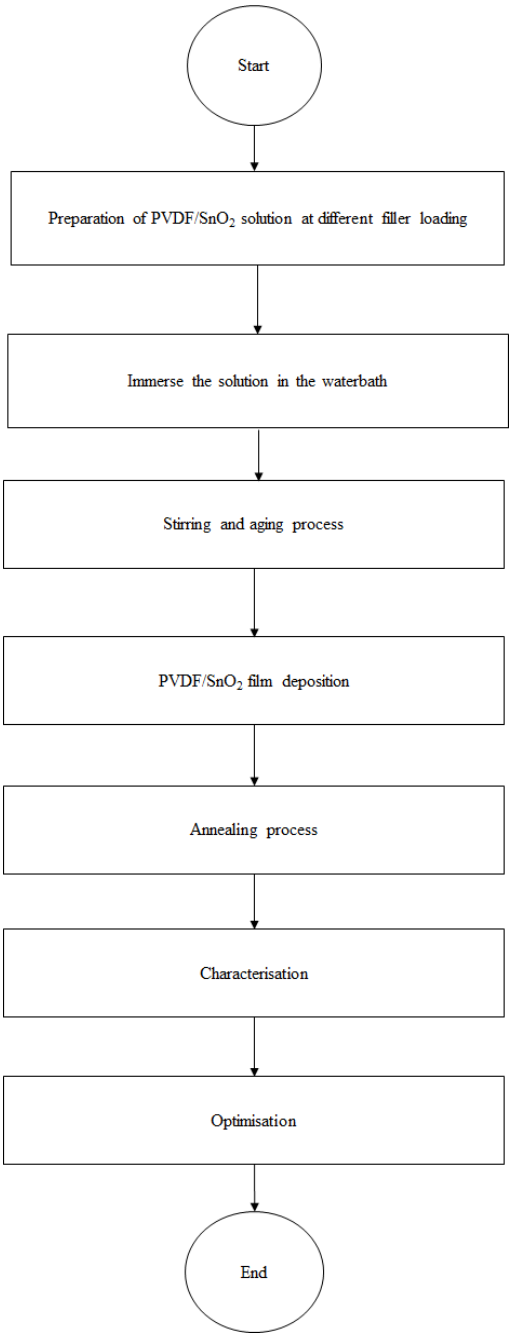

Fig. 1. The Overall Process of Deposition and Characterization of PVDF/SnO_2 Films.

A. PVDF/SnO_2 solution preparation

Prior to the deposition film, the PVDF/SnO_2 solution was prepared by dissolving the PVDF powder in N-N-Dimethylformamide (DMF) solvent at the concentration of 30g/L. Then, the solution was immersed in water bath at temperature of 70 °C. Next, the stirring and aging process was then conducted at a temperature of 70 °C and a speed of 750 rpm for 48 hours.

B. PVDF/SnO_2 film deposition

The prepared solution was dropped into a petri dish using a drop casting method. Then, the film was annealed at 120 °C for 90 minutes in oven.

C. Characterization

Surface morphology, interaction with the polymer matrix and Piezo electric response have been investigated by Fourier-Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD) and external force (2Nm) from mechanical tapper. The force and the frequency applied during piezoelectric measurement (open circuit voltage) were 2 Nm and 10 Hz respectively.

III. RESULT AND DISCUSSION

The FTIR spectra for PVDF/SnO_2 at different SnO_2 weight percentage (1 wt%,3 wt%, 5 wt%, and 7 wt%) is shown in Fig. 2 while Fig. 3 shows that FTIR spectra for 9 wt% of SnO_2. The spectra revealed all samples have semicrystalline polymer PVDF which has formation of all phases (α, β and γ). The results also indicate that 1wt% of filler SnO_2 exhibits the sharpest polymorph peaks comparison to other investigated SnO_2 filler weight percentages. From observation, peaks assigned to the α non-polar phase of PVDF, with IR bands located at 615 cm^{-1}, 764 cm^{-1} and 976 cm^{-1}, are insignificantly observed for sample 5 wt%, 7 wt%, and 9 wt%. In addition, the β phase-related peaks located at 840 cm^{-1}, 875 cm^{-1}, 1179 cm^{-1}, and 1400 cm^{-1} are predominated. It has been shown that the addition of SnO_2 filler enhanced the electroactive phase content (β phase).

However, as the filler loading increases (>3 wt%), the aligned chains get disrupted due to agglomeration of the SnO_2, and the overall β phase content reduces. Furthermore, there is no polymorph peak observed for 9 wt% film as shown in Fig. 3 which indicates that the aligned chains get disrupted. It is suggested that this condition was due to the agglomeration of the SnO_2 filler and its loose electroactive properties. This is proven by surface morphology of this film Fig. 4 where it shows agglomeration of particles.

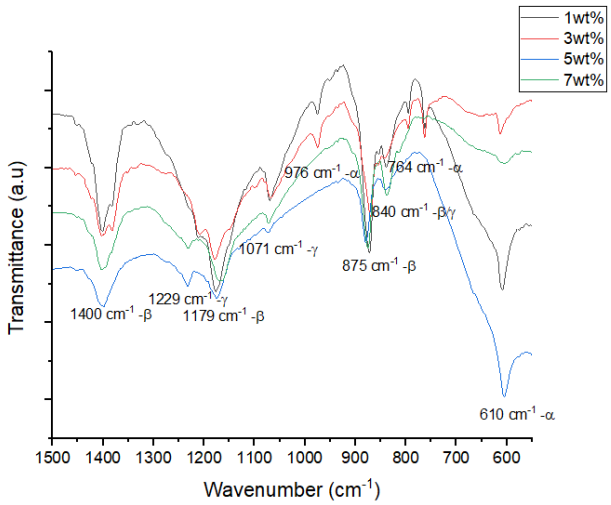

Fig. 2. FTIR Spectra for 1 wt%,3 wt%,5 wt% and 7 wt% Films

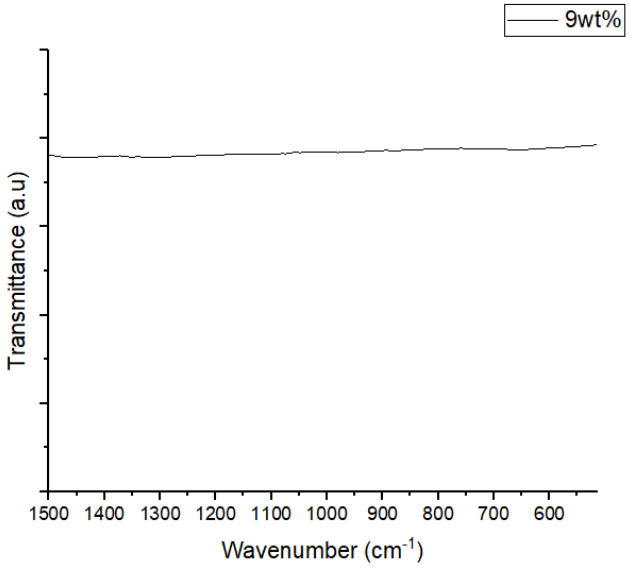

Fig. 3. FTIR Spectrum for 9 wt% Film

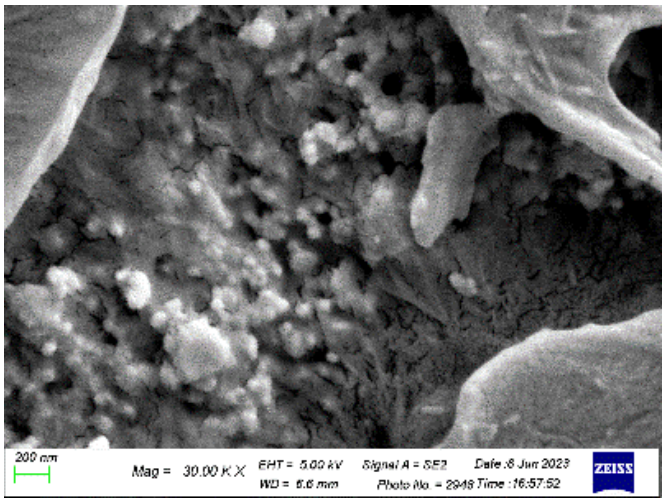

Fig. 4. FESEM image of 9 wt% film at 30K magnitude

Fig. 5 shows the X-ray diffraction (XRD) pattern of deposited films and indicates the film's highly crystalline structure. The diffraction peaks are located at 26.63°, 33.87°, 38.03°, 51.86°, 54.83° and 57.93° and are indexed at (110), (101), (200), (211), (220) and (002) planes. All the fractions are corresponding to the tetragonal rutile like SnO_2 structure, Joint Committee on Powder Diffraction Standards (JCPDS) card No. 41-1445, space group: P42/m, A_o = 4.738 Å, C_o = 3.1865 Å [11]. The XRD pattern indicates that SnO_2 was successfully synthesized in a single phase for all filler weight percentages. Additionally, the diffraction peak of the electroactive β-crystallite (2θ~20.2°) appeared prominently for sample with loading percentage 1 wt% and 3 wt%. Above 3 wt%, the peak associated with β crystalline demolished.

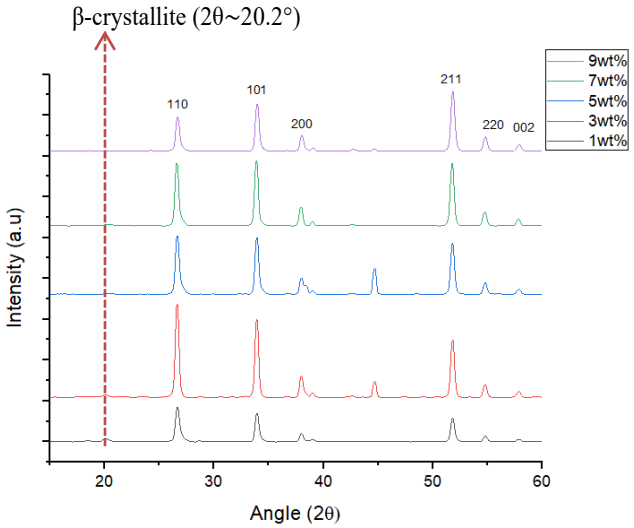

Fig. 5. X-Ray Diffraction of PVDF/SnO_2

The piezoelectric response of deposited PVDF/SnO_2 films at various SnO_2 filler loading were investigated by measuring the open circuit output voltage of the nanogenerator. The generated voltage is produced from external mechanical force via mechanical tapper and the force, and the frequency applied during measurement were 2 Nm and 10 Hz respectively.

Fig. 6 and Table 1 show the measured open circuit voltage of the deposited PVDF/SnO_2 films. According to Table 1, the open circuit voltage is insignificantly changed for 1 wt% to 3 wt% films while for 5 wt% it is significantly increased to 9.25 Vpp. The Vpp for 9 wt% film was found to decrease dramatically at 1.83 V. In addition, the Vpp result shows that the 5 wt% produced better output performance compared to other films. It is suggested that the highest performance was due to the uniform surface morphology Fig. 6 and good polymorph characteristic of the deposited films.

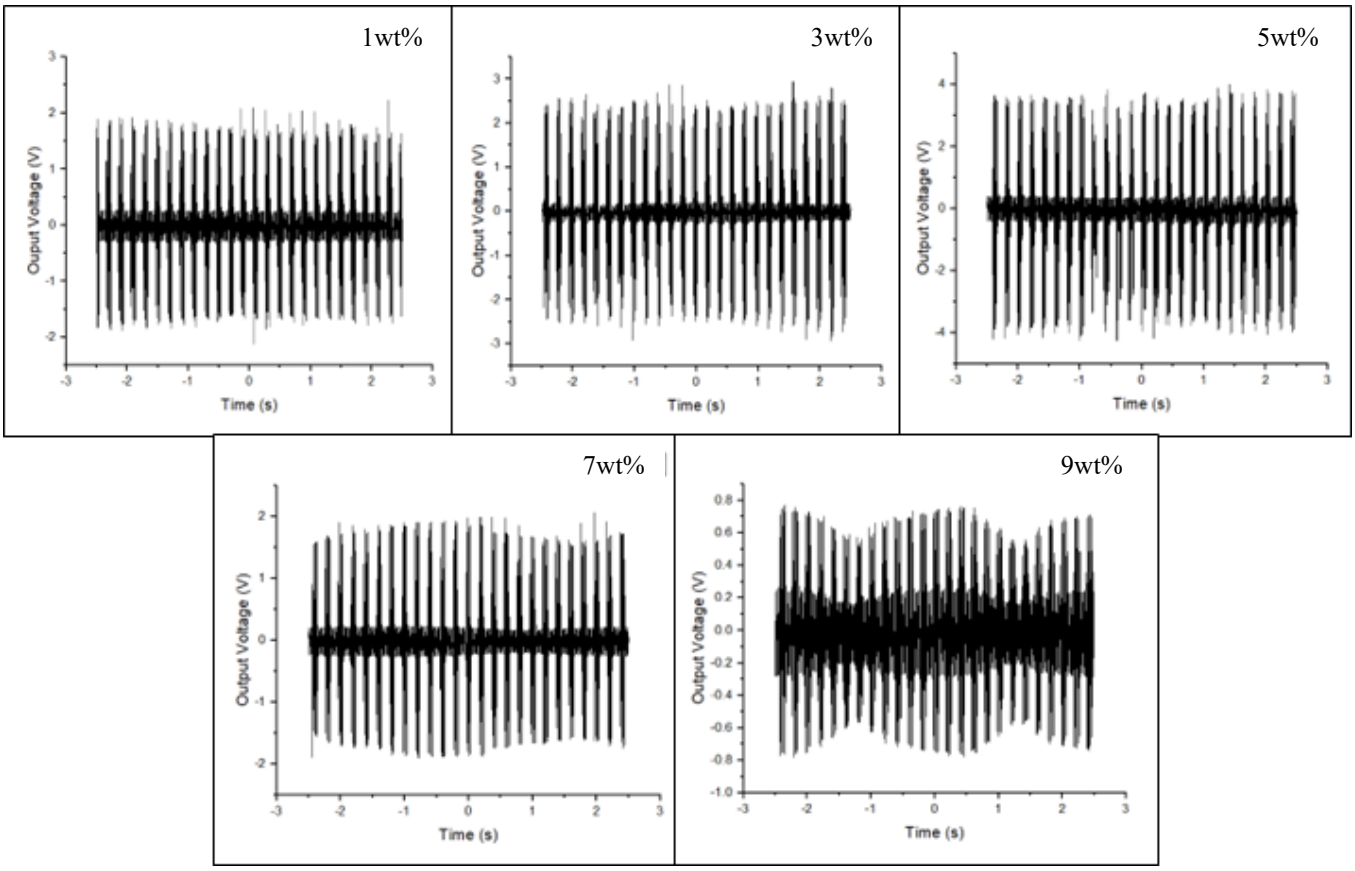

Fig. 6. Piezo electric response of PVDF/SnO_2 at different SnO_2 filler loading percentage.

TABLE I. Voltage Peak to Peak and Voltage peak for each SnO_2 filler.

Filler	V_{PP}(V)	V_P (V)
1 w%	6.51	3.26
3 wt%	7.46	3.37
5 wt%	9.25	4.63
7 wt%	6.95	3.48
9 wt%	1.83	0.92

IV. CONCLUSION

In conclusion, PVDF/SnO_2 piezoelectric nanogenerator films at different weight percentage (1 wt%, 3 wt%, 5 wt%, and 9 wt%) were successfully deposited using the solution casting method. As a result, the findings show that the relationship between SnO_2 nanofiller and the electroactive β crystal of PVDF has a crucial part in improving the piezoelectricity of PVDF/SnO_2 nanogenerator film. At 5 wt% of SnO_2 loading, the film's open circuit voltage reached its maximum output of 9.25 Vpp. The FTIR spectra analysis showed that all samples had semicrystalline PVDF with α, β, and γ phases. SnO_2 filler increased the electroactive β phase content, however, with filler loadings more than 3 wt%, the aligned chains collapsed by SnO_2 filler, resulting in a decrease in total β phase content. The absence of polymorph peaks in the 9 wt% film indicated that chain alignment had been disrupted due to severe SnO_2 filler agglomeration. The XRD analysis showed the successful single-phase synthesis of SnO_2 nanoparticles with a highly crystalline structure corresponding to tetragonal rutile-like SnO_2.

It can be concluded that the 5 wt% SnO_2 loading is the optimized loading percentage for PVDF/SnO_2 nanogenerator film which can be related to its morphology and good polymorph properties. These findings highlight the significant contribution of filler loading in PVDF composites to obtain better piezoelectric characteristics. The results provide useful insights for the development of efficient and sustainable energy harvesting systems using piezoelectric films.

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