# Reliability of PVDF/1D Se Micro-Rod Based Composite Films for Energy Harvesters

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#### 1. Introduction

Recently, harnessing various forms of abundant waste mechanical energies in the society by the advanced portable, wearable electronic technologies (piezoelectric, and triboelectric) gained massive attention due to the broad utility in various fields. These energy technologies may reduce the global energy crisis and also useful to develop the self-powered sensors/systems [1, 2].

Piezoelectric nanogenerators (PNG) requires high performance functional micro/nanostructures, and efficient polymer films. The pure organic or composite films have advantages than the high performance inorganic materials due to the high flexibility, adaptability in device structures (linear or non-linear surfaces), high durability, and simple fabrication. Therefore the investigation of various fillers in PVDF material, modulation in function properties in a more straightforward way, and innovative device designs for energy harvesting are highly necessary to improve the efficiency of the device.

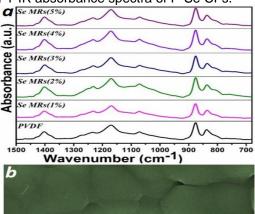
#### 2. Abstract

Multifunctional composite structures gained high attention due to a broad range of scopes such as flexibility, adaptability to measure non-linear surface motions, large scale fabrication, and high output power, accepting high mechanical force and low leakage current losses. In this study, weight ratio dependent polyvinylidene fluoride (PVDF)/selenium (Se) micro-rods (0, 1, 2, 3, 4 and 5 wt. %) based composite films (P-Se CFs) developed by the cost-effective solution casting technique. The substitution of highly crystalline, hexagonal shaped Se MRs (synthesized by solution-growth method) improves the conductivity of film and stabilizes the polar phases ( $\beta$  and  $\gamma$ ) of PVDF. The remnant polarization of 4 wt. % of P-Se CF is seven times higher than the pure PVDF film. Also investigated the energy harvesting performance of as-prepared P-Se CFs based devices by applying a perpendicular mechanical force on it. The generated electrical energy of P-Se CF devices is green energy, cost-effective, and also useful to drive the low power electronic components (five LEDs, and LCD devices).

#### 3. Results and Discussions

In the present work, flexible, PVDF/Se MRs based composite films (P-Se CFs) with the multiple

weight ratios (0, 1, 2, 3, 4, and 5 wt. %) of Se MRs fabricated by the ultrasonication process followed by the solution casting technique. Figure 1a shows the FT-IR absorbance spectra of P-Se CFs.



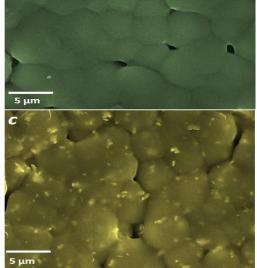


Fig. 1(a) FT-IR spectra of weight ratio dependent P-Se CFs at room temperature. (b, c) Surface morphological analysis of PVDF film and P-Se CF (4 wt. %) at 5  $\mu$ m scale.

The polar phases and non-phases were evaluated using these patterns. For the PVDF film, the calculated electroactive  $\beta$ -phase is (70.5 %) along with the minor  $\alpha$  (13.36 %) and  $\gamma$  (16.14 %) phase components. Here, the sonication process directly triggers the major part of non-polar CH<sub>2</sub>/CF<sub>2</sub> molecular chains into well aligned polar molecular chains by the rotational, stress-induced effects. After that, various amounts of Se MRs dispersed into PVDF solution to stabilize the  $\beta$ -phase, improves the semi-polar  $\gamma$ -phase along with the better electrical conductivity of the sample.

At 4 wt. % of Se MRs in PVDF decreases the  $\beta$ -phase from 70.5 % to 56.91 %, and at the same time improves the  $\gamma$ -phase from 16.14 % to 25.26 %. For other compositions, the polar phase ( $\beta$ , and  $\gamma$ ) percentage is reduced than the pure PVDF and improves the non-polar  $\alpha$  phase, will directly reduce the piezoelectric performance of P-Se CFs.

In Fig.1(b) shows the FE-SEM image of pure PVDF film shows the well-connected spherulites without any cracks. Whereas in the case of P-Se CF (4 wt. %) shows the homogeneous distribution of c-axis oriented Se-MRs in PVDF spherulites. Fig.2 confirms the existence of all the chemical elements such as F, C, and Se atoms in the obtained final film.

Se F C

Fig. 2 Elemental analysis of P-Se CF (4 wt. %) by energy dispersive X-ray spectroscopy (EDS) technique.

Figure 3 shows the polarization (P)-electric field (E) dependent hysteresis loops of as-fabricated all the P-Se CFs and confirms. The nature of P-E loops of all the films confirms the ferroelectric nature. Here, 4 wt. % of Se MRs film shows the excellent response (high remnant polarization) than all other films such as pure PVDF and other films due to the stabilized polar phases  $(\beta, \gamma)$ , and improvement in the space transport behavior (i.e., high conductivity) between the PVDF spherulites. Further, the P-Se CFs (0 and 4 wt. %) films were tested to harness the mechanical energy in the society by fabricating the traditional sandwich structure of piezoelectric nanogenerator (PNG), i.e. Ag/P-Se CF/Ag. To protect the as-fabricated devices from the harsh environments, humidity, and temperature, a PDMS packing layer used on the top/bottom of devices.

The pure PVDF PNG device generates peak-to-peak voltage 3.5 V upon 0.5 N force generated from the linear motor. Whereas, P-Se CF (4 wt. %) based PNG device generates a higher electrical response (18 V) than the PVDF PNG. This electrical output is sufficient to drive the low power consumed electronic components such as light emitting diodes and the electronic display.

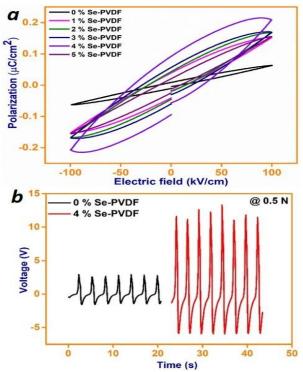


Fig. 3(a) Ferroelectric hysteresis loop at room temperature (b) Open circuit voltage of flexible piezoelectric nanogenerators upon a perpendicular force 0.5 N.

#### 4. Conclusion

In summary, efficient, flexible P-Se CFs developed by the cost-effective, simple and eco-friendly approaches. The remnant polarization of 4 wt. % of P-Se CF is seven times higher than the pure PVDF film. Morever, P-Se CF generates higher open circuit voltage than the pure PVDF film upon same mechanical force suggest the potentail candidate to drive the LEDs, and LCDs.

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