**Supporting Information for:**

Increased piezoelectric response in functional nanocomposites through MWCNT interface and fused-deposition modeling 3D printing

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**Methods**

**Method S1. 3D printing of MW-CNTs/BaTiO3/PVDF nanocomposites film**

For the cyclic load frame test, eight layers are printed with varying concentration of BT powders: 0, 6, 12, and 15 weight percentages and MWCNTs: 0, 0.1, 0.4 weight percentages. Increasing the weight content above 18%-BT would increase severe clogging within the nozzle which could potentially damage the 3D printer. In addition, increasing the weight content above 0.4%-MWCNTs would increase the electrical break down during the electric poling process. For the printing parameter, the film is printed at 230°C of nozzle temperature, 23°C of heating bed temperature, and 10mm/s of extrusion speed. The printing pattern is described in Figure S1. Final film was 0.55 mm in thickness with dimensions of 6 × 35 mm.

**Method S2. Calculation of β-phase contents for nanocomposites film**

The β-phase contents of each sample are calculated, specifically, at the absorption bands of 764 and 840 cm-1 which are characteristics of α- and β-phases respectively. Assuming that the infrared absorption follows the Lambert-Beer law, and absorbance at 764 and 840 cm-1, respectively, are given by equation (1) below.[1]:

(1)

where the subscripts α and β are defined as the crystalline phases, and are the incident and transmitted intensities of the radiation, respectively. The is defined as a sample thickness, is an average monomer concentration, is the absorption coefficient at the respective wave number, and is the degree of crystallinity of each phase.[1] For a system containing α- and β-phases, the relative fraction of the β-phase, , can be calculated using equation (2).[1]:

(2)

where (6.1 × 104 cm2/mol) and (7.7 × 104 cm2/mol) are the absorption coefficients at the respective wave number.

**Method S3. Calculation of Piezoelectric Coefficient (d31)**

To calculate the piezoelectric coefficient (d31) by using the equation (3) below:

(3)

where is the electrical displacement, is the piezoelectric coefficient, and is the applied stress. In this case, subscripts and are defined as 3 (applying force direction) and 1 (poling direction) respectively as shown in Figure 2a-i. Therefore, the equation can then be expressed as . Considering the areas of the electrode and cross-section of the sample, equation (4) can then be expressed as

(4)

where is charge, and are areas of electrode and cross-section respectively, is Poisson’s ratio which is 0.34,[2] and is an applied force. The is equal to which are capacitance and voltage, respectively. can be expressed to. Then, the piezoelectric coefficient can be expressed as

(5)

where is relative permittivity of the printed nanocomposites film, is 8.854×10-12 C/Vm, and d is its thickness. are 2.47 mm2. Then and are determined at maximum and minimum of voltages and forces as equation (6) describes.

(6)

and are 5 N and 45 N, respectively. Each attained is divided by 2 for as shown in following equation (7)

= (7)

**Figures and Tables**

**Figure S1: Printing pattern design**

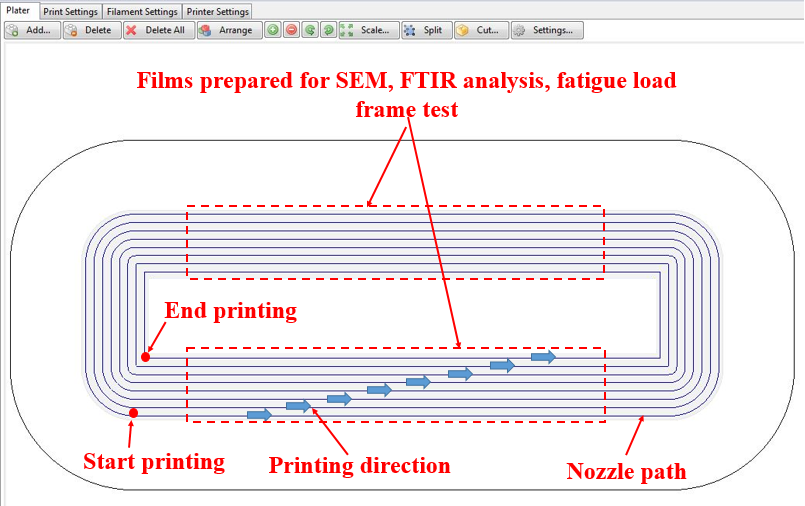
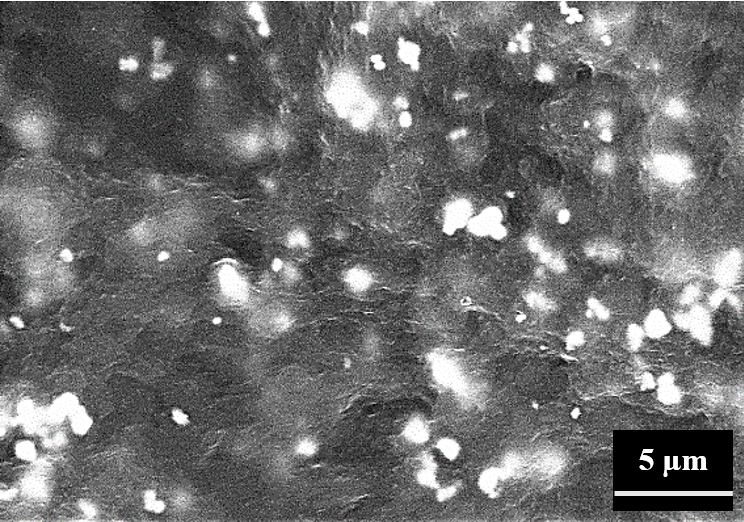
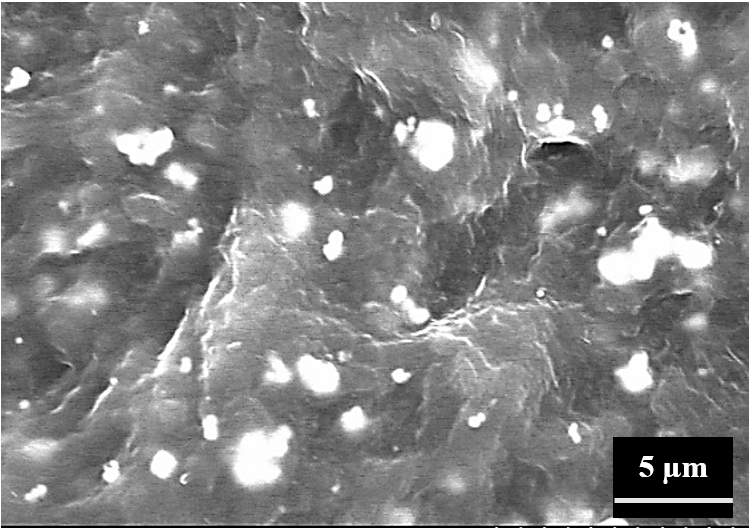


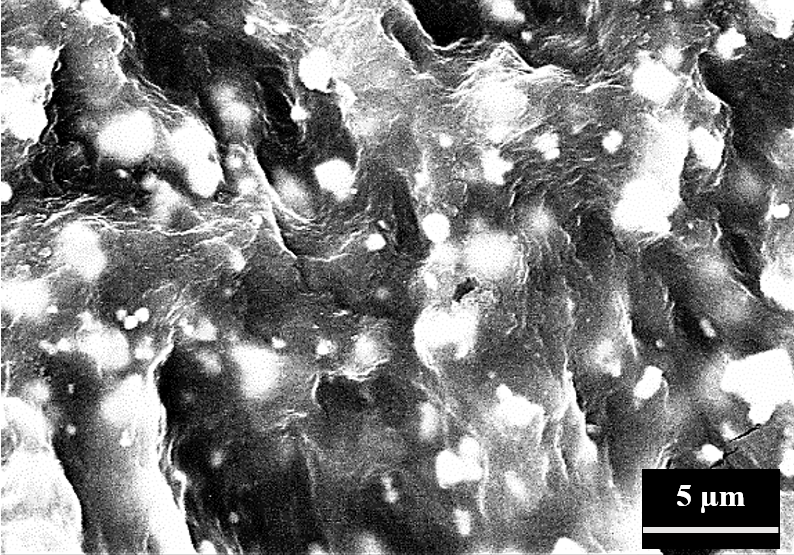
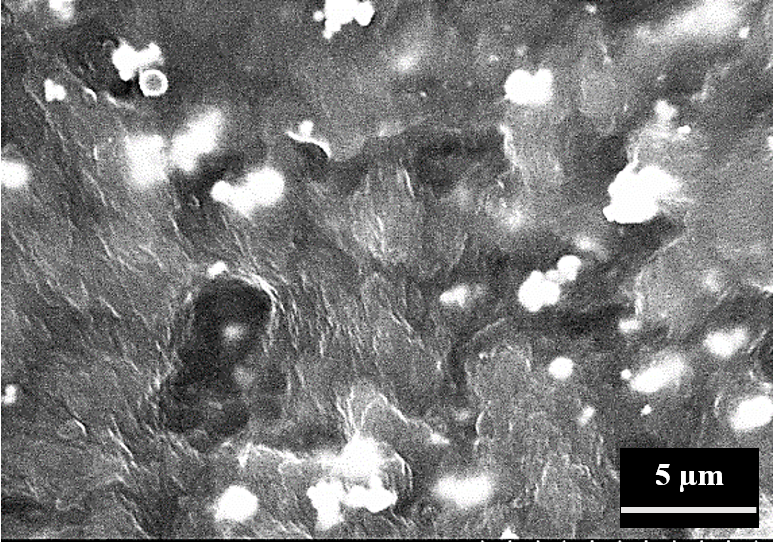
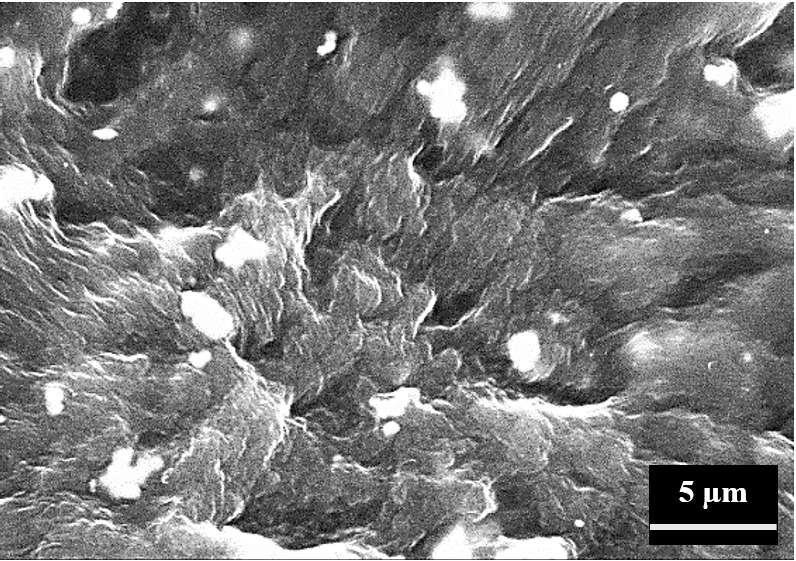
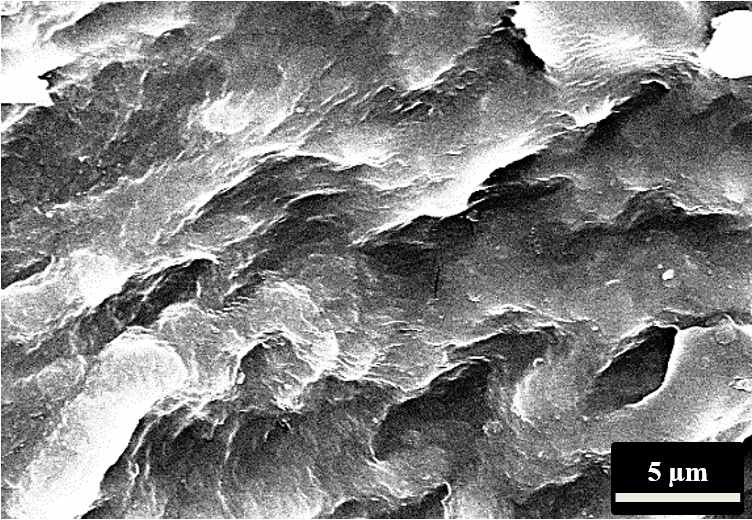
Figure S1. A captured image of concentric fill pattern design created in Slic3r software used for SEM, FTIR, and fatigue load frame test.

**Figure S2: Scanning electron microscopy images of the printed nanocomposites**



**(b)**

**(a)**



**(d)**

**(f)**

**(e)**

**(c)**

Figure S2. SEM images of (a) 12wt.%-BT/PVDF, (b) 0.1wt.%-MWCNTs/12wt.%-BT/PVDF, (c) 0.4wt.%-MWCNT/PVDF, (d) 0.4wt.%-MWCNT/6wt.%-BT/PVDF, (e) 0.4wt.%-MWCNT/12wt.%-BT/PVDF, (f) 0.4wt.%-MWCNT/18wt.%-BT/PVDF.

**Figure S3: Fourier transform infrared spectroscopy (FTIR) spectra**

1. **FTIR spectra before electric poling process**

α (763)

β/γ (840)

α (854)

γ (811)

α (795)

α (614)

α (976)

β (1275)

γ (1234)

(b)

(a)

(f)

(e)

(d)

(c)

1. **FTIR spectra after electric poling process**

Figure S3. FTIR spectra of the printed nanocomposites (1) before and (2) after electric poling: (a) 12wt.%-BT/PVDF, (b) 0.1wt.%-MWCNT/12wt.%-BT/PVDF, (c) 0.4wt.%-MWCNT /PVDF, (d) 0.4wt.%-MWCNT/6wt.%-BT/PVDF, (e) 0.4wt.%-MWCNT/12wt.%-BT/PVDF, (f) 0.4wt.%-MWCNT/18wt.%-BT/PVDF.

**Table S1: Dielectric Properties of the Printed MWCNT/BT/PVDF Nanocomposites Films**

|  |  |
| --- | --- |
| **Composition** | **Relative Permittivity ( at 1 kHz** |
| 12wt.%-BT/PVDF | 16.9 |
| 0.1wt.%-MWCNT/12wt.%-BT/PVDF | 31.2 |
| 0.4wt.%-MWCNT/PVDF | 30.5 |
| 0.4wt.%-MWCNT/6wt.%-BT/PVDF | 31.7 |
| 0.4wt.%-MWCNT/12wt.%-BT/PVDF | 25.0 |
| 0.4wt.%-MWCNT/18wt.%-BT/PVDF | 36.5 |

**References**

[1] V. Sencadas, M. V. Moreira, S. Lanceros-Méndez, A. S. Pouzada, and R. Gregório Filho, "α-to β Transformation on PVDF films obtained by uniaxial stretch," in *Materials science forum*, 2006, pp. 872-876.

[2] A. Vinogradov and F. Holloway, "Electro-mechanical properties of the piezoelectric polymer PVDF," *Ferroelectrics,* vol. 226, pp. 169-181, 1999.