Hot Melt Extrusion and 3D Printing of Thermoplastic Lead-Free Piezocomposite for Environmentally Safer Sensing Applications

Presenter

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Introduction

Research focus:

- Lead-free piezo-polymer/ceramic composite (piezocomposite) filaments for 3D printing.
- Environmentally safer solvent-free manufacturing method based on melt compounding & extrusion ➡ exclusion of solvents that pose risks to human health and environment.
- 3D printing (fused filament fabrication) of flexible and durable piezoelectric sensors and energy harvesters.

Research alignment with key European priorities in R&D of functional/advanced materials:

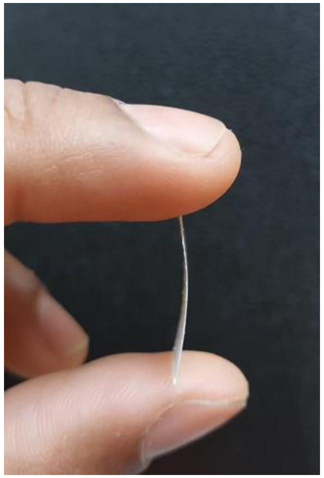
- EC "The Materials 2030 Roadmap" (2023):
  - ✓ Highlights the potential of 3D printing to revolutionize industries.
  - ✓ Priority areas "Advanced materials for additive manufacturing in health applications", "Development of efficient sensors".
- EU "Chemicals Strategy for Sustainability Towards a Toxic-Free Environment" (2020) ➡ key commitment of the Green Deal ➡ aimed at achieving a toxic-free environment.

3D printable piezoelectric composites

ktu 1922

- **Piezocomposite:** Combination of thermoplastic piezopolymer matrix (PVDF-HFP) & lead-free piezoceramic filler particles (barium titanate-BTO).
- **Advantages over conventional materials (PZT):** improved performance & functionality (e.g. high flexibility ➜ durability).
- **Benefits of 3D printing:** larger design freedom ➜ possibility to manufacture piezo-devices having advanced structural configurations (e.g. stretchable, conformable).
- **Applications:** mechanical sensors or energy harvesters (wearable or implantable smart devices, environment monitoring devices, etc.).

Custom-made piezocomposite filament



3D printed PVDF-HFP/BTO sample

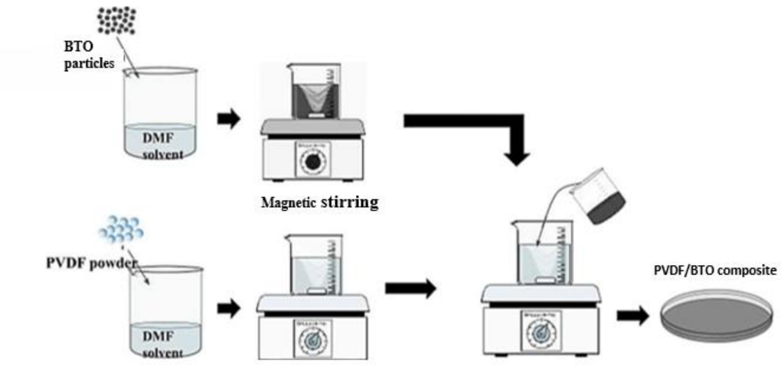
Research motivation

Piezoelectric composites are mainly manufactured using:

- Solvent-based techniques, e.g. solution processing/casting ➡ widely used in research.
- Solvent-free techniques, e.g. dry-mix preparation + hot melt extrusion ➡ popular in industrial applications.

Limitations of solution processing:

- Negative environmental impact ➡ solvent use restricted by REACH legislation ➡ more difficulties for large-scale industrial manufacturing.
- Some organic solvents (e.g. DMF) are highly toxic.
- Safer solvents (e.g. bio-based DMSO) still have potential health hazards (skin irritation, etc.) and may be harmful to environment.
- Higher clinical risks for piezoelectric medical devices (wearable, implantable).



**Shivanand M Chougule,* *Polymers and Polymer Composites, Vol. 30, 2022.*

Research motivation

Advantages of solvent-free melt-based manufacturing (vs. solution processing):

- More environmentally friendly ➡ potentially less chemical waste, e.g. no release of volatile organic compounds.
- Possibly more cost-effective ➡ easier to scale up for industrial production.
- Possibly more efficient large-scale production, compatibility with widely used industrial processes (extrusion).
- More suitable for medical devices (no need to worry about residues of harmful solvents).

Melt compounding and filament extrusion line @ KTU Institute of Mechatronics

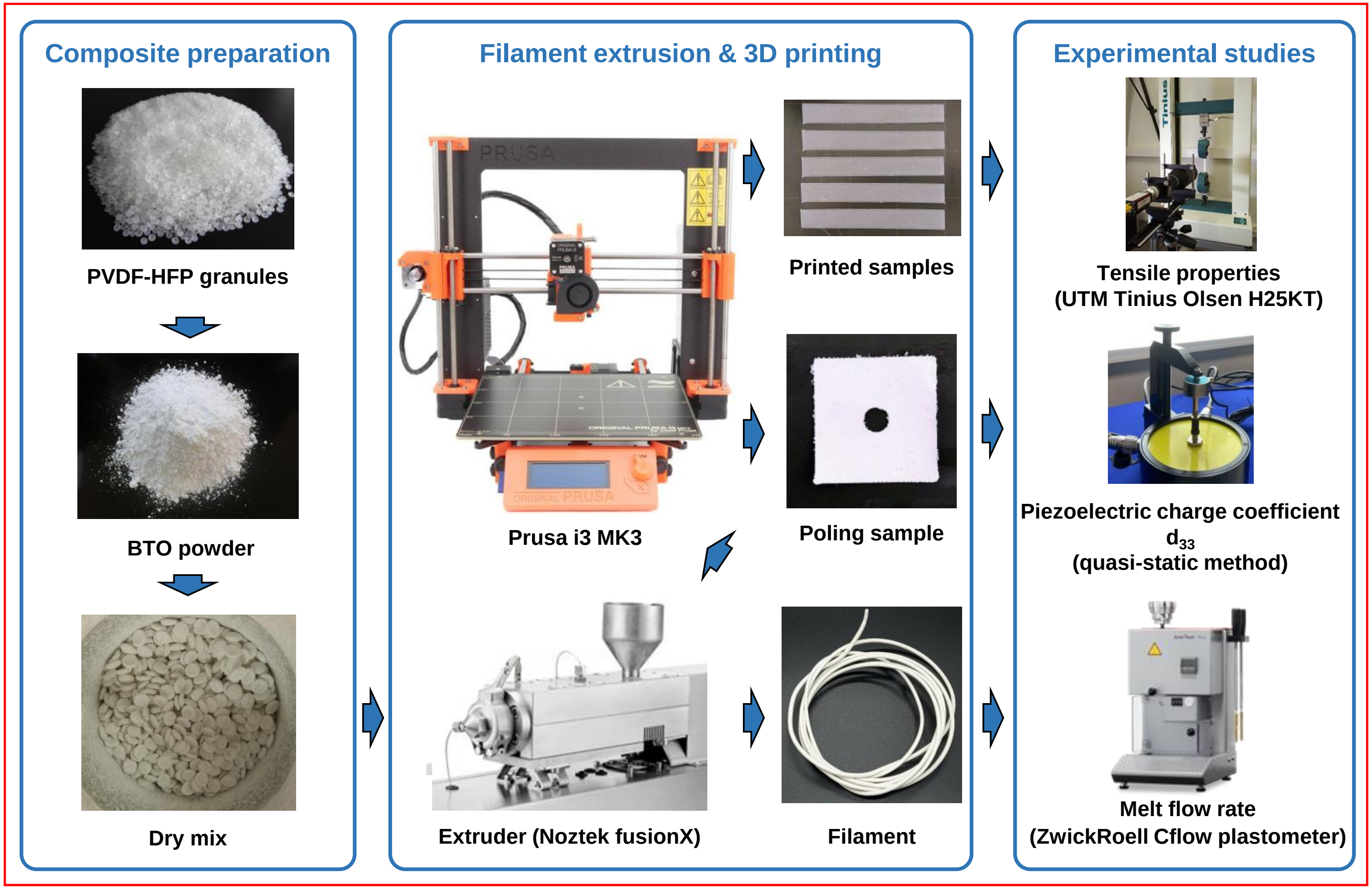
Filament winder

Tolerance puller


Roller conveyor

Single-screw melt compounding extruder

Research methodology

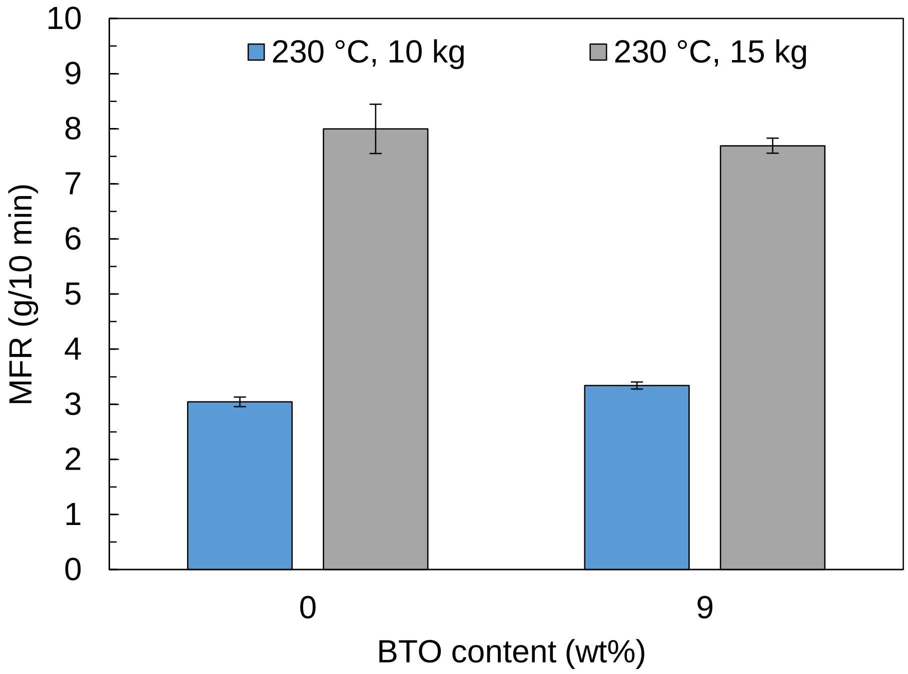


Process parameters for PVDF-HFP/BTO filament extrusion & 3D printing

Extrusion settings	Value
Extrusion zone temperature	240 °C
Mixing zone temperature	220 °C
Nozzle diameter	1.3 mm
Motor speed	36 RPM
Cooling Type	Water cooling

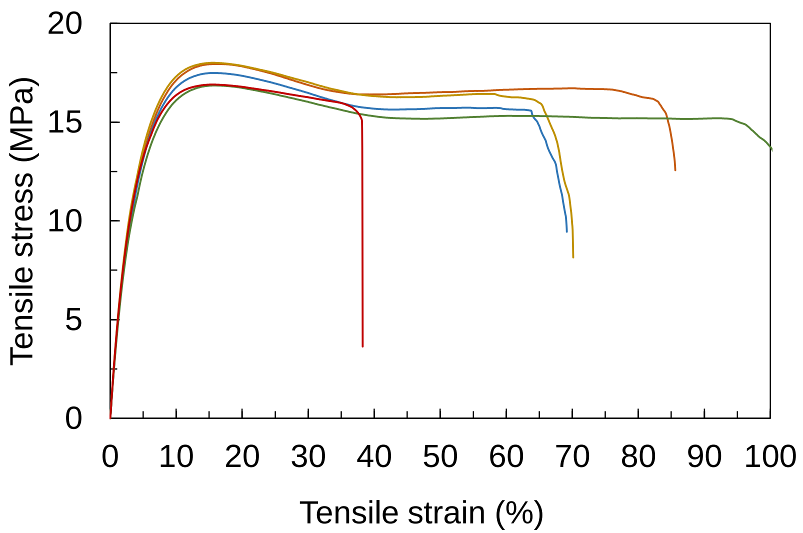
3D printing settings	Value, description
Nozzle diameter, material type	0.8 mm, Vanadium nozzle
Nozzle temperature	260 °C
Bed temperature	70 °C
Printing speed	35 mm/sec
Raster angle	+45°/-45°
Layer thickness	0.1 mm
Infill ratio	100%
Printing time	8 min.

Experimental results for mass flow rate

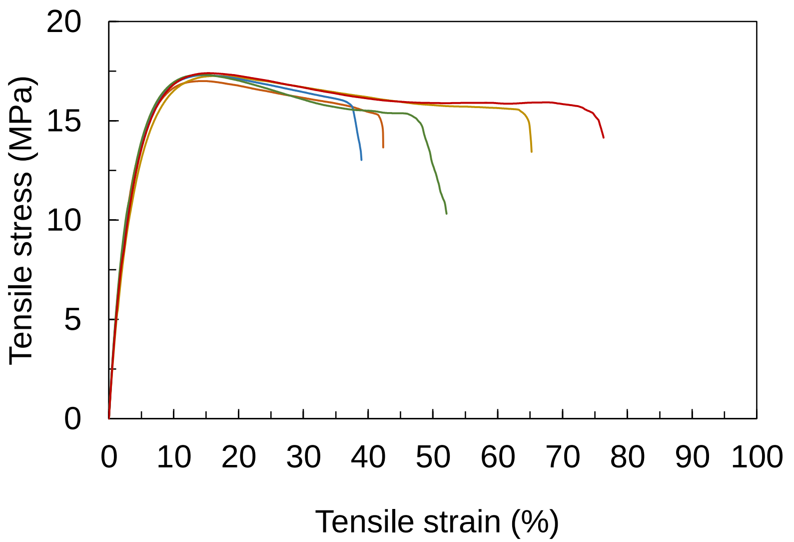


- Slight reduction in MFR was observed with increasing BTO. It suggests that increase in BTO content may not affect the composite printability.

Tensile testing



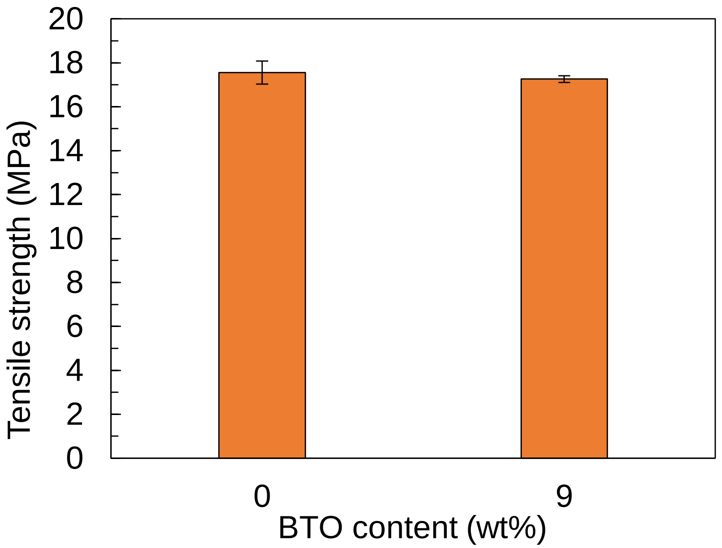
0 wt% BTO

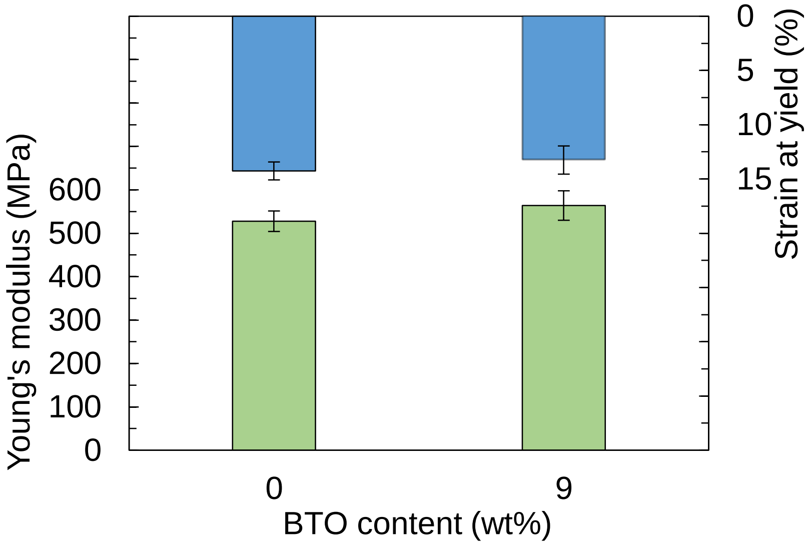


9 wt% BTO

- Stress-strain curves indicate ductile behaviour for both pristine PVDF-HFP and composite specimens.
- In all the test cases the nominal strain at break is fluctuating.

Tensile testing

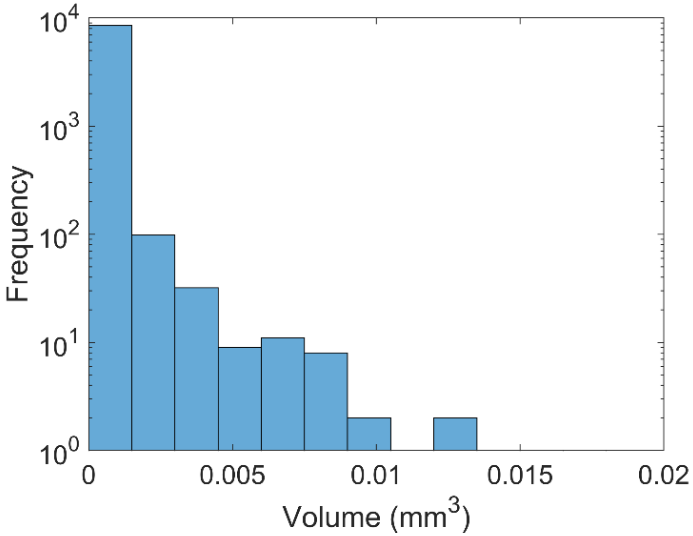


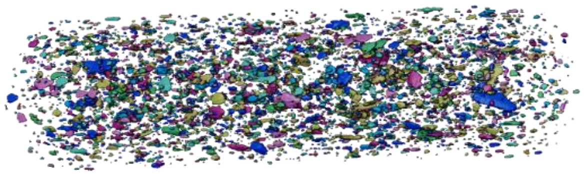


- BTO particles have not shown any significant impact on the mechanical properties of the composites.

- Tensile strength slightly decreases, and tensile modulus slightly increases with higher BTO, but the variation of average values are less than 6% in comparison to pristine PVDF-HFP specimens.

Results of X-ray microtomography

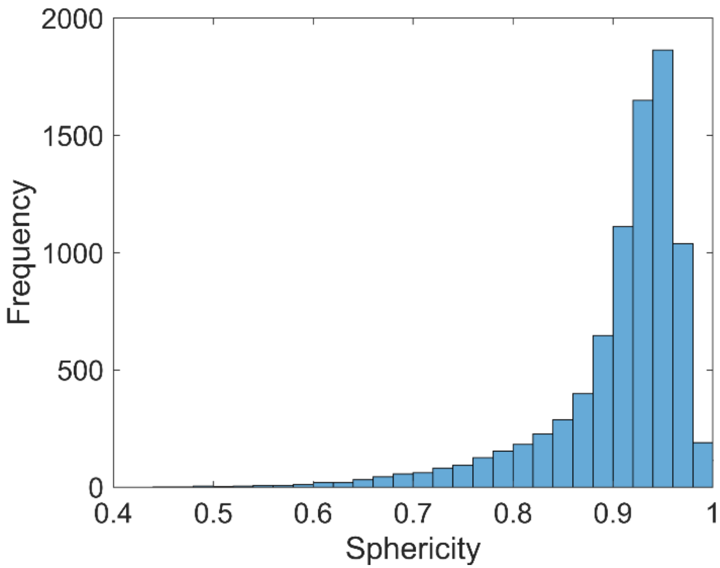


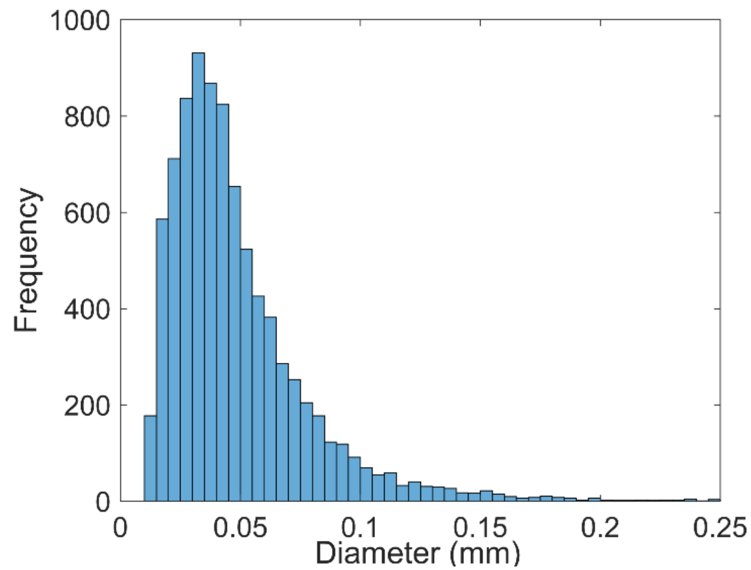


9% BTO

- Volume-frequency distributions indicate that agglomerates of the smallest volume predominate in the composite.
- The 3D visualizations of the filament indicate that the filler content was homogeneously dispersed.

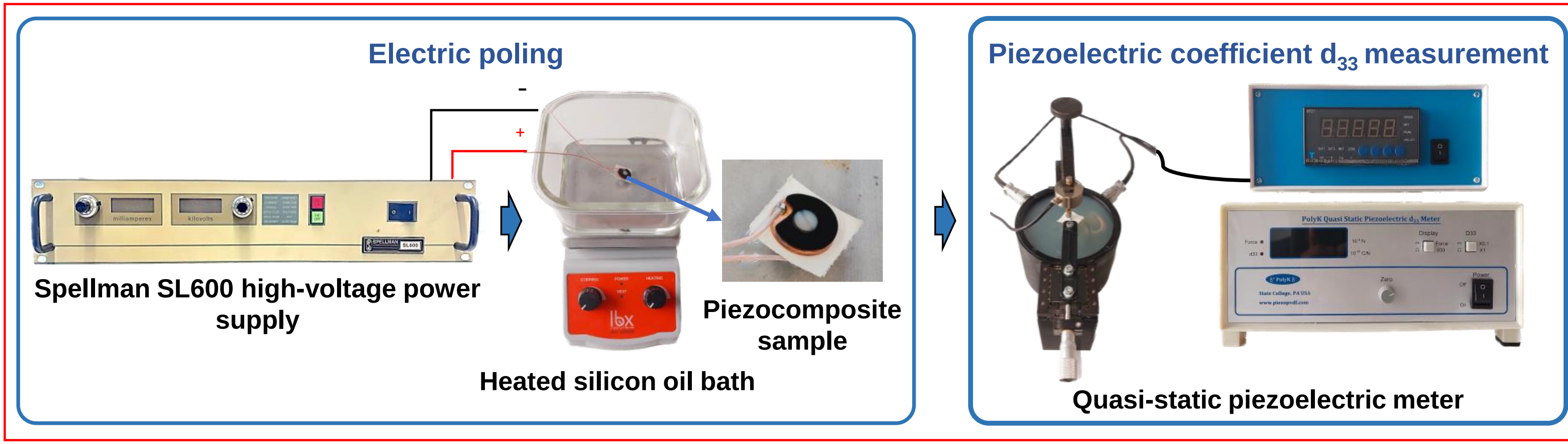
Results of X-ray microtomography





- The size of agglomerates of filler content in piezocomposite are not significantly large, which is an advantageous result regarding composite printability.

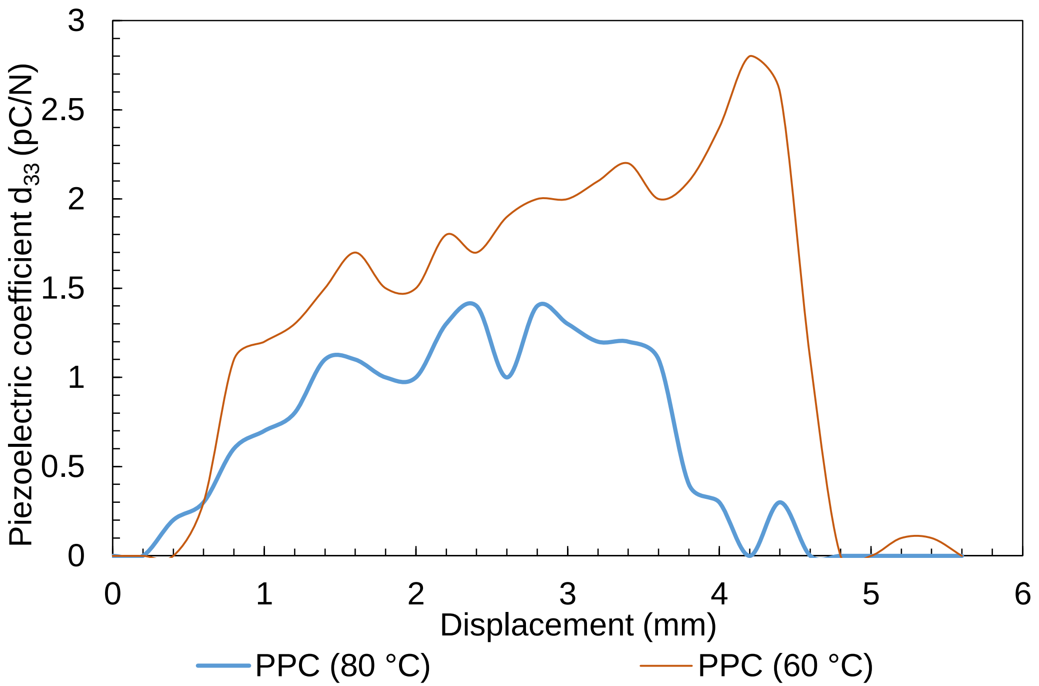
Electric poling and measurements of piezoelectric coefficient d_{33}



Parameters of electric poling (contact poling method):

- Voltage: 7 kV
- Duration: 4 hrs.
- Poling temperatures: 60 °C and 80 °C

Fluctuations of piezoelectric coefficient d_{33}



- The highest piezoelectric coefficient values of piezocomposite (PPC).
  - ✓ At 60 °C poling temperature: 2.8 pC/N.
  - ✓ At 80 °C poling temperature: 1.4 pC/N.
- Poling of piezocomposite at 60 °C is more effective vs. poling at 80 °C.

Conclusions

1. Addition of BTO microparticles to PVDF-HFP matrix had minimal negative effect on tensile properties of 3D printed piezocomposite.
2. BTO particles were uniformly dispersed within the piezocomposite matrix.
3. Incorporation of BTO particles increased the piezoelectric coefficient of electrically poled piezocomposite.

Future research objectives:

- Development of multi-stage extrusion methodology (several compounding-extrusion cycles) to improve uniformity of filler dispersion, ensure more consistent printing process and achieve higher quality printed structures for more effective poling.
- Increasing filler content & changing piezoelectric filler type to enhance the piezoelectric properties of piezocomposite.
- Development of electric poling methodology (poling integrated into 3D printing).

Thank you for your attention !