# Electrostrictive polymer - inorganic nanoparticle nanocomposites for actuator applications

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## Introduction

Ferroelectric materials such as poly(vinylidene fluoride) – P(VDF) – and its copolymer with trifluoroethylene – P(VDF-TrFE) – possess relatively large piezoelectric constants but they are limited for applications such as high precision actuators by their low strain level (< 0.2 %). By the terpolymer poly(vinylidene fluoride-trifluoroethylene-1,1-chlorofluoroethylene) P(VDF-TrFE-CFE), in short PTC, a conversion to a relaxor ferroelectric was obtained [1, 2] and along with this high electrostrictive strain and relatively high Young modulus, both essential parameters for actuator applications. It has been shown that the strain in the PVDF-TrFE-CFE, $S_{PTC}$, is best described as a second order dependence on the applied electric field [2, 3]:

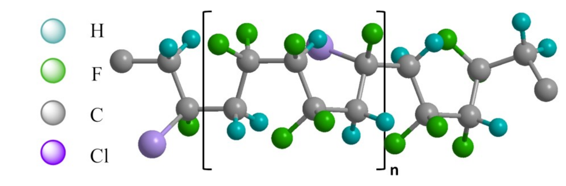
$$S_{PTC} = Q \cdot \varepsilon_0^2 \cdot (\varepsilon_r - 1)^2 \cdot E^2 = M \cdot E^2 \qquad (1)$$

with $S$ = strain; $Q$ = charge-related electrostrictive coefficient; $\varepsilon_0$ = electric permittivity in vacuum; $\varepsilon_r$ = dielectric constant of the material; $M$ = electrostrictive coefficient; $E$ = applied electric field.

In this poster, for our study on materials suitable for large deformable actuators, we consider increasing even further the strain of the electrostrictive PTC. As the strain is dependent on the $\varepsilon_r$ of a material, we attempt to increase the terpolymer's strain by mixing it with nanoparticles (NP) of high dielectric constant such as $BaTiO_3$ or $TiO_2$.

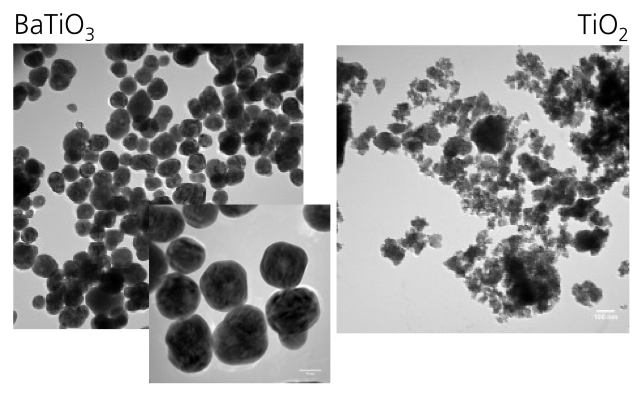
## Materials

- Polymer:
  P(VDF-TrFE-CFE), in short PTC
  - supplier Piezotech S.A.S.
  - 61.7/29.8/8.5 mol.-%
  - strain of 7 % at 170 V/µm [4]




- Nanoparticles:
  $BaTiO_3$
  - supplier: IoLiTec
  - $d \sim 100$ nm; $\varepsilon_r = 95$

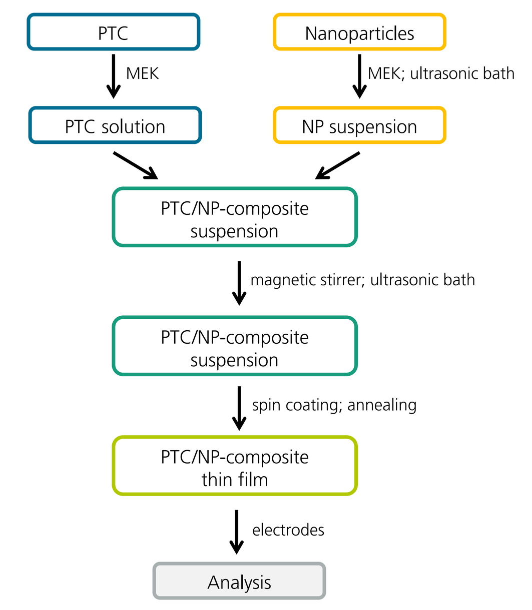
  $TiO_2$
  - supplier: IoLiTec
  - $d \sim 20$ nm; $\varepsilon_r = 110$



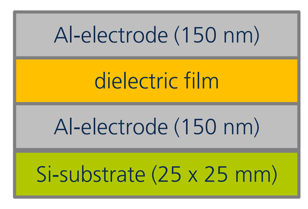

- Solvent:
  Methylethylketone (MEK)

## Thin film characterization

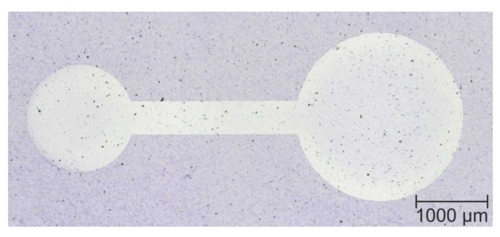
### Preparation of composite films




### Composite stack




### Top view optical microscope image of composite stack



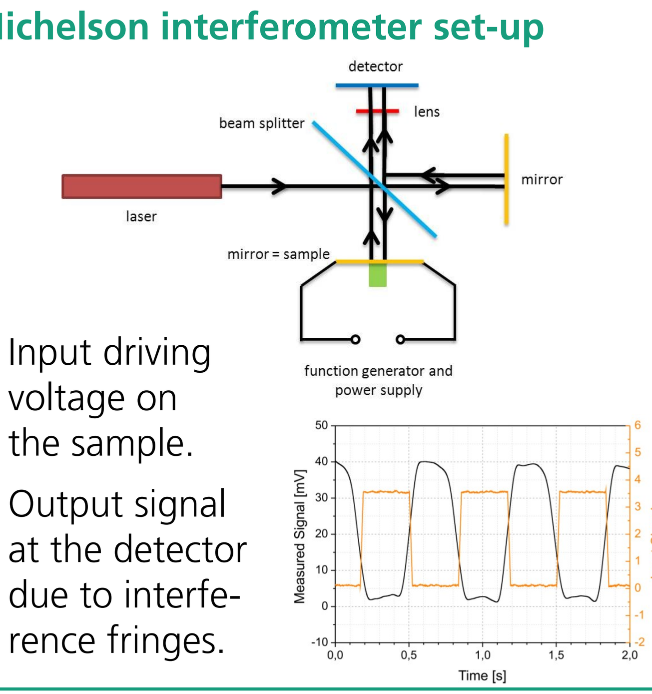

### Characterization methods

Surface roughness:
- Determination of surface roughness in dependence of annealing temperature using atomic force microscopy (AFM).

Dielectric constant:
- Impedance spectrometer Wayne Kerr model 1J6520BD2
- Measurement of capacity and dielectric loss of stacks designed as plate capacitor ($A$ = 7 mm² $d$ = 2.8 µm).
- Measurement at room temperature and 1 V (ac)

Electric field induced strain measurements:
- Michelson interferometer set-up

### Michelson interferometer set-up

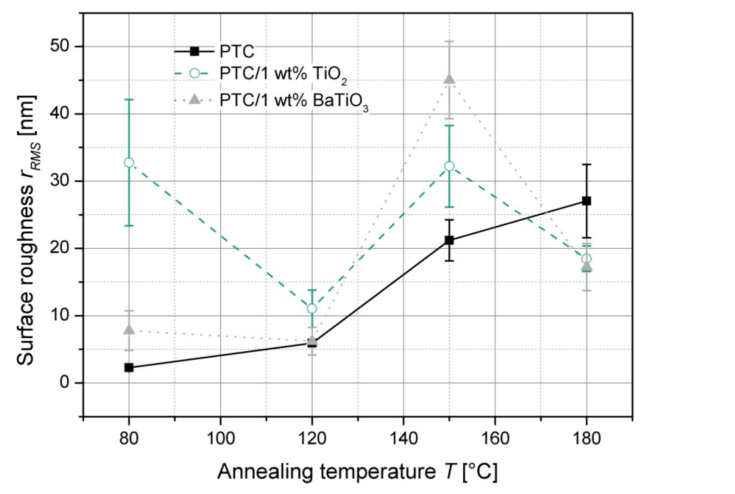



- Input driving voltage on the sample.
- Output signal at the detector due to interference fringes.

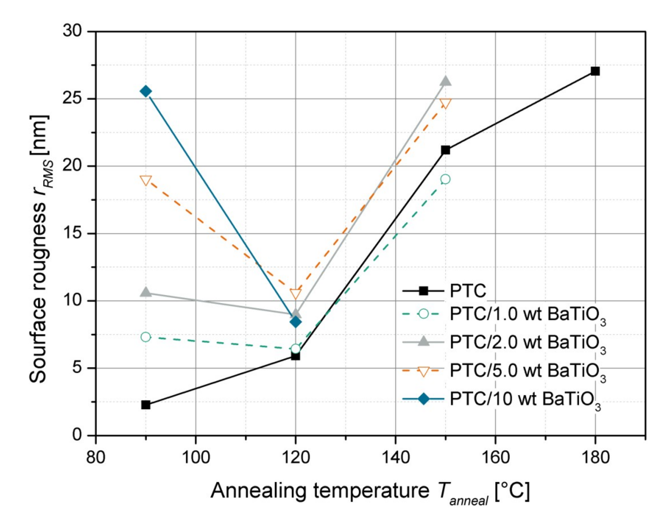
## Results

### Surface roughness inspection using AFM

- Annealing of samples in order to remove solvent and improve composites' crystallinity.
- Roughness of films was found to be dependent on annealing temperature.
- Surface roughness $r_{RMS}$ is estimated from the AFM image's contrast.




Roughness analysis of neat PTC and composites containing 1 wt% $BaTiO_3$ or $TiO_2$.

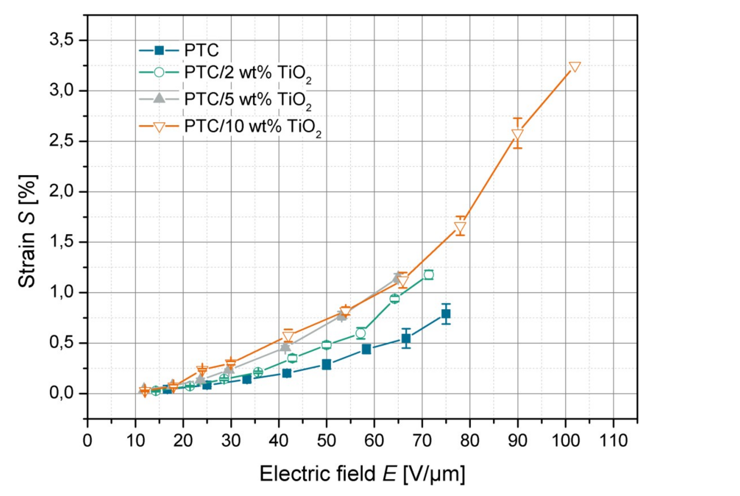



Roughness analysis of neat PTC and composites containing different weight fractions $BaTiO_3$.

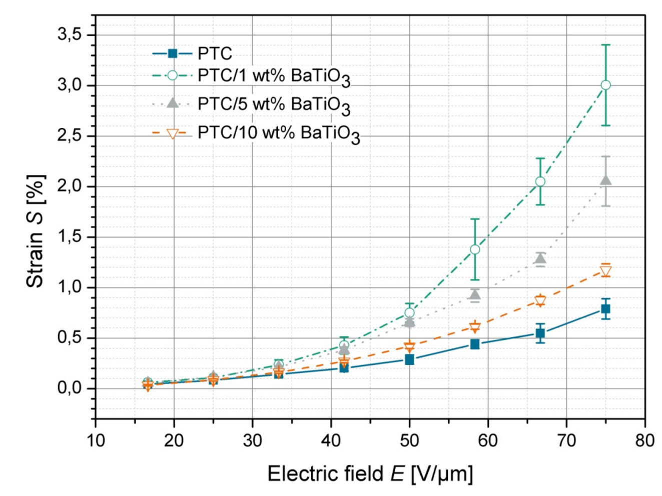
- An optimal annealing temperature for all films was found at 120 °C.

### Strain measurements using Michelson interferometer set up

- The main composites' parameter relevant for actuator application is the electric field induced strain.




Strain vs. electric field for neat PTC and PTC/*$TiO_2$* composite stacks.

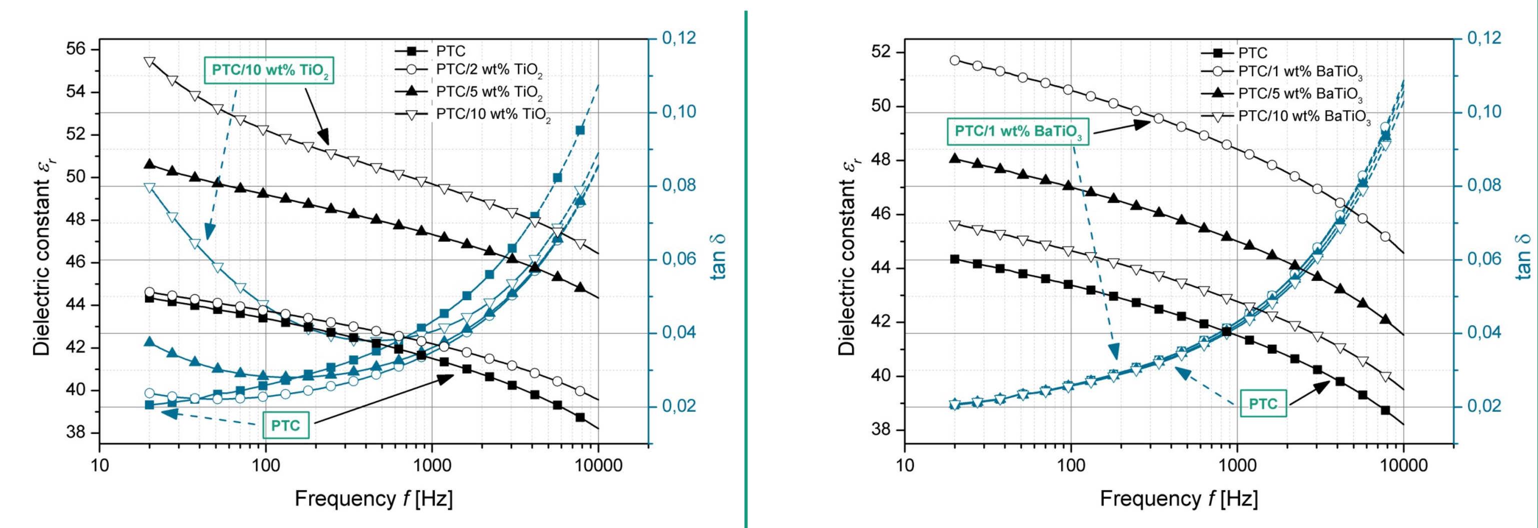



Strain vs. electric field for neat PTC and PTC/*$BaTiO_3$* composite stacks.

- The strain depends quadratically on the applied electric field for all stacks investigated, confirming electrostriction.
- Strain increases with addition of nanoparticles.
- For the PTC/$TiO_2$ composites: Strain increases with increasing nanoparticle content.
- For the PTC/$BaTiO_3$ composites: Stack made of PTC/1 wt% $BaTiO_3$ composite exhibits the largest strain. Further increase of nanoparticle content leads to a decrease in strain, but the strain is still larger than that of neat PTC.
- Largest strain could be observed for the stack made of PTC/1 wt% $BaTiO_3$ composite.

### Dielectric constant measurements

- Dielectric constant directly dictates the materials electrostriction coefficient and hence the materials strain.




Dielectric constant and loss vs. frequency for neat PTC and PTC/*$TiO_2$* composite stacks.

Dielectric constant and loss vs. frequency for neat PTC and PTC/*$BaTiO_3$* composite stacks.

- Dielectric constant decreases with increasing frequency.
- Highest dielectric constant for PTC/10 wt% $TiO_2$ and PTC/1 wt% $BaTiO_3$ composite.
- Dielectric loss, compared to PTC, is unchanged for PTC/$BaTiO_3$. For PTC/$TiO_2$ dielectric loss increases at low frequencies with increasing nanoparticle amount (pointing to changes in interaction mechanism).

## Conclusions

- We studied the influence of high-$\varepsilon_r$ $BaTiO_3$ and $TiO_2$ nanoparticles on the induced strain in terpolymer - nanoparticle (PTC-NP) composite thin films for actuators applications.

| | Material | $M$ [$10^{-18}$ m²·V⁻²] | $\varepsilon_r$ @ 1 kHz |
|---|---|---|---|
| | PTC | 1.31 | 41.5 |
| $BaTiO_3$ | PTC/1 wt% $BaTiO_3$ | 4.42 | 48.4 |
| | PTC/5 wt% $BaTiO_3$ | 3.37 | 45.0 |
| | PTC/10 wt% $BaTiO_3$ | 1.89 | 42.7 |
| $TiO_2$ | PTC/2 wt% $TiO_2$ | 2.43 | 42.2 |
| | PTC/5 wt% $TiO_2$ | 2.72 | 47.3 |
| | PTC/10 wt% $TiO_2$ | 3.03 | 49.7 |

- Capacity measurements showed that the dielectric constant of the PTC/1 wt% $BaTiO_3$ composite increased by 15 % as compared to that of the neat PTC.
- Addition of high-$\varepsilon_r$ NP, for both $BaTiO_3$-NP and $TiO_2$-NP, to neat terpolymer increases the induced strain substantially.
- Electrostrictive constant of a PTC/1 wt% $BaTiO_3$ was found to be up to 3.5 times larger than that of the neat PTC but decreased with increasing the NP content in the composite. Contrary, for $TiO_2$ the electrostrictive constant improved with increasing NP content.

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**B. Pawlik's work was funded by the European Union (ERDF) and the Free State of Saxony via the ESF project 100087859 (ENano). Additional funding from the FhG Internal Programs under Grant Nr. Attract 692123 is greatly acknowledged. Furthermore, we gratefully acknowledge support from the German Excellence Initiative via the Cluster of Excellence EXC 1056 "Center for Advancing Electronics Dresden".**