

19<sup>th</sup> International  
Symposium on Electrets



**ISE19**

18 – 22 September 2023  
Johannes Kepler University  
Linz, Austria

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# Welcome Note

Dear fellow electret enthusiasts!

We warmly welcome you to the 19<sup>th</sup> International Symposium on Electrets (ISE19), which is being held at the 'Bildungshaus Sankt Magdalena', hosted by the Soft Matter Physics Group of the Johannes Kepler University Linz. Located in the center of Europe, the city of Linz and its universities are a vibrant melting pot of cultures and a hotspot for innovations at the intersection of science, art and industry since its heydays in astronomy. In modern times, Linz and JKU became a fixed star in electret research through the pioneering work of Siegfried Bauer and his team. We dedicate this conference to his memory.

The IEEE International Symposium on Electrets (ISE) stands as the leading event for the field, bringing together scientists, engineers, and young researchers from around the world. After a 4-year pandemic-induced pause, we are glad to see the electret community meeting in person again, ready to exchange ideas and share their latest findings.

ISE19 is set to take place at the 'Bildungshaus Sankt Magdalena' Educational Center in Linz, picturesquely situated above the city's rooftops and surrounded by greenery. Much needed after years of online distancing, this venue uniquely encourages networking and interaction among attendees due to the close proximity of all conference-related activities.

ISE19 stages 17 plenary lectures, 36 oral presentations, one poster session and two focus sessions hosted by newly established IEEE DEIS Technical Committees. In a special session, we will honor Siegfried Bauer, an esteemed member of the electret community, whose life and work are closely connected with Linz. Siegfried's creativity and unwavering support of young scholars across multiple fields keep inspiring many of us. In memoriam, but in Siegfried's spirit with an eye toward the future, friends and colleagues will present a vibrant cross-section of their latest works.

Following the symposium, a workshop titled "Electroactive polymers and electrets for soft transducers" is scheduled for September 22<sup>nd</sup>. The program comprises five tutorial lectures delivered by renowned experts in the field.

Since ISE12 in 2005, the Bernhard Gross Memorial Lecture has been presented by researchers who have established an international reputation for sustained and high-quality research work in the ISE field. We would like to congratulate Professor Heinz von Seggern who had been elected Bernhard Gross Memorial Lecturer by the International Scientific Advisory Committee already at ISE18 in Shanghai, China. He will deliver his award lecture at the opening session of ISE19 on Monday, September 18<sup>th</sup> and will receive the award in appreciation of his excellent contributions to the field of electrets

Furthermore, the Dilip Das-Gupta awards for best oral and poster presentations of a young scientist will be awarded during the closing ceremony on September 21<sup>st</sup>.

Now Austria's third-largest city, Linz has a long and eventful history dating back to Celtic times, with its name origin "Lentos/Lentia" hinting at the curvature of the river Danube that runs through the city centre. The JKU campus and the conference venue are on the "Urfahr" side, snuggled against soft hills. On sunny days, the view from the 'Bildungshaus' will take us all the way to the Alps, where in the evenings the lights of the city and the modern industrial park will set the backdrop for lively discussions. An excursion right into the heart of the "City of Steel" is organized as part of the conference. We hope that you will also find some time to explore Linz and its history or enjoy the lush autumn nature of the "Mühlviertel" region, maybe with a walk along the former tracks of Europe's first public railway (then horse-powered).

The conference is sponsored by IEEE Dielectrics and Electrical Insulation Society and the Johannes Kepler University. We would like to take the opportunity to thank the members of the International Scientific Advisory Committee, our sponsors, our colleagues from the Local Organizing and Program Committees, in particular Dr. Simona Bauer for her tremendous efforts in together all the details of this conference, all supporters and all participants for their contributions to the organization and scientific excellence of this symposium.

Martin Kaltenbrunner

General Chair, on behalf of the Local Organizing Committee

Linz, September 2023

# History of the International Symposium on Electrets

- Electrical & Related Electrostatic Charge Storage Phenomena, 15 - 20 October 1967, Chicago, USA
- Electrets, Charge Storage & Transport in Dielectrics, 08 - 13 October 1972, Miami, USA
- International Symposium on Electrets and Dielectrics, 01 - 06 September 1975, São Carlos, Brazil
- Charge Storage, Charge Transport and Electrostatics with Applications, 08 - 12 October 1978, Tokyo, Japan
- 5th International Symposium on Electrets (ISE 5), 04 - 06 September 1985, Heidelberg, Germany
- 6th International Symposium on Electrets (ISE 6), 01 - 03 September 1988, Oxford, United Kingdom
- 7th International Symposium on Electrets (ISE 7), 25 - 27 September 1991, Berlin, Germany
- 8th International Symposium on Electrets (ISE 8), 07 - 09 September 1994, Paris, France
- 9th International Symposium on Electrets (ISE 9), 25 - 30 September 1996, Shanghai, China
- 10th International Symposium on Electrets (ISE 10), 22 - 24 September 1999, Delphi, Greece
- 11th International Symposium on Electrets (ISE 11), 01 - 03 October 2002, Melbourne, Australia
- 12th International Symposium on Electrets (ISE 12), 11 - 14 September 2005, Salvador, Brazil
- 13th International Symposium on Electrets (ISE 13), 15 - 17 September 2008, Tokyo, Japan
- 14th International Symposium on Electrets (ISE 14), 27 - 31 August 2011, Montpellier, France
- 15th International Symposium on Electrets (ISE 15), 10 - 13 August 2014, Baltimore, Maryland, USA
- 16th International Symposium on Electrets (ISE 16), 4 - 8 September 2017, Leuven, Belgium
- 17th International Symposium on Electrets (ISE 17), 2 - 5 September 2019, Limerick, Ireland
- 18th International Symposium on Electrets (ISE 18), 24 - 28 September 2021, Shanghai, China

## Previous Bernhard Gross Memorial Awardees

2005	Gerhard Sessler	(ISE 12, Salvador)
2008	Jacques Lewiner	(ISE 13, Tokyo)
2011	Jan van Turnhout	(ISE 14, Montpellier)
2014	James West	(ISE 15, Baltimore)
2017	Reimund Gerhard	(ISE 16, Leuven)
2019	Takeo Furukawa	(ISE 17, Limerick)

## Previous Dilip Das-Gupta Awardees for the Best Oral and Poster Presentations by a Young Scientist

2005:

- Best oral contribution: Jean-Michel Reboul (École d'Ingénieurs de Cherbourg de l'Université de Caen Basse Normandie, France)
- Best poster contribution: Françoise Toledo Reis (Instituto de Física de São Carlos, Universidade de São Paulo, Brazil).

2008:

- Best combination of oral and poster contributions: Takashi Nakajima (Faculty of Science, Tokyo University of Science, Japan)
- Best oral contributions: Chien Nguyen (School of Materials Science and Engineering, Nanyang Technological University, Singapore).

2011:

- Best combination of oral and poster contributions: Eric Dantras (University of Toulouse, France) and Gregorio Faria (Instituto de Física de São Carlos, Universidade de São Paulo, Brazil).

2014:

- Best oral contribution: Tristan Putzeys (KU Leuven, Belgium)
- Best poster contribution: Qin Chen (GE Global Research Center at New York, USA).

2017:

- Best oral contribution: Sarah Guerin (University of Limerick, Ireland)
- Best poster contribution: Tim Cornelissen (Linköping University, Sweden).

2019:

- Best oral contribution: Indre Urbanaviciute (Linköping University, Sweden)
- Best poster contribution: Tahsin Morshed (Bangladesh University of Engineering and Technology, Dhaka, Bangladesh).

# Committees, Sponsors

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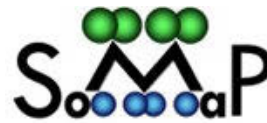


# Sponsors and Exhibitors

ISE19 is sponsored by the IEEE Dielectrics and Electrical Insulation Society along with the Johannes Kepler University Linz.

The conference is also supported by PolyK Technologies and voestalpine Stahl GmbH.

We want to convey our thanks to our sponsors and supporters!



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## List of Topics

The ISE19 topics include but are not limited to:

- Charge related phenomena in dielectrics (charge injection, transport & trapping)
- Thermally stimulated current & dielectric relaxation
- Nanoscale measurements of electrostatic phenomena
- Ferroelectric, piezoelectric & pyroelectric phenomena
- Ferroelectrets & photoelectrets
- Electrostatic & dielectric phenomena in life science: bioelectrets
- Non-linear electrical & optical effects
- Applications of thin-film ferroelectric materials
- Electrets in organic electronics
- Soft actuators & sensors
- Functional materials and dielectrics

# Sunday, September 17<sup>th</sup> 2023

Registration

16:00 - 20:00

Welcome party

18:00 - 22:00

# Monday, September 18<sup>th</sup>, 2023

09:00	Opening Session Chair: Martin Kaltenbrunner	Opening Ceremony
09:20		Heinz von Seggern <i>Ferroelectrets: The Electret Story Continues</i> Bernhard Gross Memorial Lecture
10:10	Session 1 Chairs: Jan van Turnhout, Sarah Guerin	Christiane Thielemann <i>Sustainable PLA electrets: a review</i>
10:40		<b>COFFEE BREAK</b>
11:00		Yang Cao <i>All-organic fabric based wearable electronics</i>
11:30		Xunlin Qiu <i>Improvement of the charging efficiency of ferroelectrets based on Paschen's law</i>
11:50		Thulasinath Raman Venkatesan <i>Poly(butyl vinyl ether-co-acrylonitrile) copolymer for thermal capacitive sensing and thermal energy harvesting</i>
12:10		Dennis Flachs <i>Sustainable PLA electrets: a comparison of commercial and solution-cast foils</i>
12:30	<b>LUNCH BREAK</b>	
13:45	Session 2 Chairs: Michael Wübbenhorst, Peng Fang	Hiroyuki Mitsuya <i>Highly reliable electret for heat resistive vibrational energy harvester</i>
14:15		Lin Zheng <i>Influence of interface dipole on charge build-up under high voltage</i>
14:35		Yumi Tanaka <i>Polarization and charging characteristics of perovskite-type lanthanum aluminate ceramics</i>
14:55		Jinhai You <i>Charge transport and glassy dynamics in non-stoichiometric protic ionic liquids 2-aminoethyl hydrogen</i>
15:15		Jessica Mangialetto <i>Evolving glass transition of curing network based on Diels-Alder reversible bonds studied by dielectric relaxation</i>
15:35	<b>COFFEE BREAK</b>	
15:55	Session 3 Chairs: Yuji Suzuki, Reinhard Schwödlauer	Stéphane Hóle <i>High spatial resolution for space charge measurements: limitations and possibilities</i>
16:25		Dmitry Rychkov <i>Isothermal charge decay in solid and 3D-printed polypropylene films</i>
16:45		Zhongyang Cheng <i>Multifunctional polymer-nanocellulose composites for energy harvest</i>
17:05		Leonardo Gasperini <i>Energy harvesting through piezoelectric polymeric nanofibers</i>

18:00-19:00

**DINNER**

18:00-19:30

**MEETING OF THE SCIENTIFIC  
ADVISORY COMMITTEE**

## Tuesday, September 19<sup>th</sup>, 2023

09:00	Session 4: Functional Materials and Dielectrics Chairs: Zhongyang Cheng, Takashi Nakajima	Zhongyang Cheng <i>Functional dielectrics and materials</i>
09:30		François Bauer <i>Polarization response of PVDF under ultrahigh voltage</i>
09:50		Kailiang Ren <i>Tunable flexophotovoltaic effect in PVDF nanocomposites</i>
10:10		Ehtsham-UI Haq <i>Quantitative Surface Free Energy measurements in Electrets using Micro-Colloid Probe Pairs</i>
10:30		Min Sun <i>PMN-PT single-crystal derived ferroelectric optical fibers</i>

10:50

**COFFEE BREAK**

11:10	Session 5 Chairs: Takeo Furukawa, Thulasinath Raman Venkatesan	Daisuke Yamane <i>Evaluation of Micropatterned Self-Assembled Electrets for MEMS Devices</i>
11:30		Yuya Tanaka <i>Self-assembled electret for vibrational energy harvester</i>
12:00		Tomoya Miyoshi <i>Development of skin-attached stretchable energy harvester with perfluoroelastomer electret</i>
12:20		Sebastian Engel <i>Influence of optical excitation on the ferroelectric properties of ferroelectric-semiconductor hybrid materials</i>

12:40

**LUNCH BREAK**

13:55	Session 6: Siegfried Bauer's legacy lives on – Contributions by his closest friends Chair: Martin Kaltenbrunner	Shihai Zhang <i>A new class of relaxor ferroelectric polymer exhibiting ultrahigh electromechanical response at low electric field</i>
14:15		Bernd Ploss <i>Influence of preparation conditions on structure and ferroelectric properties of thin VDF-TrFE copolymer film</i>
14:45		Reimund Gerhard <i>Electret charges and/or dipoles on dielectrics plus elastical and thermal materials properties</i>
15:15		<b>COFFEE BREAK</b>
15:35		Michael Wübbenhorst <i>Thermal wave based charge and polarization profiling - how to achieve nanometer resolution?</i>
16:05		Reinhard Schwödjaer <i>Electrostatic converter with an electret-like elastomer</i>
16:35	Christoph Keplinger <i>Artificial muscles for the lifelike robots of the future</i>	

18:00-19:00

**DINNER**

19:00-21:00

**POSTER SESSION**

## Wednesday, September 20<sup>th</sup>, 2023

09:00	Session 7: "Biodielectrics" – an initiative of IEEE Chairs: Tofail Syed, Carmo Lança	Tofail Syed <i>Opening: IEEE Technical Committee on Biodielectrics: Goals, objectives and next steps</i>
09:10		Sarah Guerin <i>Piezoelectric biomolecules for lead-free, reliable, eco-friendly electronics</i>
09:40		Kai Tao <i>Self-assembling peptides piezoelectricity</i>
10:10		Charlie O'Mahony <i>Quantitative 3D optical birefringence in peptide electrets</i>
10:30		Hema Dinesh Barnana <i>Cold sintering of biologicals for electret applications</i>

10:50

**COFFEE BREAK**

11:10	Session 8 Chairs: Xiaoqing Zhang, Stéphane Holé	Kritish Roy <i>Engineered Lysozyme bioelectrets</i>
11:30		Sarah K. Markham <i>In silico design of a biodegradable endoscopic ultrasound transducer</i>
11:50		Veronika Turiničová <i>Non-invasive measurements of excess electron charge in charged hydroxyapatite dielectric</i>
12:10		Jan van Turnhout <i>Better charging of microfiber filter media and better disinfection of seeds by the joint use of a corona discharge</i>

12:40

**LUNCH BREAK**

13:45-14:15

**CONFERENCE GROUP PHOTOGRAPH**

14:15-17:00

**EXCURSION: VOESTALPINE STEELWORLD**

17:00-21:00

**CONFERENCE DINNER**

## Thursday, September 21<sup>th</sup>, 2023

09:00	Session 9 Chairs: Heinz von Seggern, François Bauer	Takeo Furukawa <i>Towards quantitative understanding of phase transition and polarization switching in VDF-based</i>
09:30		Daniel Tan <i>Realization of stable dielectric permittivity in Pb(Ni, Nb)O<sub>3</sub>-P(Zr, Ti)O<sub>3</sub> relaxor ferroelectrics</i>
09:50		Geetu Kumari <i>Density Functional Theory (DFT): A tool for rational design of crystalline piezoelectrics</i>
10:10		Giacomo Selleri <i>Piezoelectric core-shell nanofibers for impact localization</i>
10:30		Krishna Hari <i>Amino acid crystals as high-performance, eco-friendly structural health monitors</i>

10:50 **COFFEE BREAK**

11:10	Session 10 Chairs: Bernd Ploss, Yang Cao	Jianguo Zhu <i>Realizing high energy density and efficiency simultaneously in (Bi<sub>0.5</sub>Na<sub>0.5</sub>)<sub>0.7</sub>Sr<sub>0.3</sub>TiO<sub>3</sub>-CaTiO<sub>3</sub> ceramics</i>
11:30		Yintang Yang <i>Functionally Piezoelectric Composites for Ultrasonic Transducer Applications</i>
11:50		Nian Dai <i>Electret-based noncontact sensor for human-machine interface in harsh environments</i>

12:10 **LUNCH BREAK**

13:25	Session 11 Chairs: Xunlin Qiu, Kai Tao	Thulasinath Raman Venkatesan <i>Piezo- and pyro-electricity in polynorbornene-based stretchable elastomer electrets</i>
13:55		Takashi Nakajima <i>Abnormality detection system based on piezoelectric polymer</i>
14:15		Xingchen Ma <i>Fully degradable, highly sensitive electret-based pressure sensor for biomechanical monitoring</i>
14:35		Philipp Schöffner <i>Imperceptible sensor sheet based on ultraflexible ferroelectric polymer transducers and</i>

14:55 **COFFEE BREAK**

15:25	Session 12 Chairs: Dmitry Rychkov, Christiane Thielemann	Carmo Lança <i>TSDC and surface potential measurements of charged hydroxyapatite/BaTiO<sub>3</sub> biocoatings deposited by CoBlast</i>
15:45		Sridharbabu Yarramaneni <i>Thermo-electret behaviour of PET/0.8PHB, PET/0.6PHB polymer liquid crystals</i>
16:05		Yuji Suzuki <i>Deep-learning-assisted discovery of amorphous fluorinated polymer electret with high charging performance for energy</i>
16:35		Yuji Suzuki : <i>Welcome to ISE 20</i>
16:45		Closing Ceremony

17:00 **END OF THE ISE 19 SYMPOSIUM**

18:00-19:00 **DINNER**

Friday, September 22<sup>nd</sup>, 2023

**WORKSHOP**  
**ELECTROACTIVE POLYMERS FOR SOFT**  
**TRANSDUCERS**

<i>Chairs: Martin Kaltenbrunner, Christoph Keplinger</i>	
<b>09:10</b>	Marco Fontana <i>Materials for fluid-gap electrostatic actuators</i>
<b>09:40</b>	Florian Hartmann <i>Swimming robots powered by soft electrohydraulic actuators</i>
<b>10:10</b>	Ellen Rumley <i>Fully biodegradable electrohydraulic actuators for sustainable soft robots</i>
<b>10:40</b>	<b>COFFEE BREAK</b>
<b>11:00</b>	Naoji Matsuhisa <i>Soft transducers using stretchable electronic materials</i>
<b>11:30</b>	Giacomo Moretti <i>An overview on the design and development of dielectric elastomer transducers for dynamic applications</i>

**12:00**

**END OF THE WORKSHOP**

**12:30**

**LUNCH**

Monday, September 18<sup>th</sup>, 2023

## SESSION 1

09:00	Opening Session Chair: Martin Kaltenbrunner	Opening Ceremony
09:20		Heinz von Seggern <i>Ferroelectrets: The Electret Story Continues</i> Bernhard Gross Memorial Lecture
10:10	Session 1 Chairs: Jan van Turnhout, Sarah Guerin	Christiane Thielemann <i>Sustainable PLA electrets: a review</i>
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12:10	Dennis Flachs <i>Sustainable PLA electrets: a comparison of commercial and solution-cast foils</i>	



# Ferroelectrets: The Electret Story Continues

Heinz von Seggern

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**Abstract:** Dielectric absorption phenomena, spatial polarization distributions, Paschen breakdown and radiation effects are just a small selection of Bernhard Gross' interests in dielectric sciences. I had the privilege of getting to know Prof. Bernhard Gross as doctoral student during his frequent visits at Technical University Darmstadt and as postdoc and principal investigator at Bell Laboratories in Murray Hill, USA, and later during many visits at the University of Sao Paulo, Brazil on the Campus of Sao Carlos. Here I will talk about the field of ferroelectrets, which is the newest development in electret research. Since ferroelectrets have developed mostly after Bernhard's death I will address some of Bernhard's related work to convert this talk to a Bernhard Gross Memorial Lecture.

**Keywords:** ferroelectrets, piezoelectric  $d_{33}$  coefficient, elastomers, thermoplastic polyurethane, Teflon FEP

## Introduction

In 1989 a new approach for ferroelectric polymers has been introduced by VTT Technical Research Center, Finland, which utilizes charging of nonpolar porous polypropylene (PP) to fabricate piezoelectric materials with high piezoelectric  $d_{33}$  coefficients by electrical breakdown in the air-filled pores [1]. Due to poor thermal charge stability of PP, the search for new materials and structures started. Therefore, it was not surprising that Teflon FEP and PTFE were entering the scene, known to be the presently most stable charge storage materials.

Under the up to now suggested ferroelectret structures the fusion-bonded FEP tunnel structure in 2016 was one of the most interesting one (see Figure 1).

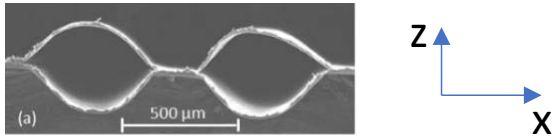


Figure 1: Fusion bonded Teflon FEP foils metallized on both sides [2]

It showed very high  $d_{33}$  coefficients up to 4600 pC/N and for the first time sizeable  $d_{31}$  coefficients of up to 32 pC/N. The large coefficients can be explained basically by the small Young's modulus of the very thin FEP foils being able to easily deform under stress in  $z$  as well as  $x$  direction both resulting in strong deformations in  $z$  direction.

## Results and discussion

Instead of relying on a single material for the electrical and mechanical properties of the ferroelectret we have suggested a new concept [3] where the electrical part of the device is separated from the mechanical part using different materials. The structure and the geometrical variables are displayed in Figure 2. The ferroelectret thereby consists of two 12.5  $\mu\text{m}$  thick FEP layers separated by a 3D printed elastomeric thermoplastic polyurethane (TPU) grid.

Poling was performed by breakdown charging to its maximum value of  $\sigma_{rem}^{max}$ . No charge built-up occurs in the spacer region due to high conductivity of TPU.

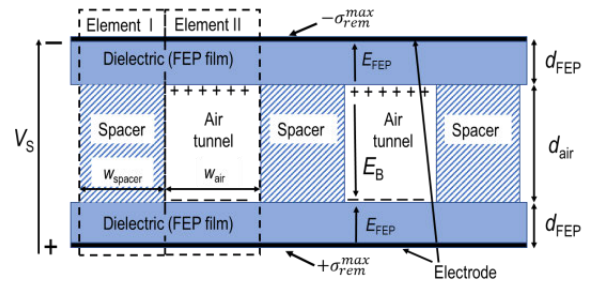


Figure 2: Structure of the newly introduced ferroelectret with  $d_{air} = 0.27 \text{ mm}$ ,  $d_{FEP} = 12.5 \mu\text{m}$ ,  $w_{spacer} = 1 \text{ mm}$  and  $w_{air} = 1 \text{ mm}$  and  $3 \text{ mm}$ , respectively.

Calculation of the elastic modulus  $Y_{total}$  by Reuss and Voigt laws and charge  $\sigma_{rem}^{max}$  [4] results in

$$d_{33} = \frac{\sigma_{rem}^{max}}{\sigma_{mech}} = \frac{w_{air}}{w_{TPU}} \times \frac{\epsilon_0 \epsilon_{FEP} E_B}{Y_{TPU} \left( \epsilon_{FEP} + \frac{2d_{FEP}}{d_{TPU}} \right)}$$

which describes the experimental results in an excellent manner (see Figure 3).

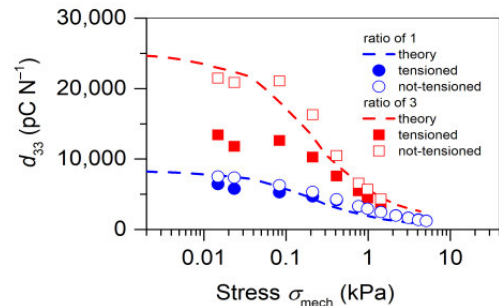


Figure 3: Experimental and theoretical  $d_{33}$  coefficients vs stress for  $w_{air}/w_{TPU} = 1$  and  $3$

Detailed experimental data and additional results as well as links to Bernhard Gross' fundamental work will be presented in the talk.

## References

- [1] A. Savolainen and K. Kirjavainen, *J. of Macromolecular Science: Part A - Chemistry*, 26, 583, 1989.
- [2] and [4] in [3] H. von Seggern et al, *Polymers* 13, 3751, 2021.

## Acknowledgement

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# Sustainable PLA electrets: a review

Christiane Thielemann and Dennis Flachs

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**Abstract:** Recently, the demand for sustainable materials for electronic devices has increased significantly. Polylactic acid (PLA) is a good alternative to conventional petroleum-based polymers due to its attractive dielectric and mechanical properties and ease of processing. Recently, PLA has been discussed as a dielectric material with piezoelectric and electret properties. The state of the art of this interesting new electret material is presented.

## Introduction

Due to growing environmental awareness and the increasing amount of electronic waste, the demand for environmentally friendly materials has increased significantly. Polylactic acid (PLA) is one of the best-known biopolymers, which is mainly used for compostable packaging. It is made from corn and in aqueous environment breaks down into molecules that are non-toxic to humans and environment [1]. Only recently, PLA has been described as a soft electroactive material with promising electret and piezoelectric properties [2-4]. First applications such as a PLA-based nanofibrous electret membrane for air filters have been proposed [2]. Also, biological applications such as biosensors or energy harvesters embedded in tissue have been suggested due to the inherent biocompatibility of PLA electrets [2]. Gong et al. presented a hybrid energy harvester for electronic skin applications comprising a piezoelectric PLLA film and a PLA-electret-based triboelectric nanogenerator [3]. Additionally, PLA-based ferroelectrets are discussed for sensor applications. Zhukov et al. presents foamed PLA sheets (360  $\mu\text{m}$ , porosity of 60 %) with large quasi-static piezoelectric coefficients of about 600 pC/N ( $d_{33}$ ) and 44 pC/N ( $d_{31}$ ). During the first 20 days after polarization, the piezoelectric activity decreased by half compared to the primary value, but then remained almost stable [4]. Dali et al. presented a partly 3D printed PLA-based ferroelectret air-coupled ultrasonic transducer [5].

## Electret properties of PLA

Even though PLA electrets have found their first applications, the charge stability of plain PLA is still significantly lower compared to fluoro-based electret materials like FEP. Research has been presented with the aim to improve the charge stability of PLA by incorporation of inorganic micro- and nanoparticles as filler materials e.g., Zn-doped  $\text{TiO}_2$  [2],  $\text{BaTiO}_3$  [6], or  $\text{SiO}_2$  [6]. Depending on the particles, improvement of charge stability was clearly achieved, where structural deviations are introduced into the polymer matrix, which may act as deep traps for charge carriers [7].

## Degradation of PLA

A major attraction of PLA is its biodegradability. However, decomposition is slow and strongly dependant on environmental conditions. In an aqueous environment polymer chains are first cleaved by hydrolysis of ester bonds. In a second step, microorganisms mineralize the resulting lower-weight molecules which are harmless for humans and environment [8]. A recent approach to accelerate and control this process that determines the functional life of a device, is the enzymatic hydrolysis. Enzymes are highly specialized proteins that act as biological catalysts for the hydrolysis. Embedding the enzyme proteinase K into the PLA polymer matrix is a promising way to accelerate and control the degradation time of PLA [9].

## Conclusion

Increasing research activities on sustainable, functional polymers in combination with first promising results indicate that PLA could be an interesting "green" electret material in the future. However, further work is needed to significantly improve the charge stability of this new electret material.

## References

- [1] Y. Tokiwa et al., *Appl. Microbiol. Biotechnol.*, 72, 244-251, 2006.
- [2] L. Ke et al., *ACS Applied Materials & Interfaces*, 15 (27), pp 32463 (2023).
- [3] S. Gong et al., *Adv.Funct. Mater.*, 30, 1908724 (2020).
- [4] S. Zhukov et al., *Appl. Phys. Lett.* 117, 112901 (2020).
- [5] O. B. Dali et al., *IEEE International Ultrasonics Symposium*, pp. 1-4 (2021).
- [6] A. Guzhova, et al., *J. Electrostat.*, 79, 1-6, (2016).
- [7] R. Kamalova *AIP Conference Proceedings*, vol. 2174, p. 020026 (2019).
- [8] M. Karamanlioglu et al., *Polymer Degradation and stability* 137, 122-130 (2017)
- [9] Q. Huang et al., *Biomacromolecules* 21(8), 3301-3307 (2020).

## Acknowledgements

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# Improvement of the charging efficiency of ferroelectrets based on Paschen's law

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**Abstract:** Charging of ferroelectrets is realized by means of dielectric barrier discharges (DBDs), the triggering of which is governed by Paschen's law. The Paschen-breakdown voltage  $V_b$  of common gases exhibits a U-shaped dependence on  $pd$  ( $p$  is gas pressure and  $d$  gap distance). For easier triggering of the DBD charging, the  $pd$  is adjusted toward  $(pd)_{\min}$  by controlling the gas pressure in the cavity. Then,  $pd$  is restored to its value at ambient pressure under the charging voltage in order to obtain a high remanent polarization. The proposed charging scheme can significantly improve the charging efficiency of ferroelectrets with a wide range of cavity geometries.

**Keywords:** ferroelectrets, dielectric barrier discharge, Paschen's law

## Introduction

Ferroelectrets (also called piezoelectrets) are internally charged non-polar polymer foams or polymer systems with cavities [1]. Charging of the cavities is realized through a series of dielectric barrier discharges (DBDs) under sufficiently high applied electric fields. After charging, the cavities, carrying positive and negative charges on the top and bottom internal surfaces, respectively, can be considered as macroscopic dipoles. It is known that the piezoelectric coefficients of ferroelectrets are proportional to their effective polarization (i.e., the density of their macroscopic dipoles). Therefore, more efficient charging is highly desired in the preparation and further optimization of ferroelectrets.

## Results and Discussion

Previous studies show that the DBD charging in ferroelectrets is strongly dependent on the breakdown strength of the cavities. Lower breakdown strength leads to easier triggering of the DBDs and higher effective polarization in the presence of the charging voltage, whereas higher breakdown strength is needed in order to have higher remnant effective polarization after charging. This prompts us to propose a novel charging strategy for ferroelectrets.

The charging scheme consists of four steps for ferroelectrets with large (small) cavities as schematically shown in Fig. 1: (1) reduce (increase) gas pressure, so that  $pd$  of the cavity approaches  $(pd)_{\min}$ ; (2) apply the optimal poling voltage  $V_p$ ; (3) hold poling voltage and restore gas pressure to ambient conditions; and (4) switch off poling voltage at ambient pressure. The proposed charging scheme is easy to operate and can significantly

improve the charging efficiency of ferroelectrets with a wide range of cavity geometries.

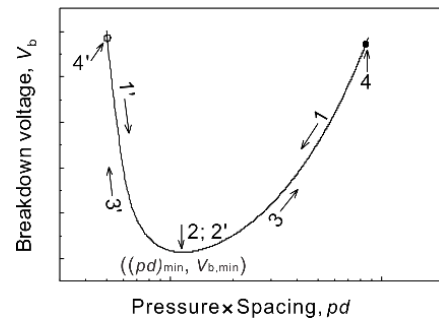


Figure 1: Paschen-breakdown voltage as a function of  $pd$ . For ferroelectrets with a large (small) cavity height,  $pd$  at atmospheric pressure is found toward the right (left) end of the Paschen curve, as indicated by the black (white) circle at point 4 (4').

## Conclusions

On the basis of the dependence of the DBD charging on the threshold voltage and Paschen's law, we propose a practical strategy for more efficient charging of ferroelectrets with a wide range of cavity geometries.

## References

- [1] X. Qiu, Y. Bian, J. Liu, Y. Xiang, T. Ding, W. Zhu, and F. Xuan, "Ferroelectrets: Recent developments", IET Nanodielectr. 5, 113 (2022).
- [2] X. Qiu, Y. Liu, C. Wu, Y. Xiang, F. Xuan, R. Gerhard "More efficient charging of ferroelectrets via tuning of the Paschen breakdown" Appl. Phys. Lett. 122, 092902 (2023).

## Acknowledgements

Financial support from the National Key Research and Development Program of China (No.2021YFC3001802), and the National Natural Science Foundation of China (Nos. 12174102 and 12025403) is gratefully acknowledged.

# Poly(butyl vinyl ether-co-acrylonitrile) Copolymer For Thermal Capacitive Sensing and Thermal Energy Harvesting Applications

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**Abstract:** In this work, alternating poly(butyl vinyl ether-co-acrylonitrile) (P(BVE-co-AN)) copolymer was found to exhibit temperature-dependent strain recovery when it was heated through its glass-transition temperature ( $T_g \sim 26^\circ\text{C}$ ). This copolymer is amorphous and contains polar side groups in its structure, thereby exhibiting a switch in permittivity when passing through the glass transition. The strain-recovery effect accompanied by the change in permittivity and thickness occurring around room temperature can be exploited in electro-active applications such as thermal capacitive sensors and energy harvesting.

**Keywords:** P(BVE-co-AN), strain recovery, capacitive sensors, thermal energy harvesting

## Introduction

Alternating poly(butyl vinyl ether-co-acrylonitrile) (P(BVE-co-AN)) containing ether and nitrile side groups was synthesized by a free-radical bulk copolymerization. It was then cast into free-standing thin films using solvent blade-casting. The copolymer's soft and amorphous nature and the presence of polar side groups make it an interesting candidate for electro-active applications. Hence, the P(BVE-co-AN) films were subjected to thermal, mechanical, and dielectric characterization.

## Results and Discussion

P(BVE-co-AN) polymer, when stretched below its glass-transition temperature ( $T_g$ ), can be given a secondary elongated shape [1]. This can be observed in Figure 1 where a P(BVE-co-AN) film is subjected to an initial RT creep experiment (blue curve with triangles) at an applied load of 5 kPa. On removal of the stress,

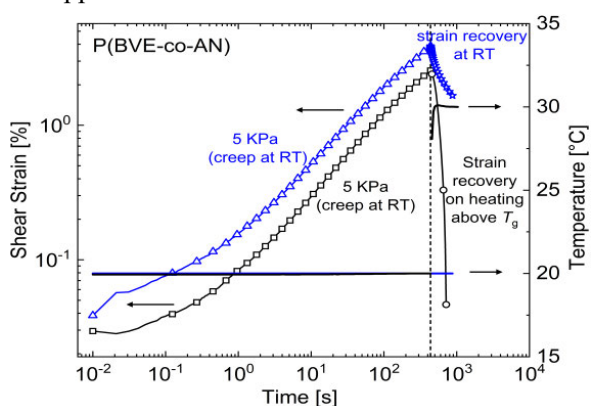


Figure 1: Initial creep curves at RT (blue curve with triangles and black curve with squares) followed by strain recovery at RT (blue curve with stars) and as the sample is heated through its  $T_g$  (black curve with circles).

the developed strain is only partially recovered (blue curve with stars). However, after the initial creep (black curve with squares), when the copolymer is heated

above its  $T_g$ , ( $\sim 26^\circ\text{C}$ ), the polymer returns back to its initial unstrained state (black curve with circles), i.e., exhibits a shape memory effect. In tensile mode, complete strain recovery is observed for films strained up to 100%.

With the onset of  $T_g$  the dipoles are unfrozen, hence it also shows an increase in dielectric permittivity in this temperature range. A change in permittivity ( $\Delta\epsilon$ ) of 5.5 is observed as the copolymer is heated from 20 to 35  $^\circ\text{C}$  at 1 Hz. This permittivity switch occurring in a small temperature range and the change in thickness between the stretched and un-stretched state could be used in thermal capacitive sensing applications and thermal energy generators (TEG). In the latter's case, combined with a metamagnetic shape memory alloy such as Heusler alloys [2], the TEG can be brought in contact with hot and cold surfaces to harvest energy continuously.

## Conclusions

An alternating P(BVE-co-AN) polymer strained under a load of 5 kPa at 20  $^\circ\text{C}$  exhibits 100% strain recovery on heating it above its  $T_g$  (26  $^\circ\text{C}$ ). The change in permittivity and thickness occurring during the  $T_g$  and between the stretched and un-stretched state, respectively, can be used in applications such as thermal capacitive sensors and thermal energy harvesters.

## References

- [1] C. Liu, H. Qin, and P. T. Mather, "Review of progress in shape-memory polymers," *J. Mater. Chem.*, vol. 17, no. 16, pp. 1543–1558, 2007
- [2] M. Gueltig *et al.*, "High-Performance Thermomagnetic Generators Based on Heusler Alloy Films," *Adv. Energy Mater.*, vol. 7, no. 5, p. 1601879, 2017

## Acknowledgements

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# Sustainable PLA electrets: a comparison of commercial and solution-cast foils

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**Abstract:** We investigate the electret properties of solution-cast PLA electrets and compare it with commercially available PLA foils fabricated by melt-extrusion. Measurements reveal that TSC peaks of solution-cast electrets are superior after full evaporation of the solvent.

**Keywords:** solution-cast film, PLA, chloroform, thermally-stimulated-current

## Introduction

Non-biodegradable petro-based polymers, such as FEP, are known to be excellent piezoelectrets which promoted a variety of flexible sensors, actuators, and energy harvesting devices. In recent years, the demand for environmentally friendly biodegradable polymers has increased due to growing environmental awareness. With this background, the sustainable substitute for petro-based piezoelectrets polylactic acid (PLA) has been proposed. PLA is produced from corn and biodegradable under certain conditions. Only recently, it has been shown that PLA piezoelectrets show very good piezoelectric  $d_{33}$ -coefficients [1]. However, charge stability of PLA is still an issue and there is an urgent need to improve the electret properties of commonly used, commercial PLA foils. One approach is the fabrication of PLA foils by solution casting with the goal to produce customized films with modified polymer composition and integrated filler materials [2]. In this work we compare commercial and solution-casted PLA foils in terms of charge stability, assuming that the solvent chloroform plays a critical role.

## Results and Discussion

Solution-cast samples were fabricated by a spin-coating process using a chloroform/PLA mixture. Thermally-stimulated-current (TSC) measurements were performed after corona-charging of solution-cast and commercial foils (approx. 30  $\mu\text{m}$  thick) and are displayed in Figure 1. As expected, PLA films show two characteristic peaks in the TSC spectra, presumably related to charge release from shallow and deep traps, respectively. PLA films cast from solution show TSC peaks at lower temperatures compared to commercial ones. This can be explained by chloroform residues in the polymer, which persist even after storage for several weeks at room temperature. After complete evaporation of the chloroform by annealing at 120  $^{\circ}\text{C}$  for 30 minutes, both TSC peaks shift towards higher temperatures. For commercial films, no shift is observed after the similar treatment, but only a broadening of the TSC peaks. For the charging at temperatures of 80  $^{\circ}\text{C}$  and 100  $^{\circ}\text{C}$ , the shallow traps

at 55  $^{\circ}\text{C}$  were no longer trapping, since charges were released immediately after capture. Thereafter, the deeper traps filled gradually, which ultimately leads to significantly improved electret properties.

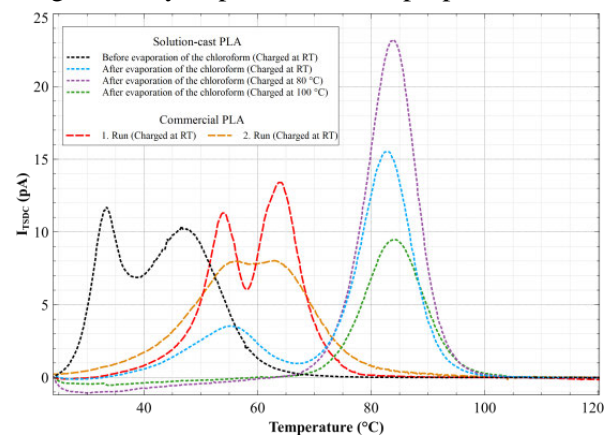


Figure 1: TSC measurement of solution-cast (33  $\mu\text{m}$ ) and commercial PLA foil (30  $\mu\text{m}$ ). Samples were corona-charged to -1kV for 3 min. The heating-rate was 4  $^{\circ}\text{C}/\text{min}$ .

Additional investigations include surface potential measurements, thermogravimetric analysis and crystallinity measurements.

## Conclusions

We investigated the properties of sustainable PLA electrets. The results show that the charge stability strongly depends on the manufacturing process, where solution-cast electrets show (after temperature treatment) deeper energy traps compared to commercially available PLA foils. More work is needed to further improve the charge stability of biodegradable electrets, f.e. incorporation of filler materials.

## References

- [1] S. Zhukov, et al. "Biodegradable cellular polylactic acid ferroelectrets with strong longitudinal and transverse piezoelectricity" *Appl. Phys. Lett.*, 117, 112901, 2020.
- [2] A. A. Guzhova, et al. "Improvement of polylactic acid electret properties by addition of fine barium titanate" *J. Electrostat.*, 79, 1-6, 2016.

## Acknowledgements

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Monday, September 18<sup>th</sup>, 2023

## SESSION 2

13:45	Session 2 Chairs: Michael Wübbenhorst, Peng Fang	Hiroyuki Mitsuya <i>Highly reliable electret for heat resistive vibrational energy harvester</i>
14:15		Lin Zheng <i>Influence of interface dipole on charge build-up under high voltage</i>
14:35		Yumi Tanaka <i>Polarization and charging characteristics of perovskite-type lanthanum aluminate ceramics</i>
14:55		Jinhai You <i>Charge transport and glassy dynamics in non- stoichiometric protic ionic liquids 2-aminoethyl hydrogen</i>
15:15		Jessica Mangialetto <i>Evolving glass transition of curing network based on Diels- Alder reversible bonds studied by dielectric relaxation</i>

# Highly reliable electret for heat resistive vibrational energy harvester

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**Abstract:** We have developed heat resistive vibrational energy harvester using silicon oxide electret. The electret in this work is known to be structurally robust owing to the five-coordinated silicon atoms in the silicon oxide molecular network. We utilize a vacuum package to suppress the degradation of electret potential at an elevated temperature of 100 °C, making it possible to produce robust energy harvesters that could be used on high-temperature equipment in factories and plants where continuous monitoring is needed using IoT type sensors.

**Keywords:** MEMS, vibrational energy harvester, electret, heat resistant, vacuum package

## Introduction

Modern factories and chemical plants are in need of establishing wireless sensor networks to keep their equipment and utilities monitored around the clock. Energy harvesters (EHs) is an ideal alternative to batteries to eliminate the need for battery replacement for such distributed sensors. Prior to this work, we studied a MEMS vibrational EH that utilizes electrostatically induced currents generated by mechanically movable electrodes coated with a silicon oxide electret film. Considering that temperature of the factory utilities is about 60°C, we developed a technique to improve the heat resistance of the electrets.

## Results and Discussion

Figure 1 shows the photographs of the EH device with the comb-shaped silicon microelectrodes. During the fabrication process, the surface of the silicon structure is thermally oxidized using an aqueous solution of KOH to include potassium, which is then electrically charged to form the five-fold atomic structures of silicon ( $\text{SiO}_5^-$ ) in the silicon oxide network as shown in Fig. 2. From the molecular dynamics simulation, such structure is known to behave as a negatively charged electret which is more stable than the usual  $\text{SiO}^-$  structures. Therefore, the degradation of electret potential is mostly caused by the external influence such as adsorbed gases and moisture. Figure 3 shows the time dependent degradation of electret potential monitored in 100 °C. The electret packaged in dry air exhibited a quick drop of po-

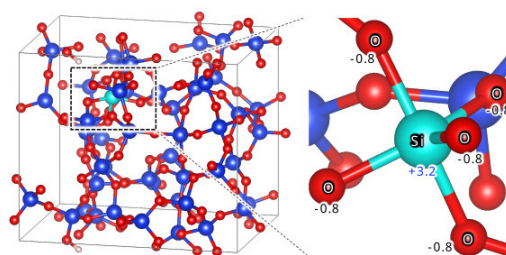


Figure 2.  $\text{SiO}_2$  layer with potassium ions have the five-coordinated  $\text{SiO}_5^-$  structure.

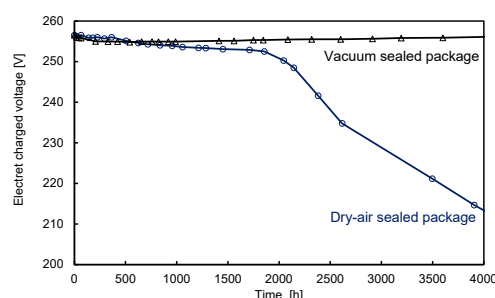


Figure 3. Time evolution of the charging voltage at 100°C.

tential after 1,900 hours, while the vacuum-sealed device maintained the potential over time. The deterioration of the epoxy resin in air was found to have caused the degradation of electret potential.

## Conclusions

Vacuum packaging was found to be effective to maintain the electret potential over time at a high temperature of 100 °C, making it possible to produce EH devices that could be used as an energy source as well as a battery-free sensor deployed in a harsh high temperature environment.

## References

- [1] T Sugiyama and G Hashiguchi, "SiO<sub>2</sub> electret generated by potassium ions on a comb-drive actuator," *Appl. Phys. Express*, vol. 4, Issue 11, 114103, 2011.
- [2] T Nakanishi et al. "Negative-charge-storing mechanism of potassium-ion electrets used for vibration-powered generators: Microscopic study of a-SiO<sub>2</sub> with and without potassium atoms," *Applied Physics Letters*, vol. 117, no. 10, 2020

## Acknowledgements

This research was also funded by JST CREST grant no. JPMJCR15Q4 and JPMJCR19Q2, Japan.

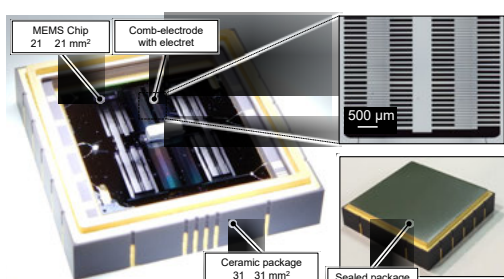


Figure 1. MEMS vibrational energy harvester

# Influence of interface dipole on charge build-up under high voltage

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**Abstract:** Interface dipole was measured in various polyethylene samples with a high sensitive pressure-wave-propagation measurement setup. The samples were then submitted to a high voltage for 24 h. Charge evolution is discussed in relation with the measured interface dipoles. Correlations are clearly observed.

**Keywords:** interface dipoles, space charge, pressure-wave-propagation (PWP) method, polyethylene

## Introduction

Charges naturally exchange through the interface between two materials and build-up a contact potential. This acts on energy levels at the interface and thus may impact charge injection through this interface. The interface dipole due to the contact potential can be detected [1] using a high-sensitive pressure-wave-propagation (PWP) method [2]. Two kinds of polyethylene samples are studied, low density (LDPE) and high density (HDPE). The samples are 1-mm thick and are coupled on each side to carbon-loaded Ethylene Vinyl Acetate (EVA) electrodes with silicone oil. Additionally, polyethylene is either coated with gold or aluminium or left uncoated. As these different interface conditions exhibit different interface dipoles, 40 kV was applied to the structure at 22°C during 24 h to assess the impact of the interface conditions on the evolution of space charges.

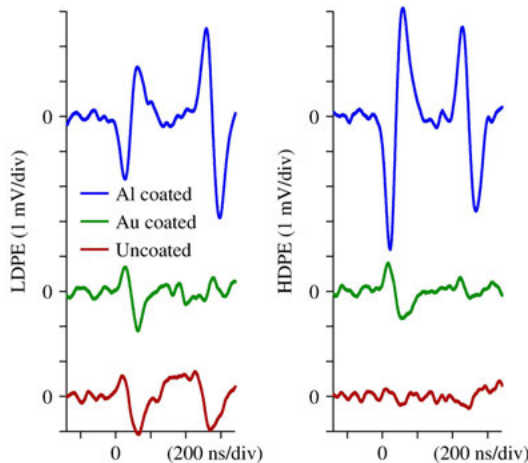


Figure 1: Raw measurements of interface dipoles for the six interface configurations.

## Results and Discussion

Figure 1 shows the raw signals. Al-coating generates an interface dipole whose polarity is opposite and amplitude is larger than in any other cases. Additionally, the interface dipole seems larger for HDPE than for LDPE. Au-coating generates similar dipoles for both kinds of polyethylene. In the case of uncoated samples, the dipole is almost zero for HDPE and is similar to the one of gold for LDPE.

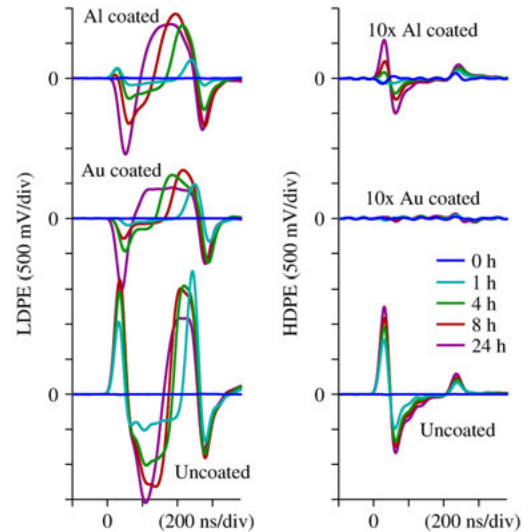


Figure 2: Raw charge measurements after various durations under 40-kV stress at 22°C.

Figure 2 shows the charge distribution under short-circuit during voltage application. The short-circuit was maintained for 2 min to carry out the measurements. In LDPE, charges greatly build-up and the dynamic is clearly different between Al-coated and Au-coated electrodes. There was less charges build-up in HDPE. Al-coating seems to facilitate injection at the cathode contrarily to Au-coating.

## Conclusions

Different electrode configurations exhibit different interface dipoles which may in direct correlation with the various charge build-up observed under 40 kV. The dipole seems to increase or reduce injection depending on its polarity. The absence of coating seems to allow more charges to be injected. The direct interface dipole measurement brings new information for insulating structures.

## References

- [1] L. Zheng; S. Holé. "Study of Contact Conditions at Conductor/Insulator Interfaces used in Space Charge Distribution Measurements," *Phys. Scr.*, 98 (2), 025802, 2023.
- [2] S. Holé; T. Ditchi; J. Lewiner, "Non-Destructive Methods for Space Charge Distribution Measurements: What are the Differences?," *IEEE Trans. Dielectr. EI.*, 10 (4), 670-677, 2003.



# Polarization and charging characteristics of perovskite-type lanthanum aluminate ceramics

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**Abstract:** To develop a high-performance ceramic-electrets, the effects of Ca<sup>2+</sup>-doping on polarization and charging characteristics of LaAlO<sub>3</sub> (LAO) ceramics were investigated. The surface potential of Ca<sup>2+</sup>-doped samples, prepared to have a  $X = \text{Ca}/(\text{La} + \text{Ca}) = 0\text{--}5\%$  (mol/mol), exhibited a volcano-shaped correlation with the  $X$ , reaching max. value of 3.7 kV at  $X \approx 0.5\%$ . This result suggests that "Ca-LAO" can become an excellent electret substrate and the optimization of the doping composition is effective in producing "Ca-LAO" electrets with a high surface potential.

**Keywords:** Ceramic electrets, Ionic conductivity, Lanthanum aluminate

## Introduction

With the recent development of the IoT society, research into electret-type vibration power generators for wireless sensor network systems has been activated. In our research group, the high-performance electrets based on ionic conductive ceramics have been tried to be developed and it was found that the concentration and diffusivity of charge carriers (mobile ions), low dielectric constant, and wide bandgap of the ceramic substrate are important factors for the ceramic electret to exhibit a high surface potential. Based on these findings, research for new ceramic electret substrates was conducted and perovskite-type lanthanum aluminate (LaAlO<sub>3</sub>; LAO) was found to be a promising candidate. Whereas there are no charge carriers in LAO with the strict stoichiometric composition, systematic control of concentration of oxygen vacancies, that can act as charge carriers, is possible by utilizing charge compensation accompanied with doping of low oxidation state cations in La<sup>3+</sup> sites. Hence, this study investigated the effects of Ca<sup>2+</sup>-doping in LAO ((La<sub>1-x</sub>Ca<sub>x</sub>)AlO<sub>3-0.5x</sub>; Ca-LAO) on their dielectric, conductivity, polarization and charging properties.

The sample powders were synthesized to have a Ca<sup>2+</sup> composition of  $X = 100x = 0\text{--}5$ , and after pressed into compact disks, sintered for 2 hours in a dry air atmosphere at 1600–1650°C to produce sintered bodies ( $\phi 10$  mm,  $T 1$  mm). The obtained disks, on which gold electrodes were sputtered on both sides, were then polarized by applying a DC electric field of 8 kVmm<sup>-1</sup> for 1 hour at 200°C. The composition of each sample was confirmed by ICP analysis, and the crystal structure was evaluated by XRD measurement. The dielectric and conductive properties were evaluated using impedance measurement, and the polarization and charging states of the polarized samples were evaluated by TSDC analysis and surface potential measurement based on the Kelvin probe method.

## Results and Discussion

Figure 1 shows the relationship between the  $X$  and the surface potential ( $V_s$ ). The value of  $V_s$  was found to increase significantly from ca. 0.4 kV (at  $X \approx 0$ ) to a maximum value of 3.7 kV (at  $X \approx 0.50$ ) in the range of  $X \approx 0$  to 0.9, indicating that LAO ceramics can

become an excellent electret substrate by replacing La<sup>3+</sup> with a small amount of Ca<sup>2+</sup>. At  $X \approx 5.0$ , however, insulation breakdown ( $>20$  mA) occurred during the polarization process, and effective value of  $V_s$  was not obtained. Considering the result of impedance measurements at 200°C (the polarization treatment temperature) for the non-polarized samples, which is the conductivity probably due to oxygen vacancies [2] increased with increasing  $X$ , it is believed that the insufficient amount of charge carriers in the un-doped sample and the progress of the charge transfer reaction in the over-doped samples may have contributed to the insufficient generation of  $V_s$ .

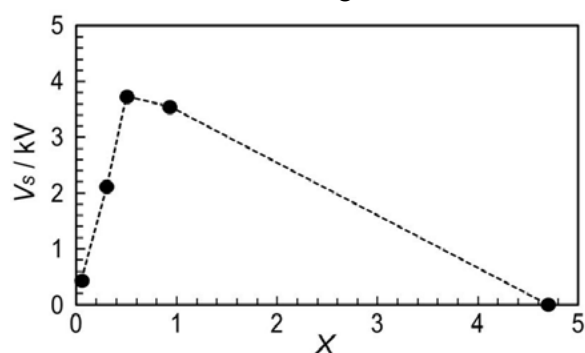


Figure 1: Change in  $V_s$  of Ca-LAO ceramics polarized at 200°C for 1 h under 8 kVmm<sup>-1</sup> with the  $X$ .

## Conclusions

This study discovered that perovskite-type lanthanum aluminate ceramics (LaAlO<sub>3</sub>) are promising candidate as electret substrate; replacing La<sup>3+</sup> with an optimized amount of Ca<sup>2+</sup> is effective in producing a "Ca-LAO" electret with a high surface potential.

## References

- [1] K. Hakamata et al., "OHA Ceramic Electret for Vibration Energy Harvesting", *J. Phys.: Conf. Series*, 1052, 012116, 2018
- [2] Changmei Lei, et al., "Dielectric relaxations of LaAlO<sub>3</sub> ceramics over broad temperature range", *J. Alloy. Compd.* 555, pp.51–55, 2013

## Acknowledgements

This work was supported by JST, CREST Grant Number JPMJCR19Q1, Japan.

# Charge transport and glassy dynamics in non-stoichiometric protic ionic liquids 2-aminoethyl hydrogen sulphate triflate

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**Abstract:** Protic ionic liquids (PILs) have been attracted growing attention due to their remarkable physicochemical characteristics. It is still imperative to improve the conductivity of PIL for actual applications. Herein, we have studied non-stoichiometric PILs based on 2-aminoethyl hydrogen sulphate triflate *via* dielectric relaxation spectroscopy, showing significantly enhanced conductivities, which are strongly coupled to the structural relaxation as manifested by VFT-behaviour.

**Keywords:** Protic ionic liquids, Charge transport, Glassy dynamics, Dielectric relaxation spectroscopy

## Introduction

Protic ionic liquids (PILs), commonly synthesized through a neutralization reaction involving a Brønsted acid and a Brønsted base, are potential electrolyte candidates for electrochemical devices due to their excellent properties including low volatility, negligible flammability, high thermal and electrochemical stability, and high ionic conductivity.[1] However, to further enhance the feasibility of commercialization, it is necessary to improve the conductivity of PILs. [2] One promising strategy to address this challenge is a non-stoichiometric blending of Brønsted acids and bases. In this work, non-stoichiometric PILs based on 2-aminoethyl hydrogen sulphate triflate in acid-rich components were studied *via* dielectric relaxation spectroscopy in terms of charge transport and molecular dynamics.

## Results and Discussion

The temperature dependence of the DC conductivity ( $\sigma_{dc}$ ) upon heating is shown in Figure 1(a). Among all compositions, the mixture with a ratio of 1:9 (purple dots) exhibits highest  $\sigma_{dc}$  values in the whole temperature range. Interestingly, all non-stoichiometric compositions reveal a temperature-dependent  $\sigma_{dc}(T)$  that follows Vogel-Fulcher-Tammann (VFT) behaviour, and the absence of any discontinuities expected for (partial) crystallization, confirming that all non-stoichiometric compositions are fully amorphous. As a result, the low temperature limit of the liquid state is largely extended from about 80 °C (the upper limit of testing in this study) to around  $-112$  °C, the glass transition temperature,  $T_g$ , for the 1:9 system. More interestingly, all  $\sigma_{dc}(T)$  curves of non-stoichiometric compositions collapse into a “master” curve (see Figure 1(b)) by scaling the temperature to their respective  $T_g$ . This observation indicates that the temperature-dependent  $\sigma_{dc}$  is dominated by cooperative liquid dynamics.

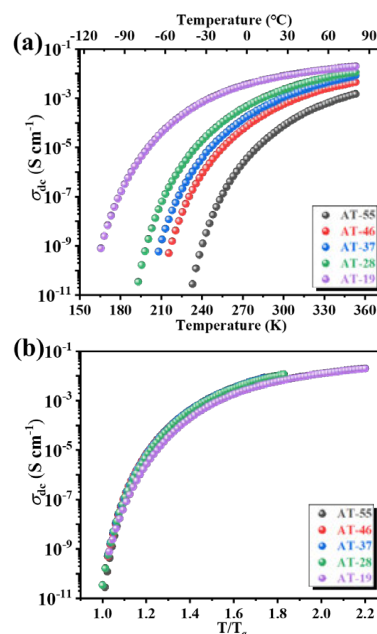


Figure 1: (a)  $\sigma_{dc}$  as a function of temperature; (b) The normalized  $\sigma_{dc}$  curve for all non-stoichiometric components scaled by their respective glass transition temperatures ( $T_g$ ).

## Conclusions

(i) Non-stoichiometric PILs show substantially enhanced conductivities over the stoichiometric reference system; (ii) All non-stoichiometric components are fully amorphous with the lowest  $T_g$  around  $-112$  °C for the 1:9 system; (iii) The temperature-dependent  $\sigma_{dc}$  obeys VFT behaviour and is thus dominated by glassy dynamics.

## References

- [1] H. Pan *et al.*, “Physicochemical study of diethylmethylammonium methanesulfonate under anhydrous conditions,” *J. Chem. Phys.*, 152(23), 234504, 2020.
- [2] L. E. Shmukler *et al.*, “The physicochemical properties and structure of alkylammonium protic ionic liquids of  $R_nH_4-nNX$  ( $n=1-3$ ) family. A mini-review,” *J. Mol. Liq.*, 321, 114350, 2021.

## Acknowledgements

J. You acknowledges China Scholarship Council (CSC) for a doctoral scholarship (Grant No. 202006310030).

# Evolving glass transition of curing network based on Diels-Alder reversible bonds studied by dielectric relaxation spectroscopy

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**Abstract:** This work concerns the systematic dielectric relaxation spectroscopy (DRS) study of a dynamic network based on the thermoreversible Diels-Alder (DA) reaction of a 4-functional furan-functionalized Jeffamine coupled with a 2-functional maleimide, focussing on the cooperative segmental dynamics as represented by the dielectric  $\alpha$ -relaxation. In a first step, the VFT parameters describing the relaxation time traces of the  $\alpha$ -process were derived for each partially cured sample. In a second step, global fits of all DRS spectra were successfully obtained without including effects due to reaction, as well as with, through the introduction of a kinetic model.

**Keywords:** glass transition,  $\alpha$ -relaxation, reversible networks, cure monitoring

## Introduction

In the past decades, the thermophysical properties of polymer networks have been extensively studied through numerous techniques, including DRS. In particular, the cure of irreversible networks has been thoroughly investigated by DRS while studies on reversible covalent network formation are notably scarce, and particularly absent for systems based on thermoreversible DA cycloadditions. Such dynamic networks are commonly developed as promising intrinsic self-healing materials. In this work, the molecular dynamics of a reversible network based on the furan-maleimide DA reaction of a 4-functional furan-functionalized Jeffamine coupled with a 2-functional maleimide, was studied systematically by DRS, with emphasis on the  $\alpha$ -relaxation, i.e., the material's glass transition temperature ( $T_g$ ).

## Results and Discussion

The relaxation times relative to the  $\alpha$ -relaxation  $\tau_\alpha$  were derived by conventional Havriliak-Negami (HN) fits of DRS spectra [1], measured in non-isothermal heating experiments from -120 to 100 °C, at frequencies between  $10^{-1}$  -  $10^7$  Hz, after isothermally curing the networks at 55 °C for different reaction times. The characteristic  $\tau_\alpha$  as a function of temperature was modelled using a Vogel-Fulcher-Tammann (VFT) law for each individual experiment. The obtained fits were consistently good. A more global approach was then attempted, where one unique set of VFT parameters was used to describe all experimental relaxation traces, initially without including effects of the reaction. This fit could describe well the temperatures where no reaction took place, but highlighted the effect of cure on the spectra, and the difficulty of determining the exact temperature interval for which  $\tau_\alpha$  is not influenced by reaction kinetic effects free of reaction kinetic effects. Another attempt for a global fit was then made by additionally introducing a kinetic model to pre-

dict the cure conversion [2], which was a clear improvement. Based on this successful procedure, a new technique for continuous cure monitoring is proposed and tested for a system curing isothermally at 55 °C. This technique allows to compute in real-time the dynamic  $T_g$  from the relaxation time  $\tau_\alpha$ , using only three VFT parameters. This promising approach might stimulate new applications of DRS-based cure monitoring.

## Conclusions

A reversible network based on the furan-maleimide DA reaction was studied by DRS with a focus on the  $\alpha$ -relaxation. The corresponding relaxation times  $\tau_\alpha$  were obtained from HN fits of dielectric spectra of partially cured samples, which were then fitted to the VFT law. A unique set of VFT parameters based on a global fit of all DRS spectra could describe well the experiments as long as the cure kinetics were ignored. A refined approach was developed by introducing a kinetic model for the DA reaction, which allowed accurate predictions of relaxation time evolutions during isothermal and non-isothermal cure experiments.

## References

- [1] J. Mangialetto, "Real-time determination of the glass transition temperature during reversible network formation based on furan-maleimide Diels-Alder cycloadditions using dielectric spectroscopy," *Macromolecules* 2023.
- [2] J. Mangialetto, "Time-temperature-transformation, temperature-conversion-transformation, and continuous-heating-transformation diagrams of reversible covalent polymer networks," *Macromolecules* (54), 412-425, 2021.

## Acknowledgements

The authors thank the Research Foundation - Flanders (FWO-Vlaanderen) for financial support (PhD fellowship of Jessica Mangialetto (1128520N)).

**Monday, September 18<sup>th</sup>, 2023**

**SESSION 3**

<b>15:55</b>	<b>Session 3</b> <i>Chairs: Yuji Suzuki, Reinhard Schwödauer</i>	Stéphane Hóle <i>High spatial resolution for space charge measurements: limitations and possibilities</i>
<b>16:25</b>		Dmitry Rychkov <i>Isothermal charge decay in solid and 3D-printed polypropylene films</i>
<b>16:45</b>		Zhongyang Cheng <i>Multifunctional polymer-nanocellulose composites for energy harvest</i>
<b>17:05</b>		Leonardo Gasperini <i>Energy harvesting through piezoelectric polymeric nanofibers</i>

# High spatial resolution for space charge measurements: limitations and possibilities

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**Abstract:** The limitations of conventional space charge distribution measurement techniques are clearly identified and various solutions can be proposed based on local scanning, or on different implementation schemes for propagation or diffusion based methods. All these methods show great interest, but none are completely ready to use.

**Keywords:** spatial resolution, space charge distribution

## Introduction

Direct and nondestructive space charge measurement methods provide information on the space charge build-up in dielectrics under voltage without requiring a model of knowledge. They are therefore very convenient for the study of new materials or structures comprising such materials. In their typical uses, however, the spatial resolution they can reach seems limited to a few microns. This is sufficient in most cases when dealing with high voltage structures, but interface phenomena or high field submitted dielectrics used in integrated devices for power switching for instance require a higher spatial resolution.

It was shown [1] that spatial resolution is limited by noise and excitation rise time in the case of propagation methods (PWP and PEA methods) and depth in the case of diffusion methods (Thermal methods). These limitations only depend on the implementation technique, which is why increasing the bandwidth has been proposed to overcome the problem. Unfortunately, spatial dispersion also increases with frequency, making conventional implementation techniques inefficient.

New setups were recently proposed in recent years to reach submicrometer spatial resolution or less. In this presentation, local probe scanning, electroacoustic reflectometry (EAR) and thermal pulse methods are discussed.

## Results and Discussion

When talking about spatial resolution, local probe scanning methods come to mind. They indeed show atomic resolution, but this is in the lateral dimensions. Information in depth are more difficult to reach due to invariance in translation of a planar layer of charges. Approach profiles can, however, be used to obtain information in depth [2].

The EAR method is a propagation method. Unlike PEA and PWP methods, the sample is excited frequency by frequency. Excitation and measurement are therefore more efficient over a broad spectrum. In addition, the measurement is based on an electrical impedance variation: it is not the product of

the interaction that is measured but the energy necessary to produce the interaction. Spatial dispersion due to the elastic coupling at the sample interfaces is therefore reduced. Micrometre or slightly less spatial resolution has been demonstrated [3] although the intrinsic dispersion of polymers may limit further enhancement.

If elastic waves require very large bandwidth for spatial resolution improvement and therefore a more complex measurement setup, a slower process might be more convenient to achieve high spatial resolution. In such a case, the thermal method may be recommended. However, the great influence of noise in the inverse problem calculation limits the confidence in the results. The measurement of the surface temperature reduces the degree of freedom of the problem and thus offers more reliable information in the nanometre range [4]. In addition signal processing in the time domain reduces the windowing effects.

## Conclusions

Current implementations of space charge measurement methods do not allow a high spatial resolution to be reached. Various approaches are tested concurrently and give interesting results although they are not completely ready for use yet.

## References

- [1] S. Holé, *Resolution of direct space charge distribution measurement methods*, IEEE Trans. Dielectr. E.I. 15, 861-871, 2008.
- [2] I. Alhossen *et al.*, *Sensitivity analysis of the electrostatic force distance curve using Sobol's method and design of experiments*, J. Phys D:Appl. Phys. 50, 035304, 2017.
- [3] E. Maréchal *et al.*, *Wide-band electrical and electromechanical properties of polyvinylidene fluoride (PVDF) and polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE) piezoelectric films using electroacoustic reflectometry*, J. Acoust. Soc. Am. 153, 2499-2505, 2023.
- [4] C. Filloy-Corbrion *et al.*, *Surface temperature measurement for space charge distribution measurements with thermal methods*, IEEE Trans. Dielectr. E.I., 22, 1506-1511, 2015.

# Isothermal charge decay in solid and 3D-printed polypropylene films

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**Abstract:** In the present work we investigate the processes of charge transport and storage in polypropylene films under isothermal conditions. The samples were manufactured either as solid films via heat-pressing, or as 3D-printed films in FDM filament printer. Isothermal surface-potential-decay measurements reveal much higher charge stability in 3D-printed samples. We attribute this to the increased number of interfaces, large surface area and, probably, surface modification via increased oxidation of said interfaces during printing.

**Keywords:** electrets, charge storage and transport, charge decay, additive manufacturing

## Introduction

Additive manufacturing (AM) is increasingly used to produce functional parts, with the most common method being fused deposition modeling (FDM) using polymers. While many studies have investigated the effects of FDM on the mechanical properties of printed parts [1], there is a gap in the literature regarding their electrical [2] and particularly electret properties [3]. This study aims to investigate the charge storage stability of polypropylene (PP) films manufactured via heat-pressing and FDM methods.

## Results and Discussion

Film samples were produced using a 3D-printing filament (Ultrafuse PP Natural, BASF) as a base material, with two sets manufactured using FDM printer (Raise 3D Pro) and the other two using a heat press (Vogt P200S). Both solid and 3D-printed films with a thickness of 200 $\mu$ m were placed on the aluminum foil to provide good electrical contact for electret measurements. Each set was charged with either -1kV or -2kV in corona discharge and then subjected to isothermal surface potential decay at 70°C. The measurements show that 3D printed films exhibit higher charge storage stability compared to heat-pressed films, with some significant variations in their curves. Moreover, the results indicate that samples with a charge density corresponding to the initial surface potential of -1kV exhibit more stable curves than those charged to -2kV.

Increased charge stability in FDM samples can be explained by the increased amount and depth of traps for the electret charge. As traps in polymers are often related to interfaces, 3D-printed films should have a higher concentration of both. Additionally, a larger surface area can increase the amount of charge that can be stored in a material. Furthermore, the increased oxidation of the interfaces in 3D-printed PP films can improve charge stability via creating deeper traps associated with oxygen-containing functional groups.

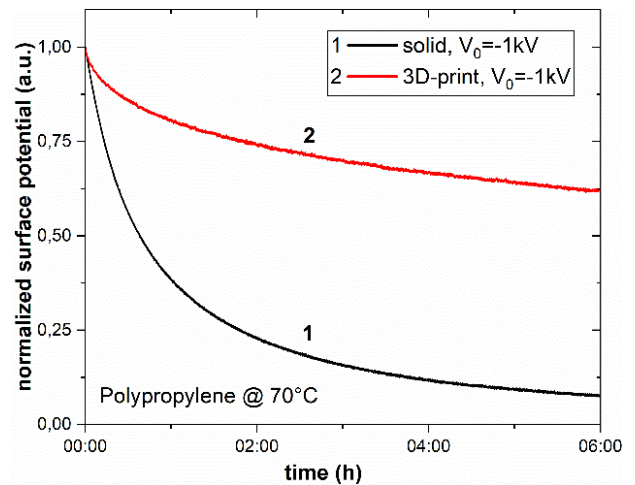


Figure 1: Isothermal surface potential decay in negatively charged polypropylene samples at 70°C. 1- solid film, 2- 3D-printed film.

## Conclusions

FDM printing, though a very useful and powerful production method, definitely changes the material properties compared to that of the bulk material. We have shown that 3D-printed polypropylene films possess much higher electret charge stability than the films produced in the usual way via heat-pressing.

## References

- [1] A. Bakır et al., "Mechanical properties of thermoplastic parts produced by fused deposition modeling: a review," *RPJ*, 27 (3), pp. 537–561, 2021.
- [2] A. Dijkshoorn et al., "Modelling of Anisotropic Electrical Conduction in Layered Structures 3D-Printed with Fused Deposition Modelling," *Sensors*, 21 (11), p. 3710, 2021.
- [3] Y. A. O. Assagra et al., "A new route to piezo-polymer transducers: 3D printing of polypropylene ferroelectrets," *IEEE TDEI*, 27(5), pp. 1668-1674, 2020.

## Acknowledgements

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# Multifunctional polymer-nanocellulose composites for energy harvest

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**Abstract:** To harvest kinetic energy, it is highly desirable to use flexible piezoelectrics. From environmental point view, renewable materials would be better to be used. Cellulose from biomass, among which cellulose nanocrystal (CNC) is piezoelectric and transparent, is renewable. In this study, a unique process is developed to fabricate polymer-CNC piezoelectric composites. The polymer-CNC composites with different compositions were prepared using the process. When the PVDF-based piezoelectric polymers are used, it is experimentally found that adding CNC can improve/enhance its insulation performance, dielectric and piezoelectric properties.

**Keyword:** cellulose nanocrystal, composite, piezoelectric, dielectric, energy harvest

## Introduction

Cellulose from biomass is renewable and green [1], among which cellulose nanocrystal (CNC) is piezoelectric with a high piezoelectric coefficient and transparent in visible range [1]. Therefore, a high electro-optic coefficient is also expected for the CNC. All these make the CNC a great candidate for the development of multifunctional materials. Harvesting kinetic/mechanical energy from environment is an important approach to meet the needs for energy, especially various localized devices and mobile devices/system. Using piezoelectric materials to harvest environmental kinetic energy is promising and has attracted a great deal of attention, but facing a critical challenge of the piezoelectric materials used that is either brittle or of a low piezoelectric coefficient. Therefore, CNC could be a promising candidate to meet this critical need. In this work, polymer-CNC composites are developed.

First, it is experimentally found that it is critical for the CNC to be per-treated to eliminate the water on the surface of CNC, for which a unique process is reported. Secondly, the orientation of CNC is the key for the composite to exhibit a high piezoelectric coefficient. A process is established to achieve an orientation degree of more than 90% [2]. Combining both processes, polymer-CNC composites with uniform structure were fabricated.

## Results and Discussion

As shown in Fig. 1, where the Polarization-Electric field loop (P-E loop) for the composite using P(VDF-HFP) with different CNC contents at their maximum electric field is presented, adding CNC can significantly improve the breakdown field and increase the permanent polarization that indicates a high piezoelectric response.

For piezoelectric materials, a high piezoelectric coefficient is usually associated with a high electro-optic coefficient. Therefore, the transparent

polymer-CNC composites can be a great candidate for the electro-optic applications.

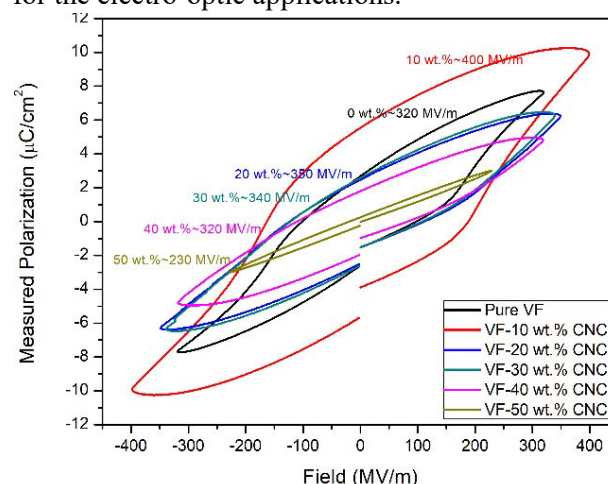


Figure 1: The P-E loop for P(VDF-HFP)-CNC composites with different CNC contents under their maximum electric field

## Conclusions

Polymer-CNC composites are promising for the development of flexible piezoelectric materials with a high piezoelectric coefficient. These composites can also be used to build high performance electro-optic devices.

## References

- [1] L. Csoka, I. C. Hoeger, O. J. Rojas, I. Peszlen, J. J. Pawlak, and P. N. Peralta, "Piezoelectric effect of cellulose nanocrystals thin films," *ACS Macro Letters*, vol. 1, no. 7, pp. 867–870, 2012.
- [2] M. Parit, P. Saha, V. A. Davis, and Z. Jiang, "Transparent and homogenous cellulose nanocrystal/lignin UV-Protection Films," *ACS Omega*, vol. 3, no. 9, pp. 10679–10691, 2018.

## Acknowledgements

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# Energy harvesting through piezoelectric polymeric nanofibers

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**Abstract:** One of the primary concerns regarding wearable electronic devices pertains to their power supply and autonomy. The harvesting of mechanical energy generated by body movement and vibrations can be achieved through the incorporation of piezoelectric materials into a suitable energy scavenging mechanism. For this purpose, 30 poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) 75/25 nanofibrous membranes were stacked and parallelly connected to charge a 1  $\mu\text{F}$  capacitor. The resulting stored energy of 30  $\mu\text{J}$  at 10 Hz could be an interesting feature for wearable applications.

**Keywords:** piezoelectric materials, energy harvesting, wearable devices

## Introduction

Small devices such as remote sensors or implantable medical systems still depend on batteries for their power source. For this reason, one of the most studied solutions in recent years is the possibility of recovering energy from the environment to replace batteries. Energy harvesting from piezoelectric materials has gained significant attention due to their potential to convert mechanical vibrations and movements into electrical energy. Among all the piezoelectric materials, piezopolymers have attracted enormous interest due to their great flexibility. Therefore, a possible solution is the use of piezopolymers in the shape of nanofibers, that can be manufactured via electrospinning. Nanofibers provide the advantage of high porosity, enabling their integration into hosting material, e.g., epoxy resin or polyurethane rubber, to fabricate multifunctional composite materials.

In this study, a stack of 30 P(VDF-TrFE) 75/25 nanofibers was employed to produce a flexible energy harvesting unit used to charge a 1  $\mu\text{F}$  capacitor at different excitation frequencies.

## Results and Discussion

Piezoelectric P(VDF-TrFE) 75/25 nanofibers were manufactured via electrospinning starting from a polymeric solution. To enhance the piezoelectric behavior of the nanofibrous mat, a poling process is then required. By soaking the nanofibers in an ester oil bath (FR3 natural ester, Cargill) and by applying an external electric field (20 kV/mm), the ferroelectric domains of P(VDF-TrFE) were aligned. The poling process took place for 10 min at 130 °C [1]. Piezoelectric samples were formed into a circular shape with a diameter of 20 mm and parallelly connected to increase the output current. An aluminum foil was used as electrodes to assemble a flexible energy harvesting unit.

A compressive sinusoidal force oscillating between 0 to 80 N was applied on the stack. The piezoelectric output current passed through a full-wave diode

bridge rectifier [2] and was used to charge a 1  $\mu\text{F}$  capacitor. Three different frequencies (2, 5 and 10 Hz) were tested, and the charging curves are reported in Figure 1.

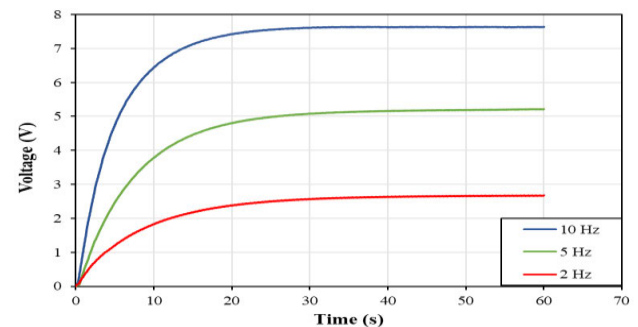


Figure 1: 1  $\mu\text{F}$  capacitor charging curves at three different frequencies (2, 5 and 10 Hz)

## Conclusions

A flexible stack of 30 P(VDF-TrFE) nanofibers samples was successfully assembled and implemented to charge a 1  $\mu\text{F}$  at different frequencies. By operating at a frequency of 10 Hz, a voltage of 7.73 V can be reached within 60 seconds, resulting in a stored energy of 30  $\mu\text{J}$ . This system could be aptly integrated into articles of clothing, backpack straps, or wearable devices to capture and harness energy that would otherwise be lost.

## References

- [1] G. Selleri *et al.*, “Study on the polarization process for piezoelectric nanofibrous layers,” *Annu. Rep. - Conf. Electr. Insul. Dielectr. Phenomena, CEIDP*, vol. 2021-Decem, pp. 61–64, 2021, doi: 10.1109/CEIDP50766.2021.9705470.
- [2] G. Selleri *et al.*, “Characterization of piezoelectric nanofibers for energy harvesting applications,” *Annu. Rep. - Conf. Electr. Insul. Dielectr. Phenomena, CEIDP*, vol. 2022-Novem, pp. 270–273, 2022, doi: 10.1109/CEIDP55452.2022.9985262.

## Acknowledgements

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**Tuesday, September 19<sup>th</sup>, 2023**

**SESSION 4**

<b>09:00</b>	<b>Session 4: Functional Materials and Dielectrics</b> <b>Chairs: Zhongyang Cheng, Takashi Nakajima</b>	Zhongyang Cheng <i>Functional dielectrics and materials</i>
<b>09:30</b>		François Bauer <i>Polarization response of PVDF under ultrahigh voltage</i>
<b>09:50</b>		Kailiang Ren <i>Tunable flexophotovoltaic effect in PVDF nanocomposites</i>
<b>10:10</b>		Ehtsham-UI Haq <i>Quantitative Surface Free Energy measurements in Electrets using Micro-Colloid Probe Pairs</i>
<b>10:30</b>		Min Sun <i>PMN-PT single-crystal derived ferroelectric optical fibers</i>

# Functional Dielectrics and Materials

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**Abstract:** Functional materials are the foundation for various sensors, actuators, and transducers. The majority of functional materials are the dielectrics. Therefore, high-performance functional dielectrics are the key for the development of next generation sensors, actuators, and transducers and should be a key research area for IEEE DEIS. Considering these, technical committee (TC) on functional dielectrics were established. The goal of this TC is to promote the research related to the functional dielectrics.

**Keyword:** Functional materials, dielectrics, sensors, actuators, transducers.

## Introduction

Materials play a critical role in the civilization. For example, the history is usually classified into the stone age, the bronze age, the iron age, and others. From engineering point of view, materials are primarily used to build a structure that can be mechanical structure (e.g., highway, buildings), electrical structure (e.g., power grid), and thermal structure (e.g., thermal insulation). The indicator of industry revolution I and II is the engine that provides power to mechanical structures. Engines are a kind of actuators that provide force or mechanical motion. The so-called high-tech devices are indicated by the usage of sensors. As the development of automation, signal/information is needed to be processed the operation of sensors and actuators. All sensors, actuators, and information process unit require power that mostly is electric power. Therefore, the conversion of energy in different forms into electric form is also critical. In other words, the engineering practices can be illustrated using Fig. 1.

## Results and Discussion

The functional materials/dielectrics are defined as the materials that exhibit coupling effects among thermal, mechanical, electrical, magnetic, and optical form of energy. In other words, for a functional material, the response and stimulus are belonged to different domains/forms of energy. For example, when different types of stimulus/input are applied to a functional material, its response can be mechanical, which is the foundation for the development of actuators. Due to the importance of functional dielectrics to current high-tech devices and systems and next-generation technologies, the Technical Committee (TC) was established under IEEE DEIS to tackle the issues facing current development of functional dielectrics [1].

The TC is working with different conferences or symposiums or meetings related to dielectrics on the efforts to promote the research and application of functional dielectrics through workshops, seminars, and focus sessions. The TC welcomes the comments and suggestions for any activities and topics for these activities.

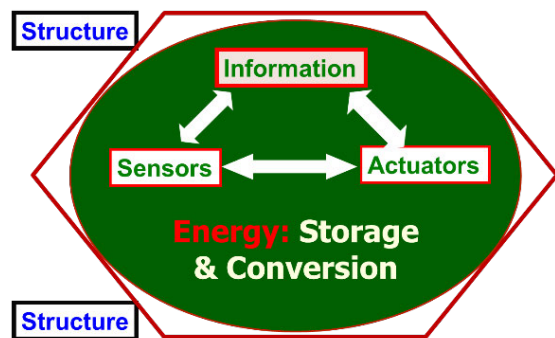


Figure 1: General engineering practices: building a structure, integrating sensors and actuators, adding information processing unit, and providing energy for last three.

## Conclusions

Functional materials/dielectrics are the foundation for the development of sensors and actuators that are the key for high-tech devices and systems and next generation technologies. To tackle the challenges facing the research, development, and applications of functional dielectrics, the TC on functional dielectrics was formed. The TC is working different meetings through workshops and special sessions to promote the research on functional dielectrics.

## References

- [1] X. Wei and Z.Y. Cheng, "Technical committees: Activities of the DEIS technical committee on functional dielectrics," *EEE Electrical Insulation Magazine*, vol. 36, no. 6, pp. 62–83, 2020.

## Acknowledgements

The TC on functional dielectrics is supported and governed by the IEEE DEIS.

# Polarization Response of PVDF under Ultrahigh Voltage

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**Abstract:** PVDF is widely used piezoelectric polymer and has been extensively studied. The polarization–electric field (P-E) loops of PVDF under different electric fields have been extensively studied. However, the polarization response of PVDF under ultrahigh electric field is studied and reported here. For PVDF under 600 MV/m, a remnant polarization of 11  $\mu\text{C}/\text{cm}^2$  was observed. For PVDF thick film with a thickness of 500  $\mu\text{m}$ , the P-E loops were obtained using ultrahigh voltage. Additionally, the abnormal peak observed in the DSC results of PVDF was explained.

**Keyword:** piezoelectricity, remnant polarization, P-E loop, PVDF

## Introduction

PVDF and P(VDF-TrFE) have been extensively studied and are widely used as the piezoelectric materials. These polymers under low and high electric fields have been reported. However, the P-E loop of these polymers under ultrahigh electric field was barely studied. Additionally, for the thick film of these polymer, due to the need of a ultrahigh electric field, there is no report on the P-E loop, by the best of our knowledge. These are very important from the application point of view and was heavily discussed at ISE-17 in Limerick, Ireland.

## Results and Discussion

In this work, bi-axially stretched PVDF films with a thickness of 25  $\mu\text{m}$  were prepared and characterized. Based on the P-E loops, it is experimentally found that the remnant polarization of these PVDF films under 600 MV/m is 11  $\mu\text{C}/\text{cm}^2$ .

For the thick films of piezoelectric polymers, an ultrahigh voltage is needed to obtain the P-E loops. That is why there is no report of the P-E loops of PVDF and P(VDF-TrFE) thick film. Here, the uni-axially stretched thick films of these polymers with a thickness of 500  $\mu\text{m}$  were prepared and characterized. The polarization curves of PVDF thick films are presented.

Although DSC results of P(VDF-TrFE) have been extensively reported, these studies were focused on the phase transition between the high-temperature paraelectric phase and low-temperature ferroelectric phase. However, a small/weak-peak, which is not due to the melting process and neither phase transition between the paraelectric and ferroelectric phase observed. For example, a small/weak DSC peak was observed at the temperature abscissa of 50-60°C in the copolymer P(VDF-TrFE) with 60% in mole of PVDF or with higher PVDF content (70%) by Dr. Thulasinath Raman Venkatesan and Prof. Reimund Gerhard [1]. Unfortunately, no much attention was paid to develop the understanding about this. In this work, a detailed study was carried out, which results in an understanding of the small/weak DSC peak at 50-60°C.

Based on these results, a short note about the “theoretical copolymerization” is presented at the end and will try to shed some light about this peak.

## Conclusions

PVDF and P(VDF-TrFE) films were prepared and characterized under ultrahigh voltage. For the bi-axially stretch PVDF film (25  $\mu\text{m}$  in thickness), a remnant polarization of 11  $\mu\text{C}/\text{cm}^2$  was obtained under 600 MV/m. For the uni-axially stretched thick films (500  $\mu\text{m}$  in thickness) the polarization response were reported. An abnormal DSC peak that is small/weak had been reported in 50-60°C for with 60-70 mole fraction of PVDF. “theoretical copolymer” was introduced and used to understand the abnormal DSC peak. Experimental data show DSC with no abnormal peak;

## References

- [1] Thulasinath Raman Venkatesan, Reimund Gerhard, “Origin of the mid-temperature transition in vinylidene fluoride-based ferro-, pyro- and piezoelectric homo-, co- and ter-polymers,” *Materials Research Express*, vol. 7, no. 6, pp. 065301, 2020.
- [2] F. Bauer et al., Brevet 05 08050, US Patent 2007/0167590 A1

## Acknowledgements

I am so proud to insert in this manuscript part of the text that we wrote with Prof. Siegfried Bauer for publication. I cannot forget Jean Blaise of Arkema, a genius engineer of who taught me the polymerization of copolymer.

Thanks to Professor Zhongyang (Z.-Y.) Cheng, Ph.D. McWane Professor, Materials Engineering and Mechanical Engineering. who help me a lot in writing this abstract for being in time with the deadline.

# Tunable flexophotovoltaic effect in 3D-printed BaTiO<sub>3</sub>/PVDF nanocomposite and its application in flexible ferroelectric memory

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**Abstract:** Recently, tremendous research effort was devoted to the flexophotovoltaic effect, in which photovoltaic current can be modulated by flexoelectricity. In this investigation, we considered the combination of BaTiO<sub>3</sub> ceramics and PVDF to fabricate a flexible BaTiO<sub>3</sub>/PVDF composite film device using direct ink writing (DIW) 3D printing technology. Moreover, the effects of flexoelectricity on the generation and transport of carriers during the bending process of the composite film were investigated based on finite element analysis and phase field simulations. At last, the BaTiO<sub>3</sub>/PVDF-15 composite film was designed as flexible ferroelectric memory. Four storage units was designed with the CAD software. Each storage unit contains 3×3 information storage points. The high flexibility, excellent optoelectronic properties and simple device fabrication process makes it possible to applied the device in the emerging foldable displays, photodetection and smart wearable devices, etc.

**Keywords:** Flexophotovoltaic effect, 3-D printed PVDF nanocomposites, ferroelectric memory;

## Introduction

Recently, tremendous research effort was devoted to the flexophotovoltaic effect, in which photovoltaic current can be modulated by flexoelectricity. In this investigation, we considered the combination of BaTiO<sub>3</sub> ceramics and PVDF to fabricate a flexible BaTiO<sub>3</sub>/PVDF composite film device using direct ink writing (DIW) 3D printing technology. Through the doping of high dielectric constant BaTiO<sub>3</sub> (BTO),  $\mu_{12}$  of the composite film can be greatly improved. In addition, the distance between the particles can be continuously adjusted by controlling the content of BTO nanoparticles using 3-D printing technology. In addition, PVDF requires a higher excitation light frequency for the photovoltaic current. The additional BTO nanoparticles can reduce the required excitation frequency and broaden the frequency range of light absorption.

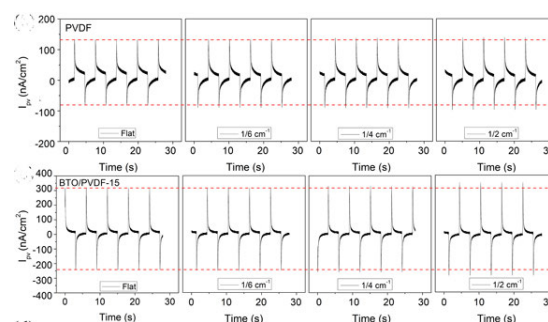
## Results and Discussion

Fig. 1(b) shows the photovoltaic current of the pristine PVDF films as a function of curvature. Compared with the flat state,  $I_{pv}$  of the pristine PVDF film increased by 10.38% (11.15 nA/cm<sup>2</sup>) to 118.47 nA/cm<sup>2</sup>, when the curvature reached 1/2 cm<sup>-1</sup>. Similarly,  $I_{pv}$  of BaTiO<sub>3</sub>/PVDF-15 increased by 13.51% (37.9 nA/cm<sup>2</sup>) to 316.56 nA/cm<sup>2</sup> compared with that of the flat BaTiO<sub>3</sub>/PVDF-15 film (Fig. 1(c)). Compared with that of pristine PVDF,  $\Delta I_{pv}$  of the BaTiO<sub>3</sub>/PVDF-15 composite film increased by 3.4 times, which was mainly ascribed to the increased flexoelectricity in the BaTiO<sub>3</sub>/PVDF-15 composite film.

## Conclusions

We investigated the flexoelectricity-enhanced photovoltaic effect (FPV) in 3D-printed

BaTiO<sub>3</sub>/PVDF composite films. Compared with the flat state,  $I_{pv}$  of the pristine PVDF film increased by 10.38% from 107.32 nA/cm<sup>2</sup> to 118.47 nA/cm<sup>2</sup> with a curvature of 1/2 cm<sup>-1</sup>. Compared with the pristine PVDF film at the same curvature,  $\Delta I_{pv}$  of the BaTiO<sub>3</sub>/PVDF-15 composite film increased by 3.4 times.



**Fig. 1.** (a) photovoltaic current ( $I_{pv}$ ) of positively poled (+120 MV/m) (b) PVDF and (c) BaTiO<sub>3</sub>/PVDF-15 as a function of curvature,

## References

B. Zhang, et al. **K. Ren\***, Flexoelectricity on the Photo-voltaic and Pyroelectric Effect and Ferroelectric Memory of 3D-Printed BaTiO<sub>3</sub>/PVDF Nanocomposite, *Nano Energy*, 104, 107897, 2022.

## Acknowledgements

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# Quantitative Surface Free Energy measurements in Electrets using Micro-Colloid Probe Pairs

Ehtsham-Ul Haq<sup>1</sup>, Yongliang Zhang, Stanislav Leesment<sup>2</sup>, Ning Liu<sup>1</sup>, Claude Becker<sup>4</sup>, Syed A. M. Tofail<sup>1</sup> and Christophe Silien<sup>1</sup>

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**Abstract missing:**

## Introduction

Surface charge and free energy of surfaces are important in electrets as well as it is critical to control wetting, adhesion, and friction properties in tribology, photonics, scaffold materials, particles for drug delivery and bio-coatings [1]. Development and validation of standardized, quantitative methods to reliably measure surface properties at relevant length scales remains an industry requirement to account for important contact phenomena such as adhesion and friction [4]. Here, a protocol for quantitative measurements and mapping of the surface free energy is presented, which reliably connects measurements at the micrometer scale to conventional measurements at the macroscopic scale [5].

## Results and Discussion

A microscale Atomic Force microscopy (AFM) colloidal probes attached onto a cantilever, the bending of which allows measuring the total force of interaction between the tip and the surface of a specimen of interest is exploited. In general, quantitative SFE measurement with AFM is hampered by relatively poor precision due to unknown tip relevant properties (e.g., geometry, contact geometry, surface physical chemistry, etc.) and, more importantly, the reliance on contact models to compute SFE from AFM observed metrics (pull-off force, snap-in, etc.). The study resulted in the development of a methodology that employs two colloidal probes (10 microns silica colloid and 10 microns polystyrene (PS) colloid, contact area: ca. 1 micron diameter). The colloids are complementary, and they operate in tandem to refine the SFE outcome. A series of laterally homogenous calibration specimens with contact-angle SFEs are then measured in order to calibrate a regression of AFM-derived main components onto the corresponding contact-angle SFEs. This indicates that the SFE is calculated using a single model derived from the contact angles (Owen Wendt's model) (Figure 1). The feasibility of the relevance of this SFE analysis protocol to materials of biological origin is demonstrated on drop casted

Methionine peptide crystals from water and ethanol solution on a clean ITO coated glass substrate.

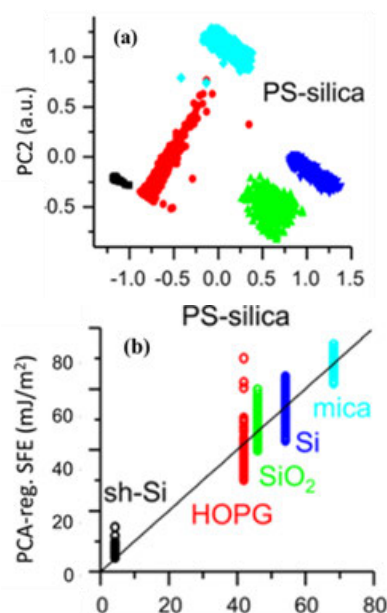


Figure 1 (a) PC2 versus PC1 scatter plots for the training set with PS and Silica colloids. The data for sh-Si are shown in black, HOPG in red, silica in green, silicon in blue, and mica in cyan. (b) Second-order regression of the PC1, PC2, and PC3 values on the CA-derived SFE values for the testing set with PS and Silica colloid.

## Conclusions

A method is described for quantitatively measuring and mapping the surface free energy. The method is particularly useful for bioelectrets, such as hydroxyapatite, Polyvinylidene fluoride (PVDF) and biological crystals where no other reliable method is available for SFE characterization.

## References

[1] E. Haq et al. Quantitative surface free energy with micro-colloid probe pairs. RSC advances (2023).

## Acknowledgements

European Union's Horizon 2020 research and innovation program, OYSTER (Open characterisation and modelling environment to drive innovation in advanced nanoarchitected and bio-inspired hard/soft interfaces) under grant agreement No 760827.

# PMN-PT single-crystal derived ferroelectric optical fibers

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**Abstract:** Single-crystal-derived ferroelectric optical fibers are fabricated by a reactive melt-in-tube thermal drawing method, combining a PMN-PT single crystal and a silicate glass tube into an optical-fiber preform. They demonstrated a graded index optical waveguide, a suitable numerical aperture, and a low transmission loss.

**Keywords:** ferroelectrics, single-crystal-derived, optical fiber, functional fiber materials

## Introduction

Ferroelectrics have excellent properties of piezoelectric, acousto-optic, electro-optic, photorefractive, and optical nonlinear, which have been widely used in the field of the optical waveguide, electro-optic modulator, and optical frequency transformation, etc [1]. Ferroelectric materials with one-dimensional optical waveguides are desirable, however, ferroelectric optical fibers have rarely been reported due to the challenge of combining the fiber core of high-refractive-index ferroelectrics and the cladding of low-refractive-index glass/crystal [2]. This is significant for the optical-fiber waveguide, miniaturization, and high efficiency of ferroelectric optical devices.

## Results and Discussion

After combining a PMN-PT single crystal of relaxor ferroelectrics and a silicate tube of optical glass into an optical-fiber preform, the single-crystal derived ferroelectric optical fibers are reported and fabricated by a reactive melt-in-tube (RMIT) thermal drawing method. Through the focused ion beam, transmission electron microscope, and piezo-response force microscopy, the fibers are found being micro-nano ferroelectric crystals in a glass matrix with hierarchical coral morphology during the fiber thermal drawing process. The multimaterial fibers exhibit a graded index optical waveguide, a suitable numerical aperture ( $NA \sim 0.29$ ), and a low transmission loss ( $L < 1.5$  dB/cm at 1.0  $\mu\text{m}$  and 1.5  $\mu\text{m}$  wavelength). Nonlinear optical experiments are underway.

## Conclusions

Multimaterial Single-crystal-derived ferroelectric optical fibers are prepared via an RMIT thermal drawing method. The multimaterial optical fibers with micro-nano ferroelectric crystals possess a graded index optical waveguide and a low transmission loss. And they are potential to be applied in the devices of the one-dimensional optical waveguide, micro electro-optic modulator, and nonlinear optical frequency transformation.

## References

- [1] X. Liu, P. Tan, X. Ma, et al. "Ferroelectric crystals with giant electro-optic property enabling ultracompact Q-switches" *Science*, 376, 371–377, 2022.
- [2] J. Wang and Y. Tseng. "ITO electrode-embedded double-cladding single-crystal LiNbO<sub>3</sub> optical fiber" *Optics Letters*, 38 (4), 452, 2013.

## Acknowledgements

We acknowledge Mr. Shaodong Cheng and Dr. Qingyuan Hu in Electronic Materials Research Laboratory of Xi'an Jiaotong University for their help with the focused ion beam, transmission electron microscope, and piezo-response force microscopy.

**Tuesday, September 19<sup>th</sup>, 2023**

**SESSION 5**

<b>11:10</b>	<b>Session 5</b> <i>Chairs: Takeo Furukawa, Thulasinath Raman Venkatesan</i>	Daisuke Yamane <i>Evaluation of Micropatterned Self-Assembled Electrets for MEMS Devices</i>
<b>11:30</b>		Yuya Tanaka <i>Self-assembled electret for vibrational energy harvester</i>
<b>12:00</b>		Tomoya Miyoshi <i>Development of skin-attached stretchable energy harvester with perfluoroelastomer electret</i>
<b>12:20</b>		Sebastian Engel <i>Influence of optical excitation on the ferroelectric properties of ferroelectric-semiconductor hybrid materials</i>

# Evaluation of Micropatterned Self-Assembled Electrets for MEMS Devices

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**Abstract:** In this paper, we present evaluation results of micropatterned unsublimated self-assembled electrets (SAEs) for microelectromechanical systems devices. We develop dedicated test chips, and experimental results suggest that even unsublimated Alq<sub>3</sub> has a surface potential comparable to that of sublimed Alq<sub>3</sub>. Both simulation and measurement results indicate that the micropatterning attenuates the surface potential of the SAEs when evaluated with Kelvin probes.

**Keywords:** self-assembled electret, through hole, microelectromechanical systems

## Introduction

Environmental vibration energy harvesters (VEHs) using electrets are expected to be stand-alone power sources in low-power wireless sensor terminals [1]. Self-assembled electrets (SAEs) are deposited at room temperature in the semiconductor process and could be integrated with various devices [2]. To use SAEs in VEHs, it is useful to form electrets inside small VEHs such as microelectromechanical systems (MEMS) devices, and to improve productivity with low-cost materials. So far, we have developed a technology to form micropatterned SAEs within MEMS devices [3]. In this paper, we report evaluation results of micropatterned SAEs using unsublimated Alq<sub>3</sub> for lower-cost SAEs.

## Results and Discussion

We used unsublimated Alq<sub>3</sub> (purity >98.0%, Tokyo Chemical Industry Co., Ltd.) as an SAE, and developed test chips with removable through-hole structures. First, the surface potential of the SAE flat film over 4- $\mu\text{m}$  thick was evaluated with a Kelvin probe (UHVKP020, KP Technology), and found to increase in proportion to the film thickness (47 V/ $\mu\text{m}$ ) which was comparable to the performance of the sublimed Alq<sub>3</sub> [4]. Next, the surface profiles of the micropatterned SAEs were evaluated and found to be deposited at about 120  $\mu\text{m}$  square with 40  $\mu\text{m}$  spacing. The SAE film profiles were not flat, and the average film thickness was about 1.67  $\mu\text{m}$ . Compared to the same amount of SAE per unit area, finite element simulations using COMSOL Multiphysics 6.1 showed that the micropatterning attenuated the surface potential by about 15%. Experimental results also confirmed the attenuation of SAE surface potential by the micropatterning, although the rate of attenuation was larger than the simulation results. The number of samples and experimental conditions will be increased to investigate the details in the future.

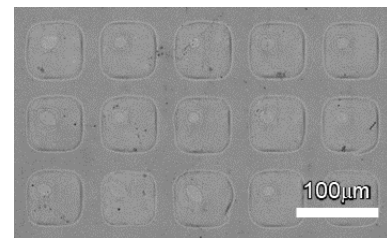


Figure 1: Photo of micropatterned unsublimated SAEs.

## Conclusions

We evaluated the micropatterned unsublimated SAEs, and the results suggested that the surface potential of the SAEs was almost the same as that of the sublimed ones. In the Kelvin probe evaluation, the attenuation of the SAE surface potential due to the micropatterning was confirmed both experimentally and by simulation.

## References

- [1] Y. Suzuki, "Recent progress in MEMS electret generator for energy harvesting," *IEEJ Trans. Elec. Electron. Eng.* 6(2), 101-111, 2011.
- [2] Y. Tanaka, N. Matsuura, and H. Ishii, "Self-assembled electret for vibration-based power generator," *Sci. Rep.* 10, 6648, 2020.
- [3] D. Yamane, H. Kayaguchi, K. Kawashima, H. Ishii, and Y. Tanaka, "MEMS post-processed self-assembled electret for vibratory energy harvesters," *Appl. Phys. Lett.* 119, 254102, 2021.
- [4] E. Ito, Y. Washizu, N. Hayashi, H. Ishii, N. Matsue, K. Tsuboi, Y. Ouchi, Y. Harima, K. Yamashita, and K. Seki, "Spontaneous buildup of giant surface potential by vacuum deposition of Alq<sub>3</sub> and its removal by visible light irradiation," *J. Appl. Phys.*, 98, 7306-7310, 2002.

## Acknowledgements

This work was supported in part by the Adaptable and Seamless Technology transfer Program through Target-driven R&D (A-STEP) from the Japan Science and Technology Agency (JST) Grant Number JPMJTR22R5, JSPS KAKENHI 22H01929, 21K05208, and 20H02810, and Grant-in-aid by Samco Foundation, Japan.



# Self-assembled electret for vibrational energy harvester

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**Abstract:** The surface potential of a thin film of 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi), which is a typical molecule used in organic light-emitting diodes, linearly increases with the film thickness due to the spontaneous orientation of the permanent dipole of TPBi. Recently, we demonstrated that TPBi can be used as an electret for vibrational energy harvesting (VEH). This means that TPBi can be regarded as a self-assembled electret (SAE). The advantage of an SAE-based VEH is that no charging process is needed during device fabrication. We believe that the application of SAEs will lead to the dissemination of VEH technology.

**Keywords:** Spontaneous orientation polarization, Giant surface potential, Self-assembled electret, Vibrational energy harvester, organic light-emitting diode, polar organic molecules

## Introduction

Organic light-emitting diodes (OLEDs) have attracted attention due to their potential applications. To understand the operating mechanism of OLEDs, it is essential to evaluate the internal potential distribution as it determines the charge behaviour inside the devices. In 2002, Ito et al. found that the surface potential of a vacuum-evaporated film of tris-(8-hydroxyquinolino)aluminium (Alq<sub>3</sub>) (Fig. 1(a)), which is a typical light-emitting material for OLEDs, linearly increased with the film thickness and reached 28 V at a film thickness of 560 nm [1]. Moreover, they revealed that this giant surface potential (GSP) originates from the spontaneous orientation of the permanent dipole of Alq<sub>3</sub>, as demonstrated by the use of second harmonic generation. This result suggests that positive and negative polarization charges exist on the film surface and reverse side, respectively (Fig. 1(b)). This phenomenon is named spontaneous orientation polarization (SOP), and after the discovery of the SOP in Alq<sub>3</sub>, much effort has been devoted to clarifying the mechanism of spontaneous orientation and the role of polarization charge in OLED [2], although Alq<sub>3</sub> is expected to be applied to a variety of devices because the GSP appears without the requirement of any charging process.

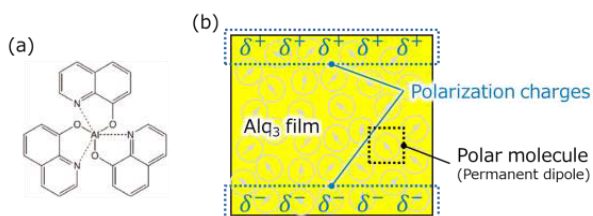


Figure 1: Alq<sub>3</sub>, (b) vacuum deposited film of Alq<sub>3</sub>.

## Results and Discussion

We inserted 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi), which is also an OLED molecule (Fig. 2(a)), between fixed and movable electrodes (Fig. 2(b)). We observed that a current flowed during the vibration of the movable electrode (Fig. 2(c)).

These results suggest that TPBi can be utilized to realize electret-based vibrational energy harvesters (VEHs) without the need for any charging process.

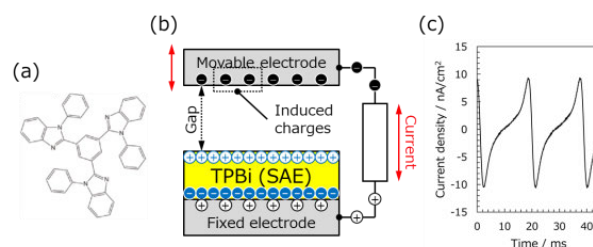


Figure 2(a) TPBi, (b) VEH, (c) generated current during TPBi-based VEH operation.

## Conclusions

We have demonstrated electret-based VEHs without requiring any charging process by utilizing TPBi which exhibits SOP. This result suggests that molecules demonstrating GSP, such as Alq<sub>3</sub> and TPBi, can be considered as self-assembled electrets (SAE). In this talk, we will discuss the mechanism of SOP in SAE and their applications.

## References

- [1] E. Ito et al., "Spontaneous buildup of giant surface potential by vacuum deposition of Alq<sub>3</sub> and its removal by visible light irradiation," *J. Appl. Phys.*, 98, 7306, 2002.
- [2] Y. Noguchi, Y. Tanaka et al., "Understanding spontaneous orientation polarization of amorphous organic semiconducting films and its application to devices", *Synth. Met.*, 288, 117101, 2022.
- [3] Y. Tanaka, N. Matsuura, H. Ishii, "Self-assembled electret for vibration-based energy generator", *Sci. Rep.* 10, 6648 (2020).

## Acknowledgements

Y.T. thanks Prof. Hisao Ishii in Chiba University and Prof. Daisuke Yamane in Ritsumeikan University for their helpful suggestions. This research was supported by the Japan Science and Technology Agency (JST), A-STEP (Grant No. JPMJTR22R5), and KAKENHI (Grants Nos. 22H01929, 21K05208, 20H02810).

# Development of Skin-Attached Stretchable Energy Harvester with Perfluoroelastomer Electret

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## Introduction

Skin electronics have been highly desired for applications in biomedical, sports, and healthcare [1]. Kinetic energy harvesting has been attracting attention as an independent power source for skin-attached electronics [2]. While an earlier developed stretchable piezoelectric energy harvester has limited output power [3], the recent development of fluorinated electret elastomer, which is as stretchable as typical silicone rubber with high surface charge density, has opened up high output power generation from skin stretch [4].

In the present study, we develop a stretchable electret energy harvester with intrinsically-stretchable fluorinated electret to capture the kinetic energy of stretching motion of human skin.

## Results and Discussion

Figure 1 shows a schematic of a stretchable electret energy harvester. We employ perfluoro-elastomer FFKM, which exhibits a record-high surface charge density of  $0.74 \text{ mC/m}^2$ , as well as an almost linear stress-strain curve with maximum elongation reaching 220 % [4].

The output power of stretchable electret energy harvester is estimated by FEM simulation with COMSOL. The electrode width is  $200 \mu\text{m}$ , and their gap is  $50 \mu\text{m}$ , while the substrate thickness is  $100 \mu\text{m}$ . The area of the interdigitated electrodes is  $2 \text{ cm} \times 2 \text{ cm}$ . With a simulation condition of a 20 % strain amplitude vibration at 1 Hz, the current amplitude of 14 nA is obtained over the  $2 \text{ G}\Omega$  load at the surface voltage of 1.4 kV, which corresponds to the output power of  $0.4 \mu\text{W}$ . In addition, the output power can be further enhanced by strengthening the fringe field using a high permittivity layer on the top [5].

Figure 2 shows the prototype of the skin-attachable energy harvester using the stretchable electret. Interdigital electrodes are microfabricated on the FFKM film using standard lithography. The electrode features a width of  $30 \mu\text{m}$ , and the gap between adjacent electrodes measures  $20 \mu\text{m}$ .

## Conclusions

A stretchable electret energy harvester has been developed by employing perfluoro-elastomer FFKM. The simulated output power is up to  $0.1 \mu\text{W/cm}^2$  at 1 Hz stretching motion. The early prototype has been successfully microfabricated through the MEMS processes.

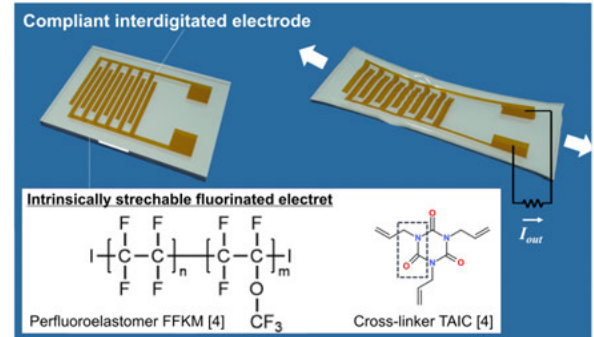


Figure 1: Schematic of stretchable electret energy harvester with perfluoroelastomer FFKM.

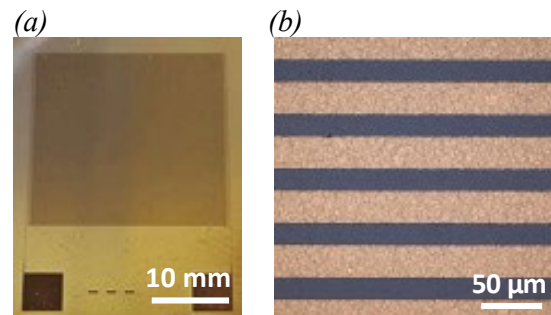


Figure 2: Photograph of stretchable electret energy harvester prototype. (a) Overall view, (b) Magnified view.

## References

- [1] J. C. Yang, et al., "Electronic Skin: Recent Progress and Future Prospects for Skin-Attachable Devices for Health Monitoring, Robotics, and Prosthetics," *Adv. Mater.*, Vol. 31, 1904765, 2019.
- [2] A. Petritz et al., "Imperceptible energy harvesting device and biomedical sensor based on ultraflexible ferroelectric transducers and organic diodes," *Nature Comm.*, 12, 2399, 2021.
- [3] Y. Suzuki, "Recent Progress in MEMS Electret Generator for Energy Harvesting," *IEEJ Trans. Electr. Electron. Eng.*, Vol. 6, pp. 101-111, 2011.
- [4] R. Wang, et al., "Intrinsically-stretchable Polymer Electret for Powering Skin Electronics," *PowerMEMS 2022*, Salt Lake City, T1A-01, 2022.
- [5] M. Takebe, et al., "Stretchable Electret Energy Harvester Using the Fringe Field," *PowerMEMS 2022*, Salt Lake City, PT-10f, 2022.

## Acknowledgements

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# Influence of optical excitation on the ferroelectric properties of ferroelectric-semiconductor hybrid materials

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**Abstract:** Ferroelectric-semiconductor hybrid materials have been investigated in terms of their structure as well as their photoconductive and ferroelectric properties. For this purpose, CdSe quantum dots (QD) were dispersed in a solution of 70/30 P(VDF-TrFE) in N-Methylformamid. The hybrid films exhibited a polarization behaviour dependent on optical excitation intensity while maintaining high optical transparency. These hybrid materials are of particular interest for future applications in the field of small and flexible sensors and actuators.

**Keywords:** ferroelectrics, semiconductor, hybrid material, quantum dots, photoconductivity, optical excitation

## Introduction

In the future suitable sensors and actuators have to become smaller and more flexible with simultaneous inconspicuousness (transparency). For this purpose, ferroelectrics represent an ideal basic material, because of their intrinsic pyro- and piezoelectric properties. It was shown that in (Cd:Zn)S-P(VDF-TrFE) composites these properties can be influenced by optical excitation.<sup>[1,2]</sup> However, the required optimum amount of 10 vol% (Cd:Zn)S particles results in yellow colored opaque films (Fig. 1a). In order to generate a more homogeneous dispersion of the semiconductor phase and therefore a better photoconductive performance, functionalized CdSe-QD were dispersed in P(VDF-TrFE) for the first time regarding their ferroelectric properties under optical excitation (Fig. 1b). Structure and ferroelectric behavior have been investigated by optical microscopy, x-ray diffraction, REM, spectroscopy, (optically excited) I-U curves, ferroelectric hysteresis and measuring the pyroelectric coefficient.

## Results and Discussion

QD-P(VDF-TrFE) hybrid materials with different contents CdSe-QD and a film thickness of about 22  $\mu\text{m}$  have been prepared by compression molding. After annealing, no influence of the amount of the QD on the degree of crystallization was determined.

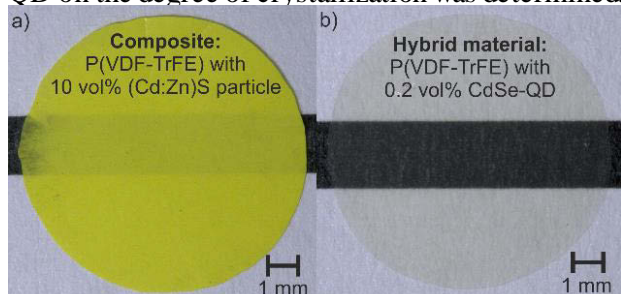


Fig. 1: Samples of ferroelectric-semiconductor films a) composite and b) hybrid material

The QDs were specifically synthesized so that their optical properties (Fig. 2a), especially the absorption behavior, were partly comparable to that of the (Cd:Zn)S-particles. Thus an optical excitation at  $\lambda = 470 \text{ nm}$  could also be performed.<sup>[2]</sup> But regarding the photoconductivity a dramatic influence of the QDs on the hybrid materials could be observed. Hybrid

films with a volume fraction of 0.2 vol% of CdSe-QD already showed similar photoelectric conductivity as composites with a semiconductor content of 10 vol% (Cd:Zn)S-particles. With this low proportion of the inorganic phase, these hybrid materials are very transparent. At the same time, the specifically adjusted photoelectric properties allow the polarization to be triggered by the optical excitation intensity (Fig. 2b). This innovative way of adjusting the ferroelectric behavior by a combination of optical excitation intensity and electric field strength was confirmed by determination of the pyrocoefficient (Fig. 2 b).

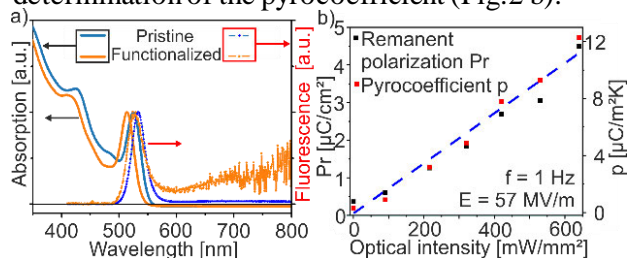


Fig. 2: a) Optical properties of the CdSe-QD and b) adjustment of the ferroelectric properties of the QD-P(VDF-TrFE) hybrid material by optical excitation.

## Conclusions

The homogeneous distribution of the very small amount of CdSe-QDs within the ferroelectric-semiconductor hybrid material enabling the control of the ferroelectric properties by the intensity of the optical excitation with a high transparency at the same time.

## References

- [1] S. Engel, D. Smykalla, Ploss, S. Gräf. and F. A. Müller, "Effect of (Cd: Zn) S Particle Concentration and Photoexcitation on the Electrical and Ferroelectric Properties of (Cd: Zn) S/P (VDF-TrFE) Composite Films". *Polymers* **9**, 650 (2017)
- [2] S. Engel, D. Smykalla, b. Ploss, S. Gräf. and F. A. Müller, "Polarization Properties and Polarization Depth Profiles of (Cd: Zn) S/P (VDF-TrFE) Composite Films in Dependence of Optical Excitation". *Polymers* **10**, 1205 (2018)

## Acknowledgements

DFG is thankfully acknowledged for financial support (EN 1331/1-1).

**Tuesday, September 19<sup>th</sup>, 2023**

**SESSION 6**

13:55		<p>Shihai Zhang  <i>A new class of relaxor ferroelectric polymer exhibiting ultrahigh electromechanical response at low electric field</i></p>
14:15	<p>Session 6: Siegfried Bauer lives on –          Contributions by his closest friends          Chair: Martin Kaltenbrunner</p>	<p>Bernd Ploss  <i>Influence of preparation conditions on structure and ferroelectric properties of thin VDF-TrFE copolymer film</i></p>
14:45		<p>Reimund Gerhard  <i>Electret charges and/or dipoles on dielectrics plus elastical and thermal materials properties</i></p>
15:15		<p><b>COFFEE BREAK</b></p>
15:35		<p>Michael Wübbenhorst  <i>Thermal wave based charge and polarization profiling - how to achieve nanometer resolution?</i></p>
16:05		<p>Reinhard Schwödauer  <i>Electrostatic converter with an electret-like elastomer</i></p>
16:35		<p>Christoph Keplinger  <i>Artificial muscles for the lifelike robots of the future</i></p>

# A New Class of Relaxor Ferroelectric Polymer Exhibiting Ultrahigh Electromechanical Response at Low Electric Field

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**Abstract:** We report a new class of relaxor ferroelectric polymers, poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene-fluorinated alkyne) (PVDF-TrFE-CFE-FA) tetrapolymer, that generate giant electrostriction at fields below 50 MV/m. Moreover, under a low DC bias of 20 MV/m, the tetrapolymer with about 2 % FA exhibits the electromechanical coupling factor  $k_{33}$  of 71% and the piezoelectric coefficient  $d_{33}$  value over 1,100 pm/V.

**Keywords:** relaxor ferroelectric polymers, electromechanical responses, critical phenomena

## Introduction

Owing to their high pliability, easy fabrication into complicated shapes and large areas, light weight, and low cost, ferroelectric polymers are attractive for a broad range of electromechanical (EM) applications such as acoustic transducers for imaging, ship navigation, sensors and artificial muscles in robots, and energy harvesting. On the other hand, the low EM properties of polymers, compared with inorganic counterparts, limit the device performance. In the late 1990s and early 2000s, relaxor ferroelectric polymers such as P(VDF-TrFE-CFE) terpolymer were developed which generate giant electrostriction under high electric fields.<sup>[1,2]</sup> Recently, it was discovered that converting small amount of CFE in P(VDF-TrFE-CFE) to FA bonds can markedly reduce the applied electric fields in generating the giant electroactuation.<sup>[3]</sup> Here, we present electromechanical responses of this new class of relaxor polymers. We will also report the study of possible origins underpinning the large EM responses at low electric fields in P(VDF-TrFE-CFE-FA) tetrapolymers.<sup>[4]</sup>

## Results and Discussion

For electromechanical applications, it is highly desired that a large electroactuation is generated at low electric fields (electric fields much below the electric breakdown field). Presented in Fig. 1 is a comparison of the thickness strains of P(VDF-TrFE-CFE-FA) 63.6/30/4.4/2 mol% tetrapolymer and the P(VDF-TrFE-CFE) terpolymer.<sup>[1-3]</sup> The data show a significantly enhanced electroactuation strain of the tetrapolymer, especially at low electric fields, compared with the state-of-the-art relaxor terpolymer. For instance, under 50 MV/m, the tetrapolymer generates a strain of more than 4%, which is about 4X of that generated by the terpolymer. Moreover, the tetrapolymer also exhibits a large piezoelectric  $d_{33}$  and electromechanical coupling factor  $k_{33}$  at low DC bias fields, see Table 1. These  $d_{33}$  and  $k_{33}$  values are

even larger than that of the piezoelectric PZT ceramics, which is the most widely used piezoceramics in the world.

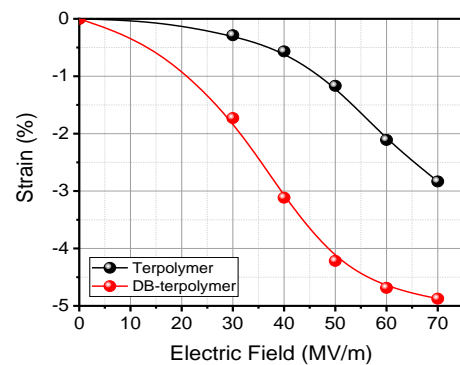


Figure 1: Comparison of the thickness strain vs applied field between the new relaxor polymer, e.g., P(VDF-TrFE-CFE-FA) tetrapolymer, and the SOA P(VDF-TrFE-CFE) terpolymer.

Table 1. Electromechanical properties of a P(VDF-TrFE-CFE) tetrapolymer at DC biased states.  $K$  is the dielectric constant

DC bias	$d_{33}$ (pm/V)	$K$	$k_{33}$
20 MV/m	-1177	64	71%
30 MV/m	-1280	60	80%
40 MV/m	-1100	47	78%

We investigated the evaluation of the relaxor behavior of the tetrapolymer as a function of FA content. One key feature of the ferroelectric relaxor is the dielectric dispersion, see Fig. 2(a) for a P(VDF-TrFE-CFE) terpolymer, in which the relaxor polymer displays a broad dielectric peak, whose position shifts progressively to higher temperature with frequency. Increasing FA content in the tetrapolymers weakens the relaxor behavior (frequency dispersion), see Fig. 2(b) for the P(VDF-TrFE-CFE-FA) 70/30/6.3/1.8 mol% tetrapolymer, in which the broad dielectric peak shows much smaller shift with frequency compared with Fig. 2(a). In addition, there is an additional broad peak at temperatures near 40 °C which

# Influence of preparation conditions on structure and ferroelectric properties of thin VDF-TrFE copolymer film

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**Abstract:** Structure and ferroelectric properties of P(VDF-TrFE) film of molar ratio 70/30 prepared from solution in MEK under various conditions have been investigated. Spherulitic lamella are growing when the solution is filtrated through a PTFE membrane filter with pore size 0.2  $\mu\text{m}$  and directly dropped on a metallized substrate before spin coating, subsequent heating above the melting temperature, and further annealing. No spherulites grow from unfiltrated solution or when the filtrated solution is stored for some seconds before deposition. This observation gives hint to a structural change of the dissolved copolymer chains from coil to rod by filtration, which persists for a short period of time only.

**Keywords:** P(VDF-TrFE), ferroelectric, polymer, structure

## Introduction

After deposition of vinylidene fluoride-trifluoroethylene (VDF-TrFE) copolymer film from solution usually an annealing process follows to optimize and tailor the ferroelectric properties [1]. It has been observed that filtration of the copolymer solution which is commonly used to remove impurities in the solution can also have significant influence on the structural and ferroelectric properties of the deposited films [2]. Various annealing procedures have been applied to VDF-TrFE copolymer film of molar ratio 70/30 deposited from filtrated and unfiltrated solution in methyl ethyl ketone (MEK) to metallized substrates, and structure and ferroelectric properties have been investigated by optical microscopy, AFM, x-ray diffraction, ferroelectric hysteresis, and pyroelectric imaging.

## Results and Discussion

VDF-TrFE copolymer film of about 1.2  $\mu\text{m}$  thickness has been prepared by spin coating from solution in MEK. The solution has been either unfiltrated or filtrated by a PTFE membrane filter with pore size 0.2  $\mu\text{m}$  and directly dropped on a metallized substrate before spin coating. Significant differences between film from unfiltrated or filtrated solution are observed when the film is heated to 159  $^{\circ}\text{C}$  which is above the melting temperature for 3 minutes, and further annealed at 145  $^{\circ}\text{C}$  for 3 hours. Microscopic images in Fig. 1 show uniformly distributed structures in the film prepared from unfiltrated solution but large plate-like structures of spherulitic origin in film prepared from filtrated solution. The plate-like structures do not appear, however, when the filtrated solution is stored for some seconds before deposition. After poling the film prepared from unfiltrated solution has the overall pyroelectric coefficient  $p=28.5 \mu\text{C}/\text{m}^2\text{K}$

while the film with the plate-like structures has only  $p=6.1 \mu\text{C}/\text{m}^2\text{K}$ . Pyroelectric images show low pyroelectric activity of the plate-like structures, indicating that these are flat-on lamellae.

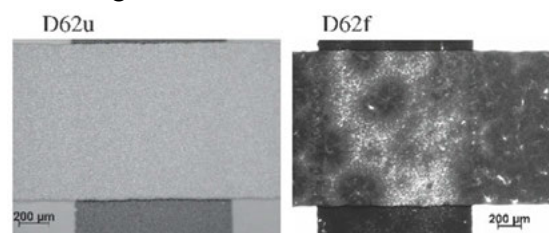


Figure 1: Microscopic images of samples D62u and D62f, prepared from unfiltrated and filtrated solution, respectively. From [2].

## Conclusions

The significant influence of filtration of VDF-TrFE copolymer solution to the structure of deposited film may be due to a structural change of the dissolved copolymer chains from coil to rod by the filtration process. This structural change is not stable, however, it reverses when the filtrated solution is stored for a short period of time before deposition.

## References

- [1] T. Furukawa, T. Nakajima, and Y. Takahashi, "Factors governing ferroelectric switching characteristics of thin VDF/TrFE copolymer films", *IEEE Trans. Dielectr. Electric. Insul.* **13**, 1120 (2006).
- [2] B. Ploss, D. Smykalla, and S. Engel, "Structure and ferroelectric properties of P(VDF-TrFE) films prepared under different conditions - Effect of filtration of the copolymer solution," *J. Adv. Dielectr.*, in print.

## Acknowledgements

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# Electret Charges and/or Dipoles on Dielectrics plus Elastical and Thermal Materials Properties Enable Piezo- and Pyroelectricity

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**Abstract:** Straight-forward arrangements of electric charges and elastic springs may be used to better understand and to predict the electromechanical behaviour of various electro-active dielectric materials. The so-called charge-spring model is essentially a macroscopic version of the microscopic Lorentz oscillator for modelling the interaction between electrons and nucleus in an atom. The charge-spring model helps to easily understand piezoelectric resonances in heterogeneous dielectrics and to predict the piezoelectric response in various materials. In this contribution, the charge-spring model and the connections between its constitutive elements and the relevant properties of established and newly designed piezoelectric materials will be briefly reviewed. Furthermore, an extension of the model to pyroelectricity in the same or other similar heterogeneous dielectrics will be attempted by introducing additional constitutive elements that represent for instance thermal expansion, entropy-related polarisation, etc. and that are again related to macroscopic sample properties. With such models, it should be possible to explain, to predict and to further optimise not only primary and secondary piezoelectricity, but also secondary and primary pyroelectricity – with respect to direct and inverse transduction.

**Keywords:** Charges and dipoles in electrets, charge-spring model, piezo- and pyroelectricity, types of electrets

## Summary

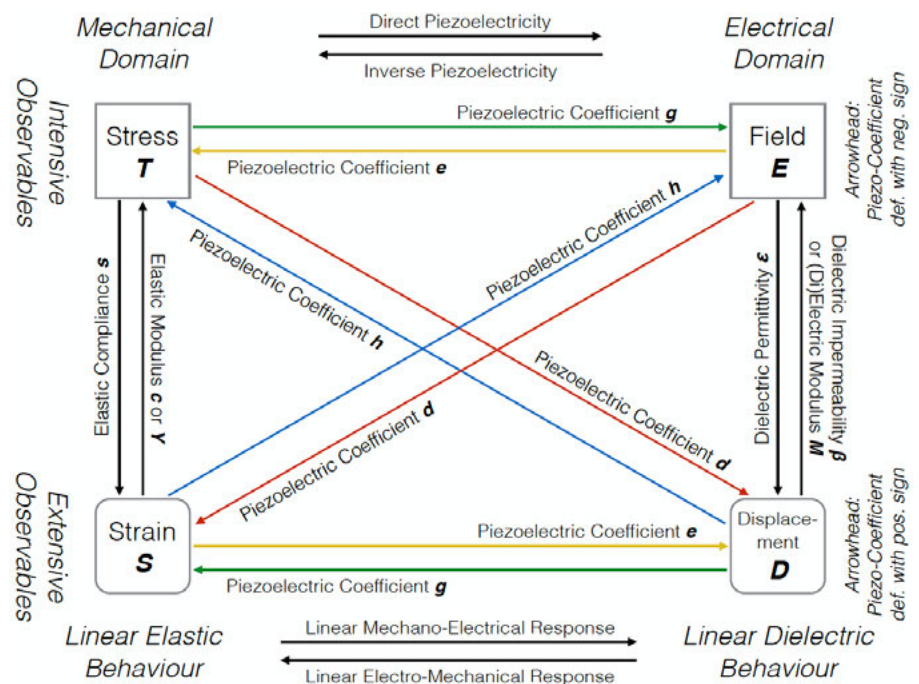
The aim of this overview is to show how the charge-spring model may be used as a unifying approach to easier understand and further develop piezoelectric properties in a large variety of materials. The adjacent **Figure (Heckmann diagram →)** almost completely illustrates the thermodynamical relations for piezoelectric coefficients, electric and elastic properties. Via the charge-spring model (plus more complex and specific models), the relevant electro-mechanical and mechano-electrical behaviour in various electrets is easily understood and predicted [1-4]. Some examples will be discussed.

Extending the charge-spring model and taking into account earlier reviews on various (pyro)electric materials [4-6], it is attempted to include secondary and primary pyroelectricity by considering thermal-expansion and entropy-related polarisation effects, etc., to test the extended model on results that are available, and to suggest a specific *Heckmann diagram* also here. It is hoped that the more comprehensive approach will help to guide the development of novel electret-based transducer materials and to include the topic in undergraduate teaching, as only basic mechanics, thermodynamics and electrostatics are involved.

## References

1. R. Gerhard, "A matter of attraction: Electric charges localised on dielectric polymers enable electromechanical transduction." *Annual Report, CEIDP*. IEEE: NY, USA, 2014, 1–10, doi: 10.1109/CEIDP.2014.6995800

2. R. Gerhard, S. Bauer, X. Qiu, "Charge-spring model for predicting the piezoelectric response of dielectric materials." *Annual Report, CEIDP*. IEEE: NY, USA, 2016, 81–84, doi: 10.1109/CEIDP.2016.7785500
3. R. Gerhard, "Piezoelectricity and electrostriction." In: F. Carpi (Ed.), *Electromechanically Active Polymers*. Springer International Publishing: Cham, Switzerland, 2016, 489–507, doi: 10.1007/978-3-319-31767-0\_21-1
4. J. Tichy, J. Erhart, E. Kittinger, J. Přívratská, *Fundamentals of Piezoelectric Sensorics*. Springer: Berlin, Heidelberg, 2010, doi: 10.1007/978-3-540-68427-5
5. S. Bauer, S. B. Lang, "Pyroelectric polymer electrets." *IEEE Transactions on Dielectrics and Electrical Insulation* **3**(5), 647-676, 1996, doi: 10.1109/94.544186
6. S. Jachalke, E. Mehner, H. Stöcker, *et al.*, "How to measure the pyroelectric coefficient?" *Applied Physics Reviews* **4**, 021303, 2017, doi: 10.1063/1.4983118



# Thermal wave based charge and polarization profiling - how to achieve nanometer resolution?

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**Abstract:** Since the proposal of the Laser Intensity Modulation Method (LIMM) by Lang and Das-Gupta in the 1980s, pyroelectric depth profiling based on thermal waves has been extensively applied to ferroelectric polymers, pyroelectric crystals and ceramics, polymer insulation materials and liquid crystals. This paper gives a review on systematic improvements of the LIMM regarding its spatial resolution, experimental sensitivity, and data analysis and interpretation based on advanced inversion methods and scale transform approaches..

**Keywords:** Pyroelectric depth profiles, charge distribution, pyroelectricity, thermal waves

## Introduction

The Laser Intensity Modulation Method (LIMM) has first been proposed in 1986 as a convenient experimental techniques for the measurement of pyroelectric depth profiles in PVDF caused by either space charges or a spontaneous polarization [1]. In contrast to well established acoustical techniques (LIPP, PWP, PPS, PEA), providing a nearly constant spatial distribution in the order of  $\mu\text{m}$  at GHz bandwidth, (thermal) diffusion wave methods like LIMM are characterized by a nonuniform spatial resolution that decreases exponentially over the sample thickness [2].

In this contribution, we will review significant milestones in the development of the pyroelectric depth profiling technique by addressing

- i) Experimental challenges, physical limits and innovations when pushing the spatial resolution limits down to the 10 nm range,
- ii) Possible strategies for reconstructing the pyroelectric distribution from the pyroelectric frequency spectra, and
- iii) We will discuss two experimental cases demonstrating the state-of-the-art resolution limits.

## Experimental Issues of Fast LIMM

Though extending LIMM towards high bandwidth seems to be conceptually simple, a couple of specific issues needed to be tackled such as heat absorption and transport on the nm-scale [2], noise scaling due to high bandwidth/low current measurements, interference of pyroelectric with thermo-elastic contributions (resonance phenomena, cf. Fig. 1) and others. In our approach, planar thermal waves are generated by modulating a 10mW fast diode laser (658nm, Lisa) at frequencies from 25 kHz to 25 MHz. The pyroelectric signal is amplified using a FEMTO high bandwidth current amplifier ( $f_c > 10\text{MHz}$ ) analyzed by a SR844 DSP Lock-in amplifier. To correct for the complex transfer function  $H(\omega)$  of the entire electronic pathway, for

each spectrum, a reference measurement using a fast PIN-diode was performed (cf. Fig. 2).

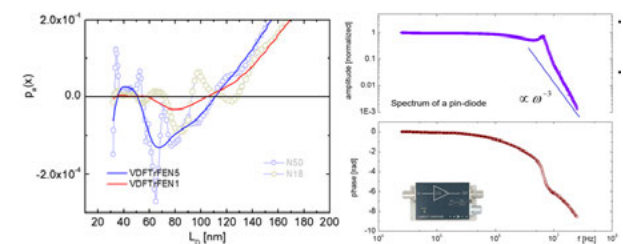


Figure 1 (left): Two transformed pyroelectric spectra before (symbols) and after removal (solid lines) of piezoelectric resonances at high frequencies. Figure 2 (right): Amplitude and phase of the complex transfer function  $H(\omega)$ .

## Reconstruction of $p(x)$

Various methods have been proposed to reconstruct the pyroelectric depth profile from the spectral response  $I(f)$ , which represents generally an ill-posed problem. Here we will focus on a Monte-Carlo based Random Walk in the multi-dimensional polarization-distribution space [3], along with the scale transformation proposed by Ploss and Bauer in 1992 [4].

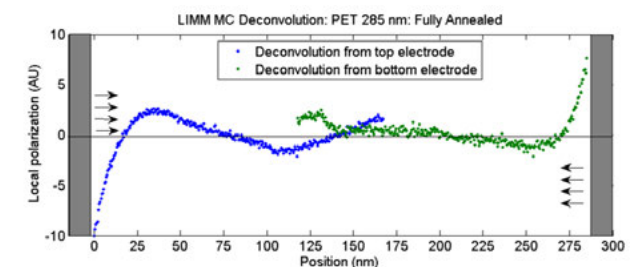


Figure 3: Pyroelectric distribution of an ultrathin PET layer reconstructed by the MC based deconvolution algorithm.

## References

- [1] Lang S B and D K Das-Gupta, 1986 Journal of Applied Physics 59 (6), 2151-2160.
- [2] B. Ploss, in 11th International Symposium on Electrets (ISE 11), Melbourne, Australia, 2002, 177-180.
- [3] T. Putzeys and M. Wübbenhorst, Phys. Chem. Chem. Phys., vol. 17, 7767-7774, 2015.
- [4] B. Ploss, R. Emmerich, and S. Bauer, Journal of Applied Physics 72 (11), 5363-5370, 1992.



# Electrostatic converter with an electret-like elastomer

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**Abstract:** We present a simple concept for an electret-based capacitive charge pump capable of working at low frequencies ( $\leq 1$  Hz) with a very low mechanical input energy and a high conversion efficiency. With a charged electret-like elastomer membrane the converter can operate without an initial bias voltage supply. A proof-of-concept demonstrator converts a mechanical input energy of  $332 \mu\text{J}$  ( $9.1 \mu\text{J}/\text{cm}^2$ ) to an electrical output energy of  $206 \mu\text{J}$  ( $5.7 \mu\text{J}/\text{cm}^2$ ) per conversion cycle. This gives a total conversion efficiency of 63%.

**Keywords:** Energy harvesting, dielectric elastomer, electret

## Introduction

Ecological as well as economical reasons have led worldwide to a strong increase in the use of low density energy sources for the generation of electricity. Notably the use of wind and solar energy is currently expanding exponentially, because these energy sources are virtually omnipresent and efficiently accessible with modern state-of-the-art technology. Besides wind and solar energy, many other ambient energy sources are readily available in various forms, e.g. with small temperature or pressure gradients, gentle movements of air or water, or small mechanical deformations, etc.; but these energy sources are at present largely unused.

With this work we propose and demonstrate an electrostatic energy converter (EEC) suitable for an efficient large scale mechanical-to-electrical energy conversion of ambient low density energy sources. [1] Our simple EEC system, illustrated in figure 1, measures ca. 10 cm in diameter, and consists of a thin elastomer membrane with a compliant electrode. A variable capacitive system is achieved with a supporting spherical dome-electrode. A membrane inflation by compressed gas decreases the capacitance and increases the voltage difference between the electrodes. A single inflation/deflation cycle with controlled charge flow can convert ca.  $9 \mu\text{J}/\text{cm}^2$  mechanical input energy into  $5.7 \mu\text{J}/\text{cm}^2$  electrical output energy.

## Results and Discussion

Before the EEC starts operation, the relaxed elastomer membrane is electrically stressed by a dc-voltage of  $-950$  V for approx. 10 min. This results in a space charge injection into the membrane surface from the aluminum dome electrode and produces a stable charge density in the order of  $\sigma \approx 10^{-8}$  C/cm<sup>2</sup>. With a periodic inflation/deflation and a controlled charge flow between the EEC and a connected storage capacitor a successive charge storage will increase the voltage as shown in figure 2.

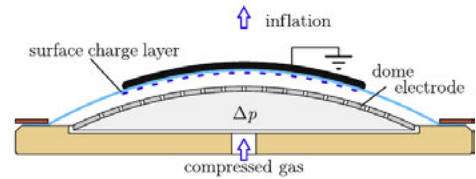


Figure 1: Cross-sectional view of the EEC showing a surface charge layer on the inner side of the elastomer.

The voltage does not continue to increase with the initially constant incremental rate of 50 V per cycle, but it is gradually getting smaller because of the progressive decay of  $\sigma$ . This decay is due to the growing field strength in the elastomer membrane.

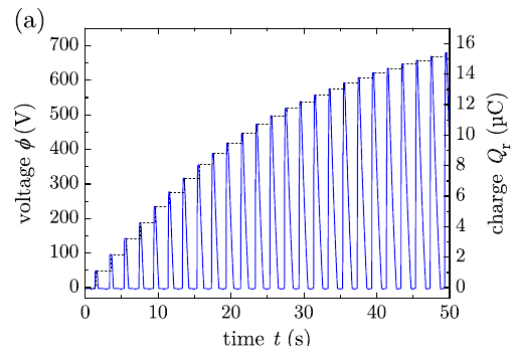


Figure 2: Cross-sectional view of the EEC showing a surface charge layer on the inner side of the elastomer.

## Conclusions

An electrostatic energy converter with a permanently charged elastomer membrane has been built and investigated for the efficient mechanical-to-electrical energy conversion of ambient low density energy sources.

## References

- [1] D. Peter, R. Pichler, S. Bauer, R. Schwödianer, "Electrostatic converter with an electret-like elastomer membrane for large scale energy harvesting of low density energy sources," *Extreme Mechanics Letters*, 4, 38-44, 2015

## Acknowledgements

Support of this work by the ERC within the Advanced Investigators Grant 'Soft-Map' and by the FWF (P22912-N20) is gratefully acknowledged.

# Artificial muscles for the lifelike robots of the future

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**Abstract:** Robots today rely on rigid components and electric motors, making them heavy, unsafe near humans, expensive, and ill-suited for unpredictable environments. Nature, in contrast, uses soft materials like muscle and skin, and has produced organisms that drastically outperform robots in terms of agility, dexterity, and adaptability. To create a new generation of lifelike robots that match the vast capabilities of biological systems, we need to develop actuators that replicate the astonishing all-around actuation performance of muscle. Hydraulically Amplified Self-healing ELectrostatic (HASEL) transducers are a new class of self-sensing, high-performance muscle-mimetic actuators, which are electrostatically driven and match or exceed most performance metrics of biological muscle. Modeling results reveal rich underlying materials science to be further explored -- in particular the physical principles that govern the behavior of solid-liquid dielectric composites under high electric fields; importantly, these modeling results also lay out a roadmap towards HASEL actuators (based on high-performance dielectrics) with drastically improved capabilities, far surpassing both biological muscle and traditional electromagnetic motors. This talk gives an overview of the latest research results and invites you to envision a future where next generation dielectrics enable revolutionary advances in robotics that substantially improve the quality of human life.

**Keywords:** Soft robotics, HASEL artificial muscles, electrohydraulic actuators, high-performance dielectrics;

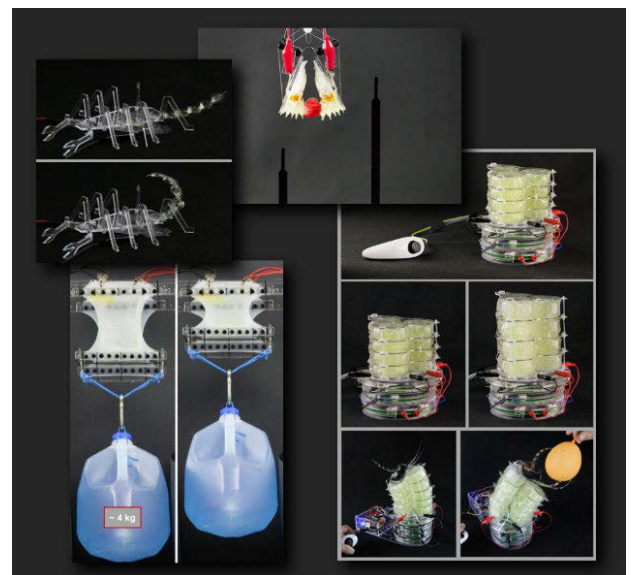
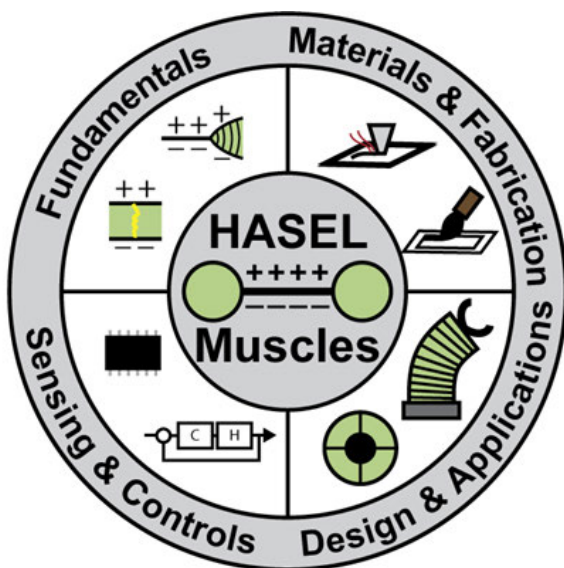


Figure 1: This talk gives an overview of the latest research results on HASEL artificial muscles.

Wednesday, September 20<sup>th</sup>, 2023

SESSION 7

09:00	Session 7: "Biodielectrics" – an initiative of IEEE Chairs: Tofail Syed, Carmo Lança	Tofail Syed <i>Opening: IEEE Technical Committee on Biodielectrics: Goals, objectives and next steps</i>
09:10		Sarah Guerin <i>Piezoelectric biomolecules for lead-free, reliable, eco-friendly electronics</i>
09:40		Kai Tao <i>Self-assembling peptides piezoelectricity</i>
10:10		Charlie O'Mahony <i>Quantitative 3D optical birefringence in peptide electrets</i>
10:30		Hema Dinesh Barnana <i>Cold sintering of biologicals for electret applications</i>

# Piezoelectric Biomolecules for Lead-Free, Reliable, Eco-Friendly Electronics

K.Hari<sup>1</sup>, G. Kumari<sup>1</sup>, T. Ryan<sup>1</sup>, C. O Malley<sup>1</sup>, S. Bhattacharya<sup>1</sup> & Sarah Guerin<sup>1,2</sup>

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**Abstract:** Billions of piezoelectric sensors are produced every year, improving the efficiency of many current and emerging technologies. By interconverting electrical and mechanical energy they enable medical device, infrastructure, automotive and aerospace industries, but with a huge environmental cost. Amino acids are the most basic biological components, and they are cheap and simple to crystallize, with significant piezoelectricity in single crystal and polycrystal forms. However this response is highly anisotropic, and precise, orientated control over crystallisation is required to maximise the piezoelectric output of a crystalline amino acid device,

**Keywords:** piezoelectrics, bioelectrets, crystals, density functional theory, energy harvesting

## Introduction

Biological crystals such as amino acids and peptides have emerged as exciting new piezoelectrics. Biomolecular-crystal assemblies can be grown at room temperature with no by-products, and do not require an external electric field to induce piezoelectricity, unlike PZT and other piezoceramics. Currently no research is focused on developing these crystals as reliable, solid-state sensors to integrate into conventional electronic devices, due to their high water solubility, uncontrolled growth, variable piezoelectric response, and difficulty in making electrical contact.

## Results and Discussion

Our research is taking on the challenge of developing biomolecular crystals as organic, low-cost, high-performance sensors, to out-perform and phase-out inorganic device components with dramatically reduced environmental impact. In this talk I will discuss our methodologies for the design, growth, and engineering of these novel piezoelectric materials under three pillars:

- An ambitious computational workflow to enable the design of super-piezoelectric crystalline assemblies by combining high-throughput quantum mechanical calculations with machine learning algorithms;
- A new method of growing polycrystalline biomolecules, allowing for easy, efficient creation of macroscopic piezoelectric structures;
- Establishing effective electromechanical testing procedures to characterise fully insulated and contacted biomolecular device components.

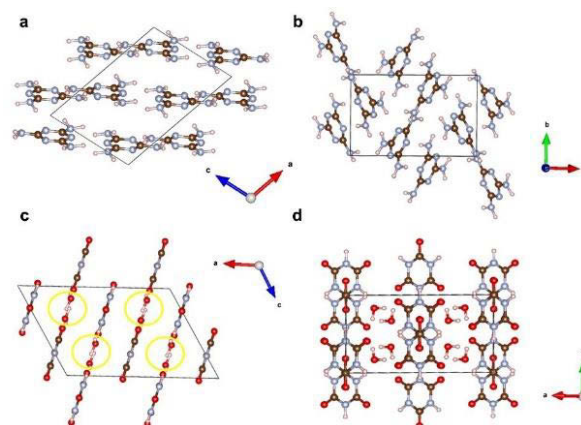


Figure 1: Unit cells of biomolecular crystals can be engineered to give tuned electromechanical properties.

## Conclusions

Even 'weak' organic piezoelectric with modest piezoelectric constants can yield significant voltages in response to strain because the piezoelectric voltages produced under an applied force are inversely proportional to the material's dielectric constant

## References

- [1] S. Guerin *et al.*, "Control of piezoelectricity in amino acids by supramolecular packing," *Nat. Mat.*, 17 (2), 180-186, 2018.
- [2] F. Okosun *et al.*, "Flexible amino acid-based energy harvesting for structural health monitoring of water pipes," *Cell Rep. Phys. Sci.*, 2 (5), 100434, 2021.

## Acknowledgements

SG acknowledge Science Foundation Ireland (SFI) for support under Grant Number 12/RC/2275\_P2 (SSPC). S.G. would like to acknowledge funding from Science Foundation Ireland under grant number 21/PATH-S/9737. S.G is funded by the European Union.

# Self-Assembling Peptides Piezoelectricity

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**Abstract:** Peptides self-assembling nanoarchitectures have been found to show intrinsic piezoelectricity, thus presenting promising potentials for diverse advanced applications. Herein, we would like to introduce our recent progress on peptides architectural piezoelectricity, focusing on the molecular mechanisms underlying piezoelectric peptide crystallization, fabrication & application of large-scale peptide crystals-arraying piezoelectricity and peptides hydrogelation piezoelectricity. Our findings suggest that the architectural piezoelectricity may bear inspiring implications on facilitating peptides self-assembly for contributing in human lives.

**Keywords:** peptides self-assembly, supramolecular architectonics, piezoelectricity

## Introduction

Since the inspiring report on piezoelectricity of diphenylalanine self-assembling nanotubes in 2010 [1], peptides supramolecular piezoelectricity has been attracting increasing interest due to its advantages to behave as promising candidates for bridging the distinctions between soft, wet, and living biological world and rigid, dry, and complex piezoelectric systems [2]. Therefore, it is crucial to study the peptides architectural piezoelectricity, in order to accelerate the incorporation of these functional resources as pivotal contributors to science and technology.

## Results and Discussion

The non-centrosymmetric peptide crystals show intrinsic piezoelectricity, thus can be used for piezoelectric power generations or energy harvesting (Fig. 1).

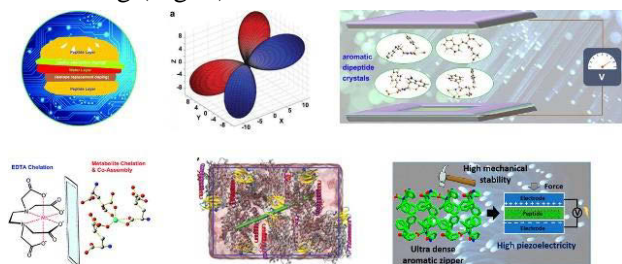


Fig. 1: Intrinsic piezoelectricity of crystallized peptides. Notably, the piezoelectric performances can be tuned by controlling the self-assembly parameters.

In addition to crystallization, the peptide self-assembling soft nanoarchitectures can also show polarity, thus giving piezoelectricity which can be employed to develop piezoelectric hydrogels for bio-machine interface and biomedical applications (Fig. 2).

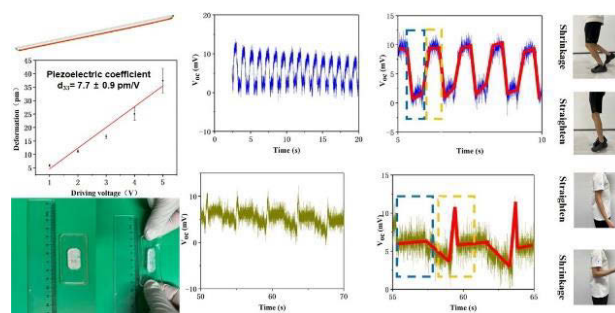


Fig. 2: Amphiphilic peptide self-assembling nanofibers show intrinsic piezoelectricity, which can be used to fabricate piezoelectric hydrogel-based sensors for tactile sensing.

## Conclusions

Piezoelectricity is undergoing a paradigm shift from traditional non-recyclable, inorganic materials to eco-friendly, bio-degradable analogues with desirable biocompatibility and multifunctionality. In this regard, the piezoelectric self-assembling peptides may be promising electromechanical coupling elements for diverse advanced bioelectronic devices, offering the modulated piezoelectric properties required for implantable and wearable bioelectronic devices along with biocompatibility and biodegradability.

## References

- [1] A. Kholkin *et al.*, Strong piezoelectricity in bioinspired peptide nanotubes, *ACS Nano*, 4 (2), 610, 2010.
- [2] I. Chae *et al.*, Review on electromechanical coupling properties of biomaterials, *ACS Appl. Bio Mater.*, 1, 936, 2018.

## Acknowledgements

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# Quantitative 3D Optical Birefringence in Peptide Electrets

Charlie O'Mahony<sup>1</sup> Aladin Mani<sup>1</sup> Daria Vasileva<sup>1</sup> Semen Vasilev<sup>1</sup> Vladimir Y. Shur<sup>2</sup> Andrei Kholkin<sup>3</sup> Christophe Sillien<sup>1</sup> Syed A. M. Tofail<sup>1</sup>

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<sup>1</sup>Department of Physics and Bernal Institute, University of Limerick, Limerick, Munster, Ireland,

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<sup>3</sup>Materials and Ceramic Engineering, University of Aveiro, Aveiro, Portugal

**Abstract:** Peptide nanotubes (PNTs) are bioelectrets that exhibit piezoelectricity, pyroelectricity, ferroelectricity and birefringence. Birefringence is an optical property that can be used to determine the degree of order, orientation, size and shape of PNTs. In this work, a custom-built optical apparatus is used to quantitatively measure birefringence in Three Dimensions, of PNTs under varying electric fields and temperature. This work also includes techniques for aligning and orienting PNTs and discusses the role of birefringence measurements in the study of PNTs.

**Keywords:** Birefringence, Optics, 3D imaging, peptide, ferroelectrets

## Introduction

Peptide nanotubes (PNTs) are unique nanoscale objects that exhibit strong piezoelectricity, pyroelectricity, and ferroelectricity. They are natural bioelectrets that have shown great potential in a variety of applications, including drug delivery, tissue engineering, and nanoelectronics. Anisotropic crystals such as PNTs should also exhibit birefringence, an optical property that depends on the electromagnetic polarization and direction of light. Optical birefringence can be a powerful tool for characterizing the structure and properties of PNTs [1-2]. This measurement technique relies on the differential refractive index of light polarized parallel and perpendicular to the long axis of the PNTs. The birefringence can be used to determine the orientation and degree of order of the PNTs, as well as their size and shape. In this work, we harness optical birefringence measurements to study PNTs, including techniques for aligning and orienting PNTs, as well as methods for measuring their birefringence [3].

## Results and Discussion

Figure 1 shows 3D birefringence in PNTs measured by a custom-built three-dimensional optical birefringence measurement apparatus. This is a first of its kind measurement of birefringence in 3D. It enables quantitative measurements of birefringence under varying electric fields and temperature. This can potentially very useful in linking piezo- and pyro-electric properties of crystals to their respective optical polarizon effects. Through the use of known orientation single crystals, a calibration of perpendicular and parallel polarizing light can be attributed in terms of retardation time and intensities.



Figure 1: 3D Optical Birefringent image of a complicated network of Nano peptides, with the yellow the parallel polarization and the blue perpendicular polarization.

## Conclusions

We demonstrate 3D Optical birefringence measurement in peptide electrets. Such measurements can be very useful in quantitative linking between electrical polarisation with optical polarisation in electrets.

## References

- [1] Handelman, A. *Molecules* **2022**, *27*, 1802.
- [2] Kumar, G.S., Ethiraj, R., & Murty, V.G. *Acta Cryst.* January 16. (1979). A35, 857-858.
- [3] Dragomir et al. *Opt. Express* **15**, 17690-17698 (2007)

## Acknowledgements

Erasmus International Credit Mobility between University of Limerick, Ireland and Ural Federal University, Yaketerinberg, Russian Federation.

# Cold Sintering of Biologicals For Electret Applications

Hema Dinesh Barnana<sup>1</sup>, Charlie O'Mahony<sup>1</sup>, Ehtsham ul Haq<sup>1</sup>, Syed A.M. Tofail<sup>1</sup>  
[dinesh.barnana@ul.ie](mailto:dinesh.barnana@ul.ie); [Tofail.Syed@ul.ie](mailto:Tofail.Syed@ul.ie)

<sup>1</sup>Department of Physics, and Bernal Institute, University of Limerick, Castletroy Limerick, Ireland, V94 T9PX.

**Abstract:** In this work, we approached the sintering and novel crystallisation of the biologicals with a cold sintering technique. Advanced characterisation techniques such as X ray diffractogram, X ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were used to study sintered soya bean powder (biological electret) pellets. Further, the electrets were prepared by contact poling and the piezoelectric properties studied with the help of piezoresponse microscopy (PFM).

**Keywords:** Electrets, Bio-compatible ferroelectrets, Atom force microscopy (AFM), and Corona poling (CP).

## Introduction

Biologicals such as amino acids, enzymes and metabolites have recently shown to generate high electricity from pressure (piezoelectricity) and temperature difference (pyroelectricity) [1,2]. With the need to improve current unsustainable piezo and pyroelectric commercial devices, made from lead, niobium or tantalum -based [3], with cheap and replaceable materials for real-life applications, biological electrets present a promising field for sustainable and requiring practical energy generating devices. Currently however, biological electrets present difficulties in real world application, with the need for some form of compaction, creating robust polycrystalline aggregates to enhance the desired piezo and pyroelectric properties. To obtain useful energy from bio piezoelectric materials conductive layers are attached, forming a capacitor. It has been difficult to attach such layers (metallization) to aggregates of biologicals, making sintered ceramics an attractive alternative.

High temperature (>350 °C) sintering is unsuitable for biological electrets, due to the loss of inherent properties. In this project, we will introduce cold sintering techniques to produce ceramics of biologicals below 350 °C. This will allow robust, sustainable, non-toxic piezo and pyroelectric devices made from biologicals. In this study, soya powder was chosen for initial studies of crystallisation but these methodologies are transferable to other biological electrets.

## Results and Discussion

The sintered biologicals bonding characteristics and vibrational modes were evaluated with the use of Raman and FTIR spectra. XRD was used to study the phase evolution in biological proteins with respect to the applied pressure and field during sintering. XPS and SEM were used to study the surface properties of the sintered biological proteins.

The sintered pellets were poled with the help of poling techniques to prepare the electrets, and to study the charge-induced dielectric properties. The PFM studies carried out on these electrets, so as to quantify the enhanced Piezoelectric properties. Also, Recent progress made in crystallisation of other biological peptides via cold sintering technique and their potential applications will be discussed.

## Conclusions

Collectively, this work provides fundamental understanding of the factors affecting piezoelectricity and structure-property relations with respect to biological electrets. It facilitates the new pathways to prepare biological crystals, for use as electrets to enhance the piezoelectric properties.

## References

- [1] S. A. M. Tofail, D. Haverty, F. Cox, J. Erhart, P. Hána, and V. Ryzhenko, "Direct and ultrasonic measurements of macroscopic piezoelectricity in sintered hydroxyapatite", *Journal of Applied Physics* 105, 064103 (2009)
- [2] Guerin, Sarah & Stapleton, Aimee & Chovan, Drahomir & Mouras, Rabah & Gleeson, Matthew & Mckeown, Cian & Noor, Mohamed & Silien, Christophe & Rhen, Fernando & Kholkin, Andrei & Liu, Ning & Soulimane, Tewfik & Tofail, Syed & Thompson, Damien, "Control of piezoelectricity in amino acids by supramolecular packing," *Nature Materials*, (2018).
- [3] Guerin, Sarah & Tofail, Syed & Thompson, Damien, "Organic piezoelectric materials: milestones and potential," *NPG Asia Materials* (2019).

## Acknowledgements

I would like to acknowledge the Dept of Physics and the Bernal Institute for allowing me to use the sophisticated facilities situated at University of Limerick.

**Wednesday, September 20<sup>th</sup>, 2023**

**SESSION 8**

<b>11:10</b>	<b>Session 8</b> <b>Chairs: Xiaoqing Zhang, Stéphane Holé</b>	<b>Krittish Roy</b> <i>Engineered Lysozyme bioelectrets</i>
<b>11:30</b>		<b>Sarah K. Markham</b> <i>In silico design of a biodegradable endoscopic ultrasound transducer</i>
<b>11:50</b>		<b>Veronika Turiničová</b> <i>Non-invasive measurements of excess electron charge in charged hydroxyapatite dielectric</i>
<b>12:10</b>		<b>Jan van Turnhout</b> <i>Better charging of microfiber filter media and better disinfection of seeds by the joint use of a corona discharge</i>



# Engineered Lysozyme Bioelectrets

Krittish Roy<sup>1,2</sup>, Charlie O'Mahony<sup>1,2</sup>, Dinesh Barnana<sup>1,2</sup>, Tewfik Soulimane<sup>2,3</sup>, Ehtsham ul Haq<sup>1,2</sup>, Syed A. M. Tofail<sup>1</sup>

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**Abstract:** Lysozyme is a well-known antimicrobial, globular protein found to be piezo, pyro and ferroelectric in its crystalline state. Here, we have fabricated a piezoelectric energy harvesting device using engineered tetragonal aggregate films of lysozyme. Deposited films exhibited both longitudinal and shear piezoelectricity between 3-13 pC/N. Subsequent output voltage/current of the device have been recorded. Considering the non-toxicity and biocompatibility, this approach offers a big advantage over inorganic/synthetic piezoelectric materials as self-powered biomedical sensor, implantable power source in body, and antimicrobial coating in medical implants.

**Keywords:** lysozyme, piezoelectricity, energy harvesting.

## Introduction

Biological building blocks are natural electrets and as such exhibit piezo, pyro and often ferroelectricity [1]. Among the natural protein crystals, lysozyme is well known as an antibacterial globular enzyme that crystallizes in different crystalline forms such as, tetragonal, monoclinic, orthorhombic, triclinic, or hexagonal. Lysozyme has shown piezo [2], pyro and ferroelectricity [3]. Piezoelectricity of biological materials has gained immense interest due to their non-toxicity, biocompatibility, and biodegradability. To adapt a self-powered piezoelectric device as an implantable system, the material used for energy harvesting or sensing must be non-toxic because under in-vivo condition, even a very low level of toxicity can cause harm to the patient. Therefore, biomaterial based piezoelectric device is the only alternative to overcome this long-standing challenge. Here, we reported the development of tetragonal aggregate lysozyme film-based bio-piezoelectric generator (Bio-PIG).

## Results and Discussion

We engineered lysozyme using a method described by Liu, Wang and Chang [4]. Chemical/structural characterisation was conducted by Raman and X-ray diffraction. Piezoelectricity was measured by Berlincourt method using a Piezometer as well as Piezoforce microscopy (PFM). Morphology was measured by optical microscopy.

Figure 1 (a) and (b) show the morphology of engineered lysozyme film under bright and dark field optical microscopy. Engineered lysozyme could retain its backbone conformation even after heat treatment (Figure 1(c)). Deposited films exhibited both longitudinal and shear piezoelectricity between 3-13 pC/N. Subsequent output voltage/current of the device have been recorded.

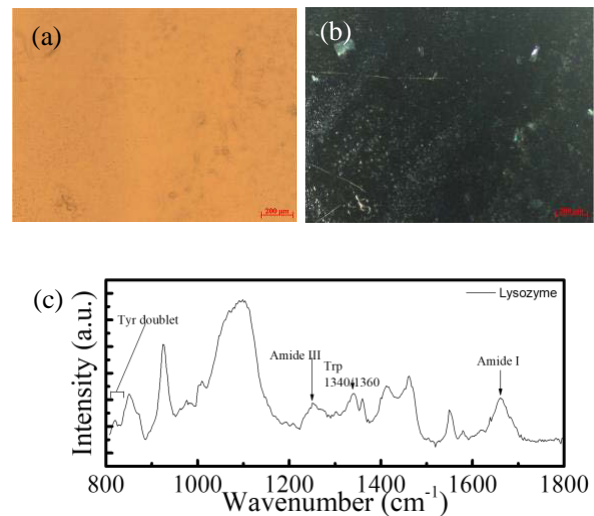


Figure 1: (a) Bright field, (b) Dark field morphology and (c) Raman spectra of engineered lysozyme film.

## Conclusions

We have successfully adapted a wet chemical approach to prepare tetragonal lysozyme bioelectret that showed piezoelectric effect in its natural state.

## References

- [1] S.A.M. Tofail, "Ferroelectricity in biological building blocks: Slipping on a banana peel?", *J. Appl. Dielect.* 13, 2341004, 2023.
- [2] A. Stapleton et al., "The direct piezoelectric effect in the globular protein lysozyme", *Appl. Phys. Lett.* 111, 142902, 2017.
- [3] A. Stapleton et al. "Converse piezoelectricity and ferroelectricity in crystals of lysozyme protein revealed by piezoresponse force microscopy", *Ferroelectrics* 525, 135, 2018.
- [4] Y. Liu, X. Wang, C. B. Ching, "Towards further understanding of lysozyme crystallization: phase diagram, protein-protein interaction, nucleation kinetics, and growth kinetics", *Cryst. Growth Des.* 10, 548-558, 2010.

## Acknowledgements

We would like to acknowledge Science Foundation Ireland (SFI) and SFI centre for medical devices (CURAM) for providing fund for this work.

# In Silico Design of a Biodegradable Endoscopic Ultrasound Transducer

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**Abstract:** In this work we examine the applicability of biocompatible, biodegradable, natural piezoelectric materials such as the amino acid glycine to replace traditional PZT (lead zirconate titanate) as the active element in endoscopic ultrasound transducer. The work is carried out *in silico* using COMSOL Multiphysics software.

**Keywords:** simulation, bioelectrets, biomedical applications

## Introduction

Piezoelectric materials are employed in a wide array of products including health care devices such as trans-dermal and endoscopic ultrasound transducers. In endoscopic ultrasound transducers, the piezoelectric element, or more typically, array of elements transmit and receive the ultrasound signal to generate an image. Due to tubular construction of endoscopes and their use within the body, endoscopes have been identified as a potential source of infection transmission[1]. In 2017, the European Society of Radiology Ultrasound Working Group issued guidelines recommending single use disposable equipment to eliminate the risk of cross contamination and medical device acquired infection.

Endoscopic ultrasound probes still currently use toxic, lead-based, piezoelectric ceramic transducer arrays that cause significant environmental and health concerns/damage[2]. Despite years of research for alternatives such as barium titanate ( $\text{BaTiO}_3$ ), bismuth sodium titanate (BNT), potassium sodium niobate (KNN), and lithium niobate ( $\text{LiNbO}_3$ ) [3], work is still needed to advance the implementation of such materials into devices.

In this work, we will examine the electrical and acoustic characteristics of a  $\gamma$ -glycine based transducer and compare with conventional materials such as PZT.

## Results and Discussion

A rectangular element of dimensions 20mm x 0.5mm with out-of-plane thickness of 4mm was constructed in COMSOL multiphysics and excited with 1 V potential. Isotropic damping factor of 0.01 was applied. No backing was simulated in these preliminary investigations. Frequency sweep was carried out from 83.5 kHz to 103 kHz.

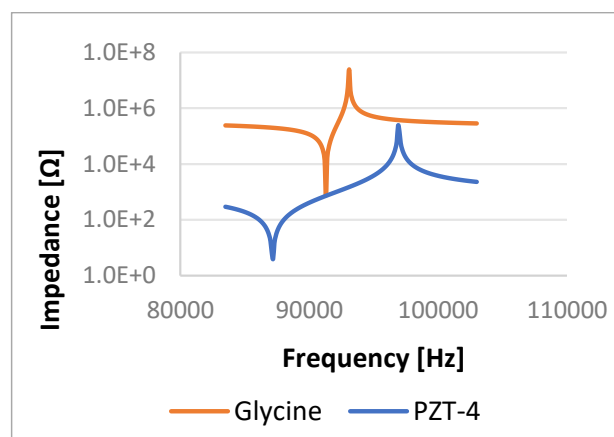


Figure 1: (a) Simulated impedance spectra of  $\gamma$ -glycine and PZT-4 transducer elements at 1V.

## Conclusions

The bandwidth of the glycine element is seen to be narrower which suggests that glycine may form a more sensitive transducer since returning signals will be stronger, however a narrowed bandwidth in a transducer will reduce the resolution.

## References

- [1] P. Rai, "Disinfection of Endoscopy and Reusability of Accessories." *J Digest Endosc* 11 (1), 61-66, 2020.
- [2] A. J. Bell, and O. Deubzer, "Lead-free piezoelectrics - The environmental and regulatory issues." *MRS bulletin* 43(8), 581-587, 2018.
- [3] E. Taghaddos, M. Hejazi, and A. Safari. "Lead-free piezoelectric materials and ultrasonic transducers for medical imaging." *J. Adv. Dielectr.* 5(02), 1530002, 2015.

## Acknowledgements

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# Non-invasive measurements of excess electron charge in charged hydroxyapatite dielectric

Veronika Turiničová<sup>1</sup>, Martin Moško<sup>1</sup>, Syed A. M. Tofail<sup>2</sup>, Pavol Ďurina<sup>1</sup>, Maroš Gregor<sup>1</sup>  
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**Abstract:** Biocompatible hydroxyapatite dielectric is known to exhibit enhanced bioactivity when irradiated by an electron beam. The value of the trapped charge induced by the beam usually strongly differs from the total irradiated charge. Therefore, a method for measuring the real value of the charge trapped in the dielectric is developed. The value of the trapped charge is determined from the shape change of the pendant drop hanging in the proximity of the charged sample. The method is simple, non-invasive, and provides reproducible results for charges of the order of nanocoulomb. Using the method, the long-term charge stability in the biocompatible hydroxyapatite is demonstrated.

**Keywords:** pendant drop, hydroxyapatite, electron beam irradiation, trapped charge measurements

## Introduction

Electrical modification techniques are often used to increase surface bioactivity of biomaterials. An exemplary system is the dielectric hydroxyapatite irradiated by an electron beam [1]. Usually, the value of the charge trapped in the material during irradiation strongly differs from the total irradiated charge and exhibits low reproducibility [2]. Thus, the real value of the trapped charge has to be measured. Most of the currently available charge measurement methods are invasive, expensive, or single-purposed. Here we develop a simple non-invasive method based on the modification of the droplet shape in presence of the electric field generated by the charge trapped in the sample.

## Results and Discussion

When the charged dielectric sample is placed beneath the water droplet, the droplet becomes polarized. As shown in Fig. 1, the electric force between the polarized droplet and charged sample causes the droplet elongation. Consequently, the surface free tension of the droplet measured by the Pendant Drop Method is effectively decreased [2, 3].

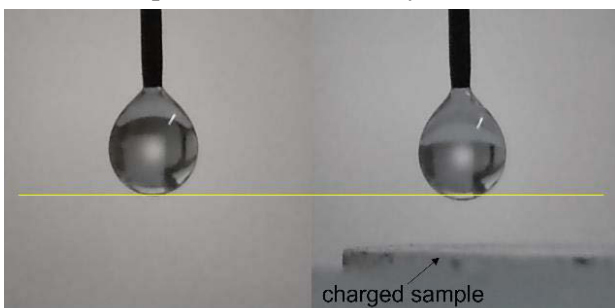


Figure 1: Shape of the pendant drop without applied electric field vs. shape of the pendant drop placed in the electric field generated by the charged sample.

Modified Young-Laplace equation is used to describe these effects theoretically as a function of the trapped charge [2]. The theory allows us to determine the trapped charge from the measured

droplet shape [2]. As a practical application of our method, a long-term stability of the charge trapped in the biocompatible hydroxyapatite irradiated by electron beam is demonstrated (see Tab. 1). Owing to the non-invasive character of the method, all 7 measurements in Tab. 1 could be performed on the same sample.

t [min]	Q [nC]	t [min]	Q [nC]
5	0.69	1440	0.39
60	0.70	2880	0.32
120	0.63	10080	0.20
330	0.55		

Table 1: The value of the trapped charge ( $Q$ ) measured as a function of the time delay ( $t$ ) after irradiation.

## Conclusions

We have developed a simple method for measuring the excess electron charge in the dielectric material. Thanks to its non-invasive character we were able to show an excellent long-term stability of the trapped charge in a single hydroxyapatite sample. Thus, our method can be useful in quantitative studies of the charging effect on the material bioactivity.

## References

- [1] T. Plecenik *et al.* “Directly created electrostatic microdomains on hydroxyapatite: Probing with a Kelvin Force probe and a protein” *J.Mater.Sci.Mater.Med.*, 23, 47-50, 2012.
- [2] V. Turiničová *et al.* “Measurement of electric charge in charged hydroxyapatite dielectric using pendant drop” *Langmuir*, 39, 7046-7056, 2023.
- [3] S. Mhatre *et al.* “Methodology to calculate interfacial tension under electric field using pendent drop profile analysis” *Proc.R.Soc.A*, 475, 2019.

## Acknowledgements

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# Better charging of microfiber filter media and better disinfection of seeds by the joint use of a corona discharge and a spray of water droplets

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## Abstract:

The combined use of a corona discharge and a mist of micro-droplets of water will be highlighted. The latter will become charged when pushed through a dc corona. If these droplets are deposited on a filter web, they charge its microfibers all-around. The microdroplets will also collect highly reactive species from the corona. They can therefore also be used for the disinfection of pathogens on seeds.

**Keywords:** ion-enriched hydrocharging, plasma activated water droplets, corona-based disinfection

## Introduction

This talk is dedicated to Siegfried Bauer, whose legacy is that he always thought out-of-the-box. The joint use of a corona discharge and a mist of water droplets is not straightforward. We will outline a few configurations and applications of this curious combination.

The microdroplets acquire two distinct hallmarks, they get charged and get loaded with anti-microbial agents. The latter is due to the many reactive molecular species that are formed in a corona discharge [1]. Hence, two types of applications are possible: one that uses the charges and another that uses the disinfecting features.

Charged microdroplets are capable to charge objects with cavities. In other words they will give an all-around charging. This implies e.g. that open porous filters made up from microfibers will be charged evenly. Likewise, seeds which often are infected with pathogens (fungi, bacteria and viruses) in crevices, are also disinfected effectively with plasma-activated water droplets.

The charging of microdroplets in a corona discharge may be dubbed: ion-enriched hydrocharging. By loading the droplets with ions, the hydrocharging does not need to rely any longer on tribo-charging, which requires a very high pressure and a large amount of water [2].

## Results and Discussion

Fig. 1 depicts the dual use of the merger of a corona discharge and nebulized water. Charged droplets can charge polymer objects in all kind of shapes. It is in particular useful for the charging of porous polymers like filter media or open cell foam. Fig. 2 shows a scheme for the charging of a filter web e.g. that for highly efficient face masks. This set up can be applied both on a small and a large scale.

A rig powered by AC for the disinfection of seeds is shown in Fig. 3. Seeds are often disinfected with hot water. This requires a lot of energy. The seeds must also be dried. The PAW microdroplet disinfection clearly is much more eco-friendly.

## Conclusions

The joint use of a corona discharge and nebulized water offers new opportunities. Using microdroplets of water as an intermediate in both processes is an

advantage. It assures that the objects will dry quickly.

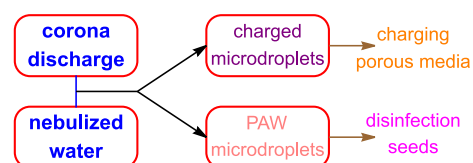


Fig. 1 The union of a corona discharge and nebulized water makes various applications feasible.

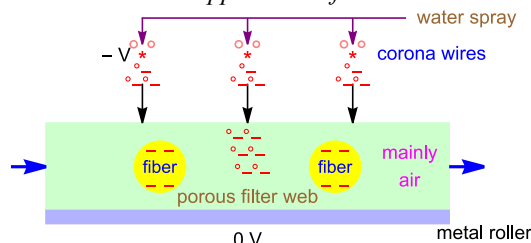


Fig. 2 Scheme on-line all-around charging of filter webs with microdroplets charged with a row of corona wires.

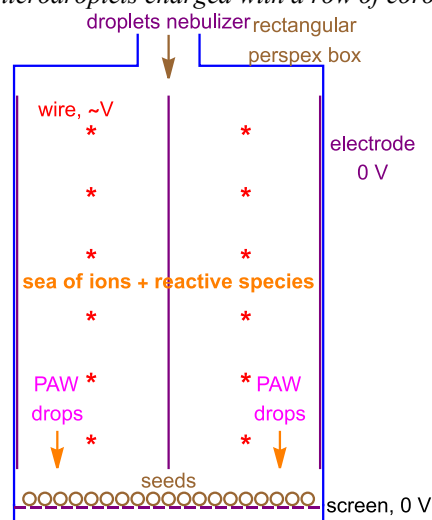


Fig. 3 The microdroplets sprayed in with a nebulizer are loaded by the corona discharge with very reactive species that disinfect the seeds from pathogens effectively.

## References

- [1] R.Thirumdas, A. Kothakota, et al., "Plasma activated water (PAW): Chemistry, physico-chemical properties, applications in food and agriculture". *Trends Food Sci. Techn.*, 77, 21-31,2018.
- [2] Z. Pan, G. Liu, et al., "Water electret charging based polypropylene/electret masterbatch composite melt-blown nonwovens with enhanced charge stability for efficient air filtration", *J. Textile Inst.*, 113, 2128-2134, 2022.

Thursday, September 21<sup>th</sup>, 2023

## SESSION 9

09:00	Session 9 Chairs: Heinz von Seggern, François Bauer	Takeo Furukawa <i>Towards quantitative understanding of phase transition and polarization switching in VDF-based</i>
09:30		Daniel Tan <i>Realization of stable dielectric permittivity in Pb(Ni, Nb)O<sub>3</sub>-P(Zr, Ti)O<sub>3</sub> relaxor ferroelectrics</i>
09:50		Geetu Kumari <i>Density Functional Theory (DFT): A tool for rational design of crystalline piezoelectrics</i>
10:10		Giacomo Selleri <i>Piezoelectric core-shell nanofibers for impact localization</i>
10:30		Krishna Hari <i>Amino acid crystals as high-performance, eco-friendly structural health monitors</i>

# Towards quantitative understanding of phase transition and polarization switching in VDF-based ferroelectric polymers

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**Abstract:** The copolymer of vinylidene fluoride with trifluoroethylene are overviewed on its ferroelectric nature. The transitions from ferroelectric to molten phase via. antiferroelectric and paraelectric phases occur due to successive loss of intermolecular and intramolecular and crystalline dipolar order. Chain dynamics together with conformational entropy play a key role. The ferroelectric polarization switching is proven to progress via. nucleation-growth mechanisms. A crystalline motion of an Arrhenius type exists commonly to all phases and reaches 1GHz on melting. A slow dynamics is suggested to exist by a gradual decrease in dielectric permittivity.

**Keywords:** ferroelectric polymer, phase transition, polarization switching, chain dynamics

## Introduction

Structural, dielectric and thermal studies have shown [1] that the copolymer of vinylidene fluoride (VDF) with trifluoroethylene (TrFE) exhibits multiple transitions among ferroelectric [F], anti-ferroelectric [AF], paraelectric [P], and molten [M] phases (Fig. 1). The dipolar order associated with all-trans conformation and parallel packing in [F] is lost intermolecularly in [AF], intramolecularly in [P] and becomes random in [M]. The copolymer containing 50-80mol% VDF exhibits typical Curie transition and melting resulting from the competition between conformational entropy and cohesive energy

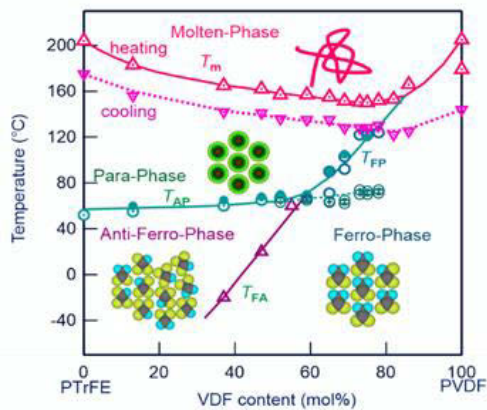


Figure 1: Phase diagram and structural changes of VDF/TrFE copolymers.

## Results and Discussion

Frequency spectra of permittivity  $\epsilon$  revealed an Arrhenius-type relaxation of ca. 50kJ/mol in the kHz-MHz range to reach 1GHz on melting. On cooling from [P] to [F],  $\epsilon$  decreases with time suggesting slow dynamics to reduce dipole fluctuations. As shown in Fig. 2, the bias field causes a reduction in  $\epsilon$  to induce higher Curie point (left) and the transition from [P] to [F] phase (right). The kinetics of the [P]-[F] transition was shown to occur via. fluctuation enhancement, structural changes and slow dynamics towards reduced defects [2].

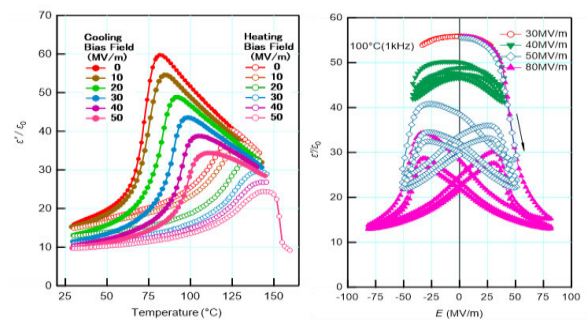


Figure 2: Temperature and bias-field dependence of dielectric permittivity of VDF(75)/TrFE(25).

The polarization switching becomes faster with applied field obeying an exponential-to-power law and reaches 1ns at 800MV/m. Time-resolved Piezo-Force-Microscopy proved the nucleation-growth mechanism [Fig. 3]. The switching time depends on various factors such as waiting time and electrode.

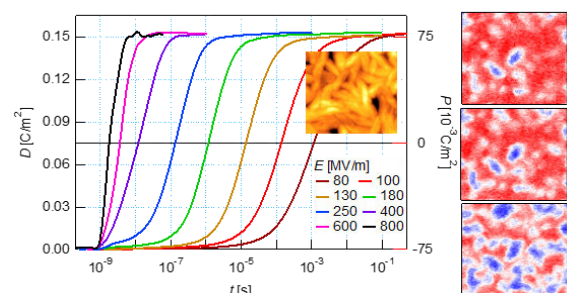


Figure 3: Switching transients and PFM images during polarization reversal in VDF(75)/TrFE(25).

## Conclusions

The introduction of 20-50mol% TrFE into PVDF causes relative stability of transbonds and a decrease in lattice energy to induce [F]-[P] transition. TrFE-rich copolymers tends to exhibit diffuse transitions.

## References

- [1] T. Furukawa, "Ferroelectric properties of vinylidene fluoride copolymers", *Phase Transitions*, **18**,143,1989.
- [2] Y. Takahashi, and T. Furukawa, "Kinetics of ferroelectric-to-paraelectric transition of copolymers of VDF and TrFE", *Macromolecules*, **37**, 2807, 2004.

# Realization of stable dielectric permittivity in Pb(Ni, Nb)O<sub>3</sub>-P(Zr, Ti)O<sub>3</sub> relaxor ferroelectrics

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**Abstract:** Piezoelectric buzzers, acoustic sounding and alarming systems render advantage of compact and high frequency design in replacing electromagnetic systems. However, the traditional PZT ceramics have lower dielectric permittivity and higher temperature dependence (-40~85°C) hardly meeting the key requirements. The authors systematically studied solid solutions of PZT and Pb(Ni<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> (PNN) by varying PNN/PZT ratio and the corresponding Zr/Ti ratio to obtain the stable permittivity compositions. Effectively controlling the dielectric permittivity around 2000 with the minimal temperature dependence below +/- 6% using lower PNN/PZT ratio outperforms the piezoceramic performance in the market. The authors investigated the phase transition behaviours from tetragonal to rhombohedral structure by increasing the Zr/Ti ratios and temperatures using X-ray diffraction and Electron microscopy techniques.

**Keywords:** dielectric permittivity, relaxor ferroelectric, piezoelectric, phase transition

## Introduction

Traditional PZT piezoelectric ceramics exist in a wide range of applications such as power generation and imaging technologies. However, their lower dielectric permittivity and higher temperature dependence (-40~85°C) cannot meet some key requirements in such applications as acoustic sounding and alarming systems. Piezoelectric product manufacturers are eagerly seeking the materials solution for stable piezoelectric ceramics with relatively high permittivity value. [1] The authors systematically studied a number of solid solutions of PZT and Pb(Ni<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> (PNN) and achieved excellent results. [2-4]

## Results and Discussion

By varying PNN/PZT ratio and the corresponding Zr/Ti ratio, the authors effectively control the dielectric permittivity to around 2000 and minimize its temperature dependence below +/- 6% which outperforms the piezoceramic performance in the market (Figure 1). The analysis shows that the Zr/Ti ratio near the morphotropic phase boundary (MPB) of the PNN-PZT compositions is preferable. In addition, minor dopants of critical oxides are also found helpful for optimum results. The authors investigated the phase transition from tetragonal to rhombohedral structure by increasing the Zr/Ti ratios and test temperatures using X-ray diffraction and Electron microscopy techniques.

## Conclusions

The investigation of PNN-PZT compositions with various Zr/Ti ratios resulted in the minimal temperature dependence of dielectric permittivity. Dielectric test, XRD, and TEM analyses shed some

light on the phase transition of the corresponding compositions.

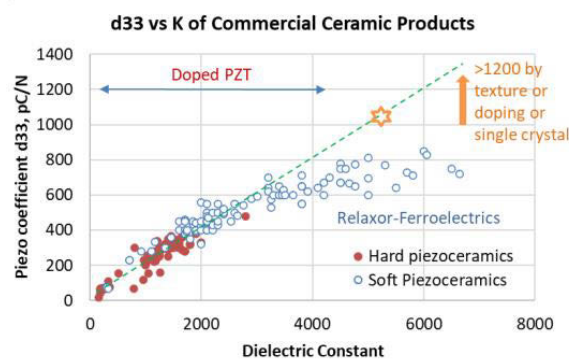


Figure 1: The relationship between piezoelectric coefficient and dielectric permittivity of current piezoelectric ceramic products and compositions.

## References

- [1] A. A. Bokov, Z.-G. Ye, *J. of Mater. Sci.* 41, 3 1–5 (2006).
- [2] N. Vittayakorn et al, *Cann, J. Appl. Phys.* 96, 5103 (2004).
- [3] J.J. Zhou et al, *J Mater Sci: Mater Electron* 25:2540–2545 (2014).
- [4] Masao Kondo et al, *Jpn. J. Appl. Phys.* 38 5539 (1999).

## Acknowledgements

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# Density Functional Theory (DFT): A tool for rational design of crystalline piezoelectrics

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**Abstract:** Crystallizing biomolecules creates a network of unit cell dipoles identical to the mechanisms of classical inorganic piezoelectrics, which allows for biological single crystals to easily fulfill the role of piezoceramics, e.g., in stack actuation. Biomolecular piezoelectric materials are considered a strong candidate for biomedical applications due to their robust piezoelectricity, biocompatibility, and low dielectric property. A combination of modeling and characterization can provide much-needed insight into how piezoelectric properties are modulated by unit cell properties, such as dipole moments, molecular packing, and composition.

**Keywords:** Piezoelectricity, DFT, Biomolecules, Pb-FREE, material design.

## Introduction

By interconverting electrical and mechanical energy they enable medical device, infrastructure, automotive and aerospace industries, but with a huge environmental cost. The majority of piezoelectric sensors contain Lead Zirconium Titanate (PZT), the fabrication of which requires toxic lead oxide. Prominent lead-free alternatives are heavily processed, and rely on expensive, non-renewable materials such as Niobium.

Biological materials such as amino acids and peptides have emerged as exciting new piezoelectrics. Biomolecular-crystal assemblies can be grown at room temperature with no by-products, and do not require an external electric field to induce piezoelectricity, unlike PZT and other piezoceramics.

## Results and Discussion

Convergence in calculated energy, volume, and lattice parameter values with respect to the vdW cut-off radius used for dispersion corrected DFT calculations. The excellent quantitative correspondence of DFT predicted stiffness, permittivity and piezoelectricity tensors with those obtained from experiment conducted in the present study and in the literature highlights the potential that DFT calculations now demonstrate to identify materials with significant piezoelectric response, and to estimate the expected magnitudes of individual piezoelectric constants.

The DFT values are calculated at 0 K, so it should be noted that systems could exhibit a deviation between predicted DFT values and properties measured at room temperature. Comparison of piezoelectric charge coefficients calculated with Finite Differences and Density Functional Perturbation Theory (DFPT) methods.

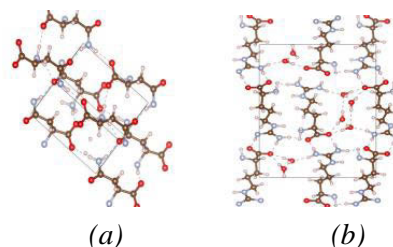


Figure 1: a. Unit cell of a. Anhydrous Asparagine, b. Arginine dihydrate.

## Conclusions

High polarization, low elastic stiffness, and low dielectric permittivity are the three main performance indicators that can be used to break down high piezoelectric responsiveness. As a result, this approach will make it easier to create a convolutional neural network that can analyze any crystal structure and forecast the likelihood of a strong piezoelectric response. TensorFlow will be the first software of choice for this work, but as the project moves forward, we'll try to use the most recent breakthroughs in the machine learning field.

## References

- [1] Sarah Guerin, Ning Liu, Tewfik Soulimane, Syed A. M. Tofail, Damien Thompson, "Control of piezoelectricity in amino acids by supramolecular packing", *Nature materials*, 17, 180–186, 2018
- [2] De Jong, Maarten, et al. "A database to enable discovery and design of piezoelectric materials." *Scientific data* 2.1 2015: 1-13.
- [3] Kiely, Evan, et al. "Density functional theory predictions of the mechanical properties of crystalline materials." *CrystEngComm* 23.34 2021: 5697-5710

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# Piezoelectric core-shell nanofibers for impact localization

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**Abstract:** Self-sensing composite materials based on piezoelectric nanofibers are attracting great interest in the last years thanks to their self-powering capability and the low-intrusiveness on the mechanical structure of the material. In this study, core-shell piezoelectric nanofibers are used to fabricate a sensor which is able to localize a mechanical impact occurring on its surface. The peculiar disposition of the nanofibers allowed to lead back to the impact position by comparing the output voltages which refer to each specific area of the sensor.

**Keywords:** core-shell piezoelectric nanofibers, electrospinning, composite materials, impact localization.

## Introduction

In the last decades, sensors and smart materials for the robotic field and for artificial intelligence systems have attracted enormous interest. In particular the use of self-powered sensors, such as the triboelectric and piezoelectric ones, represents a suitable strategy to design self-sensing systems which do not rely on an external power supply. The transducing mechanism of a piezoelectric material is based on the induced polarization as consequence of a mechanical deformation of the crystal lattice. Therefore, by interleaving piezoelectric nanofibers in a hosting material, such as epoxy resin or composite materials, it is possible to fabricate smart self-sensing materials. The use of nanofibers does not induce mechanical defects thanks the high porosity of such a membranes which allows the embedding medium to penetrate in the air pores. In this work, a flexible sensor based on core-shell piezoelectric nanofibers was designed and developed with the aim to localize the position of a mechanical impact occurring on its surface.

## Results and Discussion

Aligned core-shell piezoelectric nanofibers were electrospun and aligned in a matrix-like disposition, as shown in Figure 1. The whole membrane was then metalized with a thin layer of gold. In this way, each core-shell nanofiber was composed by an inner electrically conductive portion (core, PEDOT:PSS), a piezoelectric one (PVDF-TrFE) and an external conductive coating [1], [2]. Therefore, when a mechanical impact occurs, the piezo-generated electrical charges can be collected by the inner electrode and the outer metallization, thus fabricating a mat where each nanofiber works as a nanometric sensor. The whole mat was then embedded in a flexible polyurethane matrix, with a 4 x 4 cm dimensions. By placing conductive paint on the edge of the sensor, multiple nanofibers were connected together, thus creating four sensitive portions on the surface of the specimen, as shown in Figure 1. Electromechanical tests were performed by impacting with a 80 N force the surface of the self-sensing composite materials in the four

positions and comparing the peak-to-peak output voltages generated by the piezoelectric mat. For the whole different tests, the maximum output voltage was systematically measured in the on the impacted zone, as represented for instance in Figure 1, where the impact occurred blue-highlighted area.

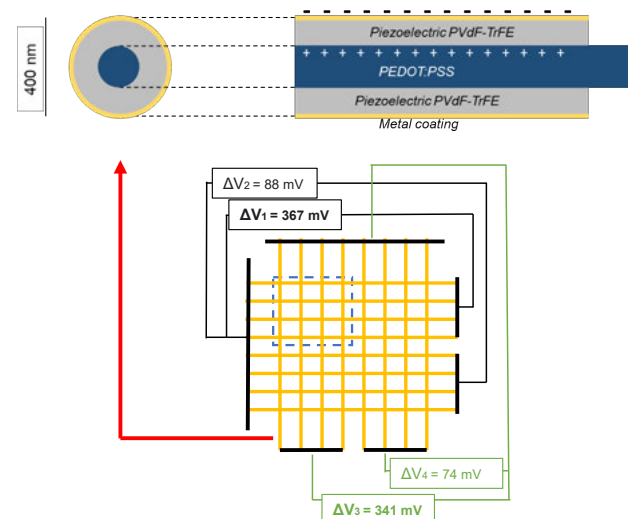


Figure 1 Schematic layout of the piezoelectric sensor.

## Conclusions

Piezoelectric core-shell nanofibers were successfully embedded in a flexible matrix to create a sensor able to detect the position of a mechanical impact occurring on its surface, as demonstrated by the electromechanical tests. The manufactured piezoelectric sensor represents a proof of concept for the technique of impact localization exploiting core-shell piezoelectric nanofibers.

## References

- [1] D. Fabiani *et al.*, "Nanofibrous piezoelectric structures for composite materials to be used in electrical and electronic components," *Proc. Nord. Insul. Symp.*, no. 26, pp. 1–5, 2019, doi: 10.5324/nordis.v0i26.3263.
- [2] T. Sharma, S. Naik, J. Langevine, B. Gill, and J. X. J. Zhang, "Aligned PVDF-TrFE nanofibers with high-density PVDF nanofibers and PVDF core-shell structures for endovascular pressure sensing," *IEEE Trans. Biomed. Eng.*, vol. 62, no. 1, pp. 188–195, 2015, doi: 10.1109/TBME.2014.2344052.

# Amino acid crystals as high-performance, eco-friendly structural health monitors.

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**Abstract:** In the past ten years, biological piezoelectric materials have emerged as the potential next generation of cost-effective, green electromechanical sensors<sup>1, 2</sup>. The piezoelectric voltages produced under an applied force are inversely proportional to the dielectric constant of the material and so even ‘weak’ organic piezoelectrics (with modest piezoelectric constants compared to inorganic ceramics<sup>3, 4</sup>), can generate large voltages in response to strain. Amino acids are the simplest biological units, and are inexpensive and easy to crystallise, and demonstrate measurable piezoelectricity in single crystal and polycrystalline forms<sup>1-6</sup>.

**Keywords:** piezoelectricity, amino acids, polycrystalline, energy harvesting, structural health monitoring.

## Introduction

Recently we have experimentally validated flexible glycine-based sensors for pipe leak detection and monitoring in real-time, for a variety of flow rates and leak sizes using a custom fluid test rig developed for the validation of PVDF patches<sup>7</sup>. This is the first time that glycine crystals have been grown and characterised as a high-concentration, polycrystalline aggregate for piezoelectric sensing<sup>8</sup>. However, a key limitation of this study is that the piezoelectric response of the film was less than that of glycine single crystals due to the random orientation of glycine crystallites.

## Results and Discussion

In this work, we will systematically study the effect of crystallisation growth parameters on a number of polycrystalline amino acid films in order to modulate the piezoelectric response and increase the detection sensitivity and voltage output of amino acid-based piezoelectric devices. Moreover, we will investigate and optimise different parameters involved in the polycrystalline film growth and characterise the formed polycrystalline films using Scanning Electron Microscopy, X-Ray Diffraction, and Scanning Probing Microscopy.

## Conclusion

The study will highlight the potential of low-dielectric, non-centrosymmetric biomolecular crystal films for widespread monitoring of built infra-structure systems by showing how reliably and sustainably they may be used as sensors for structural health monitoring (SHM) applications.

## References

- [1] Guerin, S.; Tofail, S. A.; Thompson, D., Organic piezoelectric materials: milestones and potential. *NPG Asia Materials* 2019, 11 (1), 1-5.
- [2] Chorsi, M. T.; Curry, E. J.; Chorsi, H. T.; Das, R.; Baroody, J.; Purohit, P. K.; Ilies, H.; Nguyen, T. D., Piezoelectric biomaterials for sensors and actuators. *Advanced Materials* 2019, 31 (1), 1802084.
- [3] Zhang, S.; Xia, R.; ShROUT, T. R., Lead-free piezoelectric ceramics vs. PZT? *Journal of Electroceramics* 2007, 19 (4), 251-257.
- [4] Panda, P.; Sahoo, B., PZT to lead free piezo ceramics: a review. *Ferroelectrics* 2015, 474 (1), 128-143.
- [5] Kumar, R. A.; Vizhi, R. E.; Vijayan, N.; Babu, D. R., Structural, dielectric and piezoelectric properties of nonlinear optical  $\gamma$ -glycine single crystals. *Physica B: Condensed Matter* 2011, 406 (13), 2594-2600.
- [6] Heredia, A.; Meunier, V.; BdiKin, I. K.; Gracio, J.; Balke, N.; Jesse, S.; Tselev, A.; Agarwal, P. K.; Sumpter, B. G.; Kalinin, S. V., Nanoscale ferroelectricity in crystalline  $\gamma$ -glycine. *Advanced Functional Materials* 2012, 22 (14), 2996-3003.
- [7] Okosun, F.; Cahill, P.; Hazra, B.; Pakrashi, V., Vibration-based leak detection and monitoring of water pipes using output-only piezoelectric sensors. *The European Physical Journal Special Topics* 2019, 228 (7), 1659-1675.
- [8] Okosun, F.; Guerin, S.; Celikin, M.; Pakrashi, V., Flexible amino acid-based energy harvesting for structural health monitoring of water pipes. *Cell Reports Physical Science* 2021, 2 (5), 100434.

## Acknowledgements

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Thursday, September 21<sup>th</sup>, 2023

**SESSION 10**

11:10	Session 10 Chairs: Bernd Ploss, Yang Cao	Jianguo Zhu <i>Realizing high energy density and efficiency simultaneously in <math>(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.7}\text{Sr}_{0.3}\text{TiO}_3</math>-<math>\text{CaTiO}_3</math> ceramics</i>
11:30		Yintang Yang <i>Functionally Piezoelectric Composites for Ultrasonic Transducer Applications</i>
11:50		Nian Dai <i>Electret-based noncontact sensor for human-machine interface in harsh environments</i>

# Realizing high energy density and efficiency simultaneously in $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.7}\text{Sr}_{0.3}\text{TiO}_3\text{-CaTiO}_3$ Ceramics

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**Abstract:** Dielectric capacitors, storing energy with the aid of dielectric polarization, are widely applied in a broad variety of advanced electronic systems due to their ultrafast discharge rates, ultrahigh power densities, and excellent chemical stabilities.  $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  (BNST)-based relaxor ferroelectric ceramics were prepared through new material design and component optimization strategies.  $(1-x)\text{BNST-xCT}$  ceramics show the excellent energy storage properties (high  $W_{\text{rec}}$  of  $\sim 7.00 \text{ J/cm}^3$ , large  $\eta$  of  $\sim 90.90\%$ , and ultrahigh of  $E_b \sim 660 \text{ kV/cm}$ ). The intrinsic and extrinsic origins of enhanced energy storage properties are illustrated from different scales.

**Keywords:** Bismuth sodium titanate, Relaxor ferroelectric ceramics, Energy storage properties.

## Introduction

Driven by the increasingly prominent energy and environmental issues, energy storage devices for collecting and storing the electrical energy generated by renewable energy technologies are attracting global attention.<sup>1,2</sup> Constructing ternary solid solutions was a productive route to delay polarization saturation and boost  $E_b$ . Based on these views, a combinatorial optimization strategy is proposed to achieve obviously improved overall energy storage performances (ESP) by using a ternary model system of  $(1-x)(0.70\text{BNT-0.30ST})\text{-xCaTiO}_3$  [ $(1-x)\text{BNST-xCT}$ ]. The samples were prepared via a conventional solid-state reaction method. The corresponding preparation processes and detailed characterization methods for  $(1-x)\text{BNST-xCT}$  ceramics are briefed in the ESI.†

## Results and Discussion

To assess the energy storage capability of the  $(1-x)\text{BNST-xCT}$  samples, their unipolar  $P$ - $E$  loops are detected at various electric fields. The field dependence of  $W_{\text{rec}}$  for the ceramics with low CT content is linear, revealing the existence of polarization saturation,<sup>17</sup> while the curves of 0.70BNST-0.30CT and 0.60BNST-0.40CT ceramics are nearly parabolic, revealing their similar behavior to linear dielectrics. Owing Encouragingly, the ESP of 0.60BNST-0.40CT ceramics exhibited outstanding frequency stability.

The  $T_f$  values of the 0.60BNST-0.40CT ceramics are the lowest, revealing that most of the nanodomains can switch back to their initial states after the electric field is removed. Therefore, the high  $\eta$  and delayed saturation polarization are expected to be achieved in 0.60BNST-0.4CT ceramics.

since the breakdown process of ceramics, includes multiple factors such as electrical, thermal, and electromechanical breakdown, the enhanced  $E_b$  in 0.60BNST-0.40CT ceramics can be partially explained by the inverse correlation between  $E_b$  and  $\epsilon_r(\tan \delta)$ . On the one hand, the moderate  $\epsilon_r$  in

0.60BNST-0.40CT ceramics is beneficial to avoid large electrostrictive strain, thereby reducing the possibility of electromechanical breakdown; on the other hand, the ultralow  $\tan \delta$  ( $\sim 0.0058$ ) in 0.60BNST-0.40CT ceramics corresponds to less generated heat, which is beneficial to reduce the possibility of a thermal breakdown.

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## Conclusions

In summary, excellent comprehensive performances with an ultrahigh  $W_{\text{rec}}$  of  $7.0 \text{ J cm}^{-3}$  and a large  $\eta$  of 90.9% are realized simultaneously in BNST-based ceramics via introducing the linear dielectric  $\text{CaTiO}_3$ .

## References

- [1] H. Pan, S. Lan, S. Xu, et al., "Ultrahigh energy storage in superparaelectric relaxor ferroelectrics," *Science*, 374(6563): 100-104, 2021.
- [2] O. Ellabban, H. Abu-Rub and F. Blaabjerg, "Renewable energy resources: Current status, future prospects and their enabling technology," *Renewable Sustainable Energy Rev.*, 39, 748–764, 2014.
- [3] X. Li, J. Xing, F. Wang, et al., "Realizing high energy density and efficiency simultaneously in  $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ -based ceramics via introducing linear dielectric  $\text{CaTiO}_3$ ," *J. Mater. Chem. A*, 10, 18343, 2022.

## Acknowledgements

This work is supported by the National Natural Science Foundation of China (12004267 and 52032007).

# Electret-based noncontact sensor for human-machine interface in harsh environments

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**Abstract:** This work introduces an electret-based noncontact sensor with moisture resistance and a large detection range (>2 m). These features are achieved by an air-bubble structure design and electrostatic field superposition of multilayer electret films. The key innovations in work include: (1) a 3×3 cm<sup>2</sup> five-layer sensor produces ~2.5 V output voltage with good stability; (2) the surface potential of the sensor can recover to about -1000 V even after 20 cycles of soaking-drying process; (3) a 5×5 cm<sup>2</sup> five-layer sensor can detect human movements at a distance of 2 m.

**Keywords:** electret-based noncontact sensor, large detection range, harsh environments

## Introduction

Noncontact sensors have attracted much attention in recent years because of their wide applications in the human-machine interface. In this work, we developed an electret-based noncontact sensor with an air-bubble structure and multilayer electret films by using fluorinated ethylene propylene (FEP) as the electret material, polydimethylsiloxane (PDMS) as the spacer, indium tin oxide (ITO) as electrode material, polyethylene terephthalate (PET) as substrate, and hot-melt adhesive. This work expands the application area of self-powered electret-based noncontact electronics in harsh environments, such as public toilets.

## Results and Discussion

The schematic diagram of the basic structure and working mechanism is shown in Figure 1a. The output performances of the sensor with a size of 3×3 cm<sup>2</sup> were characterized by a linear motor to provide controllable approaching motions, as depicted in Figure 1b. The sensor was fixed on a 3D stage and the open-circuit output voltage values were measured by an NI USB 6341 data acquisition system. A 3×3 cm<sup>2</sup> five-layer sensor produces ~2.5 V output voltage with good stability. The surface potential generated by the charges on the FEP electret film was probed by an electrometer (Trek 347). After 20 cycles of soaking-drying process, the surface potential of the sensor with air-bubble structure could recover to about -1000 V. The output signals generated by the sensor with size of 5×5 cm<sup>2</sup> could detect human movements at a distance of 2 m, as shown in Figure 1c.

## Conclusions

In summary, a flexible electret-based noncontact sensor has been developed to perceive changes in surrounding electric fields with excellent output performances. In addition to its moisture resistance,

this sensor is capable of detecting human movements over 2 m. Hence, this self-powered noncontact sensor has the potential to be utilized in harsh environments, such as public toilets.

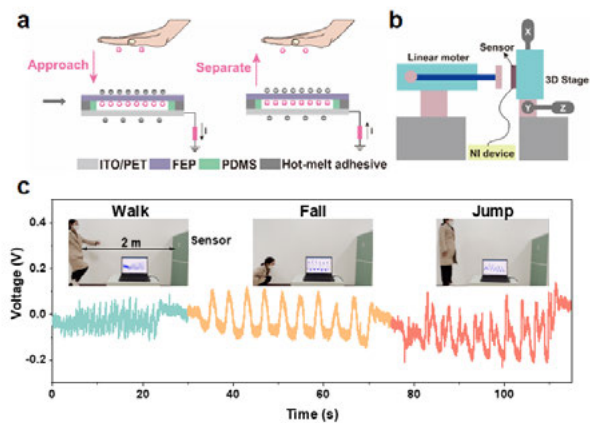


Figure 1: Working mechanism, measurement condition, and demonstration of the electret-based noncontact sensor. (a) Schematic diagram of working mechanism and (b) measurement condition. (c) Noncontact sensing signals generated by the sensor when a volunteer walks, falls, and jumps.

## References

- [1] L. Lu, C. Jiang, G. Hu, J. Liu, B. Yang, "Flexible noncontact sensing for human-machine interaction." *Adv. Mater.* 33, 2100218, 2021.
- [2] S. An, H. Zhu, C. Guo, B. Fu, C. Song, P. Tao, W. Shang, T. Deng, "Noncontact human-machine interaction based on hand-responsive infrared structural color." *Nat. Commun.* 13, 1446, 2022.

## Acknowledgements

We acknowledge the funding support from the Science and Technology Development Fund, Macau SAR (FDCT) (File No. 0059/2021/AFJ, 0040/2021/A1), the National Natural Science Foundation of China (U21A20479), the CAS Youth Innovation Promotion Association (Y2022094), and the Shenzhen Fundamental Research Program (JCYJ20200109114805984).

# Functionally Piezoelectric Composites for Ultrasonic Transducer Applications

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**Abstract:** High-performance ultrasound transducers aim to achieve ultrasound imaging with high contrast and high spatial resolution, where composite transducers have outstanding advantages due to their high sensitivity and broad bandwidth. This work uses theoretical calculation, finite element simulation and experimental preparation as the research method, combined with the artificial intelligence algorithm to optimize the structure and material parameters, and prepare the preparation of high-performance ultrasonic transducer with functionally piezoelectric composites, and realize ultrasonic imaging applications in biomedicine, non-destructive testing.

**Keywords:** Piezoelectric composites, ultrasonic transducer, artificial intelligence algorithm

## Introduction

Ultrasonic transducers are widely used in medical diagnosis and non-destructive testing applications based on ultrasound systems [1]. As the needs for application areas increase, including clinical diagnosis that requires ultrasound imaging with higher definition and a larger imaging range, ultrasonic transducers with higher spatial resolution and sensitivity are called for. In recent decades, many researches have focused on piezoelectric components of ultrasonic transducers, aiming at improving the performance of the devices. One of the effective attempts is to develop novel piezoelectric composite materials with excellent performance. Piezoelectric composites combine the advantages of piezoelectric and polymer materials.

## Results and Discussion

Many scholars and our previous work have verified that traditional piezoelectric composites, such as 1-3, 2-2 and 1-3-2 composites, have the advantages of low impedance and high electromechanical coupling factor, which are suitable for underwater ultrasonic applications.

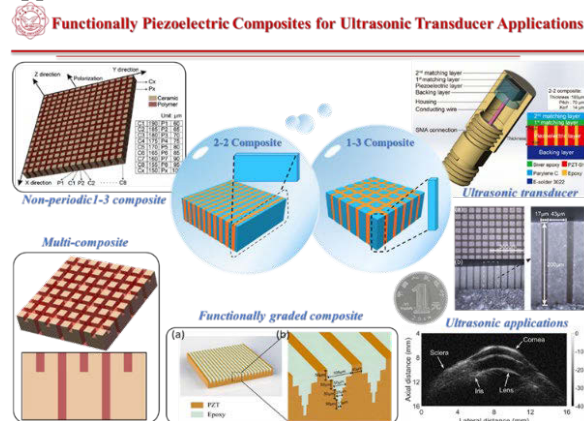


Figure 1: Evolution of functional piezoelectric materials, including structural design, preparation and ultrasonic applications of piezoelectric composite materials.

Recently, we have further improved the performance of piezoelectric composites by optimizing their microstructure and geometry [2][3]. In the whole study on the optimization of functionally piezoelectric composite materials, theoretical calculation, finite element simulation and experimental preparation were employed as the research methods, combined with the artificial intelligence algorithm to optimize the structure and material parameters. We put forward a variety of functionally piezoelectric composite transducer design methods, which improved the bandwidth, sensitivity and electromechanical coupling coefficient of piezoelectric ultrasonic transducers.

## Conclusions

It is verified that the proposed optimization method can enhance the acoustic and electrical properties of piezoelectric materials, guide the design of high-performance composite ultrasonic transducers and the prepared transducers have great potential for ultrasonic imaging of biological tissues, nondestructive testing and acoustic tweezer applications.

## References

- [1] K. K. Shung, "High frequency ultrasonic imaging," J. Med. Ultrasound, vol. 17, no. 1, pp. 25–30, 2009.
- [2] C. Fei et al., "Fabrication and Characterization of High-Sensitivity Ultrasonic Transducers with Functionally Graded Design," IEEE Sens. J., vol. 19, no. 16, pp. 6650-6654, 2019.
- [3] P. Fei et al., "Novel multi-layer-composites design for ultrasonic transducer applications," Compos. Struct., vol. 245, no. 1, pp. 112364, 2020.

## Acknowledgements

This work was supported by the the National Natural Science Foundations of China (No: 61974110) and the Cooperation Program of XDU-Chongqing IC Innovation Research Institute (No: CQIRI-2022CXY-Z07).

Thursday, September 21<sup>th</sup>, 2023

**SESSION 11**

13:25	Session 11 Chairs: Xunlin Qiu, Kai Tao	Thulasinath Raman Venkatesan <i>Piezo- and pyro-electricity in polynorbornene-based stretchable elastomer electrets</i>
13:55		Takashi Nakajima <i>Abnormality detection system based on piezoelectric polymer</i>
14:15		Xingchen Ma <i>Fully degradable, highly sensitive electret-based pressure sensor for biomechanical monitoring</i>
14:35		Dennis Flachs <i>Sustainable PLA electrets: a comparison of commercial and solution-cast foils</i>
14:55		Philipp Schäffner <i>Imperceptible sensor sheet based on ultraflexible ferroelectric polymer transducers and</i>

# Piezo- and Pyro-electricity in Polynorbornene-Based Stretchable Elastomer Electrets

Thulasinath Raman Venkatesan<sup>1</sup>, Francis Owusu<sup>1,2</sup>, Frank A. Nüesch<sup>1,2</sup> and Dorina M. Opris<sup>1,3\*</sup>

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**Abstract:** A novel piezo- and pyro-electric elastomer electret was prepared using polar amorphous polynorbornene (PNBE) as the electroactive filler in a polydimethylsiloxane (PDMS) matrix. Under the influence of an electric field, the composite was heated above the glass transition of the filler and subsequently cooled back to room temperature (RT), thereby freezing the oriented dipoles. The resultant composites with 30 wt.% of PNBE showed a high piezoelectric  $d_{31}$  coefficient of 37 pC/N and a quasi-static pyroelectric coefficient of 0.54  $\mu\text{C}/\text{m}^2\text{K}$ .

**Keywords:** Piezoelectricity, Pyroelectricity, Elastomer Electrets, Electroactive Elastomer Composite

## Introduction

The currently available pyro- and piezo-electric devices are mostly based on ceramic materials, which limits their flexibility and applicability to large and non-uniform surface areas. On the other hand, fluorinated polymers such as polyvinylidene fluoride and its copolymers are environmentally unfriendly and suffer from limited stretchability. To overcome these limitations, free-standing composite elastomer electret films were prepared by introducing polar amorphous PNBE filler particles in a PDMS matrix and their piezo- and pyro-electric effects were investigated.

## Results and Discussion

The pyroelectric coefficient ( $p$ ) was measured at RT by subjecting the poled composite to a sinusoidal temperature variation and measuring the resultant pyroelectric current. The calculated  $p$  coefficients for both the composite and filler plotted as a function of poling field in Figure 1 exhibit a non-linear trend as

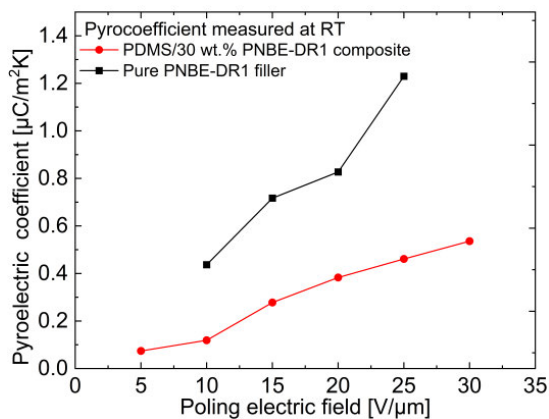


Figure 1: Pyroelectric coefficient measured at RT for a 30 wt.% PNBE-DR1 filled PDMS matrix compared with neat PNBE-DR1 filler

expected. The  $p$  coefficient of the composite is comparable with that of other non-fluorinated polar polymers from the literature, as inferred from Table 1. Since pyroelectric materials are also piezoelectric by nature, the piezoelectric coefficient was measured in the

$d_{31}$  direction while subjecting the composite film to a 50% strain along the planar axis. A  $d_{31}$  value of 37 pC/N was recorded, which is the highest among the reported elastomer electrets [1].

Table 1: Pyroelectric  $p$  coefficient at RT for the elastomer composite in comparison with other non-fluorinated polar polymers from the literature [2]

Polymer	$p$ [ $\mu\text{C}/\text{m}^2\text{K}$ ]	Poling field [V/ $\mu\text{m}$ ]
PDMS/30 wt.% PNBE-DR1 composite	0.46/0.54	25/30
PNBE-DR1	1.23	25
PVA with azobenzene alkoxy side chains	0.24	25
P(AN-co-VAc)	1.94	30

## Conclusions

Elastomer electret composite films based on polynorbornene filler particles in a PDMS matrix after poling show attractive piezo- and pyro-electric properties that could be exploited in energy generators or as sensors taking advantage of their stretchable nature in combination with their flexibility and easy processability.

## References

- [1] F. Owusu *et al.*, "Stretchable High Response Piezoelectric Elastomers Based on Polable Polynorbornene Fillers in a Polydimethylsiloxane Matrix," *Adv. Funct. Mater.*, vol. 32(41), p. 2207083, 2022.
- [2] H. K. Hall *et al.*, "Novel Cyano-Containing Copolymers of Vinyl Esters for Piezoelectric Materials," *J. Polym. Sci. A Polym. Chem.*, vol. 30(11), pp. 2341–2347, 1992.

## Acknowledgements

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# Abnormality detection system based on piezoelectric polymer

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**Abstract:** We have developed a method to realize piezoelectric polymers into disposable and large-area flexible sensors. A machine learning algorithm that uses both the output from the piezoelectric PVDF and the amount of charge in the vibration energy harvester as features is shown to enable battery-less and highly accurate fault diagnosis. Furthermore, the matrix-array PVDF stress sensor was found to be highly accurate using a crosstalk elimination algorithm based on linear programming.

**Keywords:** piezoelectric, energy harvesting, machine learning, sensor, linear programming

## Introduction

Piezoelectric polymers have potential applications in large-area, disposable flexible stress sensors. By utilizing machine learning and linear programming to interpret this sensor output, complex signal processing can be achieved with high accuracy. In this study, we report on the development of a batteryless monitoring system for abnormal conditions and a system for evaluating stress distribution with a matrix sensor structure.

## Results and Discussion

Figure 1 shows a system that detects anomalies, including compressor overturn, and diagnoses its condition using machine learning [1]. The electric power generated by vibration power generation was charged into a capacitor, and the sensor voltage data of the PVDF film was intermittently transmitted to a remotely installed PC. At this time, the amplitude of the PVDF output voltage and the time interval of wireless transmission were learned according to the compressor's normal or abnormal state. Then, it was confirmed that the system was able to discriminate with 99% accuracy, when the state was diagnosed during test data transmission. This system operates without batteries and can acquire information in the environment permanently. We concluded that the use of vibration energy harvester is advantageous in that its accuracy can be improved by using the wireless transmission interval related to the amount of electricity generated as a feature value.

Figure 2 shows a matrix-array PVDF sensor with electrodes formed on a grid, measuring occlusal force distribution. Although the matrix array structure can simplify the element configuration, the problem of signal crosstalk becomes apparent. It was found that the piezoelectric charges induced at the top and bottom electrodes, respectively, are detected using a charge amplifier and a differential amplifier circuit, and that the superposition of crosstalk can be eliminated by a linear programming method. This crosstalk elimination algorithm is adaptable to any

piezoelectric material and is expected to measure stress distribution in flexible, arbitrarily shaped objects.

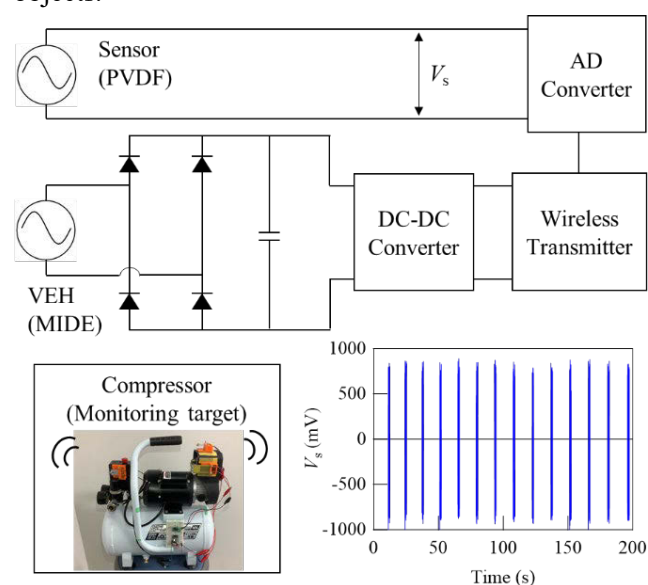


Figure 1: Experimental setup for diagnosing failures of air compressor.

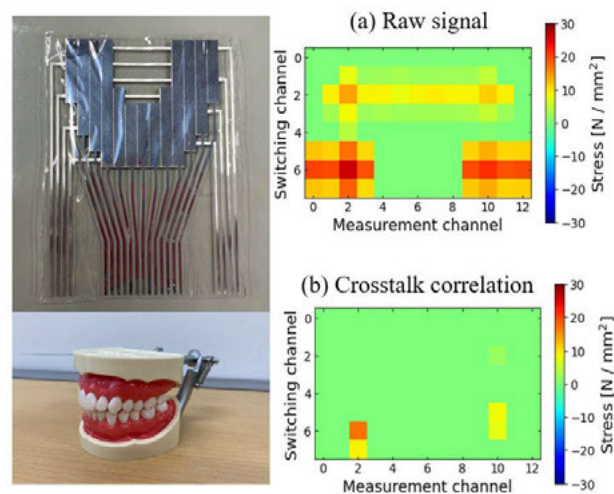


Figure 2: Bite force distribution measurement using PVDF sensor.

[1] T. Sato, M. Funato, K. Imai and T. Nakajima Y. Takase, *Sens. Mater.*, 34, 1909-1916, 2022.

# Fully Degradable, Highly Sensitive Electret-Based Pressure Sensor for Biomechanical Monitoring

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**Abstract:** Given the global environmental crisis caused by electronic waste (e-waste), the development of the advanced electronics using sustainable materials have attracted great interests, however, their preparation still remains a challenge. In this work, we proposed a fully degradable pressure sensor with cellular polylactic acid (PLA) with serrated wavy structure as electret layer and molybdenum (Mo) as electrodes. The developed pressure sensor shows a high sensitivity of 10 V/kPa and a prominent pressure resolution of 0.91%. This kind of biodegradable devices may pave a way for the development of novel sustainable electronics.

**Keywords:** biodegradable, cellular PLA electret film, pressure sensor, sustainable electronics

## Introduction

Nowadays, humans are experiencing a digital world with an increased link to all kinds of electronics, which greatly benefit our life and renovate our productivity drastically. Nevertheless, electronic devices are often with limited lifetime, and they may produce electronic litter on the earth after their service [1]. As an important element in a variety of electronics, new types of electromechanical transducers with the features of biodegradability, and excellent electromechanical coupling properties are greatly desired [2].

## Results and Discussion

Figs. 1(a) and (b) present the digital photograph and cross-sectional schematic illustration of the assembled pressure sensor, where serrated wavy

PLA electret film with charges in different polarities on the upper and lower surfaces was sandwiched into two pieces of metal molybdenum sheets. The serrated wavy structure of the PLA electret film can provide large compression deformation, resulting in prominent sensitivity when external pressure is applied. Fig. 1(c) shows the generated voltage-time response curve of the pressure sensor under external pressures ranging from 0.03 to 62.4 kPa. The response voltage of the device is increasing in parallel with the pressure applied, indicating that the device is capable of sensing and distinguishing among different levels of forces. Additionally, the device reaches open-circuit voltage of ~70 V under pressure of 62.4 kPa.

## Conclusions

In summary, the present work justified the suitability of using cellular PLA electret films for the construction of fully degradable, high-performance pressure sensors, implying their great potential in sustainable wearable electronics both in vivo and in vitro.

## References

- [1] H. Liu, Q. Shu, H. Xiang, H. Wu, Z. Li, H. Zhou, "Fully degradable triboelectric nanogenerator using graphene composite paper to replace copper electrodes for higher output performance," *Nano Energy*, 108, 108223, 2023.
- [2] X. Ma, Q. Hu, Y. Dai, P. He, X. Zhang, "Disposable sensors based on biodegradable polylactic acid piezoelectret films and their application in wearable electronics," *Sensors & Actuators: A. Physical*, 346 113834, 2022.

## Acknowledgements

Xingchen Ma and Yi Qin contributed equally to this work. This work was supported by the National Natural Science Foundation of China (NSFC, Grant Nos. 62201392 and 61761136004).

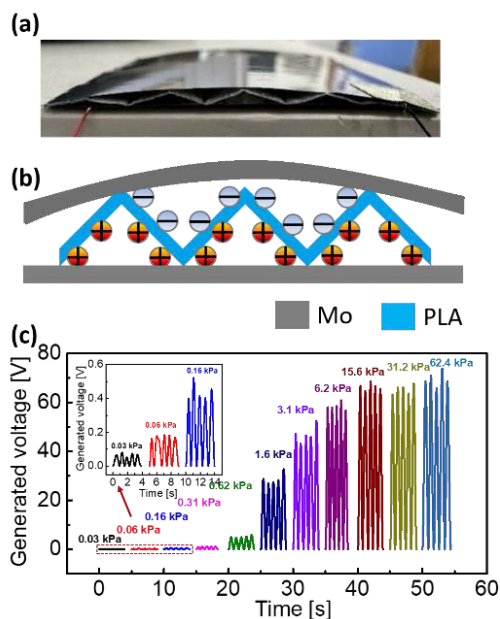


Figure 1: Structure design and sensing performance of the PLA electret-based transducer. (a) Digital photograph of the device, (b) schematic illustration of its cross-sectional structure, (c) Generated voltage of the device with different applied pressures.

# Imperceptible sensor sheet based on ultraflexible ferroelectric polymer transducers and active matrix integration

Philipp Schäffner<sup>1</sup>, Andreas Petritz<sup>1,2</sup>, Esther Karner-Petritz<sup>1,2</sup>, Jonas Groten<sup>1</sup>, Takafumi Uemura<sup>2,3</sup>, Naoko Namba<sup>2,3</sup>, Teppei Araki<sup>2,3</sup>, Tsuyoshi Sekitani<sup>2,3</sup>, and Barbara Stadlober<sup>1</sup>

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**Abstract:** Energy autonomy and conformability are essential elements in the next generation of wearable and flexible electronics for healthcare, robotics and cyber-physical systems. We present 2.5  $\mu\text{m}$  thin sensor sheets relying on the piezoelectric P(VDF-TrFE) and show their integration with an active matrix readout electronics based on organic thin film transistors.

**Keywords:** P(VDF-TrFE), ultraflexible, ultrathin piezoelectrics, active matrix

## Introduction

Polymer piezoelectric materials offer the advantage that they can be processed to ultrathin layers that are flexible and perfectly conform to moving and complex 3D surfaces like the human body. We used an ultrathin layer of P(VDF-TrFE) on a 1  $\mu\text{m}$  thin parylene substrate to build an imperceptible biomedical sensor, which also has the potential for self-sustained operation.[1]

Furthermore, we show an active matrix pressure sensor where organic transistors are monolithically integrated with the ferroelectric transducers. More than 100 pixels at a pitch of  $\approx 3\text{mm}$  are addressed in this way. [2]

## Results and Discussion

The ferroelectric properties of ultraflexible P(VDF-TrFE)-based transducers (UFPTs) were optimized through thermal annealing resulting in an increased crystallinity and remanent polarization (up to 70  $\text{mC}/\text{m}^2$ ). As predicted by numerical simulations, the ultrathin design improved sensitivity to strain and pressure as compared to devices on rigid thick substrates with values up to 15  $\text{nC}/\text{N}$ . They have a fast response ( $\ll 10 \text{ ms}/\text{N}$ ) and excellent mechanical stability (stable under bending around 40  $\mu\text{m}$ ).

For the active matrix sensor (Figure 1), the ultrathin transducers were combined with organic thin film transistors featuring ultralow noise level. The thickness of only 2.8  $\mu\text{m}$  renders the organic active matrix sensor sheet ultraflexible and therefore virtually imperceptible on the human skin. Real-time monitoring of tactile modes in a subset of  $8 \times 3$  pixels and of the pulse wave including heart rate and blood pressure using four sensors of the matrix is demonstrated.

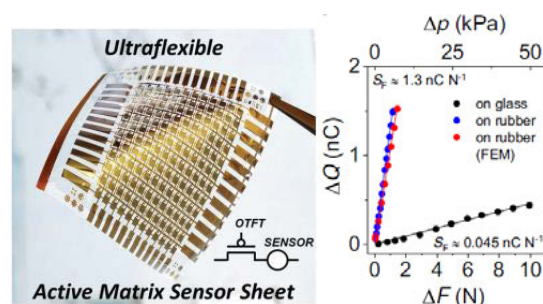


Figure 1: An ultraflexible  $12 \times 12$  active matrix sensor sheet consisting of P(VDF-TrFE) transducers and organic thin film transistors.

## Conclusions

The presented ultrathin piezoelectric transducers have high potential for use as self-sustained wearable biomedical sensors and feature high sensitivity combined with good spatial and temporal resolution.

## References

- [1] A. Petritz, E. Karner-Petritz, T. Uemura, P. Schäffner, T. Araki, B. Stadlober, T. Seketani, "Imperceptible energy harvesting device and biomedical sensor based on ultraflexible ferroelectric transducers and organic diodes", *Nat. Comm.*,12:2399, 2021.
- [2] E. Karner-Petritz, A. Petritz, T. Uemura, N. Namba, T. Araki, T. Seketani, B. Stadlober. „Ultraflexible Organic Active Matrix Sensor Sheet for Tactile and Biosignal Monitoring”, *Adv. Electron. Mater.*, 2201333, 2023.

## Acknowledgements

This work has been supported financially by the Austrian Science Fund (FWF) (J4145-N30, I5967-N), Japan Science and Technology Agency (JST) FOREST Program (grant numbers JPMJFR2035 and JPMJFR2022), JST Moonshot R&D Program (Grant Number JPMJMS2012), and Japan Society for the Promotion of Science (JSPS) Bilateral Program (Grant Number JPJSBP120222002).

Thursday, September 21<sup>th</sup>, 2023

## SESSION 12

15:45	Session 12 Chairs: Dmitry Rychkov, Christiane Thielemann	Carmo Lança <i>TSDC and surface potential measurements of charged hydroxyapatite/BaTiO<sub>3</sub> biocoatings deposited by CoBlast</i>
16:05		Sridharbabu Yarramaneni <i>Thermo-electret behaviour of PET/0.8PHB, PET/0.6PHB polymer liquid crystals</i>
16:25		Yuji Suzuki <i>Deep-learning-assisted discovery of amorphous fluorinated polymer electret with high charging performance for energy</i>
16:55		Yuji Suzuki : <i>Welcome to ISE 20</i>
17:05		Closing Ceremony

# TSDC and surface potential measurements of charged hydroxyapatite/BaTiO<sub>3</sub> biocoatings deposited by CoBlast

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**Abstract:** When a hydroxyapatite (HAP) coated implant is surface charged, the early stages of osteointegration are accelerated. Adding a piezoelectric material to the coating, such as biocompatible barium titanate (BT), can help to increase surface charges and contribute to a faster patient recovery. HAP and HAP/BT coatings were deposited on Ti-6Al-4V alloy substrates using CoBlast<sup>TM</sup>. To compare between materials, coatings were charged by DC contact polarization or by corona discharge at high temperature. Thermally stimulated discharge currents (TSDC) and surface potential measurements were performed.

**Keywords:** TSDC, hydroxyapatite, corona charging, contact charging, hard tissue engineering

## Introduction

In hard tissue engineering, HAP is widely as coating for implants, such as for hip replacement, the structural component is made of a titanium alloy (Ti-6Al-4V) coated with plasma sprayed HAP. The high temperature of the plasma leads to the formation of amorphous calcium phosphates resulting in a too fast dissolution rate of the coating (that must biodegrade at a similar rate of new bone growth). Techniques such as CoBlast<sup>TM</sup>, a room temperature (RT) blasting process, maintains the original crystalline hydroxyapatite. It is known that surface charges on the coating act as cells' cues to accelerate the regenerative process of the bone. Addition of materials that can increase surface charge, such as biocompatible piezoelectric ceramics, may lead to faster bone regeneration.

## Results and Discussion

Cubic BT (cBT) nanopowders and tetragonal BT (tBT) micropowders and HAP micropowders (Altakitin) were used as coating materials. For comparison, 100% HAP coatings by plasma spray (PS) were made. 100% HAP and 80/20%(m/m) HAP/tBT and HAP/cBT were coblasted (CB) together with abrasive alumina (50/50% m/m).

Corona charging was made from RT to 300°C, needle tip potential -5 kV and grid potential -1 kV (for 1 and 5 min). The highest surface potential measured was -2 kV (300 °C, 5 min) for PS HAP, one order of magnitude higher than all other results. For coblasted HAP, the highest value was registered for room temperature. For CoBlast<sup>TM</sup>, the coating film has a thickness of 6 µm and for PS of 13 µm with a surface roughness of comparable values [1]. This results in higher electrical conductivity for CB HAP. With temperature increase, the coating becomes enough conductive to reduce surface charging. The HAP/BT samples had the highest

potential for 250 °C. Comparing cBT (nanopowders) and tBT (micropowders), the potential was lower for the cBT. Since charging and measurements were made above the Curie temperature, the difference observed is related with powders size.

DC contact charging/poling conditions were 200 °C,  $E = \pm 10$  kV/mm, 1h. TSDC measurements were made from RT to 250 °C at  $\beta=10$  °C/min. Some samples were not charged and others underwent a thermal cycle (1h at 200 °C,  $E=0$ ). In fig. 1 it is seen the thermogram for HAP/tBT, with the non-poled coating showing a wide peak around 160 °C.

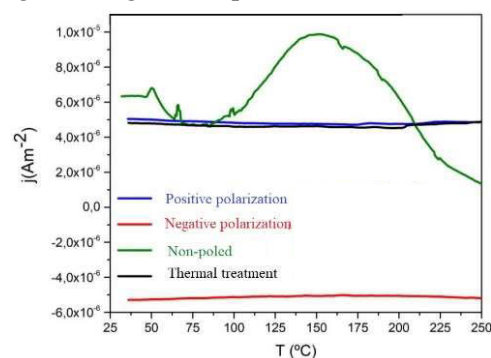


Figure 1: TSDC results for HAP/tBT showing the results for the total charge density.

## Conclusions

PS HAP has higher charge than CB coatings, including the ones with BT. This can mainly be caused by the CB films being thinner than PS deposited ones. CB HAP/tBT have higher charge density compared to CB HAP and CB HAP/cBT.

## References

- [1] I.J.G. Dias, A.S. Pádua, E. A. Pires, J.P. M.R. Borges, J.C. Silva, and M.C. Lança, Hydroxyapatite- Barium Titanate Biocoatings Using Room Temperature Coblasting, "Crystals, 13 (4), 579-, Mar. 2023

# Thermo-Electret Behaviour of PET/0.8PHB, PET/0.6PHB Polymer Liquid Crystals

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**Abstract:** Thermo-electret behaviour of PET/0.8PHB and PET/0.6PHB polymer liquid crystals were investigated using thermally stimulated depolarization current (TSD current) technique from room temperature to 250°C. Thermo-electrets were prepared at polarizing temperatures 90°C and 180°C, polarizing field was 95.2kV/cm and 129.0kV/cm. TSD current spectra consists of three current maxima around 60°C, 130°C and 180°C representing three kinds of relaxation phenomenon termed as  $\beta'$ -,  $\beta$ -, and  $\alpha$ -relaxations respectively. Dependence of relaxation temperature on polarizing temperature was observed.

**Keywords:** Thermo-electret, PET/0.6PHB, PET/0.8PHB, TSDC

## Introduction

Electrets have attracted scientists and engineers because of their applications in variety of areas including novel electret nano fibrous membranes<sup>1,2</sup>, ionic electrets<sup>3</sup>, photo responsive OFET memory<sup>4</sup>, etc. However, a little work was reported on the electret behaviour of PET/x.PHB polymer liquid crystals<sup>5,6</sup>, for x=0.6 and 0.8 (x is the molar concentration of liquid crystalline PHB sequences in the copolymer). The material used in the present study is one of the first known thermoplastic polymer liquid crystals poly(*p*-hydroxybenzoic acid-co-ethylene terephthalate) usually written as PET/x.PHB.

In the present paper thermo-electrets of polymer liquid crystals were prepared at polarizing temperatures 90°C and 180°C, polarizing fields 95.2kV/cm and 129.0kV/cm.

## Results and Discussion

TSD currents of PET/0.8PHB & PET/0.6PHB at Polarizing fields 95.2kV/cm and 129kV/cm are shown in Figure 1. TSD currents were obtained by heating the polarized samples at a constant heating rate i.e. 2°C/minute (room temperature- 250°C) using Keithley's high precision electrometer 610C. The spectra consist of three current maxima around 60°C, 130°C and 180°C representing three kinds of relaxation phenomenon termed as  $\beta'$ -,  $\beta$ -, and  $\alpha$ -relaxations respectively. It is clear from the spectra that the magnitude of TSD currents depends on the polarizing fields. The low temperature relaxation appears to be closely associated with dipolar relaxations of both PET & PHB phases<sup>5</sup>. High temperature peak (180°C to 210°C) is assigned to the space charge relaxation mechanism. The maxima appearing in the range of 120°C to 150°C is due to the electric dipole orientation polarization<sup>5</sup>.

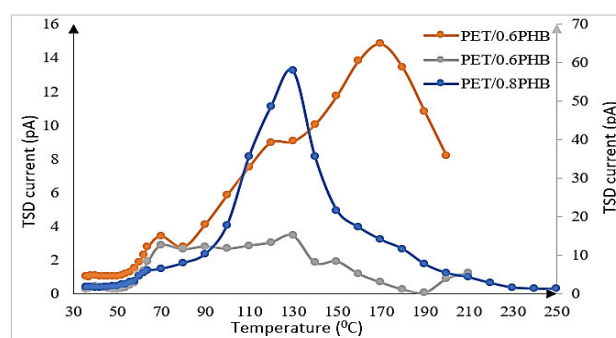


Figure 1: TSD currents for PET/0.8PHB polarized at 180°C and for PET/0.6PHB polarized at 90°C, 180°C, Polarizing fields 95.2kV/cm and 129kV/cm. Right side y-axis is for PET/0.8 PHB and left side y-axis is for PET/0.6PHB.

## Conclusions

PET/x.PHB polymer liquid crystals consist of mainly three relaxations termed as dipolar, dipolar orientation and space charge.

## References

- [1] Shan Wang et al., "Electret polyvinylidene fluoride nanofibers ... for high-efficiency air filtration," ACS Appl. Mater. Interfaces, 8, 36, 23985-23994, 2016.
- [2] Huiming, X. et al., "A Flexible Electret Membrane with ... Harvesting. Sci Rep 7, 8443 (2017).
- [3] Logan S. McCarty et al., "Ionic Electrets: Electrostatic ... Contact." Journal of the American Chemical Society, 129, 13, 4075-4088 (2007).
- [4] Rengjian Yu et al., "Electret-Based ... Computing," ACS Appl. Mater. Interfaces 12, 15446-15455 (2020).
- [5] Sridharbabu, Y. et al., "TSDC ... samples," Journal of Materials Science, 39, 4651-4653 (2004).

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# Deep-learning-assisted Discovery of Amorphous Fluorinated Polymer Electret with High Charging Performance for Energy Harvesting

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## Introduction

Electret-based vibration energy harvesting (EH) is advantageous in terms of higher output power at low frequencies and small volumes [1]. We previously found that CYTOP (AGC Chemicals), which is amorphous fluorinated polymer, offers high surface potential. Although the number of repeat units is over 1000, the charging performance is very sensitive to the functional group at both ends [2].

We recently found through the quantum chemical analysis that the trapped charge is localized at the amide bond, which is formed by the dehydration reaction between the amine added and the carboxyl end group of CYTOP CTX-A [3,4].

In this talk, our recent studies on deep-learning-assisted discovery of new CYTOP-based polymer electret are discussed.

## AI-driven Discovery of CYTOP Electret [5]

We performed optimization on the functional groups of CYTOP by seeking in a large chemical database for promising amines which can react with the carboxylic groups in CTX-A. We employ the solid-state vertical ionization potential (IP) as a descriptor for the charging performance estimation. The electret discovery workflow is presented in Figure 1. After training MatErial Graph Network (MEGNet) models [6] with 5,522 IP data via quantum chemical computation, three molecules out of 1,176,591 candidates from the database are successfully identified and synthesized to validate their charging performance experimentally. The computational speed is  $10^7$ - $10^8$  times faster than the DFT/PCM-based rigorous computations.

One of the best candidates is 1,4-Bis(3-amino-propyl)piperazine (BAPP) with the solid-state IP of 5.32 eV, which exhibits -3.49 kV of surface potential with a 15  $\mu\text{m}$ -thick film. Even in the high temperature of 115  $^{\circ}\text{C}$ , which is above the glass transition temperature, the decay of surface potential is slow. Its estimated decay time at 80  $^{\circ}\text{C}$ , which is the maximum operation temperature for consumer products, is over 140 years, and is much longer than our previous electret material [4].

## Conclusions

Machine learning based on MEGNet is used to evaluate the charging performance in the amorphous polymer electret. The potential of the deep-learning-

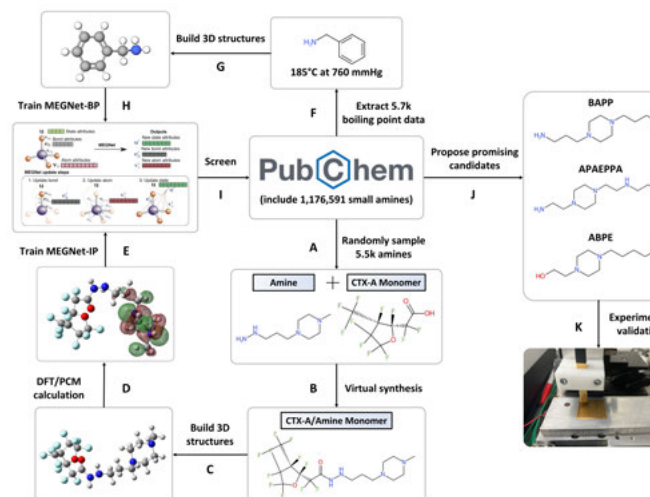


Figure 1: Work procedure for fast screening promising electret candidates from PubChem and experimentally validate the charging performance [5].

based model is clearly shown for polymer electret discovery.

## References

- [1] Y. Suzuki, "Recent Progress in MEMS Electret Generator for Energy Harvesting," *IEEJ Trans. Electr. Electron. Eng.*, Vol. 6, pp. 101-111, 2011.
- [2] K. Kashiwagi, et al., "Nano-Cluster-Enhanced High-Performance Perfluoro-Polymer Electrets for Energy Harvesting," *J. Micromech. Microeng.*, Vol. 21, 125016, 2011.
- [3] S. Kim, et al., "Solid-State Electron Affinity Analysis of Amorphous Fluorinated Polymer Electret," *J. Phys. Chem. B*, Vol. 124, pp. 10507-10513, 2020.
- [4] Y. Zhang, et al., "Discovery of Polymer Electret Material via de Novo Molecule Generation and Functional Group Enrichment Analysis," *Appl. Phys. Lett.* Vol. 118, 223904, 2021.
- [5] Z. Mao, et al., "AI-driven Discovery of Amorphous Fluorinated Polymer Electret with Improved Charge Stability for Energy Harvesting," *Adv. Mater.*, submitted.
- [6] C. Chen, et al., "Graph Networks as a Universal Machine Learning Framework for Molecules and Crystals," *Chem. Mater.* Vol. 31, 3564-3572, 2019.

## Acknowledgements

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Friday, September 22<sup>nd</sup>, 2023

# WORKSHOP

## ELECTROACTIVE POLYMERS FOR SOFT TRANSDUCERS

*Chairs: Martin Kaltenbrunner, Christoph Keplinger*

**09:10**

Marco Fontana  
*Materials for fluid-gap electrostatic actuators*

**09:40**

Florian Hartmann  
*Swimming robots powered by soft  
electrohydraulic actuators*

**10:10**

Ellen Rumley  
*Fully biodegradable electrohydraulic actuators for  
sustainable soft robots*

**10:40**

**COFFEE BREAK**

**11:00**

Naoji Matsuhisa  
*Soft transducers using stretchable electronic materials*

**11:30**

Giacomo Moretti  
*An overview on the design and development of dielectric  
elastomer transducers for dynamic applications*

**12:00**

**END OF THE WORKSHOP**

**12:30**

**LUNCH**



# Materials for fluid-gap electrostatic actuators

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**Abstract:** There has been a growing interest in soft robotics towards new types of electrostatic actuators that use dielectric fluids and insulating polymer-based thin-films, providing advantages like high power density, quick response, and cost-effectiveness. This contribution aims at exploring how the use of different dielectric materials for realization of such devices can influence their performance and introduce a possible solution for the future improvement of fluid-gap zipping electrostatic actuator systems.

**Keywords:** multilayer dielectrics, fluid-gap, hasel, ebm,

## Introduction

Soft robotics has seen a surge of interest in novel electrostatic actuators that use fluidic gaps, offering high power density, rapid response, and affordability. There are multiple actuation approaches that employ dielectric fluids in conjunction with flexible, insulating polymer-based thin-films, which are deformed through the application of high electric fields [1-5]. The performance of such actuators is strongly influenced by the properties of the employed polymeric materials. The capacitive nature of these devices calls for the use of materials that exhibit high breakdown field, large dielectric constant, and low conductivity. However, the presence of multiple adjacent layers of materials that are exposed to high electric fields can give rise to charge accumulation phenomena, which can lead to a degradation in the performance of the system. This study demonstrates how different combinations of materials can be intentionally selected to mitigate the impact of charge accumulation.

## Results and Discussion

An experimental setup was developed with a specific focus on assessing the time-dependent force response of fluid-gap capacitive actuators. The setup involved constructing a capacitor comprising a solid and liquid dielectric layer, with one of the electrodes suspended by a relatively flexible beam. Application of voltage resulted in an attractive force between the electrodes, causing a deflection in the beam that was measured using optical methods (see Fig.1-left), providing an accurate estimation of the developed attractive force.

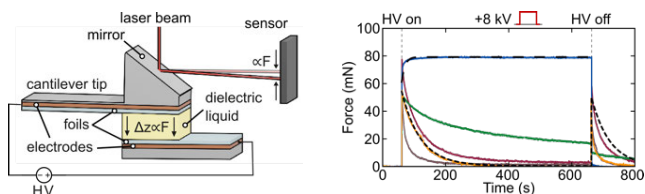


Figure 1: Left schematics of the employed setup and (right) different response over time of different solid dielectric materials when a step electric field is applied.

Various combinations of dielectric materials were utilized and tested, as depicted in Fig.1-right. The results revealed a significant dependence of the time

response on the specific combination of materials selected, with certain examples exhibiting a sharp decline in force, while others demonstrated no evidence of force decay.

## Conclusions

An experimental investigation has been undertaken on fluid-gap zipping actuators fabricated from a range of materials to demonstrate the impact of charge accumulation on force decay in liquid-gap electrostatic actuators. The results of this study hold the potential to develop a new category of fluid gap zipping actuators that exhibit superior energy densities, stability during steady-state operation, and high power efficiency.

## References

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- [1] Kellaris, N., Gopaluni Venkata, V., Smith, G.M., Mitchell, S.K. and Keplinger, C., 2018. Peano-HASEL actuators: Muscle-mimetic, electrohydraulic transducers that linearly contract on activation. *Science Robotics*, 3(14), p.eaar3276.
- [2] Moretti, G., Duranti, M., Righi, M., Veretchy, R. Fontana, M., 2018, March. Analysis of dielectric fluid transducers. In *Electroactive Polymer Actuators and Devices XX* (Vol. 10594, pp. 142-154). SPIE.
- [3] Sîrbu, I.D., Moretti, G., Bortolotti, G., Bolignari, M., Dirè, S., Fambri, L., Veretchy, R. and Fontana, M., 2021. Electrostatic bellow muscle actuators and energy harvesters that stack up. *Science Robotics*, 6(51), p.eaaz5796.
- [4] Taghavi, M., Helps, T. and Rossiter, J., 2018. Electro-ribbon actuators and electro-origami robots. *Science Robotics*, 3(25), p.eaau9795.
- [5] Leroy, E., Hinchet, R. Shea, H., 2020. Multimode hydraulically amplified electrostatic actuators for wearable haptics. *Advanced Materials*, 32(36), p.2002564.

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This study was conducted in a collaborative effort between the Soft Matter Physics (SoMaP) Division at Johannes Kepler University and the Department of Industrial Engineering of the University of Trento.

# Swimming robots powered by soft electrohydraulic actuators

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**Abstract:** Undulating fin and tail propulsion—used by marine animals across many size scales—represents an efficient locomotion method, both on and underwater. It is silent and enables a variety of maneuvers. Robotic swimmers can achieve such life-like locomotion using soft actuators but typically measure several tens of centimeters, preventing applications that benefit from smaller scales. Here we present the design, material approaches, and fabrication processes of soft mm-scale electrohydraulic actuators. Our actuators use zipping of metalized polymer films to displace a dielectric fluid, which generates the bending of fins, creating a periodic undulation. With these actuators, we demonstrate flatworm-inspired robots that locomote both on or under water.

**Keywords:** soft electrohydraulic actuators, electrostatic zipping, swimming robots

## Introduction

Maritim animals, such as the flatworm or the cuttlefish, move through the water using undulating fin propulsion. This locomotion pattern allows versatile maneuvers while being energy efficient. The same propagation mechanism can be employed in swimming robots, harnessing the advantages of soft electrohydraulic actuators. Driven by high voltage these actuators generate undulations in soft fins and allow forward propagation and rapid turns. This undulation allows the robot to swim underwater or on the water's surface. We present the design, material approaches, and fabrication processes of soft mm-scale electrohydraulic actuators, which are integrated into a 45 mm-long swimming robot.

## Results and Discussion

The flatworm-inspired design features two actuators on each side that generate a traveling wave locomotion in soft fins. Through a high-voltage signal, actuators generate a bending motion that drives the undulation. To realize this motion, our actuators use zipping of metalized polymer films to displace internal dielectric fluid and, in combination with a stiffening layer on the top side of the actuator, results in a downward bending motion. We developed a fabrication strategy based on multilayer lamination to enable actuators that operate reliably when submerged in water at 500 V to 2 kV. The actuators are fast, capable of operation up to 100 Hz, and provide suitable amplitudes for swimming, with bending angles up to 15 degrees. With these actuators, we demonstrate flatworm-inspired robots, only a few tens of millimeters long, that locomote both on or under water. The robots are capable of various fast maneuvers, from swimming forward to making clockwise or anticlockwise turns. Introducing high-performance dielectrics, the driving voltage is lowered to <600 volts, allowing untethered locomotion of these robots.

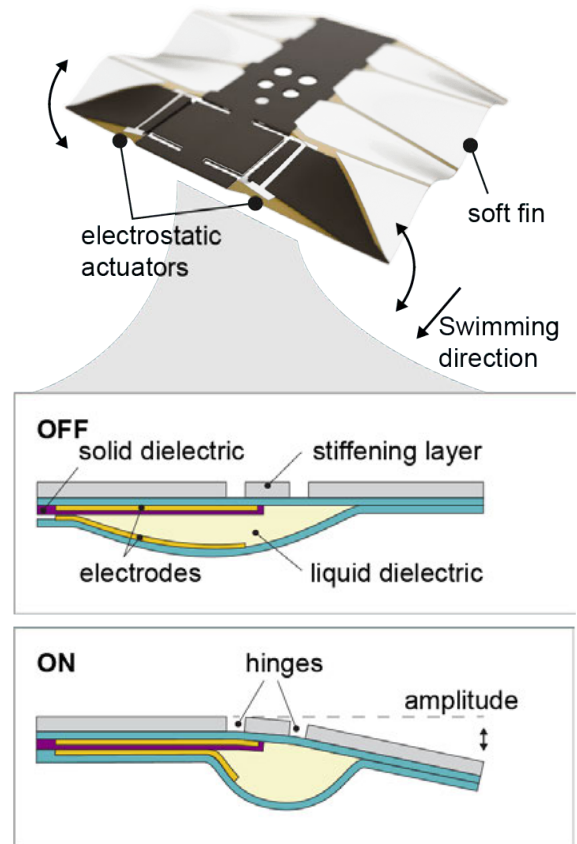


Figure 1: Illustration of a 45-mm-long swimming robot powered by soft electrohydraulic actuators.

## Conclusions

This work presents small-scale swimming robots driven by soft electrohydraulic actuators. These robots locomote on the water's surface through undulating fin propulsion. These robots are fast, agile, and durable and present a platform to build a versatile class of robots for aqueous environments.

## Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No101016411.

# Fully biodegradable electrohydraulic actuators for sustainable soft robots

Ellen H. Rumley<sup>†1,2</sup>, David Preninger<sup>†3,4</sup>, Alona Shagan Shomron<sup>1</sup>, Philipp Rothmund<sup>1,2</sup>, Florian Hartmann<sup>3,4</sup>, Melanie Baumgartner<sup>3,4</sup>, Nicholas Kellaris<sup>2,5</sup>, Andreas Stojanovic<sup>3,4</sup>, Zachary Yoder<sup>1</sup>, Benjamin Karrer<sup>1,3,4</sup>, Christoph Keplinger<sup>\*1,2,5</sup>, Martin Kaltenbrunner<sup>\*3,4</sup>

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**Abstract:** For key components of soft robots, such as soft actuators, it is important to seek sustainable options like bio-derived and biodegradable materials to mitigate environmental pollution. Here, we introduce a materials system to develop biodegradable electrohydraulic soft actuators, which are capable of operating at high electric fields, performing comparably to non-biodegradable counterparts, and displaying high actuation lifetime, proving that biodegradability does not inhibit actuation performance. We use biodegradable actuators to actuate a robotic gripper that is readily compatible with commercial robot arms, demonstrating the wide applicability of biodegradable materials systems in soft robotics.

**Keywords:** electrohydraulic soft actuators, biodegradable, sustainability, artificial muscles, soft robots

## Introduction

Electrostatic soft actuators, among the promising actuator technologies, are typically made from acrylics, silicones, and other unsustainable materials that contribute to environmental pollution at their end-of-product-life [1], warranting the need to explore sustainable material options for their future development.

## Results and Discussion

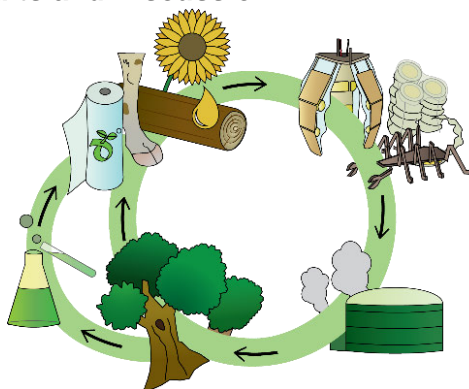


Figure 1: Representative life cycle of fully biodegradable electrohydraulic soft actuators.

We developed soft electrohydraulic actuators using NaCl-infused gelatin, 2 types of biodegradable polymer films (BOPLA and biopolyester), and a biodegradable liquid dielectric (FR3 fluid). We explored their material compatibilities and robustness for electrostatic applications using a dielectric breakdown strength test setup, and manufactured electrohydraulic soft actuators from them to compare their electromechanical performances to non-biodegradable counterparts.

Biodegradable electrohydraulic actuators were capable of tolerating high electric fields of 200 V/ $\mu\text{m}$  (BOPLA) and 74 V/ $\mu\text{m}$  (biopolyester) while exhibiting high lifetimes surpassing 100,000 actuation cycles (in the case of biopolyester actuators). We found that physical defects of commercial bioplastics (unrelated to biodegradability) currently inhibit the performance of biodegradable plastics comprising actuators, and efforts to improve manufacturing quality will further elevate actuator performance.

## Conclusions

We determined that biodegradable materials can exhibit desirable dielectric properties for electrohydraulic soft actuators and other high voltage applications, and laid the groundwork for a systematic approach towards identifying compatible materials systems for future material exploration.

## References

- [1] F. Hartmann, M. Baumgartner, M. Kaltenbrunner, Becoming Sustainable, The New Frontier in Soft Robotics. *Adv Mater* 33, (2021).

## Acknowledgements

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# Soft transducers using stretchable electronic materials

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**Abstract:** Soft electronic devices can possess mechanical properties similar to human skin, offering a platform for next-generation wearable devices and electronic skins for robots. In this talk, I will discuss a range of soft transducers using stretchable electronic materials. For example, we have developed a conducting polymer that can be intricately patterned in high resolution (<10  $\mu\text{m}$ ). These high optoelectrical properties have been fully harnessed in soft electronic devices, including skin-like transparent sensor arrays, highly skin-conformable displays, and stretchable semiconductor devices.

**Keywords:** stretchable electronics, conducting polymers, wearables

## Introduction

Conventional electronic materials are stiff and brittle, although our skin is soft and highly deformable. Therefore, developing soft and stretchable electronic materials is important to realize future wearable devices. Here I introduce soft electronic materials and the devices that can be conformably attached to our skin.

## Results and Discussion

Transparency of skin-attached wearable devices can potentially increase the adherence of the devices to the users because appearance will be one of the decision criteria in whether to wear them[1]. Our stretchable transparent conductor consists of conducting polymer, PEDOT:PSS, and Li salt ionic plasticizer. Although conventional conducting polymers, such as PEDOT:PSS, are brittle, ionic plasticizers can significantly improve ductility by altering the morphology. In addition, our stretchable polymer conductor can be patterned in a high resolution of less than 10  $\mu\text{m}$  by laser ablation[2] (Figure 1).

Fully utilizing the optoelectronic property, we realized several soft transducers. One of the examples is a capacitive touch sensor array. The sensor can be placed on our hand as a large-area interface to a computer or on robots as the skin for interaction with people.

Our transparent and stretchable conducting polymer is also useful for fabricating stretchable displays. The display is based on an electrochromism, and fabricated by sandwiching a solid electrolyte layer with two sheets of the stretchable PEDOT:PSS. The electrochromic display (ECD) showed a clear color contrast at a low voltage of less than 2 V, and a stretchability of 50%. The stretchable display is useful for showing information obtained by sensors. We recently succeeded in improving the skin

conformability of the ECD by reducing the total thickness to less than 10  $\mu\text{m}$ .



Figure 1: Transparent and stretchable polymer conductors patterned by UV laser ablation.

## Conclusions

Stretchable electronic materials enable skin-like soft transducers which can seamlessly connect human and electronics. The soft sensors accurately measure signals from human in long term. Displays on skin will alter the interaction between human and computers.

## References

- [1] T. Shimura, S. Sato, P. Zalar, and N. Matsuhisa, "Engineering the comfort-of-wear for next generation wearables," *Adv. Electron. Mater.*, p. 2200512, Oct. 2022.
- [2] T. Shimura *et al.*, "A high-resolution, transparent, and stretchable polymer conductor for wearable sensor arrays," *Adv. Mater. Technol.*, vol. 8, no. 12, Jun. 2023, doi: 10.1002/admt.202201992.

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# An overview on the design and development of dielectric elastomer transducers for dynamic applications

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**Abstract:** This contribution deals with design of dynamic systems with dielectric elastomer (DE) transducers. We examine two applications: energy harvesting from ocean waves, and coil-free DE loudspeakers. We propose a modelling/design framework that encompasses different applications in which the DE dynamics are functional to the accomplishment of a task, and we show experimental results relative to the considered applications.

**Keywords:** dielectric elastomers, energy harvesting, loudspeaker, dynamics, transducer.

## Introduction

Dielectric elastomers (DEs) are stretchable polymers that can be used to build lightweight variable-capacitance actuators and generators, with potential applications in robotics, mechatronics, and energy harvesting [1]. Some relevant applications involve the integration of DEs onto oscillating systems. For example, DEs can be used as generators in mechanical energy harvesters (from human motion, sea waves, etc.), which exploit oscillations of a primary mover excited by an external force to drive the deformation of the generator. Other applications involve using high-frequency deformations of DE membranes to build coil-free loudspeakers. In other applications, high-frequency voltage-induced deformations of DE membranes are used to develop coil-free loudspeakers. Despite their diversity, these applications share some functional requirements, e.g., the need for mechanically resonant designs, in which the natural frequency of the DE transducer (or any coupled system) is matched to a target values.

## Results and Discussion

We have developed a comprehensive modelling framework that utilizes energy-based formulations to describe the dynamics of complex DE systems, including hydro-elastic or aero-elastic interactions. Using this framework, we designed resonant wave energy converters that match the natural frequency of incoming waves, optimizing power capture. We conducted tank testing of small-scale prototypes (Fig. 1), achieving significant power outputs ranging from 1-10 W, among the largest DEG prototypes demonstrated to date [2].

Additionally, we developed models for high-frequency voltage-driven vibrations and acoustic response of DE membranes. We validated those models were validated through measurements of velocity distributions on the DE using a 3D laser vibrometer (Fig. 1). Leveraging these analyses, we designed multi-function DE actuators capable of producing linear actuation while generating sound through voltage-driven structural vibrations in

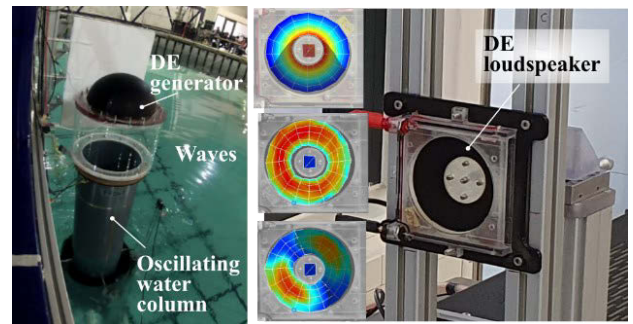


Figure 1. (a) Scaled prototype of a wave energy converter with DE generator; (b) Imaging of the vibration modes in a DE membrane loudspeaker.

different directions [3]. We applied this principle to develop multi-function audio-tactile user interfaces that provide combined acoustic and tactile feedback using multi-chromatic voltage inputs.

## Conclusions

Dynamic systems based on DEs generally need to work close to resonance to perform efficiently. We developed models of DE-based dynamic systems and used them to design wave energy converters tuned to work efficiently at frequencies matching the waves, and multi-function user interfaces utilizing different vibration modes of a single DE structure for combined audio-tactile feedback.

## References

- [1] Hajiesmaili, E., & Clarke, D. R. (2021). *Dielectric elastomer actuators*. *Journal of Applied Physics*, 129(15), 151102.
- [2] Moretti, G., Herran, M. S., ..., & Fontana, M. (2020). *Advances in the development of dielectric elastomer generators for wave energy conversion*. *Renewable and Sustainable Energy Reviews*, 117, 109430.
- [3] Gratz-Kelly, S., Rizzello, G., ..., & Moretti, G. (2022). *A Multi-Mode, Multi-Frequency Dielectric Elastomer Actuator*. *Advanced Functional Materials*, 32(34), 2201889.

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Tuesday, September 19<sup>th</sup>, 2023

POSTER SESSION

P1	<u>N. Maier</u> , M. Larsson, A. Yassine, P. Woias, A. Fischer <i>Approach to improve SiO<sub>2</sub>-based electrets with AlO<sub>x</sub> deposited by atomic layer deposition (ALD)</i>
P2	<u>A. Guliakova</u> , A. Henderyckx, A. Rychkov, N. Shishkin and <u>D. Rychkov</u> <i>The influence of crystallinity and isotacticity on charge decay in polypropylene blends</i>
P3	<u>S. Sabzpoushan</u> , P. Woias, <i>Protecting spontaneous-polarization electrets from light illumination</i>
P4	B. Lyu, J. Zhang, <u>K. Tao</u> <i>Flowing water enables steerable charge distribution on electret surface</i>
P5	<u>J. van Turnhout</u> <i>Ion enhanced hydrocharging of filter webs</i>
P6	<u>J. van Turnhout</u> <i>Using corona gas discharges for the disinfection of seeds and the defouling of biofilms</i>
P7	Y. Yang, J. Xu, <u>X. Zhang</u> , Y. Liang <i>Synergistic effect of positive electret combined with 5- fluorouracil on growth inhibition of scar fibroblasts</i>
P8	Q. Hu, <u>X. Ma</u> , <u>X. Zhang</u> <i>Biodegradable cellular polylactic acid ferroelectrets for acoustoelectric transducers</i>
P9	M. Galikhanov, <u>X. Zhang</u> , <u>X. Ma</u> <i>The effect of modifier on electret properties and hardness of epoxy composite material</i>
P10	L. Zhou, <u>X. Zhang</u> <i>Thermally stable piezoelectric fibers based on ferroelectrets</i>
P11	<u>Y. Yasuno</u> <i>Underwater microphone with cellular polymer electrets)</i>
P12	<u>T. Rößler</u> <i>Electrical limitation of expanding PEDOT:PSS films</i>
P13	<u>Y. Iguchi</u> , M. Narasaki, A. Uesugi, H. Honma, K. Sugano, <u>Y. Isono</u> <i>Atomic layer deposited nano-thick Al<sub>2</sub>O<sub>3</sub> electret films for surface-potential-modulation of carrier transport in SiNWs</i>
P14	<u>T. Sugano</u> , H. Kodama, <u>T. Furukawa</u> , <u>T. Nakajima</u> <i>Study on piezoelectric properties of ferroelectric Nylon 11 film</i>
P15	<u>M. Kober</u> , <u>D. Smykalla</u> , <u>B. Ploss</u> , M. Stelter, <u>S. Engel</u> <i>Spatially defined polarization of ferroelectric-semiconductor hybrid materials by optical excitation</i>

<b>P16</b>	<u>D. Smykalla</u> , <u>B. Ploss</u> , <u>S. Engel</u> <i>3D high resolution pyroelectric distributions in P(VDF-TrFE) matrix composites</i>
<b>P17</b>	Y. Bian, <u>X. Qiu</u> , X. Luo, G. Zhu <i>Fully transparent flexible piezoelectric composite films based on electro-spun PVDF and their device applications</i>
<b>P18</b>	H. Li, L. Xie, Z. Tan, J. Xing, X. Li, H. Chen, Y. Cheng, <u>J. Zhu</u> <i>Utilization of non-stoichiometric Nb<sup>5+</sup> to optimize comprehensive electrical properties of KNN-based ceramics</i>
<b>P19</b>	<u>T. Yovcheva</u> , <u>A. Viraneva</u> , M. Marudova, A. Grigorov <i>Polyelectrolyte multilayers deposited on corona charged porous composite polylactic acid / poly(<math>\epsilon</math>-caprolactone) substrates with potential for drug delivery systems</i>
<b>P20</b>	<u>A. Viraneva</u> , M. Marudova, A. Grigorov, S. Milenkova, <u>T. Yovcheva</u> <i>Benzydamine loaded casein nanospheres embedded in polyelectrolyte multilayers</i>

Note : Underlined participants are registered for the conference

# Approach to improve SiO<sub>2</sub>-based Electrets with AlO<sub>x</sub> deposited by Atomic layer deposition (ALD)

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**Abstract:** To improve SiO<sub>2</sub>-based electrets for mechanical energy harvesters (MEH), very thin AlO<sub>x</sub> layers are deposited on thermal SiO<sub>2</sub>. For the deposition, ALD was chosen because of extremely uniform coatings even at thicknesses under 10 nm leading to favourable electrical properties for electrets. The charging is done by corona discharge and surface potential is measured contactless under a controlled environment. The layers are further characterized with SEM, X-Ray Reflectivity (XRR), XPS and electrically with a Mercury Probe (CV and IV).

**Keywords:** atomic layer deposition, layered electret, corona discharge

## Introduction

Mechanical energy harvesters (MEHs) offer the possibility to have wireless sensor nodes at places like machine housings, tires etc. where e.g. solar cells would be useless. For MEHs, an alternative to piezoelectric or magnetic harvesters are electrostatic systems with electrets. Their unique selling point is the easy integration into micro-electronic mechanical systems (MEMS). In electret research, mostly fluorinated polymers are used as they can be charged up to thousands of volts [1]. However, most polymers are unsuited for MEMS due to high process temperatures and harsh chemicals during production. Hence, we are focusing on SiO<sub>2</sub> as electret material, which already has a good performance [2] and try to improve its charge density and retention. Therefore, thin AlO<sub>x</sub> layers were deposited on SiO<sub>2</sub> by ALD.

## Theory and Methods

For our electrets, different silicon substrates with SiO<sub>2</sub> are coated with amorphous AlO<sub>x</sub> in a thermal or plasma-enhanced (PE)ALD process. Because of the extremely uniform coatings of ALD, every possible defect on the SiO<sub>2</sub> should be effectively covered, increasing the resistivity of the electret. AlO<sub>x</sub> also has a higher permittivity than SiO<sub>2</sub> lowering the E-field in the latter after charging. Besides, in [3] it was mentioned that the increasing bandgap from AlO<sub>x</sub> to SiO<sub>2</sub> could have a positive impact on the charge stability by limiting the migration of charges. The electrets are made by charging to different surface potentials via corona discharge. Then, the resulting charge stability is measured with a surface voltmeter in a chamber with controlled humidity and temperature. To be able to interpret the results, the thickness (SEM, XRR), density (XRR), bandgap (XPS), permittivity (CV) and electrical breakdown (IV) of the oxide layers (thermal and PE-ALD) are determined.

## First Results

First data of the thermal AlO<sub>x</sub> layer are compared to literature in the following table (also see figure 1):

	therm. AlO <sub>x</sub>	literature
growth / cycle	1.13 Å	1.25 Å [4]
density	2.91 g/cm <sup>3</sup>	3 g/cm <sup>3</sup> [4]
bandgap	6.1 eV	6.2-6.8 eV [5]
elec. breakdown	8.5-9.5 MV/cm	~7.5 MV/cm [4]
permittivity	5.9	7.8 [4]

It could be shown already that AlO<sub>x</sub> by PEALD has a much a higher breakdown strength. Electret charging and characterization will be done in the next few months.

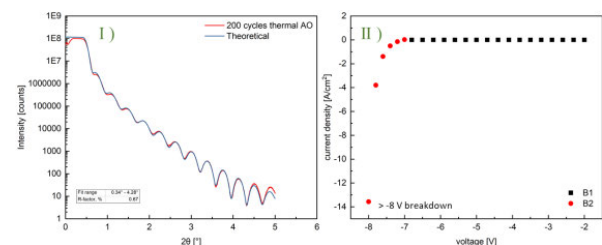


Figure 1: Thermal AlO<sub>x</sub> characterization: I) XRR for density + thickness II) IV-curve for elec. breakdown.

## References

- [1] S. Boisseau, G. Despesse, B. Ahmed "Electrostatic conversion for vibration energy harvesting" in "Small-scale energy harvesting", *InTech*, 2012.
- [2] G. Peter, X. Zhongfu "Transport of detrapped charges in thermally wet grown SiO<sub>2</sub> electrets", *J. Appl. Phys.*, **74**(12), 7269–7274, 1993.
- [3] A. Diaz-Ballester, S. Castillo-Anguera, et al. "Charge storage and retention in electret dielectric layers for energy harvesting applications", *IEEE 9th IberoAmerican Congress on Sensors*, Bogota, Colombia, 1–4, 2014.

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# The influence of crystallinity and isotacticity on charge decay in polypropylene blends

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**Abstract:** In the absence of chemical treatments or additives acting as deep charge trapping centres, the charge decay within a semi-crystalline polymer is generally governed by the physical traps originating from certain molecular configurations and charge-trapping sites at the crystalline-amorphous interface. By varying the crystalline content in polypropylene blends we have observed a marked increase of electret charge stability in the samples with higher crystallinity. Certain features on the charge-decay curves could be traced to the molecular relaxation within the material.

**Keywords:** polypropylene, homopolymer, isotacticity, charge decay

## Introduction

For semi-crystalline polymers, such as polypropylene, the crystallinity and crystal size are commonly seen as major parameters determining both the mechanical characteristics as well as their charge storage properties [1,2]. Generally, the traps originating from the crystal-amorphous interfaces and physical defects are considered to be shallower than traps of chemical nature [1]. However, some counter examples have been recently described in literature, as well. To determine the effect of crystallinity, the thermally stimulated surface potential decay (TSSPD) for a series of high isotactic polypropylene and low isotactic polypropylene blends has been investigated in combination with differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) measurements.

## Results and Discussion

Extruded films with a thickness of 50 µm of high isotactic polypropylene (HB12XF, MFI 12, Polychim Industrie FR) and low isotactic polypropylene (S901, MFI 50, Idemitsu Kosan JP) [3] blends were used. For TSSPD measurements the samples were poled in a positive corona to the initial surface potential value of 2kV. The surface potential of the electret was then measured continuously as the temperature was increased with the constant rate of 8 K/min (Fig. 1). DSC (Mettler Toledo DSC3) was performed at a rate of 10K/min, while DMA data (Mettler Toledo DMA 1) were obtained at 1Hz and heating rate of 3K/min.

TSSPD curves clearly indicate the influence of the crystalline content on charge decay. Decreasing overall crystallinity resulted in more shallow traps seen as a shift of the TSSPD curves to lower temperatures and the loss of the most stable charge traps at higher temperatures. Clear proof of lower

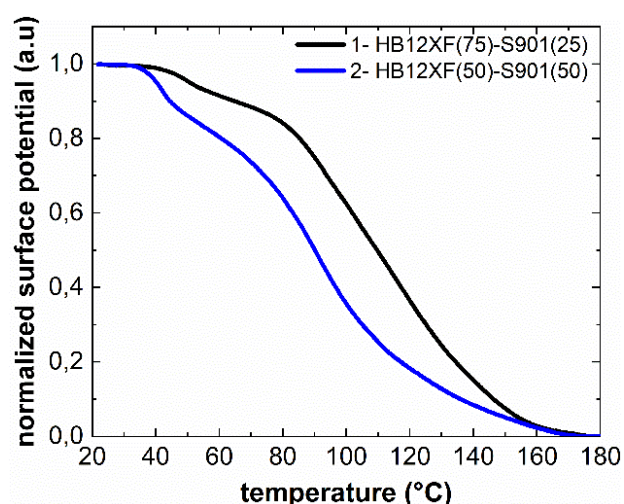


Figure 1: Thermally stimulated surface potential decay in different blends ratios as indicated.

crystallinity by increasing the fraction of low isotactic PP was noted with both techniques besides indications of a molecular relaxation in the polypropylene crystals before the melting onset.

## Conclusions

Decreasing crystallinity leads to more shallow traps at the cost of the high temperature charge stability. DSC and DMA confirm the lower crystallinity which affects the charge decay profile.

Indications of a molecular relaxation associated with the polymer crystals were observed with DSC and DMA.

## References

- [1] J. Wang et al. "The influence of orthophosphoric-acid modification on charge-storage enhancement in polypropylene electrets," *J. Appl.Phys.* 128,034102, 2020.
- [2] R. Nath et al. "Effect of crystallinity on charge storage in polypropylene and polyethylene," *IEEE Trans. on Electr. Ins.*, Volume 24, № 3, June 1989.
- [3] Y. Minami. et al. "Development of low isotactic polyolefin," *Polymer Journal*, 47.227-234, 2015.

# Protecting spontaneous-polarization electrets from light illumination

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**Abstract:** By providing comparable surface charge density with no need for a charging process, faster and more cost-effective fabrication would be possible using spontaneous-polarization electret materials. However, rapid degradation of surface potential when exposed to heat or light during or after deposition is the most important challenge for such electrets. Hence, developing practical methods to protect them against ambient illumination (particularly in UV-Vis) is of great interest. Here, the effect of implementing protective layers on Alq<sub>3</sub> as a spontaneous-polarization electret is investigated.

**Keywords:** electret, spontaneous-polarization, irradiation, transmittance, surface potential, vacuum deposition

## Introduction

One of the most important applications of electret materials is in the vibrational energy harvesters. Recently, among the candidate electrets for this purpose, spontaneous-polarization (SP) electrets have grabbed considerable attention. Conventionally, these materials are being used as the electron transport layer in OLED's and photovoltaics [1] among which Alq<sub>3</sub> and TPBi [2] are two famous ones. When deposited by dry coating methods, i.e. vacuum evaporation, an electrostatic potential ( $V_s$ ) is built up on the surface of the deposited film of such materials. Recent studies have tried to investigate different aspects of SP electrets. These include interpretation of the source of  $V_s$  [1], effect of deposition rate on the slope of  $V_s$  versus film thickness as well as on the control of molecular orientation [2], and effect of doping ratio of electret with nonpolar materials such as NPB on the degree of orientation polarization and hence the surface charge density [1]. Moreover, although some formulations have been proposed for lifetime prediction of conventional electrets, no reliable relation has been yet reported for SP electrets. Wider utilization of SP electrets in energy harvesting depends on the proposal of applied solutions to elongate stability of  $V_s$ . In this regard, the effects of illumination as well as atmospheric pressure have been studied. It is revealed that the environmental pressure has an almost negligible effect on degradation of  $V_s$  compared to illumination [3]. For the latter one, some remedies have been proposed such as using more durable electrets (e.g. TPBi instead of Alq<sub>3</sub>) [3], co-deposition of two SP electrets [4], irradiating nonpolar UV light on the substrate during deposition [1], covering electret surface or vacuum encapsulation of the device [5]. However, longer lifetime extension is still required.

## Results and Discussion

As target SP electret, Alq<sub>3</sub> mostly absorbs light within UV range with peak wavelength of about 375 nm and emits light at less energy level with peak wavelength of about 480 nm [6]. Therefore, the covering layer must not be UV-transparent. A good cover layer is not only optically protective, but also can increase the mechanical durability of the electret when there is a possibility of impact between fixed and moving sides of a harvester under gap-closing

motion (Fig. 1(a)). With respect to dielectric and UV-barrier properties, metal oxide-doped PDMS can efficiently protect Alq<sub>3</sub> while maintaining the harvester performance. After vacuum deposition of Alq<sub>3</sub>, PDMS should be rapidly spun-coated and dried at room temperature. Then, time variation of  $V_s$  of the protected electret film can be measured using an electrostatic voltmeter setup as shown in Fig. 1(b) and compared with that of the bare electret.

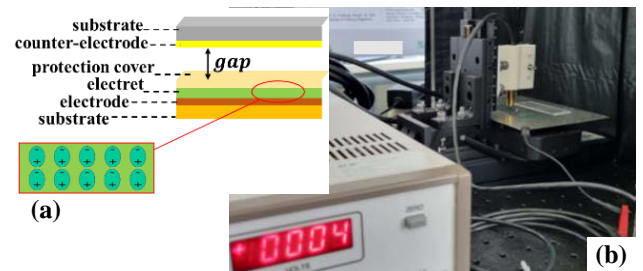


Figure 1: Schematic of harvester layers, and surface potential measurement setup.

## Conclusions

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## References

- [1] Y. Noguchi, ..., "Understanding spontaneous orientation polarization of amorphous organic semiconducting films and its application to devices," *Synthetic Met.*, 288, 117101, 2022.
- [2] Y. Tanaka, ..., "Enhancement of output power in self-assembled electret-based vibrational energy generator: control of molecular orientation by changing deposition rate," *IEEE PowerMEMS*, pp. 1-4, 2019.
- [3] Y. Tanaka, ..., "Self-assembled electret for vibration-based power generator," *Sci. Rep.*, 10 (1), 6648, 2020.
- [4] Y. Tanaka, ..., "Electret-based vibrational energy generator composed of polar molecules for OLED," *IEEE AM-FPD*, pp. 135-136, 2021.
- [5] D. Yamane, ..., "MEMS post-processed self-assembled electret for vibratory energy harvesters," *Appl. Phys. Lett.*, 119 (25), 254102, 2021.
- [6] T. Hoshi, ..., "Electronic absorption and emission spectra of Alq<sub>3</sub> in solution with special attention to a delayed fluorescence," *J. Luminescence*, 128 (8), 1353-1358, 2008.

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# Micro-patterning of electret charge distribution by selective liquid-solid contact electrification

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**Abstract:** Contact electrification (CE) has been documented for over 2600 years, but its mechanism remains ambiguous and is not fully understood, especially for liquid-solid cases. For the first time, we proposed an electret micro-patterning charging method using flowing tap water. The water charging method can be further used for droplet-based electricity power generation and water-drop self-powered sensing applications. This work demonstrates the feasibility and effectiveness of the innovatively proposed electret water charging method.

**Keywords:** Contact electrification, oxygen plasma treatment, electret, water energy harvesting.

## Introduction

With regard to water/liquid energy collectors, existing technology relies on the random contact with water to generate uncontrolled output and signal waveforms. How to achieve steerable contact between liquid-solid interfaces remains a long-standing challenge, and it is difficult to control the contact between water and electret only in certain areas [1-2]. The controllable water charging method proposed in our paper is expected to solve this problem.

## Results and Discussion

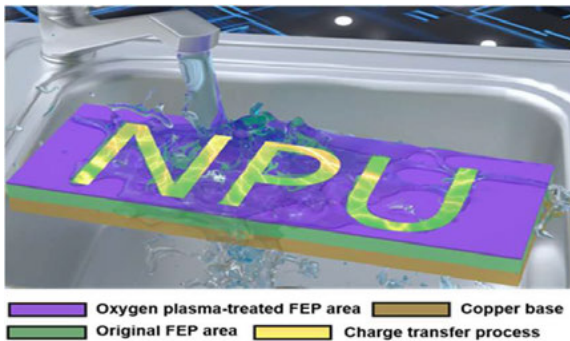


Figure 1: Schematic diagram of forming an "NPU" charge distribution on the FEP electret surface by flowing tap water.

To achieve a uniform charging profile, the flowing tap water is used to flush on the FEP surface directly (as Fig.1 shown), allowing plenty of water to contact with FEP surface at the same time. Fig. 2(d) illustrates the SEM image of the N-shaped oxygen plasma-treated pattern with a width of 200 $\mu$ m. Figs. 2(c) and 2(d) show the scanning electron microscope (SEM) images and the contact angles of the original FEP surface and the 300W power oxygen plasma-treated FEP surface, respectively. Fig. 3 shows the NPU-shaped surface potential map measured with the 3D scanner, respectively. Hit by flowing tap water, the whole FEP surface could be divided into "red" and "green" areas in the potential distribution map, representing the neutrally and the negatively charged areas, respectively.

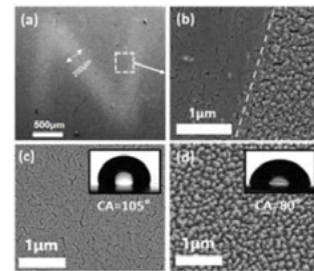


Figure 2: (a-b) The SEM image of N-shaped plasma-treated FEP area and the boundary; (c-d) The SEM image and the contact angle of original FEP surface and plasma-treated FEP surface.

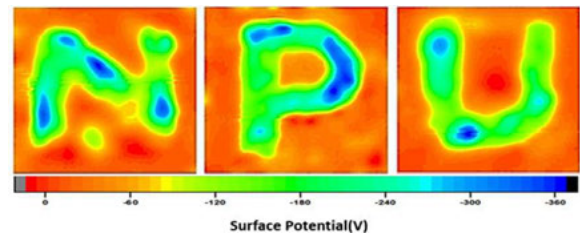


Figure 3: The NPU-shaped potential distribution map on the FEP surface was achieved with a 3D surface potential scanner.

## Conclusions

In this work, a micro-patterning water charging method is innovatively proposed. By flushing the plasma treated FEP surface with flowing tap water, an NPU-shaped charge distribution has been mapped.

## References

- [1] K. Tao, B. Lyu, et al, "Micro-Patterning of Electret Charge Distribution by Selective Liquid-Solid Contact Electrification," in Journal of Microelectromechanical Systems, vol. 31, no. 4, pp. 625-633, Aug. 2022.
- [2] B. Lyu et al., "Flowing Water Enables Steerable Charge Distribution on Electret Surface," 2023 IEEE 36th International Conference on MEMS, Munich, Germany, 2023, pp. 740-743.

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# Ion enhanced hydrocharging of filter webs

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**Abstract:** A more eco-friendly hydrocharging of filter media is described. It relies on the corona charging of nebulized water droplets. The spraying in of water under a very high pressure can thus be avoided. It also greatly reduces the drying time. By using microdroplets as charge carrier an all-around charging of the microfibers is achieved. Ion enriched hydrocharging can be done on both a small and large scale. Small scale IEH enables the reuse of filters, it makes in particular the reuse of face masks possible.

**Keywords:** ion-enriched hydrocharging, charging microdroplets, electret filter media, reuse face masks

## Introduction

The fibrous web in highly efficient filter media like face masks is charged. So its microfibers, which usually consist of PP-fibers of 1  $\mu\text{m}$  in diameter, are turned into electrets. This is usually done by corona charging. However, more recently also hydrocharging with deionized water is used [1-3]. This requires a high flow rate, so a very high pressure.

Hydrocharging has the advantage over corona charging that the fibers are charged more *uniformly*. This will clearly still be the case, when the hydrocharging is performed with microdroplets. The latter can be generated with a nebulizer. In order to get rid of a high pressure, the microdroplets are charged by pushing them through a DC corona.

## Results and Discussion

Apart from charging a filter web with a water aerosol, we have tried to charge a wetted filter by the injection of ions, see Fig. 1. This failed, any charge on the filter being quickly dissipated by the relative high conductivity of distilled water.

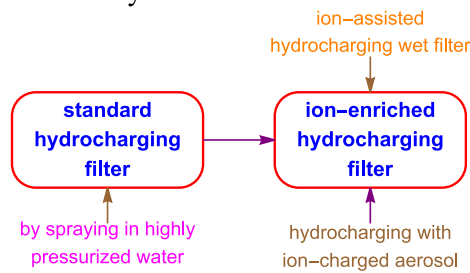


Fig. 1 Ion-enriched hydrocharging, was only successful when we loaded the droplets of an aerosol with ions.

Fig. 2 depicts a scheme of IEH for the mass production of electret filter web. The web is actually moved along 2 rollers and so gets charged from above and below.

Disposed filters cause plastic waste, so reuse should be promoted. Face masks can be disinfected quite easily. They can next be recharged with a DC-corona, however we better recharge them with IEH microdroplets, because these charge the microfibers more evenly, cf. Figs. 3 and 4.

## Conclusions

A modification of hydrocharging of filter webs is presented, which has three advantages: it does not need a high pressure, strongly reduces the drying time and can be applied on a small scale in a DIY kit.

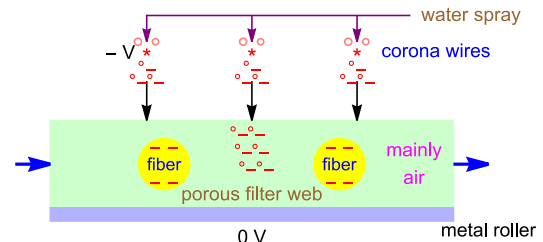


Fig. 2 On-line all-around charging of filter webs with microdroplets charged with a row of corona wires.



Fig. 3 Disposed face masks can be recharged either by corona charging or IEH microdroplet charging. Interestingly, these processes can be invoked for disinfection as well, because both are chemically reactive.

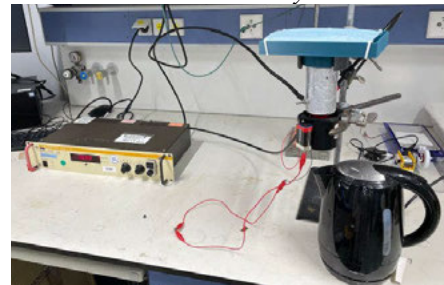


Fig. 4 From [4] provisional set up for IEH of reused filter from a face mask.

## References

- [1] Z. Wang, G. Chen et al., "Study on charge characteristic of meltblown polypropylene electret fabric by hydrocharging technique," *J. Electrostatics*, 116, 103683, 2022, pp. 5.
- [2] X. Zhang, Y. Wang, "Thermal-resist hydro-charged air filters (HCAFS) with charge stability for long-term efficient fine particle removal," *Separ. Purif. Techn.*, 303, p. 122236, 2022, pp. 9.
- [3] H. Wang, Y. Wu, et al., "Triboelectric charging of melt-blown nonwoven filters with high filtration efficiency", *Scientific Reports*, 12, 1146, 2022. pp. 9.
- [4] T. Adema, W. Brouwers, T. Linger, O. van Poppel, "Giving disposed face masks a new life with hydrocharging", *BSc-thesis, TU-Delft*, 20 January, 2023.

## Acknowledgements

We like to thank the Hydro Team of 4 BSc-students, the authors of [4], for carrying out the first experiments on ion-enriched hydrocharging.

# Using corona gas discharges for the disinfection of seeds and the defouling of biofilms

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**Abstract:** A corona discharge can be seen as a chemical reactor that produces a myriad of antimicrobial species. It can therefore be used for the disinfection or inactivation of a variety of biofilms. Such films often contain pathogens like fungi, bacteria and viruses, for instance those on seeds or food. Two devices are briefly outlined for carrying out the disinfection of seeds and the defouling of marine biofilms. The corona-plasma processes are compared to other methods much more eco-friendly.

**Keywords:** corona-based disinfection, disinfection of seeds, disinfection of surfaces, plasma defouling of biofilms

## Introduction

It is often overlooked that a corona discharge generates in addition to ions, all kind of reactive species. It can thus also be applied for the inactivation of micro-organisms, see Fig 1.

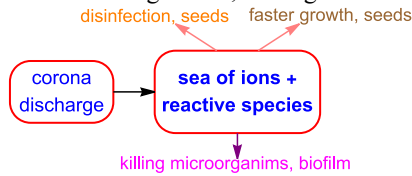


Fig.1 A corona discharge produces many antimicrobial agents and can be used for the inactivation of all sorts of biofilms.

Micro-organisms show up e.g. as pathogens on seeds and in marine biofilms, cf. Figs 2 and 3.



Fig.2 Leaf spots on sunflower caused by *Alternaria fungus*



Fig.3 A biofilm will increase the flow resistance and lead to a higher fuel consumption.

## Results and Discussion

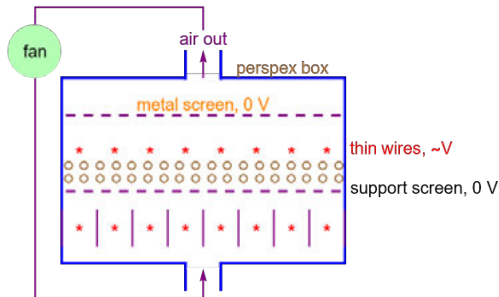


Fig. 4 Corona disinfection of seeds swirling in fluidized bed for an all-around treatment and with an extra boost of microbial species in the lower part.

Fig. 4 shows a device for the disinfection of seeds. In order to expose the whole surface of the seeds, it makes use of a fluidized bed.

Fig. 5 displays the growth pattern of a biofilm. The micro-organisms building up in the early stages will be the most vulnerable to a corona plasma.

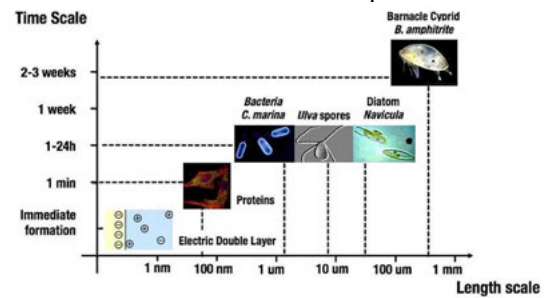


Fig.5 In particular the early micron-sized bio-growth will be inactivated by a corona discharge.

Fig. 6 shows a mobile corona-plasma device for the defouling of ships.

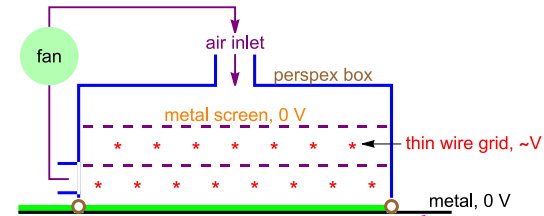


Fig 6. Mobile set up for corona defouling of biofilms using 2 wire grids and recirculating air.

## Conclusions

The use of corona discharges can be extended to the control of microbiological processes. In this way it offers the food-industry and agriculture an eco-friendly route to disinfection [1]. Corona defouling is likewise environmentally more attractive than the current methods. Corona-plasma disinfection can clearly further be engaged in the disinfection of medical equipment.

## References

[1] N.N. Misra, O.K. Schlüter, P.J. Cullen, eds: *Cold plasma in food and agriculture—Fundamentals and applications*, Academic Press 2016.

# Synergistic effect of positive electret combined with 5-fluorouracil on growth inhibition of scar fibroblasts

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**Abstract:** Objective: To investigate the effect of electret on the growth and migration of scar fibroblasts and its possible mechanism. Methods: The effects of positive electret with different surface potential combined with 5-FU on scar fibroblasts were detected. R-T PCR was used to study the expression changes of p53 et al.mRNA in fibroblasts growing under electrostatic field. Conclusion: 5-FU can inhibit the growth of scar cells. The combination of positive electret and 5-FU had a synergistic effect on the inhibition of cell growth. 5-FU and positive electret inhibit scar cell growth with similar mechanism: inhibiting cell growth by inhibiting cell DNA synthesis.

**Keywords:** electrostatic field; electret; 5-fluorouracil; scar fibroblasts

## Introduction

Mechanical stimulation and local infection at the injured site can lead to abnormal healing of skin wounds, even causing the formation of keloids. The migration, growth and proliferation of cells play a vital role in the process of wound repair. Experiments have shown that the behavior of biological tissues is highly correlated with the flow by electric charges [1,2]. In this paper, we study the effects of electrostatic fields provided by electret combined with pentafluorouracil (5-FU) on the growth, cell cycle and apoptosis of isolated cultured scar fibroblasts, which may provide new ideas for the prevention and treatment of pathological scarring.

## Results and Discussion

1. MTT method was used to measure the effects of 5-FU on scar fibroblasts and positive electrets with different surface potentials combined with 5-FU on scar fibroblasts for 48h. The effects on fibroblast proliferation were shown in the table. The effects of 5-FU on the proliferation of fibroblasts were shown in the table. The results showed that the cell inhibition rate increased significantly with the increase of electret surface potential at the same observation time (48h).

2. The effect of positive electret on the growth cycle of scar fibroblasts was studied by flow cytometry. After 5 000 V electret treatment combined with 5-FU for 48 h, the proportion of cells in G1 phase was higher than that in the control group significantly increased from 76.81±0.44% to 88.87±0.55%.

3. The expression of *p53*, *fas*, *Bax* and *fasl* mRNA in scar fibroblasts growing in electrostatic field was studied by real-time quantitative PCR. The experimental results showed that the expression of *p53*, *fas*, *Bax* and *fasl* mRNA in fibroblasts increased significantly after positive electret treatment.

ug/ml	Inhibition rate (%)		
	10	40	160
5-FU	0.99±0.028	0.99±0.028	0.99±0.028
1000V+5-FU	0.97±0.030	0.64±0.036	0.40±0.029
2000V+5-FU	0.96±0.042	0.63±0.023	0.38±0.025
5000V+5-FU	0.93±0.040	0.60±0.026	0.36±0.040

Figure 1: Effects of positive electrets with different surface potentials combined with 5-FU on scar fibroblasts (n=12)

	<i>p53</i>	<i>fas</i>	<i>Bax</i>	<i>fasl</i>
control groups	1.00±0.00	1.00±0.01	1.00±0.02	1.00±0.03
5-FU	1.60±0.06	2.23±0.11	1.81±0.13	2.01±0.19
5000V+5FU	1.92±0.14	2.81±0.29	2.20±0.17	2.49±0.21

Figure 2: Expression levels of *p53*, *fas*, *Bax* and *fasl* mRNA after positive electret treatment of scar fibroblasts (n=3)

## Conclusions

The electric field can induce the change of the cell cycle of fibroblasts, so as to regulate cell differentiation and proliferation. Positive electret can inhibit fibroblast growth by blocking G1 phase. The electrostatic field generated by electret regulates the growth of fibroblasts by regulating the expression of mRNA such as *p53* in cells.

## References

- [1] Liang, Y., et al. Research progress on the correlation between bacterial biofilm microenvironment and charge regulation. *IEEE Trans. Dielectr. Electr. Insul.* 29(4), 1540–1545(2022). <https://doi.org/10.1109/tdei.2022.3183663>
- [2] Yao, G., et al.: A programmable and skin temperature-activated electromechanical synergistic dressing for effective wound healing. *Sci. Adv.* 8(4), eabl8379(2022). <https://doi.org/10.1126/sciadv.abl8379>

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# Biodegradable cellular polylactic acid ferroelectrets for acoustoelectric transducers

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**Abstract:** This paper presents on the acoustic performance of the acoustoelectric transducer based on biodegradable polylactic acid (PLA) ferroelectrets, involving transmitters and receivers. For a transmitter with a diameter of 20 mm, driven by a voltage of 300 V ( $V_{pp}$ ), the sound pressure level (SPL) generated by it increases from 60 to 103 dB (Ref. 20  $\mu$ Pa) as frequency increases in a broadband range of 1 to 80 kHz. Besides, the maximum value of sensitivity of the receivers (microphones) can reach to 4.2 mV/Pa ( $\sim$ 47.5 dB/Ref. 1 V/Pa) at 1 kHz. The frequency response curve of the device is flat in the frequency range of 300 to 3000 Hz.

**Keywords:** ferroelectrets, acoustoelectric transducer, biodegradable materials.

## Introduction

Ferroelectrets are an ideally piezoelectric material for flexible acoustoelectric transducers since they have strong piezoelectric effect, low density and small acoustic impedance very close to air [1]. This paper reports the electro-acoustic properties of a biodegradable cellular polylactic acid (PLA) ferroelectret [2-3], which enables the possibility of environmentally friendly electroacoustic devices with excellent performance.

## Results and Discussion

As a transmitter, the transducer has a resonant frequency of 80.8 kHz (Fig. 1(a)). The sound pressure level (SPL) increases with increasing frequency before the resonant frequency, and the SPL also enhances with the driving voltage as expected. The maximum SPL is 103.8 dB SPL at the resonant frequency with a 300  $V_{pp}$  driving voltage.

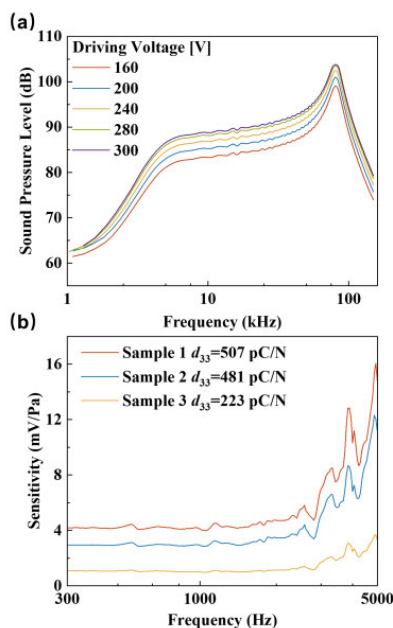


Figure 1: (a) Emitter frequency response curve at different driving voltage; (b) Receiver frequency response curve for different samples.

*response curves with different quasi-static  $d_{33}$  piezoelectric coefficients*

The response curves of the PLA ferroelectret-based receivers are quite flat in the frequency range of 300 to 3000 Hz (Fig.1 (b)). The sensitivity of the devices increase with the quasi-static  $d_{33}$  piezoelectric coefficient for the samples with a similar thickness. The average sensitivity in the frequency range of 300 to 3000 Hz is about 4.2 mV/Pa ( $\sim$ 47.5 dB Ref.1 V/Pa).

## Conclusions

This study proposes a biodegradable flexible acoustoelectric transducer based on PLA films. It has an excellent performance in both transmitter and receiver working modes. For the transmitter, the maximum SPL up to 103.8 dB at its resonant frequency is achieved. For the receiver, the sensitivity of 4.2 mV/Pa at 1 kHz is obtained, and the frequency response curve is quite flat from 300 to 3000 Hz. Thus, the biodegradable PLA ferroelectret is an ideal material for environmentally friendly acoustic devices.

## References

- [1] S. Bauer, R. Gerhard-Multhaupt, G. M. Sessler, "Ferroelectrets: Soft electroactive foams for transducers," *Physics Today*, 57, 37-43, 2004.
- [2] S. Zhukov, X. Ma, H. von Seggern, G. M. Sessler, O. Ben Dali, M. Kupnik, et al, "Biodegradable cellular polylactic acid ferroelectrets with strong longitudinal and transverse piezoelectricity," *Applied Physics Letters*, 117 (11), 112901, 2020.
- [3] X. Ma, S. Zhukov, H. von Seggern, G. M. Sessler, O. Ben Dali, et al, "Biodegradable and Bioabsorbable Polylactic Acid Ferroelectrets with Prominent Piezoelectric Activity," *Advanced Electronic Materials*, 9 (3), 2201070, 2023.

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# The effect of modifier on electret properties and hardness of epoxy composite material

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**Abstract:** The paper describes network polymer electrets made of epoxy oligomer DER-331, epoxy-urethane modifier PEF-3A and polyaminoamide L-20 as a curing agent. Electret properties of the corona electrets produced by simultaneous curing and polarization of the samples with different modifier content were not affected by modifier content after 20 days. Polarized samples were harder compared to uncharged samples according to Shore D hardness test.

**Keywords:** thermal electret, epoxy polymer, chemical modifier,

## Introduction

One of the ways to get polymer materials with the required properties is adjustable modification of commonly-used oligomer-based polymers by addition of modifiers. Reactive modifiers are added to epoxy resin composites resulting in high impact and wear resistance and elasticity of cured materials. Simultaneous curing of the modified composition and exposure to constant electric field allows manufacturing thermal electrets with the required strength and stress-strain behaviour [1, 2].

The objective of the paper was to study the stability and hardness of thermal electrets based on epoxy oligomer DER-331 modified by epoxy-urethane oligomer PEF-3A at different modifier content.

## Results and Discussion

The manufactured samples consisted of epoxy oligomer DER-331, epoxy-urethane oligomer PEF-3A as a modifier (from 0 to 10 mass %) and polyaminoamide L-20 as a curing agent in stoichiometric ratio. Electret samples were obtained by simultaneous curing at a temperature of 120 °C and polarization at a voltage of 5 kV for 2 hours.

Decays of the surface potential, electric field strength and effective surface charge density had the same behavior. The increase in PEF-3A modifier content up to 5 mass % led to smaller decay of electret properties within first 10 days. After 20 days of storage at room temperature the values of electret properties were similar and unaffected by the PEF-3A modifier content in the composition.

Composition of DER-331 and L-20 testing by thermally-stimulated depolarization showed peaks attributed to devitrification of the polymer and occurrence of post-curing chemical reaction described earlier.

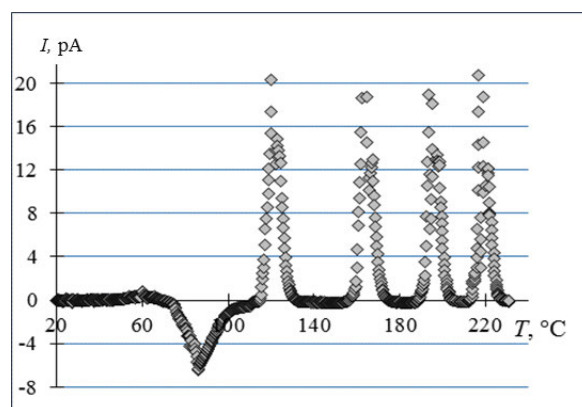


Figure 1: Thermally stimulated depolarization currents of DER-331 oligomer cured by L-20

Shore D hardness studied for polarized and untreated samples revealed that polarized samples were harder compared to uncharged samples. The higher the electret properties of the samples were, the greater the difference in hardness of polarized and uncharged samples was. The increase of modifier content in the epoxy polymer composition did not lead to increase in Shore D hardness.

## Conclusions

Therefore, adjusting composition of epoxy polymer one can get different three-dimensional structures with required electret and mechanical properties based on one oligomer. These epoxy polymer electrets can be used as a basic material for electret sensors.

## References

- [1] Yu-Cheng Liu, Yasuhiro Aoyagi & D. D. L. Chung, "Development of epoxy-based electrets," *Journal of Materials Science* 43 (5), 1650–1663, 2008.
- [2] Y. K. Mikryukova, E. N. Mochalova, M. F. Galikhanov and S. S. Akhtyamova, "Influence of the conditions of simultaneous curing and polarization on the characteristics of modified chemoelectrets on the based on oligomer DER-331," *AIP Conf. Proc.*, 2313, 050049, 2020.



# Thermally Stable Piezoelectric Fibers Based on Ferroelectrets

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**Abstract:** Very thin and thermally stable piezoelectric fibers with a coaxial structure, consisting of a conductive core, a polyfluoroalkoxy (PFA) ferroelectret layer, a shielding electrode, and an outer jacket, are successfully fabricated. The diameter of such fibers is only 0.4 mm, which make them very flexible and suitable to be woven in clothing or integrated in thin substrates. The piezoelectric sensitivity of the fibers, up to 0.76 pC/(m\*N), is achieved, and very stable even at an aging temperature of 150 °C. Therefore, the novel piezoelectric fibers are expected to be employed in high temperature environment.

**Keywords:** piezoelectric fiber, ferroelectret, thermally stable activity

## Introduction

Currently, advanced functional fibers can make common textiles smart by traditional textile process without losing their basic features such as flexibility, breath ability, and wash ability [1]. Ferroelectrets, featuring strong piezoelectric activity, flexibility, lightweight, and low cost, are advanced material and have attractive prospects for various sensors and actuators [2]. In this paper, we report a piezoelectric fiber with a polyfluoroalkoxy (PFA) ferroelectret layer in which the “macro-dipoles” are aligned in radial direction.

## Results and Discussion

As shown in Fig. 1(a), the piezoelectric fiber consists of a core electrode, a cellular PFA electret layer with oriented “macro-dipoles” in radial direction, a shield electrode, and an outer jacket. As can be seen from SEM image of piezoelectric fiber cross-section (Fig. 1(b)), the diameter of the obtained fiber is ~400 μm.

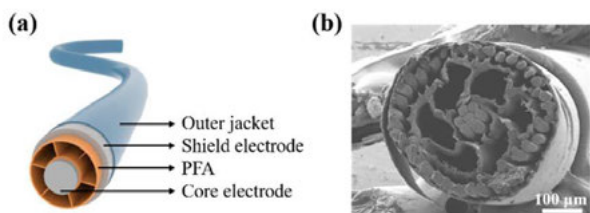


Figure 1: Structure of PFA piezoelectric fiber. (a) Schematic image of the fiber; (b) SEM image of the cross-section of the fiber.

Results on the isothermal stability of the hydrostatic piezoelectric coefficient at an annealing temperature of 150 °C for the samples polarized at various voltages are shown in Fig. 2. This figure indicates that the initial piezoelectric sensitivity of the sample polarized at -1500 V is 0.77 pC/(m\*N), and the piezoelectric activity is very stable. For the sample annealed at 150 °C, there is no observable decay of the sensitivity even after 24 h annealing time. This

is much superior to the piezoelectric cables based on the ferroelectric polymer PVDF whose highest operating temperature is around 85 °C. Therefore, such PFA piezoelectric fibers are very suitable for the applications that the devices must work at elevated temperatures.

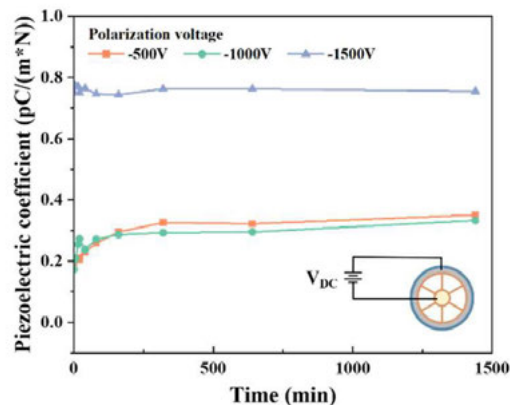


Figure 2: Piezoelectric coefficient of the fiber under the condition of thermal aging at 150 °C.

## Conclusions

Advantages of the present piezoelectric fiber include easy fabrication process, self-powered, self-shielding, slim structure and high thermal stability, making it well applied to scenarios such as human motion monitoring, smart homes, and high-temperature environments.

## References

- [1] Xiang, X., et al., Threadlike Piezoelectric Sensors Based on Ferroelectrets and Their Application in Washable and Breathable Smart Clothing. *Advanced Materials Technologies*, 2023: p. 2202130.
- [2] Bauer, S., R. Gerhard-Multhaupt, and G.M. Sessler, Ferroelectrets: Soft Electroactive Foams for Transducers. *Physics Today*, 2004. 57(2): p. 37-43.

## Acknowledgements

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# Underwater microphone with cellular polymer electrets

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**Abstract:** The measurement of underwater noise is critical for preserving the marine environment. To assess audible sound at frequencies lower than 10 kHz, we developed and evaluated an underwater microphone utilizing cellular polypropylene (CPP) for its high sensitivity compared to traditional microphones. Our prototype demonstrated a sensitivity of  $-63.5$  dB/Pa ( $183$  dB/ $\mu$ Pa), which is 28 dB higher than the reference microphone. Moreover, the microphone displayed nearly flat characteristics up to 10 kHz.

**Keywords:** piezoelectricity, piezo-electret, hydrophone, cellular polypropylene

## Introduction

In recent years, there has been growing interest in electrets made from cellular structured polymers as a new type of piezoelectric material with a high piezoelectric  $d_{33}$  coefficient exceeding 100 pC/N. Previous research has focused on improving the physical characteristics and applications of porous polypropylene film [1,2]. In this study, we explore the use of cellular polypropylene (CPP) as an underwater microphone for evaluating audible sound. We present the experimental results of our prototype underwater microphone.

## Experiment

The prototype underwater microphone comprises a cylindrical substrate with a  $10\text{ mm} \times 10\text{ mm}$  CPP film fixed onto it, covered with a waterproof silicon cap. The electret function of the CPP material induces an electric signal that is fed to an integrated circuit with an input capacitance of a few picofarads. Figure 1 illustrates the measurement system. An underwater speaker UA60 (made by UETAX) was used as the sound source, with a frequency range of 50–10 kHz. The sound source was placed at the bottom of a  $500 \times 425 \times 810\text{ mm}^3$  water tank, directed toward the water surface. The experimental sample was immersed at a distance of 100 mm from the sound source.

## Results and Discussion

The sound pressure frequency characteristics [A] of the underwater speaker were obtained using a referenced hydrophone (Type 8103), which is a calibrated microphone with a reference for measurements. Then, divide the sound pressure frequency characteristics [B] by [A] using the experimental microphone at the same location to obtain the frequency characteristics. The reference hydrophone was used to ensure flat characteristics. The pressure sensitivity of the hydrophone  $|S_p|$  was calculated from  $|S_p| = B/A|S_R|$ , where  $|S_R|$  is the pressure sensitivity of the reference hydrophone. Figure 2 depicts the sensitivity frequency

characteristics of the prototype microphone in air and water. We found that measurements in air and water produced nearly identical mean frequency properties.

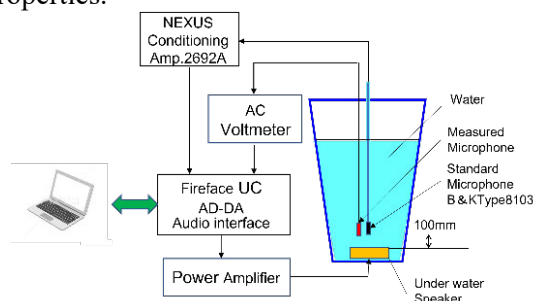


Figure 1 Underwater evaluation system

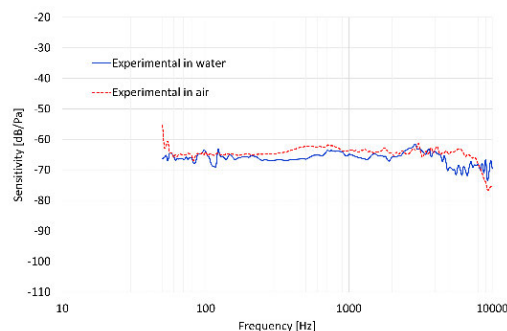


Figure 2 Sensitivity frequency characteristics of the prototype microphone in air and water.

## Conclusions

The prototype underwater microphone demonstrated a sensitivity of  $-63.5$  dB/Pa ( $-183$  dB/ $\mu$ Pa), which is approximately 28 dB higher than the reference microphone. Moreover, the prototype displayed nearly flat characteristics up to 10 kHz.

## References

- [1] J. Lekkala et al., "EMFi - New electret material for sensor and actuators," *Proc. ISE10*, 743-746, 1999.
- [2] G. M. Sessler et al. "Electromechanical response of cellular electret films." *Appl. Phys. Lett.* 75 (21), 3405-3407, 1999.

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# Electrical limitation of expanding PEDOT:PSS films

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**Abstract:** Conjugated polymers are widely used in the field of soft actuators where a redox-driven ion exchange with a surrounding electrolyte leads to reversible volume expansions. Here, the actuation of poly(3,4-dioxoethylene thiophene):poly(4-styrenesulfonate) (PEDOT:PSS) has been studied. The response of thin films (40 nm to 1.5  $\mu\text{m}$ ) has been studied by atomic force microscopy (AFM) and electrochemical impedance spectroscopy (EIS) under chronoamperometric conditions. In particular, the influence of applied potential and the film thickness on actuation has been determined and thickness-dependent limitations have been observed.

**Keywords:** soft actuators, conjugated polymer, atomic force microscopy, impedance spectroscopy

## Introduction

Conjugated polymers such as polyanilines, polypyrroles, and polythiophenes are widely used in the field of soft actuators. This systems shows a redox-driven ion exchange with a surrounding electrolyte, which leads to reversible volume expansion. These electroactive polymers are often utilized in macroscopic layer structures.[1]

Atomic force microscopy (AFM) allows for in-situ studies of actuation on the nm-scale.[2] For that purpose, thin polymer films are often deposited onto an electrode surface *via* electropolymerization. Here, we determined the actuation of thin PEDOT:PSS films *via* chronoamperometry in dependence of the film thickness and the applied redox potential by AFM and electrochemical impedance spectroscopy (EIS).

## Results and Discussion

We prepared thin films of PEDOT:PSS on gold electrodes *via* electropolymerization. First, we varied the reduction potential and observed an increase in the charge density and volume expansion for higher potentials, which was expected. Moreover, we studied the influence of film thickness on relative expansion. The overall volume expansion increased for thicker films as expected (cf. Figure 1). However, the expansion normalized to the film thickness decreased as well as the volume charge density. The corresponding impedance spectra were frequency-shifted for thicker films indicating increased confinement for charge carriers. The observed decay of the normalized expansions has been previously reported. [2, 3] Hence, we suggest thin actuator films show an electrical hindrance for an increased thickness, which is in-line with the EIS measurements.

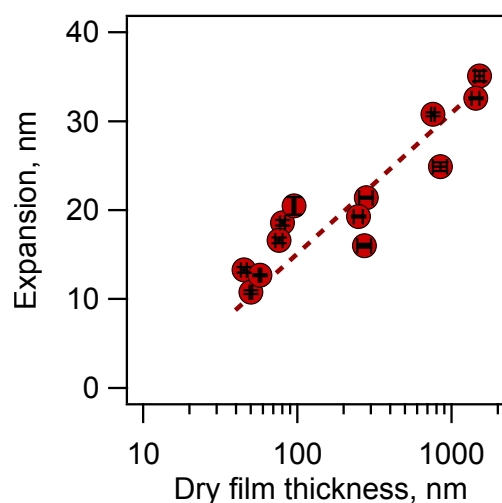


Figure 1: Volume expansion of thin PEDOT:PSS films in 100 mM KCl while reducing at  $-1$  V after oxidation at  $0.4$  V (vs. Ag/AgCl).

## Conclusions

In this work, we studied the actuation of thin PEDOT:PSS films for different redox potentials and film thicknesses. We found an increase in the volume expansion for both, higher potentials and thicker films. However, the normalized expansion decreases for the latter. Based on chronoamperometry and EIS, we consider a charge gradient normal to the film limiting the actuation process in thicker films.

## References

- [1] Y. Li *et al* "Soft and flexible PEDOT/PSS films for applications to soft actuators", *Smart Materials and Structures*, 23, 074010, 2014
- [2] M. J. Higgins *et al* "Visualizing dynamic actuation of ultrathin polypyrrole films", *Langmuir*, 25 (6), 3627-3633, 2009
- [3] R. Wu *et al* "Mass and charge transport kinetics in an organic mixed ionic-electronic conductor", *Chem. Mater.*, 34 (21), 9699-9710, 2022

## Acknowledgements

Tamino Rößler thanks the Elite Network of Bavaria and the Studienstiftung des Deutschen Volkes for funding.

# Atomic Layer Deposited Nano-thick Al<sub>2</sub>O<sub>3</sub> Electret Films for Surface-potential-modulation of Carrier Transport in SiNWs

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**Abstract:** In this study, an electretization technique for Al<sub>2</sub>O<sub>3</sub> during atomic layer deposition (ALD) has been established to control the carrier transport properties of silicon nanowires (SiNWs) by surface-potential-modulation. The electron irradiation to Al<sub>2</sub>O<sub>3</sub> films based on the photoelectric effect was found to charge the films with a charge density of 50-350 nC/cm<sup>2</sup>. The effects of bias voltage during electron irradiation on the charge density of Al<sub>2</sub>O<sub>3</sub> films are discussed. It is also demonstrated that the Al<sub>2</sub>O<sub>3</sub> electret film induces a hole accumulation layer at the interface of p-type silicon substrate.

**Keywords:** atomic layer deposition, Al<sub>2</sub>O<sub>3</sub>, photoelectric effect, surface-potential-modulation

## Introduction

Nanometer-thick electrets are effective in modulating the carrier transport properties of semiconductor nanowires (NWs) as well as MEMS power generators [1]. We previously reported on the carrier transport properties of SiO<sub>2</sub>- and Al<sub>2</sub>O<sub>3</sub>-coated p-type SiC nanowires employed as channels in FET configuration devices [2]. We found that the carrier transport of the nanowires is sensitively modulated by the electrostatic field of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> due to the large surface area to volume ratio of the nanowires.

To control carrier mobility by electret film coating of semiconductor nanowires, we have established a nanometer-thick Al<sub>2</sub>O<sub>3</sub> electret film deposition technique that can control charge density. Atomic layer deposition (ALD) with electron irradiation based on the photoelectric effect has been employed as the deposition technique for Al<sub>2</sub>O<sub>3</sub> electret films because of its ability to deposit uniform films on a three-dimensional structure. This paper reports on the changes in charge density of Al<sub>2</sub>O<sub>3</sub> electret films under various deposition conditions.

## Results and Discussion

The fixed charge densities of Al<sub>2</sub>O<sub>3</sub> electret films was estimated from the *C-V* curves, measured by the quasi-static capacitance-voltage method. The charge densities of the Al<sub>2</sub>O<sub>3</sub> films deposited at a temperature of 320 °C and irradiated at a bias voltage of 20 to 45 V increased with increasing bias voltage during irradiation, reaching a peak value of -350 nC/cm<sup>2</sup> at 40 V. The electric field of the Al<sub>2</sub>O<sub>3</sub> films induced by the fixed charge is roughly estimated to be in the order of minus several ten to hundred thousand volts per centimeter. This magnitude is compatible with the electric field of metal-oxide-semiconductor FETs. The charge density of the films changed even when the deposition temperature and irradiation dose were varied. In addition, we examined the influence of Al<sub>2</sub>O<sub>3</sub> electret films on a carrier transport in p-type Si substrate, with a

resistivity of 1-20 Ωcm. Figure 1 shows *I-V* characteristics of the 2-μm-thick Si substrate coated with the Al<sub>2</sub>O<sub>3</sub> electret films. Although the drain current is less than ±10nA@±2V on the Si substrate without the electret coating, for the coated substrate, the negative drain current increased rapidly under negative drain voltage. This is due to the electrostatic field of the electrets, which induced a hole accumulation layer at the interface. They exhibit the similar behaviour as the depletion mode of a p-channel FET. We will apply the electrets to n-type SiNWs in the future.

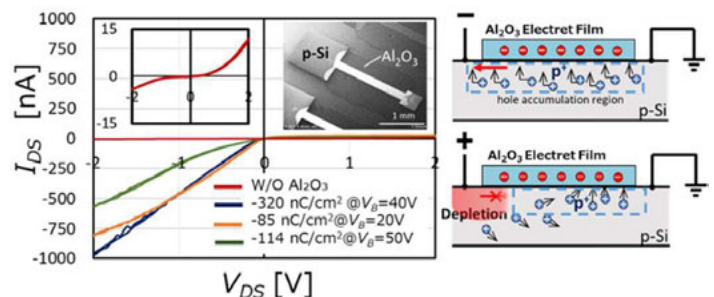


Figure 1: The *I-V* characteristics of p-type Si substrate coated with Al<sub>2</sub>O<sub>3</sub> electrets deposited at 320 °C and irradiated at a bias voltage of 20 to 50V.

## Conclusions

This study established deposition and electron irradiation conditions for Al<sub>2</sub>O<sub>3</sub> electret films in ALD. These nano-thick electret films are considered to be effective for controlling the electrostatic field of FETs using nano-semiconductors.

## References

- [1] H. Honma *et al.*, “A power-density-enhanced MEMS electrostatic energy harvester with symmetrized high-aspect ratio comb electrodes”, *J. of Micromech. and Microeng.*, **29**, (2019) 084002, (9pp).
- [2] A. Uesugi *et al.*, “Surface-potential-modulated piezoresistive effect of core-shell 3C-SiC nanowires”, *Nanotechnology*, **33**, (2022) 505701, (11 pp).

## Acknowledgements

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# Study on piezoelectric properties of ferroelectric Nylon 11 film

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**Abstract:** The temperature dependence of the permittivity, elastic moduli, electromechanical coupling coefficients and piezoelectric constants of the ferroelectric polymer Nylon 11 was systematically evaluated using broadband dielectric spectroscopy. Electromechanical coupling coefficients varied moderately up to a temperature range of 180°C, confirming that Nylon 11 exhibits excellent thermal stability. The piezoelectric  $d$  constants increased with increasing temperature, which was quantitatively determined by the change in electromechanical coupling coefficients and the increase in permittivity and decrease in elastic moduli.

**Keywords:** Nylon 11, ferroelectric polymer, piezoelectricity, broadband dielectric spectroscopy

## Introduction

Nylon 11, an odd-numbered Nylon, is one of the representative ferroelectric polymers and a unique material in that hydrogen bonding is involved in its ferroelectric stability. There are reports on the evaluation of the piezoelectricity of Nylon 11 film by the direct piezoelectric measurement, and it has been reported that the piezoelectricity is maintained stably at high temperatures [1]. In this study, broadband dielectric spectroscopy of ferroelectric Nylon 11 film was performed in the temperature range from room temperature to 180°C. The tensor components of elastic modulus, electromechanical coupling coefficient, and piezoelectric constant were obtained by piezoelectric resonances.

## Results and Discussion

Nylon 11 films were fabricated using the solvent casting method and stretched 3 times. The remanent polarization obtained by  $D$ - $E$  hysteresis loop was 50 mC/m<sup>2</sup>. Piezoelectric resonances associated with length, width, and thickness extension modes were observed. Temperature dependence of permittivity  $\epsilon'/\epsilon_0$  at 1 MHz, elastic modulus, coupling coefficient, and piezoelectric  $d$  constant are summarized in Figure 1. The permittivity is about 4 at room temperature and increases with increasing temperature. Young's modulus  $1/s_{11}$  and  $1/s_{22}$  show anisotropy. The elastic stiffness  $c_{33}$  is two times larger than  $1/s_{22}$  due to hydrogen bonding in the film thickness direction. The electromechanical coupling coefficients  $k_{3i}$  increased with increasing temperature. This is presumably due to the fact that the elastic modulus of the amorphous part decreases in the composite structure of amorphous and crystalline parts in the main chain direction, and stress is concentrated on the crystalline part, which induces a large piezoelectric polarization. In addition,  $k_{32}$  and  $k_{33}$  decreased gradually. As for the piezoelectric  $d_{3i}$  constants, each constant

increased.  $d_{3i}$  can be obtained from the following equations relating  $k_{3i}$ , permittivity  $\epsilon^T$ , and elastic compliance  $s_{ij}$ .

$$k_{3i}^2 = \frac{d_{3i}^2}{\epsilon^T s_{ii}} \quad (i = 1,2), k_{33} = \frac{e_{33}^2}{\epsilon^T c_{33}} \quad \dots (1)$$

It was understood that  $d_{3i}$  increases due to the competition between the increases in both  $\epsilon^T$  and  $s_{ii}$ , while  $k_{3i}$  does not decrease significantly during the temperature increase process.

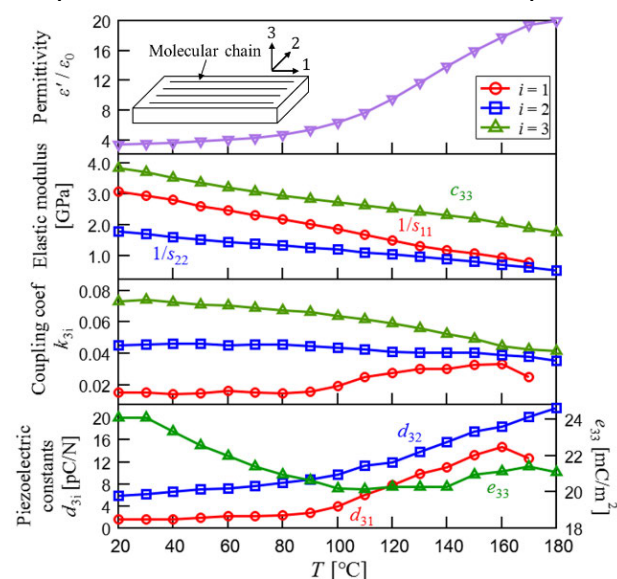


Figure 1: Temperature dependence of electrical and mechanical tensor components for Nylon 11.

## Conclusions

The experimental data show thermal stability of Nylon 11 in its piezoelectric properties, which can be interpreted from the results of the temperature dependence of the electrical and mechanical tensor components.

[1] Y. Takase, *Macromolecules*, 24, 6644-6652, 1991.

# Spatially defined polarization of ferroelectric-semiconductor hybrid materials by optical excitation

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**Abstract:** The influence of spatially defined optical excitation during hysteresis poling on the resulting polarization between a single pair of electrodes was investigated. For this purpose 30  $\mu\text{m}$  thick bilayer films made of a (Cd:Zn)S particle/P(VDF-TrFE) composite and a pristine P(VDF-TrFE) layer were prepared, and selected regions of the semi-transparent Au top electrode were illuminated (470 nm wavelength) during poling. polarization distribution in the samples was characterized using the laser intensity modulation method. It was possible to generate polarization in geometrically defined regions including specified polarization direction within the area between the electrodes.

**Keywords:** composite, ferroelectrics, semiconductor, photoexcitation

## Introduction

It is known that photoexcitation leads to an increase in electrical conductivity in composites of semiconductor particles and P(VDF-TrFE) [1]. If poling takes place under illumination with light of a suitable wavelength, this is also associated with an increase in the remanent polarization and the pyroelectric coefficient [2]. On this basis, bilayer films of a 10 vol% (Cd:Zn)S particle/P(VDF-TrFE) composite and a pristine P(VDF-TrFE) layer were investigated regarding this effect could be utilized to generate spatially selective polarisation by optical excitation during poling.

## Results and Discussion

Figure 1a shows a laser intensity modulation method (LIMM) measurement with high resolution [3] carried out on a film, whose top electrode was partially illuminated in a geometrically defined area during poling. A region of increased polarization occurs exclusively in the area, which was optically excited during poling.

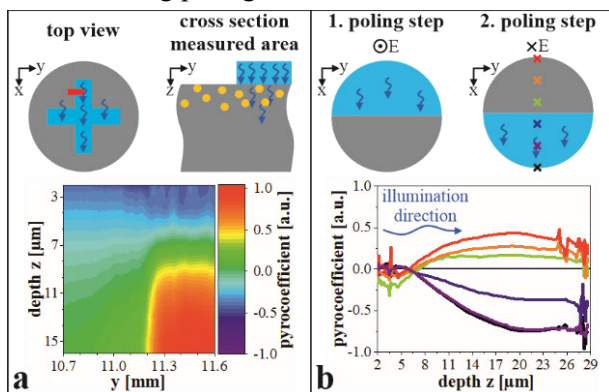


Figure 1: a) Cross-illumination of the electrode during poling and LIMM tomography along the red line. b) Illumination and last half cycle electric field direction within the poling sequence as well as LIMM profile measured at the marked spots. For poling a triangular voltage with 50 MV/m amplitude and 1 Hz frequency was applied for 2 minutes.

Figure 1b shows a test sequence in which the two half-sides of the top electrode were alternately illuminated and the electric field direction of the last poling half cycle was reversed in the two poling steps. The LIMM measurement illustrates that the two half-sides have opposite polarization directions, whereby the polarization of the upper half set in the first step has decreased slightly during the second poling step.

The increased polarization in the illuminated areas is attributed to an increase of the local electric field strength due to charge carrier injection as well as to improved dipole stabilisation due to increasing charge carrier density, both resulting from photoexcitation in the composite layer.

## Conclusions

Optical excitation of semiconductor-P(VDF-TrFE) hybrid materials allows spatially defined and directionally adjustable polarization in the area of a single pair of electrodes. In combination with their adjustable conductivity there is a high potential for developing multifunctional sensor and actuators systems. The use of light as an external trigger gives the process a high degree of adaptability as well as a high technological efficiency.

## References

- [1] S. Engel et al., "Effect of (Cd:Zn)S particle concentration and photoexcitation on the electrical and ferroelectric properties of (Cd:Zn)S/P(VDF-TrFE) composite films", *Polymers*, 9 (12), 650, 2017.
- [2] S. Engel et al., "Polarization properties and polarization depth profiles of (Cd:Zn)S/P(VDF-TrFE) composite films in dependence of optical excitation", *Polymers*, 10 (11), 1205, 2018.
- [3] D. Smykalla et al., "Measuring 3D pyroelectric distributions with high resolution in thin films by a laser scanning microscope", *Rev. Sci. Instrum.*, 94 (2), 2023.

## Acknowledgements

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# 3D high resolution pyroelectric distributions in P(VDF-TrFE) matrix composites

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**Abstract:** Composite systems of vinylidene fluoride-trifluoroethylene (VDF-TrFE) copolymer matrix of molar ratios 70/30 and zinc oxide nano wire are fabricated by infiltration. Corona poling at room temperature generates an inhomogeneous polarization in sample. The polarization profiles are recorded with the laser intensity modulation method and show distribution with 1  $\mu\text{m}$  lateral resolution.

**Keywords:** P(VDF-TrFE); ferroelectric; pyroelectricity; structure

## Introduction

The combination of new materials in the vinylidene fluoride-trifluoroethylene (VDF-TrFE) copolymer matrix is a way to produce systems with tailored dielectric and polarization properties [1]. Such matrix composites are of high interest for new ferroelectric devices like membranes or sensors. The Laser Intensity Modulation Method (LIMM) is utilized to measure the pyroelectric distribution inside various thin films with dispersed BaTiO<sub>3</sub> particles, (Cd:Zn)S particles or ZnO nano wire with a lateral resolution of 1  $\mu\text{m}$  [2].

## Results and Discussion

Zinc oxide (ZnO) nano wire with a height of 10-20  $\mu\text{m}$  and diameter of 200 nm have been grown on silicium substrate. VDF-TrFE copolymer of molar ratio 70/30 from Solvay has been dissolved in methyl ethyl ketone (MEK) and infiltrated between the nano wire structures. After cutting the film from the substrate, it was melted on a glass substrate with a 1 mm wide aluminium bottom electrode, annealed at 120°C for 2h. Subsequently, a 1mm wide top electrode was thermally evaporated and the sample was corona poled.

The pyroelectric coefficient of the full sample is  $p = 8.2 \mu\text{C}/\text{m}^2\text{K}$ , the measurement was done with a sinusoidal temperature variation with amplitude of  $\vartheta = 1 \text{ K}$  around 20 °C and period of  $T = 100 \text{ s}$ . Afterwards the pyroelectric distribution was measured with a Laser-Scanning-Microscope and the pyroelectric depth profile  $p(d)$  was calculated from the pyroelectric spectrum  $Re(I_p) - Im(I_p)$ . Fig. 1 shows the pyroelectric image of the top and bottom side of the sample with  $d = 1 \mu\text{m}$  penetration depth. Additionally, a polarization profile at a 225 $\mu\text{m}$  long line with constant  $x$  was scanned in depth direction, the position is marked with the red line on the bottom electrode. It is shown, that the pyroelectric coefficient at the bottom side is positive and highest close to the electrode. At the top side the pyroelectric coefficient points in negative direction in some parts. The charge injection in the nano wire during

poling can cause a negative electric field, which leads to the opposite sign pyroelectric coefficients at parts with higher nano wire concentration.

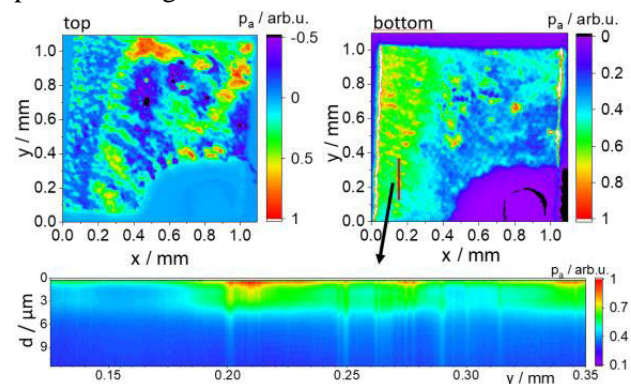


Figure 1: Pyroelectric distributions of a 1x1 mm and 11 $\mu\text{m}$  thin P(VDF-TrFE) sample with ZnO nano wire.

## Conclusions

The high-resolution measurement of pyroelectric distributions is utilized to determine concentration variations of ZnO nanowire in P(VDF-TrFE) matrix. It is presented, that the overall ferroelectric parameters of a 1x1 mm sample are not comparable with the local parameters in micrometer scale. The pyroelectric distributions can vary in a large scale inside a single sample, and with the measurements it is possible to determine errors in the sample production or to test the homogeneity of the samples with resolution up to 1 $\mu\text{m}$  in lateral direction.

## References

- [1] S. Engel et al, "Effect of (Cd:Zn)S Particle Concentration and Photoexcitation on the Electrical and Ferroelectric Properties of (Cd:Zn)S/P(VDF-TrFE) Composite Films", *Polymers* 9(12):650, 2017.
- [2] D. Smykalla et al, "Measuring 3D pyroelectric distributions with high resolution in thin films by a laser scanning microscope" *Rev Sci Instrum* 94, 023703, 2023

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# Fully transparent flexible piezoelectric composite films based on electro-spun PVDF and their device applications

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**Abstract:** Piezoelectric polymer films with simple and stable structure are desired for flexible sensors. Here, polyvinylidene fluoride (PVDF) microfiber films containing high  $\beta$ -phase content of about 75% are prepared via electrospinning technique. Due to the nearly-identical refractive index of PVDF and polydimethylsiloxane (PDMS), highly transparent piezoelectric composite films, with a transmittance of above 87% over the visible light range, are obtained by filling the PVDF microfiber film with PDMS. The piezoelectric PVDF/PDMS film exhibits a  $d_{33}$  coefficient of 8pC/N, and flexible piezoelectric sensors are prepared and tested for detection of body signals and environmental weak mechanical excitation.

**Keywords:** polyvinylidene fluoride, electrospinning, polydimethylsiloxane, piezoelectric composite film

## Introduction

Electrospinning is a low-cost and effective way to fabricate  $\beta$ -phase PVDF microfiber films [1, 2]. Here, a new type of fully transparent flexible piezoelectric PVDF/PDMS composite is prepared based on electro-spun PVDF films in combination with PDMS. Its microstructure and piezoelectric properties are characterized and flexible piezoelectric sensors are prepared for monitoring of body and weak mechanical signals.

## Results and Discussion

PVDF microfiber films with high  $\beta$  phase content of about 75% is prepared via electrospinning technology. By filling the electro-spun PVDF with PDMS via scrape coating, a flexible PVDF/PDMS piezoelectric composite film with ultra-high transparency are successfully obtained (Figure 1).

The longitudinal piezoelectric test shows that the piezoelectric  $d_{33}$  coefficient of PVDF/PDMS samples is 8pC/N under a static force of 1N, while the  $d_{33}$  of electro-spun PVDF is only 5.8pC/N. In terms of transverse piezoelectric test, under specific bending strain, the  $V_{oc}$  and  $I_{sc}$  of PVDF/PDMS can reach 13.12V and 17.01nA, superior to those of PVDF films with 10.96V and 11.5nA, respectively.

Flexible piezoelectric sensors have been prepared, and employed in detecting human body signals and environmental sound signals. the amplitude of the human pulse signals measured by the PVDF/PDMS devices reaches 5mV, and the signal amplitudes of finger tapping and finger bending are close to 1V, both are better than the respective values of the electro-spun PVDF sensors. The environmental sound signal amplitude of the PVDF/PDMS devices reaches to 0.27V, and the sensors are capable of

accurately capturing the sound frequency and pressure.

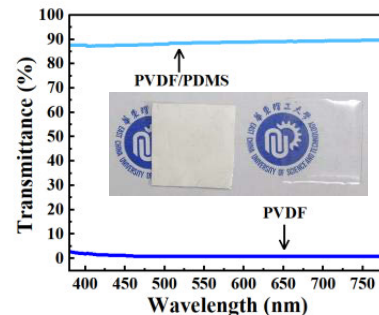


Figure 1: Transmittance of an electro-spun PVDF microfiber film and a PVDF/PDMS film. The inset shows an optical image of the two films placed on top of the logo of ECUST.

## Conclusions

A fully transparent flexible piezoelectric PVDF/PDMS composite film is prepared, which exhibits a  $d_{33}$  of 8pC/N and can detect body signals and environmental weak mechanical excitation.

## References

- [1] D. H. Reneker and I. Chun, "Nanometre diameter fibres of polymer, produced by electrospinning", *Nanotechnology*, 7 (3), 216-223, 1996.
- [2] F. Xu, J. Yang, R. Dong, H. Jiang, C. Wang, W. Liu, Z. Jiang, X. Zhang, G. Zhu, "Wave-Shaped Piezoelectric Nanofiber Membrane Nanogenerator for Acoustic Detection and Recognition", *Adv. Fiber Mater.*, 3, 368-380, 2021.

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# Utilization of non-stoichiometric Nb<sup>5+</sup> to optimize comprehensive electrical properties of KNN-based ceramics

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**Abstract:** An easy approach is suggested to obtain excellent piezoelectric performances in KNN-based ceramics simultaneously with high  $T_C$ . Herein, a KNN-based ceramics system with non-stoichiometric Nb<sup>5+</sup> is designed. A high  $T_C = 300$  °C and large  $d_{33} = 450$  pC/N can be simultaneously obtained in the KNN-based ceramics with non-stoichiometric Nb<sup>5+</sup>.

**Keywords:** Lead-free ceramics; potassium sodium niobate; non-stoichiometric Nb<sup>5+</sup>

## Introduction

There is an increasing request for the use of environmentally-friendly lead-free ceramics in piezoelectric devices. To get high-performance KNN-based ceramics that can replace lead-based ones, a lot of efforts have been made to improve their piezoelectricities<sup>1</sup>. High-performance KNN-based ceramics is always obtained at low  $T_C$ , and with poor temperature stability, however, these results are not sufficient for practical applications. How to overcome the contradiction between large  $d_{33}$  and high  $T_C$  has become a hot research issue for lead-free piezoelectric ceramics.

## Results and Discussion

Appropriate excessive Nb<sup>5+</sup> content can be incorporated into the B-site lattice, which can improve the phase structure, densification, grain growth, and domain structure of KNN-based ceramics, as shown in Figure 1a. The Nb<sup>5+</sup> in the lattice matrix of KNN-based ceramics decreases the size of domains, thus leading to more domains, as shown in Figure 1b. From Figure 1c, a high  $T_C = 300$  °C and  $d_{33} = 450$  pC/N can be simultaneously obtained in the KNN-based ceramics with non-stoichiometric Nb<sup>5+</sup>. Furthermore, the introduction of excess Nb<sup>5+</sup> leads to the domain wall pegging effect, which can benefit the improvement in the temperature stability of  $d_{33}$  values.

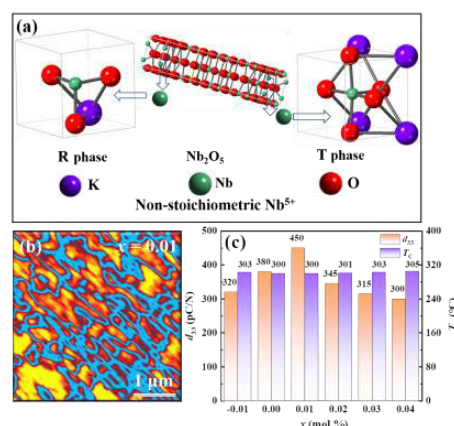


Figure 1: (a) schematic representations of Nb<sup>5+</sup> into the lattice matrix of KNN; (b) amplitude images of PFM for ceramics; (c)  $d_{33}$  and  $T_C$  of samples with different amounts of Nb<sup>5+</sup>.

## Conclusions

The comprehensive electrical properties of KNN-based ceramics can be tuned by optimizing the content of non-stoichiometric Nb<sup>5+</sup>.

## References

1. H. Tao, "Ultrahigh performance in lead-free piezoceramics utilizing a relaxor slush polar state with multiphase coexistence," J. Am. Chem. Soc., 141(35) 13987-94, 2019.

## Acknowledgements

This work is supported by the National Natural Science Foundation of China (12004267).

# Polyelectrolyte multilayers deposited on corona charged porous composite polylactic acid / poly( $\epsilon$ -caprolactone) substrates with potential for drug delivery systems

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**Abstract:** In the present paper polyelectrolyte multilayers (PEMs) deposited on porous composite polylactic acid (PDLA)/poly( $\epsilon$ -caprolactone) (PEC) substrates were investigated. The substrates obtained were charged in a corona discharge. The dependences of the normalized surface potentials on the storage times of charged substrates were studied. Layer-by-layer (LbL) technique was used for multilayer deposition on the substrates. A model drug Benzydamine hydrochloride was loaded in the casein layers. A study of the drug release kinetics in saline buffer was carried out and the amount of the released drug was calculated spectrophotometrically.

**Keywords:** corona discharge, porous composite biopolymer, polyelectrolyte multilayers, drug release

## Introduction

Biodegradable polymer films, comprised of different materials such as polylactic acid (PDLA) and poly( $\epsilon$ -caprolactone) (PCL), are one of the fastest developing materials and find a number of applications in the field of biomedicine [1]. Polymer blending of two different kinds of biopolymers in different ratios has been demonstrated to improve the film properties, when compared to pure films [2]. The implementation of corona discharge can further improve the properties of the polymer blends as it is often implemented for the creation of multilayers on pure polymer films for drug delivery [3].

## Results and Discussion

Time dependences of the normalized surface potential for positively and negatively charged PDLA, PEC and PDLA:PEC (at the desired ratios 25/75, 50/50 and 75/25) electrets were studied. The results obtained show that the normalized surface potential for samples, charged in a positive corona, are higher than those for samples, charged in a negative corona, independently of the material type. It was also established that the values of the normalized surface potential for the porous composite electrets are higher than those of non-porous one independently of the corona polarity.

The morphology of the obtained porous substrates was examined by means of scanning electron microscopy (SEM).

Casein/chitosan polyelectrolyte multilayers (PEMs) were created on the substrates obtained. The benzydamine hydrochloride release from PEMs assembled was investigated. The obtained results show that the benzydamine hydrochloride release profile could be controlled by varying the composite of the substrate and its surface charge. Based on the drug release results, the release kinetics dependences were fitted to Korsmeyer-Peppas model.

## Conclusions

The benzydamine hydrochloride release from chitosan/casein PEMs, assembled on different porous composite substrates, was examined in this paper. It was shown that the steady state values of the normalized surface potential for PDLA electrets are the lowest compared to others investigated films independently of the corona polarity. The benzydamine hydrochloride loading and release profile could be controlled by changing the polarity and the substrates and the PDLA:PEC ratio.

## References

- [1] H. Shakeri, M. Nazarpak, R. Imani, L. Tayebi, Poly (l-lactic acid)-based modified nanofibrous membrane with dual drug release capability for GBR application, *Int. J. Biol. Macrom.*, 231, 123201, 2023.
- [2] B. Zhu, T. Bai, P. Wang, Y. Wang, C. Liu, C. Shen, Biodegradable poly(lactic acid) nanocomposites reinforced and toughened by carbon nanotubes/clay hybrids, *Int. J. Biol. Macrom.*, 153, 1272 – 1280, 2020.
- [3] T. Yovcheva, A. Viraneva, A. Marinova, S. Sotirov, G. Exner, I. Bodurov, M. Marudova, B. Pilicheva, Y. Uzunova, I. Vlaeva, Insulating chitosan/casein multilayers on corona charged polylactic acid substrates, *IEEE Trans. on Dielect. and Electr. Insul.*, 25, 766-771, 2108.

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# Benzydamine loaded casein nanospheres embedded in polyelectrolyte multilayers

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**Abstract:** Polyelectrolyte multilayers films containing Benzydamine hydrochloride loaded casein nanoparticles were developed with the aim to increase the structural drug loading efficiency and to prolong the drug release. The multilayers were built on biodegradable polyester substrates, which are previously charged in a corona discharge. High molecular weight chitosan was used as a partner in the multilayer formulation. The chitosan and the casein nanoparticles were deposited on the substrate using the layer-by-layer (LbL) spraying technique. The drug loading efficiency and the release kinetics in artificial saliva were determined spectrophotometrically.

**Keywords:** polyelectrolyte multilayers, casein nanoparticles, loading efficiency, drug release

## Introduction

Polyelectrolyte multilayer films are emerging as successful and widely used drug delivery systems. They are flexible, soft, small (thin) and provide comfort to the patient while extending the contact time of the drug and increasing its bioavailability. A major drawback of these films is their low drug loading efficiency, which makes it difficult to reach the required drug dose [1].

Another approach for drug delivery is the use of nanoparticles [2]. Their main advantages are high loading efficiency, the ability to control the release process of the medicinal substance, protection of the drug from biological degradation, and improved bioavailability. At the same time, however, nanoparticles cannot ensure an extended time of contact between the medicinal substance and the treated tissue.

The present research proposes the construction of new drug-delivery systems from nanoscale structures embedded in multilayer polyelectrolyte films.

## Results and Discussion

Benzydamine hydrochloride loaded casein nanoparticles were synthesized by spray drying technique [3]. Their size was  $(149.2 \pm 2.6)$  nm and the  $\zeta$ -potential was  $(-16.3 \pm 0.5)$  mV.

Casein nanoparticles/chitosan polyelectrolyte multilayers (PEMs) were created on the preliminary corona treated substrates from biodegradable polyester. For this purpose, a chitosan solution with a concentration of 0.1% and a dispersion of casein particles with different concentrations were used. The chitosan and the nanoparticles were adsorbed on the polyester surface by spraying at constant pressure.

The embedment of the nanoparticles into the PEMs was proved using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

The loading efficiency of the structures and the Benzydamine hydrochloride release kinetics were examined spectrophotometrically by measuring the amount of the free drug in the artificial saliva.

The obtained results show that the benzydamine hydrochloride release profile could be controlled by varying the composite of the PEMs. The release kinetics dependences were fitted by different mathematical models.

## Conclusions

The benzydamine hydrochloride release from casein nanoparticles/chitosan PEMs, assembled on corona treated substrates, was examined in this paper. It was shown that the casein nanoparticles were successfully embedded into the PEM structure.

The benzydamine hydrochloride loading and release profile could be controlled by changing the casein nanoparticles concentration.

## References

- [1] I. Vlaeva, B. Pilicheva, A. Marinova, I. Bodurov, T. Yovcheva, A. Viraneva, ... & M. Marudova, Investigation of flexible polyelectrolyte multilayered structure by using different techniques, *AIP Conf. Proc.*, 2075, 1, 160007, 2019.
- [2] S. Khatun, T. Appidi, & A. Rengan, Casein nanoformulations-Potential biomaterials in theranostics, *Food Bioscience*, 102200, 2022.
- [3] N. Zahariev, M. Marudova, S. Milenkova, Y. Uzunova, & B. Pilicheva, Casein micelles as nanocarriers for benzydamine delivery, *Polymers*, 13, 24, 4357, 2021.

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## Notes