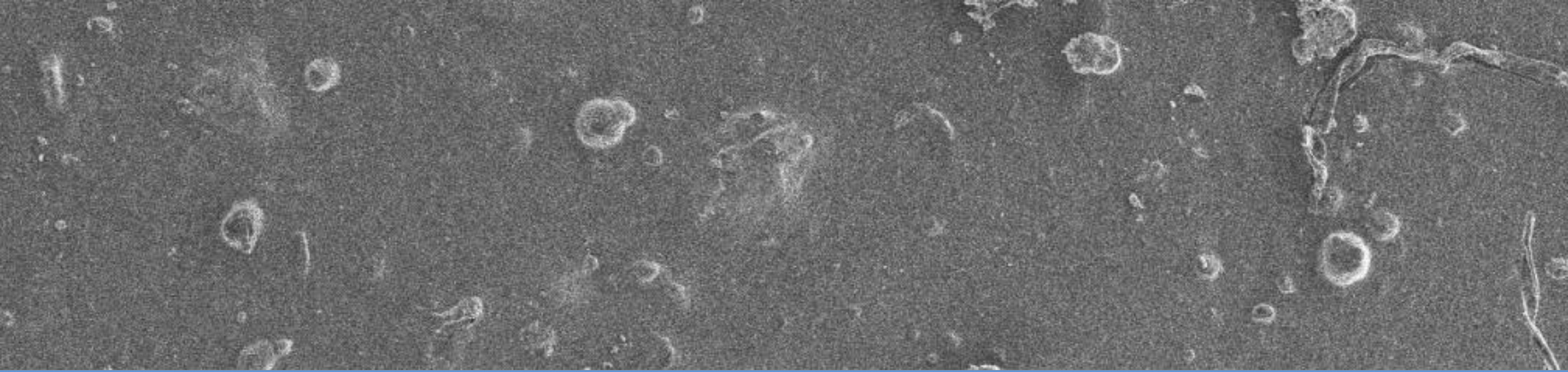


NUMERICAL MODELLING OF PVDF/HA/AGNO3 PIEZOELECTRIC COMPOSITE

Ieva Markūnienė, PhD.:Kaunas University of Technology, Studentu str. 56, Kaunas, LT 51373, Lithuania; ieva.markuniene@ktu.edu;

Prof. **Giedrius Janušas**: Kaunas University of Technology, Studentu str. 56, Kaunas, LT 51373, Lithuania; giedrius.janusas@ktu.lt;

Abstract

*Many biosensors based on biocompatible piezoelectric materials have recently emerged. These biological sensors can be integrated into biological systems. Modern piezoelectric biosensors have been developed using new materials and advanced technologies to avoid the toxicity of conventional lead-containing piezoelectric materials. Polyvinylidene fluoride - PVDF polymer has been recognised to have good ferroelectric properties and is biocompatibility and also the cheapest inter fluoride polymers [3]. **HA** - hydroxyapatite brittleness and poor bending strength - limits its application. To compensate for the mechanical weakness of HA, a number of formulas for HA and polymer composites have been developed. HA / polymer composites have excellent biocompatibility as a result of the amount of HA in the overall composition. **PVDF** films with a high -phase content of **β-phase** up to 98.8% are obtained using dimethylsulfoxide (**DMSO**) as the solvent at optimized crystallization [6]. The addition of a conductive phase, such as silver, can be helpful. The conductive phase improves the charge transfer, enhancing the sensitivity of the piezoelectric response. These reasons led to the choice of materials: PVDF, HA, AGNO3. A solvent casting method was used to produce PVDF films in DMSO solvent. The energy extracted from the samples was measured using a micro power meter and force. Piezoelectric constants were measured using a piezoelectric meter. Using the acquisition properties of piezoelectric and COMSOL Multiphysics program, a numerical model of the samples was created.*

Materials – Ag, HA and DMSO

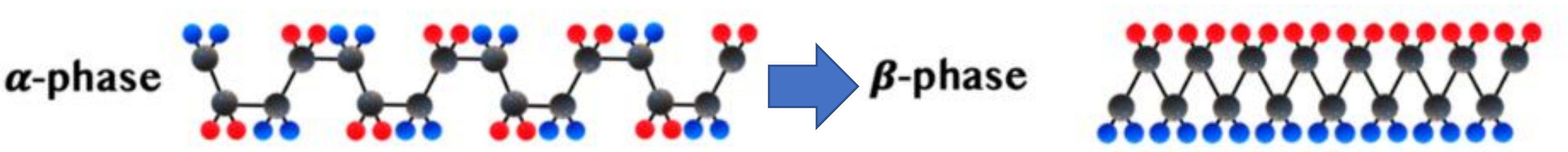
Conductive phase such as **silver** can be beneficial because the conductive phase improves the charge transfer by increasing the sensitivity of the piezoelectric response and a suitable amount of **Ag** deposition gives the piezoelectric activity, while a higher Ag loading decreases the piezoelectric activity (concentration properties studied **0.12, 0.21, 0.52%,** 1 ml) [3].

HA has the capacity to form chemical bonds with ambient hard materials with the forming of a HA interfacial ply. The similar chemical and physical characteristics of natural HA with bone do it biocompatible [9].

DMSO - dimethyl sulfoxide is an aprotic solvent that also miscible with polar solvents because it has a dipole moment. These properties make DMSO a potential solvent for the solubilization of other polymers.

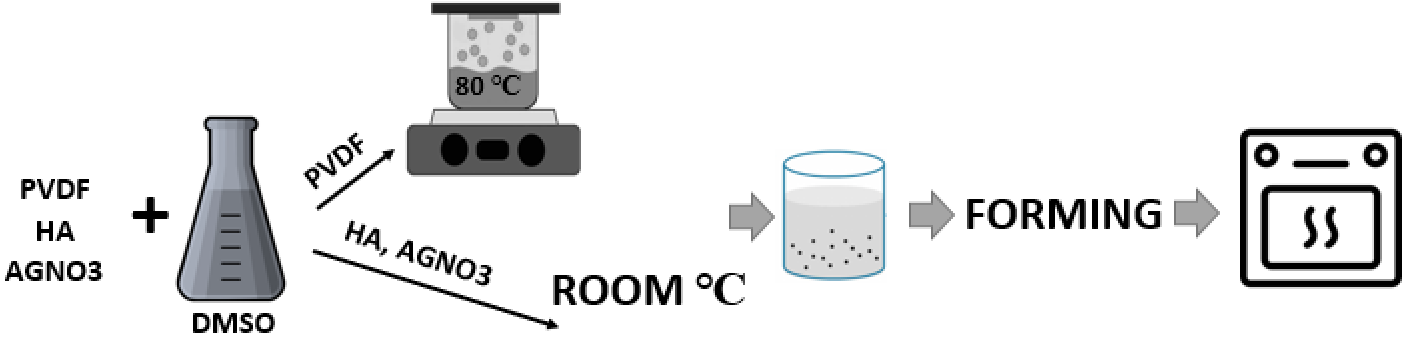
Materials - PVDF

Polyvinylidene fluoride - **PVDF** films with high content of **β-phase** up to 98.8% are obtained by using DMSO as the solvent at optimized crystallizing temperature of 60 °C. The corresponding PVDF film with high β-phase content presents excellent ferroelectric and piezoelectric properties. Finally, PVDF films can be prepared by solvent casting. To evaluate the effect of crystallization temperature on the amount of **β-phase,** different crystallization temperatures (50–160 °C) can be applied to prepare PVDF films using the optimal DMSO solvent [10]. The same polar solvent can form all three phases of PVDF. Different phases of PVDF can be obtained by changing the solution temperature using the polar DMSO solvent. Annealing conditions lead to the presence of different phases and the transformation of one phase into another PVDF phase. The β-phase, which is important for ferroelectric applications, is obtained by using a polar solvent and appropriate annealing. The maximum β phase in the films exists when the PVDF films are annealed at 90°C for 5 h. [6].



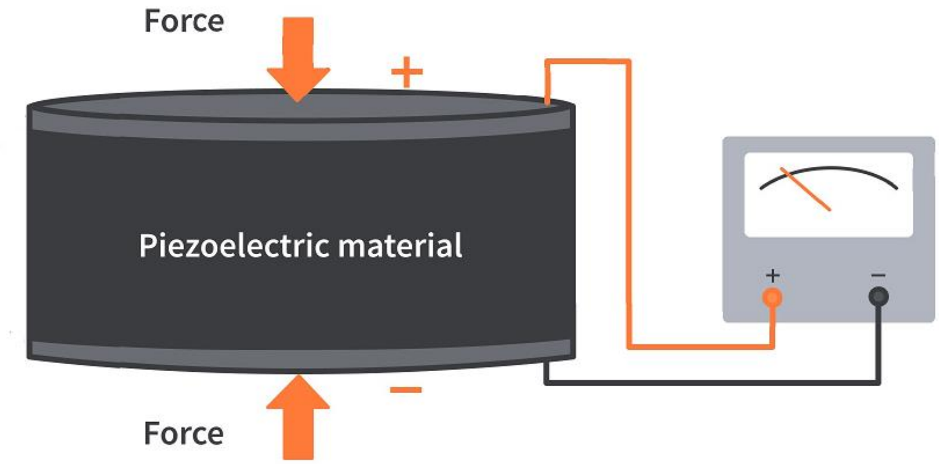
Preparing - Solvent casting method

Films are obtained using DMSO - dimethyl sulfoxide as a solvent at an optimized temperature of 80 °C. Polyvinylidene fluoride - PVDF beads and DMSO solvent were first mixed and dissolved at 80 °C for 4–5 h until a homogeneous solution was formed. Silver nitrate and hydroxyapatite (HA) were also dispersed in DMSO solvent, but at room temperature and stirred until evenly distributed or dissolved. Finally, all the components are mixed and poured onto the base, and the film is formed with forming rods and dried in an oven at 60 °C for 5-6 hours.



Piezoelectric

- Ag can be beneficial because the conductive phase improves the charge transfer by increasing the sensitivity of the piezoelectric response and a suitable amount of Ag deposition gives the piezoelectric activity, while a higher Ag loading decreases the piezoelectric activity (concentration properties studied 0.12, 0.21, 0.52%, 1 ml) (Soroush et al., 2021).
- The corresponding PVDF film with high β-phase content presents excellent ferroelectric and piezoelectric properties (Satapathy et al., 2011).
- Ceramics such as hydroxyapatite (HA) has excellent piezoelectric properties.



Piezoelectric constants

The piezoelectric effect is an interaction between the mechanical and electrical behaviour of the material, and to a linear approximation, this interaction can be described by the expressions:

$$S = S^E T + dE$$
$$D = \varepsilon^T E + dT$$

where, E – electric field strength, D – dielectric displacement, T - applied stress, S – strain, s – compliance, ε – permittivity.

In this formula, k is the electromechanical coupling coefficient, k^T is a dielectric constant under constant tension, and s^E is the elastic correspondence (10 m N^{-1}) in the constant electric field. The following are the two main constants [10]:

$$d_{31} = k_{31}\sqrt{\varepsilon_0 k_3^T s_{11}^E} \quad (C\ N^{-1})$$
$$d_{33} = k_{33}\sqrt{\varepsilon_0 k_3^T s_{11}^E} (C\ N^{-1})$$

The d constants are related to the large mechanical displacements commonly found in motion transducer equipment. Conversely, the coefficient can be considered to be related to the load assembled on electrodes under mechanical stress, d33 applies when the force acts in three directions - parallel to the axis of polarization - and acts on the same surface from which the load is taken, d31 is applied when the load is collected from the same surface as d33, but the force acts perpendicular to the axis of polarization. They are known to have the following empirical connection [10]:

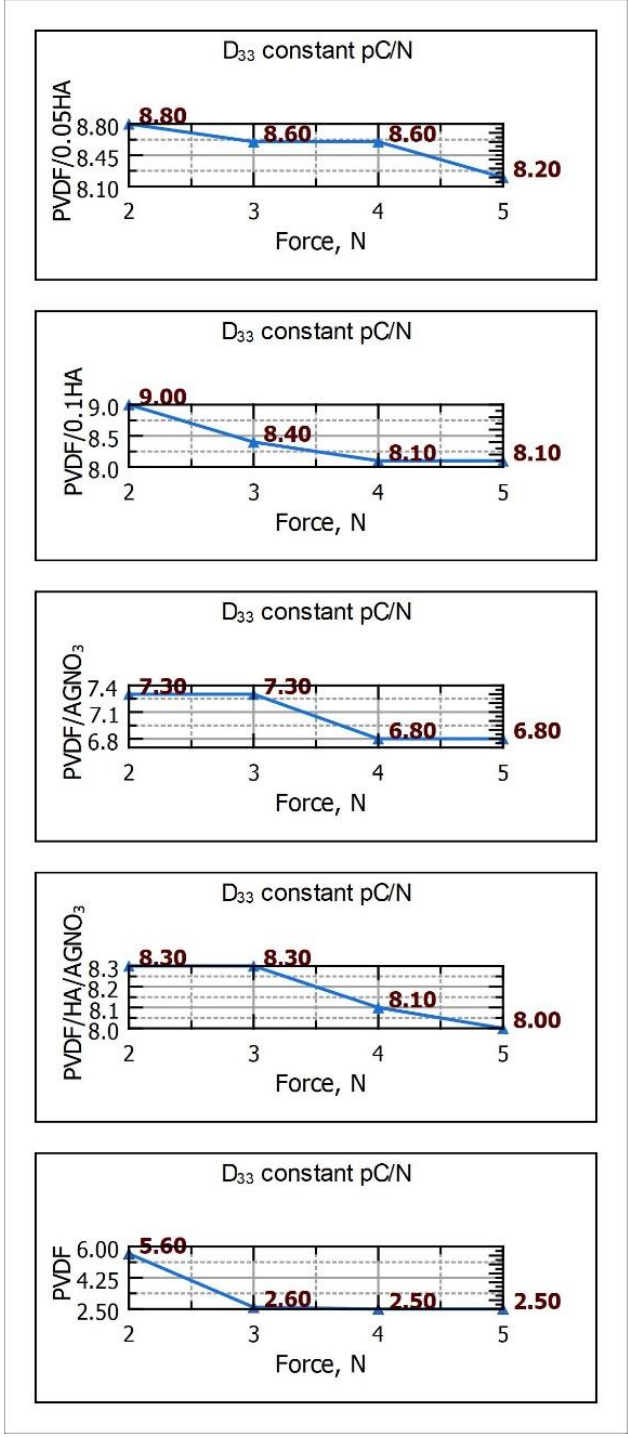
$$d_{33} \approx -2{,}5 \times d_{31}$$

The piezoelectric charge coefficient connecting the electrical charge generated per piece area with the mechanical force is applied and calculated by coulombs - Newton units (C N-1). This constant is most commonly used for the evaluation of piezoelectric material.

$$d = \frac{\text{Strain developed}}{\text{Applied field}} = \frac{\text{Charge density (open circuit)}}{\text{Applied stress}}$$

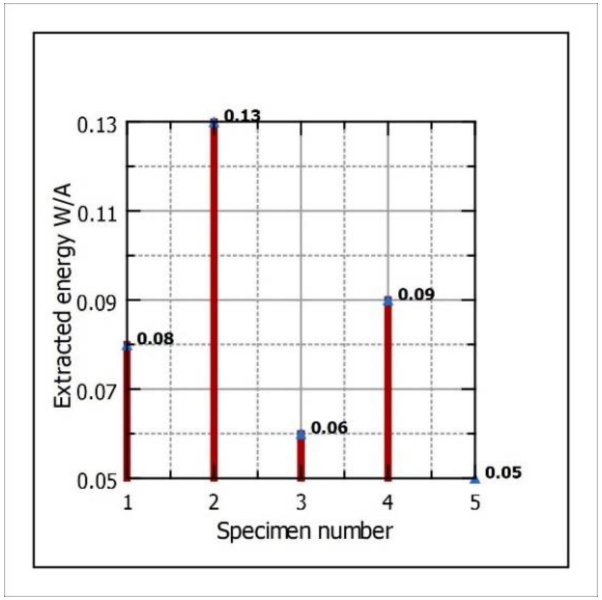
d_{33} constant

d_{33} constant was measured using Polyk Quasi Static Piezoelectric d_{33} Meter. Each sample was measured with a different force in the range [2-5 N]. The piezoelectric metre showed the lowest result for the PVDF sample, which is 5.6 pC/N with a force of 2 N and decreased steadily. The best results showed PVDF/HA samples, which is 8.8-9 pC/N with a force of 2 N and decreased steadily. Sample PVDF/HA/$AGNO_3$ also shows good results and the d_{33} constant is 8.3 pC/N at a force of 2 N. The best results are with a force load of 2 N.



Extracted energy

Using multimeter and Zwick/Roell automated testing system was measured generated energy by specimens. The registered energy ranges from 0.06 to 0.13 ± 0.002 W/A. HA increases electrical durability, as samples 3 and 5 without HA showed the lowest energy values. The measurements of the generated power confirm that the samples containing HA have better piezoelectric properties. For example, the energy generated by PVDF/0.05HA, PVDF/0.1HA and PVDF/HA/AGNO3 samples is at least 30% higher.



1 – PVDF/0.05HA; 2 – PVDF/0.1HA; 3 – PVDF/AGNO3; 4 – PVDF/HA/AGNO3; 5 – PVDF

Characteristics for simulation

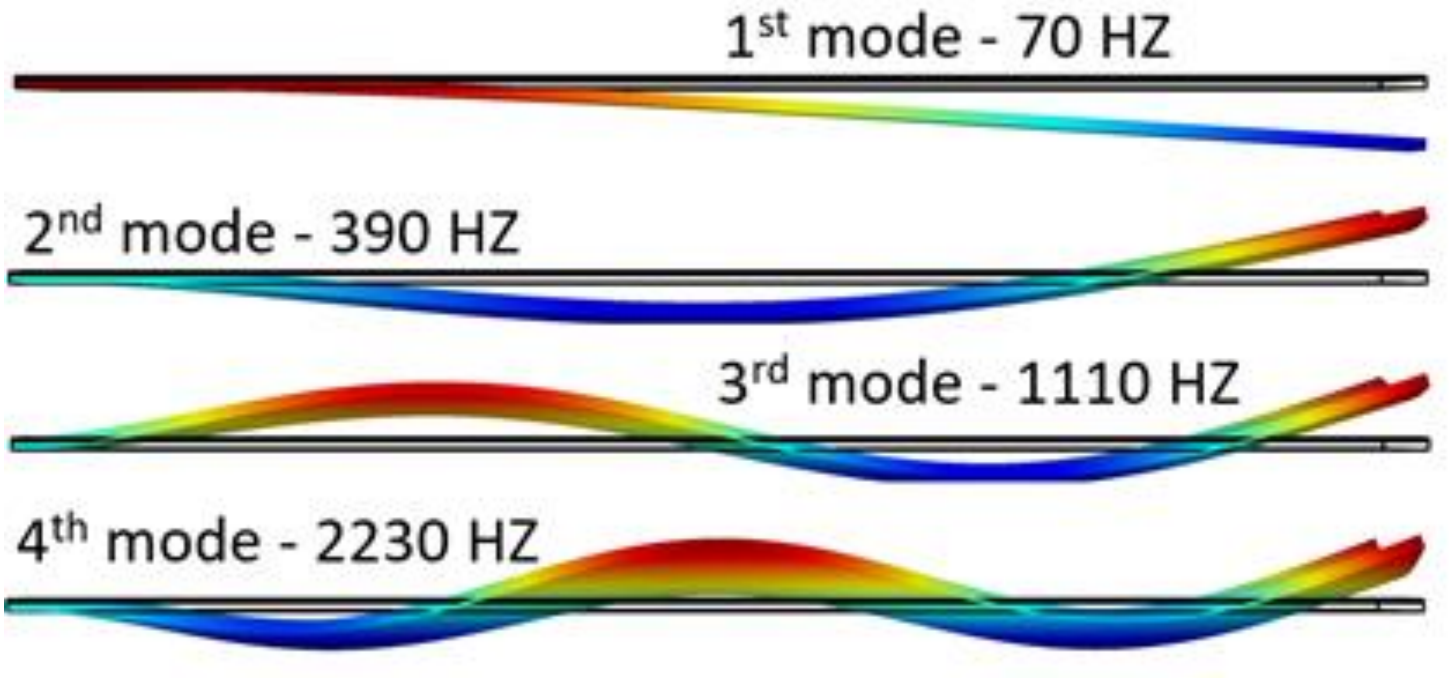
COMSOL Multiphysics is a simulation software used in engineering, manufacturing, and research. The software provides fully coupled Multiphysics and single-physics simulation capabilities, simulation data management, and functions for building simulation applications.

Was created a numerical model of sample **PVDF/0.05HA/AgNo3** was selected with the obtained parameters, which are presented in Table:

Sample	Specimens Thickness (piezoelectric layer), mm	Extracted energy (W/A)	D_{33}, 10^{-12} C/N (Force, 2 N)	D_{31}	Mass, g	Density kg/m^3	Size of specimens, mm
PVDF/0.05HA/AgNo3	0.100	0.09	8.3	3.32	0.19	0.08	30x80

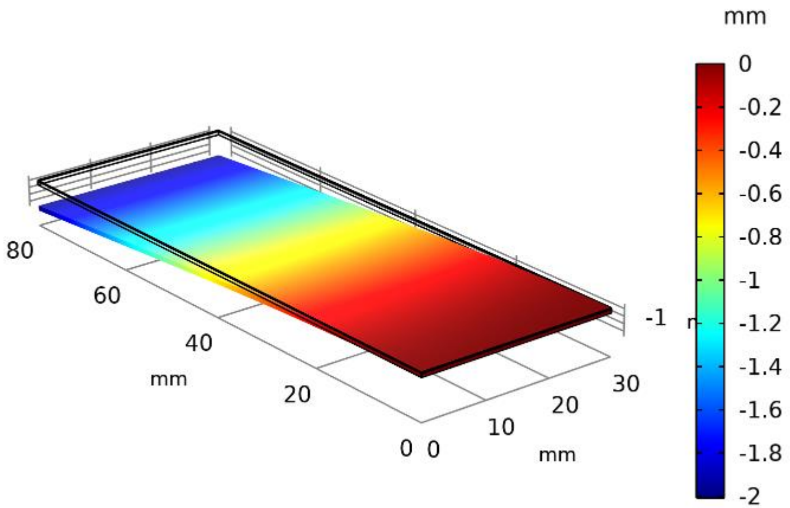
Vibration modes

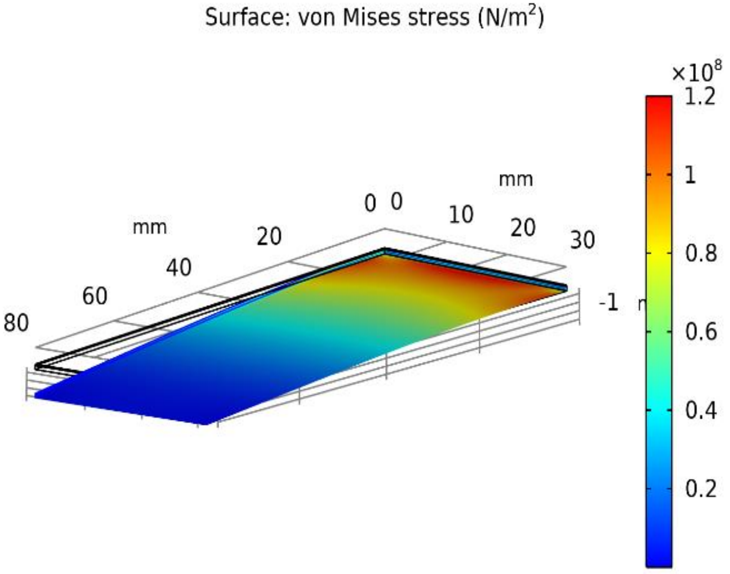
For the model verification, two tests were performed: Eigen frequency and deformation analysis. The first four eigenvalues and Eigen frequencies are presented. Since the thickness of the formed samples is 300 µm, they are characterized by low resonant frequencies. The first eigenvalue is observed when the sample is excited at a frequency of 70 Hz, the second at 390 Hz, the third at 1110 Hz and the fourth at 2230 Hz.



Displacement of electric potential and Mises stress

The COMSOL Multiphysics program performed calculations of the displacement and stresses of the sample PVDF/0.05HA/AgNo3 under the influence of a 2N force. The maximum deformation of the specimen was determined to be 2 mm, and the surface tension was 120 MN/m2. The theoretical results match the experimental ones with 15 % error.





Application

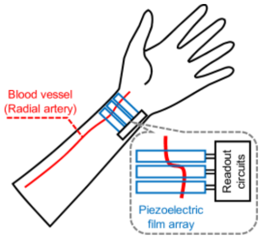
1

Pressure sensors

2

Vibration sensors

3



Pulse sensors

4

Biomedical sensors

Conclusions

The piezoelectric meter showed the lowest result for the PVDF sample, which is 5.6 pC/N with a force of 2 N and decreased steadily. The best results showed PVDF/HA samples, which is 8.8-9 pC / N with a force of 2 N and decreased steadily. Sample PVDF/HA/AGNO3 also shows good results and the d33 constant is 8.3 pC/N at a force of 2 N. The best results are obtained with a force load of 2N.

Using Multimeter 2002 and Force machine Zwick/Roell was measured generated voltage by specimens. HA increases electrical durability, as samples 3 and 5 without HA showed the lowest energy values. The measurements of the generated power confirm that the samples containing HA have better piezoelectric properties. The multimeter showed a maximum energy of ~0.125 ± 0.002 W/A when using a load with a Zwick machine. **HA increases piezoelectric properties, as samples PVDF/AGNO3 and PVDF showed the lowest energy values.** For a sample PVDF/0.05HA/AgNo3 numerical model was created and verified. **The theoretical results match the experimental ones with 15 % error. The created piezoelectric composite material is suitable for sensing applications in flexible electronic devices.**

Thank you