Conservation of the piezoelectric response of PVDF films under irradiation

G. Melilli, D. Lairez, D. Gorse, E. Garcia-Caurel, A. Peinado, O. Cavani, B. Boizot, M-C Clochard
Material of interest: **Poly(vinylidene fluoride) (PVDF)**

piezoelectric PVDF membrane has experienced a resurgence of interest for energy harvesting.

- decrease of energy consumption
- Robustness and flexibility allows an easier integration respect to conventional piezoelectric materials such as PZT ceramics

How to enhance piezoelectric properties in miniaturized objects?

- Multilayers or nanostructuration
- Structural modification: SHI irradiation and e-beam*, **

PVDF polymorphism: crystalline phases $\alpha$, $\beta$, $\delta$ and $\gamma$ phases.

PVDF crystalline phases:

- **PVDF $\alpha$**
  - Monoclinic cell
  - Non net dipole moment
  - $a=4.96$ Å, $b=9.64$ Å, $c=4.62$ Å

- **PVDF $\delta$**
  - Orthorombic cell
  - Net dipole moment
  - $a=4.97$ Å, $b=9.67$ Å, $c=9.24$ Å

- **PVDF $\beta$**
  - Orthorombic cell
  - Net dipole moment
  - $a=8.58$ Å, $b=4.91$ Å, $c=2.56$ Å

Poling process:

- (T $\approx$ 95°C, $\Delta V = 50 \div 100$ MV.m$^{-1}$)

Hysteresis loop for piezo-PVDF

Dipole moments are randomly oriented ($\beta$ and $\delta$ phase)

Piezoelectricity is defined as the aptitude to convert mechanical strain in electrical charge and vice versa.

**Constitutive equations**

\[ D = \varepsilon^T E + d_{33} T \]
\[ S = d_{33} E + s^E T \]

D : electric displacement (C.m\(^{-2}\))  
E : electric field (V.m\(^{-1}\))  
T : stress (N.m\(^{-2}\))  
S : strain  
\( \varepsilon^T \) : dielectric constant  
\( s^E \) : compliance (inverse of the young’s modulus)  
d\(_{33}\) : piezoelectric constant (m.V\(^{-1}\) or C.N\(^{-1}\)) in z direction

**Curie Brothers**  
Direct piezoelectric effect  
1880
Piezoelectricity is defined as the aptitude to convert mechanical strain in electrical charge and vice versa.

**Constitutive equations**

\[
D = \varepsilon^T E + d_{33} T \\
S = d_{33} E + s^E T
\]

- $D$: electric displacement (C.m$^{-2}$)
- $E$: electric field (V.m$^{-1}$)
- $T$: stress (N.m$^{-2}$)
- $S$: strain
- $\varepsilon^T$: dielectric constant
- $s^E$: compliance (inverse of the young’s modulus)
- $d_{33}$: piezoelectric constant (m.V$^{-1}$ or C.N$^{-1}$) in z direction

---

**Direct piezoelectric effect (sensors)**

- **Applied Stress**
- **Induced $\Delta V$**
Piezoelectricity is defined as the aptitude to convert mechanical strain in electrical charge and vice versa.

**Constitutive equations**

\[
D = \varepsilon^T E + d_{33} T \\
S = d_{33} E + s^E T
\]

- **D**: electric displacement (C.m\(^{-2}\))
- **E**: electric field (V.m\(^{-1}\))
- **T**: stress (N.m\(^{-2}\))
- **S**: strain
- **\(\varepsilon^T\)**: dielectric constant
- **\(s^E\)**: compliance (inverse of the young’s modulus)
- **\(d_{33}\)**: piezoelectric constant (m.V\(^{-1}\) or C.N\(^{-1}\)) in z direction
Mechanical stretching allows to transform $\alpha$ phase (spherulite) in $\beta$ phase (fibrillar).

The bi-oriented piezo PVDF film is an anisotropic system with majority $\beta$ phase

- Nominal Thickness (um): 9 $\mu$m
- Electromechanical coupling factor $K_T$ (%): 10 to 15
- $d_{33}$ (pC/N): 27 ± 20%
- Young’s modulus (GPa): 2.5
- Crystallinity content (%): 36±2
Investigated e-beam range doses: 5, 10, 25, 50 and 100 kGy
(*Gy absorption of one joule of radiation energy per kilogram of matter)

Irradiations were performed under He atmosphere.

Defects in PVDF:
- Radicals + gas release
- Chain scission

Primary beam interacts with valence electrons generating defects.

Investigated doses for SHI irradiation: 0.076 kGy, 0.76 kGy and 7.6 kGy

$^{136}$Xe$^{48+}$
7.46MeV.amu$^{-1}$

Gel dose $\approx$ 10kGy

Crosslinking

low doses range, leads mainly to main-chain scission

higher molecular mobility.
Electrical measurements

Characterisations
Home-made experimental set-up

- Simultaneous registration of pressure and $V_{\text{output}}$
- Clamped membrane under bending stress
- Testing area: 0.785 cm$^2$

Gold electrodes sputtered on both sides (100 nm)

Solenoid Valve controls the pressure:

- Frequency ($f=1 \div 10$ Hz)
- Load application time ($T=20$ ms $\div 1.25$ s)
Simultaneous registration of pressure and \( V_{\text{output}} \)

Clamped membrane under bending stress

Testing area: 0.785 cm\(^2\)

Gold electrodes sputtered on both sides (100 nm)

Solenoid Valve controls the pressure:

- Frequency \( f = 1 \div 10 \text{Hz} \)
- Load application time \( T = 20 \text{ms} \div 1.25 \text{s} \)
Output voltage **versus** pressure

Output voltage under cycling bending stress condition

Electrical circuit:

Piezoelectric PVDF is considered as capacitor with a *RC time constant* $\tau$
The energy conversion efficiency is the ratio between the total electrical energy ($W_e$) and the total mechanical energy ($W_m$).

The conversion efficiency was found to be around 0.8%

Electrical efficiency:
Load=0.6Bar, f=0.4Hz, $R = 1\, \text{M} \Omega$, tested volume=$5.73\times10^{-3}\, \text{m}^3$

\[ \eta(\%) = \frac{W_e}{W_m} \times 100 \]

\[ W_e = \int \frac{V^2}{R} \, dt \]

\[ W_m = \frac{1}{T} \int PV \, dt \]
Electrical measurements

Characterisations
Dielectric measurement

- Permittivity is directly linked with the dipole moment density of the sample:

\[ D = \varepsilon_r \varepsilon_0 E \]

- No variation of the permittivity with the doses.

The density of the dipoles not changes with the range doses investigated.

<table>
<thead>
<tr>
<th>Freq. [kHz]</th>
<th>(\varepsilon_r) PVDF ref</th>
<th>(\varepsilon_r) PVDF irr. 5kGy</th>
<th>(\varepsilon_r) PVDF irr. 10kGy</th>
<th>(\varepsilon_r) PVDF irr. 25kGy</th>
<th>(\varepsilon_r) PVDF irr. 50kGy</th>
<th>(\varepsilon_r) PVDF irr. 50kGy</th>
</tr>
</thead>
</table>

24/04/17
Elastic Modulus

- The polymer is stressed in the elastic regime.

- The polarization generated at applied stress \( T \) is proportional to the piezoelectric coefficient \( d_{33} \):

\[
D = d_{33}T
\]

\[
d_{33} \propto \sqrt{\frac{\varepsilon^{T}_{33}}{Y_{33}^{E}}}
\]

- The young’s modulus is not affected by the irradiation, except for 10 and 50 kGy.

Combined effect of crosslinking and chain scissions lead to increase the young’s modulus at 10 and 50 kGy.
Crystallinity content by DSC

- Shift of the melting peak with irradiation dose increase meaning creation of smaller crystallites.
- The crystalline content reaches the maximum at 10 kGy. At higher irradiation dose (10-20kGy gel dose), competition crosslinkings/chain scissions.

\[ X_c(\%) = \frac{H_f}{H_{0f}} \cdot 100 \]

*\( H_f \) is the heat of fusion for the tested sample.
*\( H_{0f} = 104.7 \text{ J/g (Nakagawa and Ishida, 1973)}, the heat of fusion for the 100\% crystalline sample.*
X-ray diffraction

- Comparison of the area of the crystallites peak fits for different doses.

\[
\beta \text{ Fraction (\%)} = \left( \frac{A_\beta}{A_\beta + A_\alpha} \right) \times 100
\]

- Referring to DSC data the degree of crystallinity of the \( \alpha \) and \( \beta \) phases

<table>
<thead>
<tr>
<th>Dose [kGy]</th>
<th>Degree XX from DSC (%)</th>
<th>% ( \alpha ) phase</th>
<th>% ( \beta ) phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>35,08</td>
<td>10,07952</td>
<td>25,00048</td>
</tr>
<tr>
<td>5</td>
<td>40,75</td>
<td>9,68688</td>
<td>31,06312</td>
</tr>
<tr>
<td>10</td>
<td>42,92</td>
<td>10,56043</td>
<td>32,35957</td>
</tr>
<tr>
<td>25</td>
<td>40,74</td>
<td>11,05309</td>
<td>29,68691</td>
</tr>
<tr>
<td>50</td>
<td>37,25</td>
<td>10,10486</td>
<td>27,14514</td>
</tr>
<tr>
<td>100</td>
<td>35,33</td>
<td>8,99655</td>
<td>26,33345</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>phase</th>
<th>(hkl)</th>
<th>2( \Theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta )</td>
<td>(200)</td>
<td>20.668</td>
</tr>
<tr>
<td></td>
<td>(110)</td>
<td>20.828</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>(110)</td>
<td>20.119</td>
</tr>
</tbody>
</table>
Conclusion

- SHI and e-beam irradiation not affect the electrical efficiency of the PVDF in a range between 0 and 100kGy. The dipoles density is maintained under relative strong doses (100kGy) and the elastic modulus not shows relevant variation in that range doses.

- Chain scissions are responsible to increase the crystallization and in particular between 5 and 10kGy (before the gel dose). XRD technique combined with the DSC shows that the increase of crystallinity correspond to the increase of the $\beta$ phase.

- The increase of the $\beta$ phase not correspond with an increase of the piezoelectric response.

The sensitivity of the instrument is not enough to detect the variation of the piezo-response of the irradiated PVDF.

High electric field needs to polarized the additional $\beta$ phase: Hysteresis loops will be performed.
Exploiting SHI irradiation...

I. PVDF Ions Irradiation

II. Chemical etching

Nanostructuration to enhance piezoresponse

- Exploiting interfacial polarization between filler (nanowire) and matrix (PVDF)

Increase piezoelectric response
Thank you for the attention
Output voltage \textit{versus} pressure

Output voltage under cycling bending stress condition

Output voltage peak vs Pressure

Non-linear response

PVDF generator

Piezoelectric PVDF is considered as capacitor with a $RC$ time constant $\tau$

Local curvature not allowed a complete extension of the membrane.
Output voltage versus pressure

Output voltage under cycling bending stress condition

PVDF generator

Piezoelectric PVDF is considered as a capacitor with an $RC$ time constant $\tau$

Output voltage peak vs Pressure

Linear response

The pressure extends the membrane to the shape of a spherical cap.