POLYMERIC SPACE-CHARGE ELECTRETS

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1. A little bit of history and some introduction: Electrophore or space-charge electret?
2. Charge-storing polymers for electret applications: Typical materials and essential requirements
3. Acoustical and thermal charge-probing techniques: Looking inside without cutting the polymer open
4. The mystery of charge-trapping mechanisms: Chemical trapping, physical trapping or both?
5. Conclusions and outlook

School on Polymers and Composites for Microelectronics and Robotics

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Short History of Electret Science until 1900

- Thales of Miletus (∼640–546 B.C.): Knowledge about the attractive force of magnets and amber
- William Gilbert (1544–1603): Clear distinction between “magnets” and (di-)“electrics”
- Otto von Guericke (1602–1686): Electrification of sulfur and demonstration of electric forces
- Stephen Gray (1666–1736): Discovery of several electret materials and of electrical conduction
- Petrus van Musschenbroek (1692–1761) and Ewald Georg von Kleist (∼1700–1748): Discovery of the “Leiden” or “Kleist” jar (glass capacitor)
- Benjamin Franklin (1706–1790): Theory of the “electrical fire” (including charge conservation)
- Franz Ulrich Theodosius Aepinus (1724–1802): Qualitative theory of electro- and magnetostatics
- Johan Carl Wilcke (1732–1796) and Alessandro Volta (1745–1827): Invention of “electrophorus”
- Charles-Augustin Coulomb (1736–1806): Law of the forces between electric charges on bodies
- Oliver Heaviside (1850–1925): First proposal of the name “electret” (in analogy to “magnet”)

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(Injected) homocharge (left) and (separated) heterocharge (right) in a polymer electret.
Typical space-charge electret polymers (fluoroethylene-propylene copolymer, polyimide, polyethylene terephthalate, cycloolefin copolymer, polypropylene) and some properties

<table>
<thead>
<tr>
<th>Name</th>
<th>Acronym</th>
<th>Density</th>
<th>Melting/Degrad.</th>
<th>Permittivity</th>
<th>Resistivity</th>
<th>Elasticity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon</td>
<td>FEP</td>
<td>2.15 Mg/m$^3$</td>
<td>$\approx 270 ^\circ$C</td>
<td>$2.0 \varepsilon_0$</td>
<td>$&gt; 10^{16} \Omega$ m</td>
<td>480 MPa</td>
</tr>
<tr>
<td>Kapton</td>
<td>PI</td>
<td>1.42 Mg/m$^3$</td>
<td>($&gt;400 ^\circ$C)</td>
<td>$&gt;3.0 \varepsilon_0$</td>
<td>$&gt; 10^{15} \Omega$ m</td>
<td>2.5 GPa</td>
</tr>
<tr>
<td>Mylar</td>
<td>PETP</td>
<td>1.39 Mg/m$^3$</td>
<td>$\approx 255 ^\circ$C</td>
<td>$3.3 \varepsilon_0$</td>
<td>$\approx 10^{16} \Omega$ m</td>
<td>4.8 GPa</td>
</tr>
<tr>
<td>Topas</td>
<td>COC</td>
<td>1.02 Mg/m$^3$</td>
<td>$\approx 260 ^\circ$C</td>
<td>$2.35 \varepsilon_0$</td>
<td>$&gt; 10^{14} \Omega$ m</td>
<td>3.2 GPa</td>
</tr>
<tr>
<td>many</td>
<td>PP</td>
<td>0.91 Mg/m$^3$</td>
<td>$\approx 165 ^\circ$C</td>
<td>$2.2 \varepsilon_0$</td>
<td>$&gt; 10^{16} \Omega$ m</td>
<td>1.8 GPa</td>
</tr>
</tbody>
</table>

Note: Names are usually protected as registered trademarks and vary from manufacturer to manufacturer. Only one typical trade name for each electret polymer is given here.
Chemical formula of polyethylene terephthalate (PETP or PET)
Trade names: Mylar, Hostaphan, Terphane, Melinex, etc.
Teflon Fluoropolymers for Space-Charge Electrets

\[
\begin{bmatrix}
F & F \\
C & C \\
F & F
\end{bmatrix}_n
\]

Polytetrafluoroethylene (Teflon PTFE)

\[
\begin{bmatrix}
F & F \\
C & C \\
F & F
\end{bmatrix}_n + \begin{bmatrix}
F & CF_3 \\
C & C \\
F & F
\end{bmatrix}_m
\]

Tetrafluoroethylene-co-hexafluoropropylene
(Fluoroethylene-propylene, Teflon FEP)

\[
\begin{bmatrix}
F & F \\
C & C \\
F & F
\end{bmatrix}_n + \begin{bmatrix}
C_3F_7 \\
F & O \\
F & F
\end{bmatrix}_m
\]

Tetrafluoroethylene-co-perfluoropropoxyethylene
(Perfluoroalkoxy, Teflon PFA)

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Laser-Induced Pressure Pulses (LIPPs) for probing charge and polarization-gradient profiles in polymer films
1. $e^-$-Beam

2. LIPP

Teflon FEP 25$\mu$m

TIME (ns)

10 keV

20 keV

30 keV

50 keV

CURRENT RESPONSE (mA)

DEPTH ($\mu$m)
Uniform Volume-Charge Distributions

- in Pressure-Pulse Experiments
  \[ I(t) \sim g(x); \text{ e.g. LIPP} \]

- in Pressure-Step Experiments
  \[ I(t) \sim E(x) \sim \int g(x) \, dx; \text{ e.g. PPS} \]
Piezoelectrically Generated Pressure Steps for the Detection of Electric-Field Profiles

\[ I(t) = \frac{Ap}{\rho_0 cs} (\gamma + 1) \int_0^{x=ct} \rho(\xi) d\xi \]

\[ = \frac{Ap}{\rho_0 cs} (\gamma + 1) \varepsilon_0 \varepsilon E(x = ct) \]
Pressure Step about to enter the sample

Pressure Step just inside the sample

Pressure Step passing the charge layer

Pressure Step leaving the sample

(Thickness change exaggerated)

Oscilloscope image
Pressure Step about to enter the sample

Pressure Step just inside the sample

Pressure Step at the center of the sample

Pressure Step leaving the sample

(Thickness change exaggerated) Oscilloscope image
Electric-displacement profile in negatively corona-charged Teflon FEP
($V_c=-15$ kV, $T_c=20^\circ$C, $t_c=60$ min, maximum charge density $\approx 1600$ C/m$^3$)
Electric-displacement profile in positively corona-charged Teflon PFA ($V_c = -15$ kV, $T_c = 200$°C, $t_c = 60$ min, maximum charge density $\approx 500$ C/m$^3$)
Electric-displacement profile in negatively corona-charged Teflon PFA ($V_c=-15$ kV, $T_c=20^\circ$C, $t_c=60$ min, maximum charge density $\approx 2000$ C/m$^2$)
Electric-displacement profile in negatively corona-charged Teflon FEP ($V_c = -15 \text{ kV}$, $T_c = 200^\circ\text{C}$, $t_c = 60 \text{ min}$, maximum charge density $\approx 500 \text{ C/m}^3$)
Side view (a) and cross section (b) of special PEA equipment for *in-situ* measurements on HV cables (after Hozumi *et alii* 1994)

(a)

(b)
"Pulsed electroacoustic" (PEA) method for the measurement of charge distributions in dielectrics
(after Takada and Li 1992)

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Development of the space-charge distributions in a high-voltage cable during application of ±70kV

(after Hozumi et alii 1994)
Development of the space-charge distributions in a high-voltage cable during application of $\pm 350kV$

(after Hozumi et alii 1994)
The 6 most relevant schemes for non-destructive probing of space charge in electret films

<table>
<thead>
<tr>
<th>Probing technique</th>
<th>Mechanism of operation</th>
<th>Excitation mechanisms</th>
<th>Detection of signal</th>
<th>Spatial resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal pulse</td>
<td>Time-dependent non-uniform expansion</td>
<td>Light flash or pulsed laser</td>
<td>Voltage with oscilloscope</td>
<td>depends on depth</td>
</tr>
<tr>
<td>Thermal step</td>
<td>Time-dependent non-uniform expansion</td>
<td>Heat reservoirs or continous laser</td>
<td>Voltage with oscilloscope</td>
<td>depends on depth</td>
</tr>
<tr>
<td>Thermal wave</td>
<td>Frequency-dependent periodic expansion</td>
<td>Chopped light or modulated laser</td>
<td>Current/voltage with lock-in amp.</td>
<td>depends on freq.</td>
</tr>
<tr>
<td>Acoustic pulse</td>
<td>Propagation of thin compression zone</td>
<td>Piezo-transducer or pulsed laser</td>
<td>Current via 50Ω with oscilloscope</td>
<td>≥1μm</td>
</tr>
<tr>
<td>Acoustic step</td>
<td>Propagation of steep compression front</td>
<td>Cable discharge + piezo-transducer</td>
<td>Current via 50Ω with oscilloscope</td>
<td>≥1μm</td>
</tr>
<tr>
<td>Acoustic wave</td>
<td>Propagation of field-induced acoustic wave</td>
<td>Electric pulse on electrodes</td>
<td>Piezo-transducer + oscilloscope</td>
<td>depends on pulse</td>
</tr>
</tbody>
</table>

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Response Equations for the Probing of Charge and Polarization Profiles in Thin Dielectrics by Non-Uniform Temperature or Stress Excitation

Total current density inside the sample:

\[ i(t) = \rho_r(x, t)v(x, t) + \frac{\partial D(x, t)}{\partial t} \quad \text{with} \quad D(x, t) = \varepsilon_0\varepsilon(x, t)E(x, t) + P(x, t) \]

General response equation \((T \equiv \text{temperature or stress})\):

\[ I(t) = \frac{A}{s} \int_0^s \left[ \frac{1}{\varepsilon \frac{dT}{dx}} \left( \frac{d\varepsilon}{dx} - \frac{1}{dx} \right) \varepsilon_0\varepsilon E(x) + \frac{dP(x)}{dT} \right] \frac{\partial T(x, t)}{\partial t} dx \]

Response equation for thermal excitation (e.g. heat pulse):

\[ I(t) = \frac{A}{s} \int_0^s \left[ (\alpha - \varepsilon_0\varepsilon \alpha_x) \varepsilon_0\varepsilon E(x) + \lambda(x) \right] \frac{\partial T(x, t)}{\partial t} dx \]

Response equation for mechanical excitation (e.g. pressure pulse):

\[ I(t) = \frac{A}{s} \int_0^s \left[ -(\gamma + 1)\varepsilon_0\varepsilon E(x) + \varepsilon_{33}(x) \right] \chi \frac{\partial p(x, t)}{\partial t} dx \]
Response Equations for Specific Experimental Probing Techniques

Laser-Intensity Modulation Method (LIMM) (Lang and Das-Gupta 1981)

\[
I(t) = \frac{A}{s} \int_{0}^{s} \left[ (\alpha_\epsilon - \alpha_\tau) \int_{0}^{x} \rho_r(\xi)d\xi + (\alpha_\rho + \alpha_\tau - \alpha_\epsilon)P(x) \right] \frac{\partial T(x,t)}{\partial t} dx
\]

Thermal Pulser Technique (Collins 1975)

\[
\Delta V(t) = \int_{0}^{s} \left[ \frac{\alpha_\tau}{\varepsilon_0 \varepsilon} \int_{0}^{x} \rho_r(\xi)d\xi + \frac{\alpha_\rho + \alpha_\tau - \alpha_\epsilon}{\varepsilon_0 \varepsilon} P(x) \right] \Delta T(x,t) dx
\]

Laser-Induced Pressure-Pulse (LIPP) Technique
(Sessler, West and Gerhard-Multhaupt 1981)

\[
I(t) = \frac{A p r}{\rho_0 s} \left[ (\gamma + 1) \varepsilon_0 \varepsilon \rho(x) - \frac{d \varepsilon_3(x)}{dx} \right]_{x=ct}
\]

Piezoelectrically Generated Pressure-Step (PPS) Method
(Eisenmenger and Haardt 1982)

\[
I(t) = \frac{A p}{\rho_0 c s} \left[ (\gamma + 1) \int_{0}^{x} \rho(\xi)d\xi - e_3(x) \right]_{x=ct}
\]
Conclusions and outlook

- Space charge (i.e. extra charge) provides external electric field for applications
- Good charge retention related to excellent insulation properties and high thermal stability
- A few special polymers (plus some inorganic materials) highly suitable for electrets

- Non-destructive space-charge probing with acoustic-wave (pressure) propagation or thermal-wave (heat) diffusion possible
- Space-charge stability possibly a combination of deep (chemical) trapping on macromolecule and restricted (physical) mobility of macromolecules