Composites piézoélectriques et diélectriques à base de polymères fluorés

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Created: 1990

Director: Prof. J.-A. Månson

Direction: P.-E. Bourban, Y. Leterrier, V. Michaud, C. Plummer

Staff: 20 members (postdocs, PhDS, engineers)
LTC creates the scientific base for the next generation of materials and processes in the fast-growing fields of polymers and composites:

- incorporating unique additional functionality
- developing new routes to cost-effective materials and manufacturing
- scaling up to an industrial context (aerospace, automotive, building, medical, electronics, sports…)

Research domains

- Advanced Thermoset Composite Processing
- Thermoplastic Composite Manufacturing
- **Smart Composites**
- Nanostructured materials
- Biocomposites
- Multilayer films
- Cost and implementation strategies

Main industrial sponsors

- DaimlerChrysler, Ford, VW, Renault, USCAR
- Johnson Controls, Vetrotex, ABB, Bekaert, KB
- DuPont, Dow, EMS Chemie, Firmenich, Konarka, Solvay
- Essilor, Tetra Pak, Ailinghi, Solar Impulse, Swatch Group
Outline

• Why dielectric and piezoelectric polymer composites

• Process – structure – property analyses
  • Solvent based and melt processing
  • Morphology and crystallinity
  • Thermomechanical properties
  • Barrier properties
  • Dielectric and piezoelectric properties

• Application case
  • Self-sensing high pressure H₂ storage vessel

• Conclusions and outlook
Why dielectric and piezoelectric composites
Dielectric and piezoelectric composites: applications

Underwater applications

Sonar (40 kHz - 10 MHz)

Hydrophone (<40 kHz)

Energy harvesting and vibration control

AIST (www.aist.go.jp)

Materials Systems Inc. (www.matsysinc.com)

APC International, Ltd. (www.americanpiezo.com)

Vermon SA (http://www.vermon.com)

Imran Patel (2011) www.intechopen.com

Biomedical imaging and Non Destructive Testing (NDT)

…and more…
Dielectric and piezoelectricity

**Dielectric material**

Relative permittivity $\varepsilon_r(f)$

Dielectric loss tangent $\tan\delta(f)$

Breakdown strength $E_{\text{max}}$

**Piezoelectric material**

Before poling

After poling

Poled piezoelectric material

Coercive field $E_c$ ($E_p > E_c$)

Piezoelectric coefficient $d_{33} \left[ \frac{pC}{N} \right] = \frac{Q[pC]}{F[N]}$
**Why dielectric and piezoelectric composites**

**Perovskite ceramics**
- Relative permittivity >1000 ✔
- Breakdown strength < 100 kV/mm ✗
- Piezoelectric coefficient >100 pC/N
- Difficult processing and shaping
- Brittleness and high stiffness
- High density

**Energy harvesters:**
- High piezoelectric coefficient
- Compliance

**Transducers:**
- High piezoelectric coefficient
- Low dielectric losses
- Compliance

**(Fluoro)polymers**
- Relative permittivity ~10 ✗
- Breakdown strength > 1000 kV/cm ✔
- Dielectric loss tang. < 0.01
- Piezoelectric coefficient ~-30 pC/N
- High coercive field 500 kV/cm
- Ease of processing
- Flexibility and compliance
- Low density

D. Tan and P. Irwin (2011)
Why dielectric and piezoelectric composites

High energy density capacitors:
- High breakdown strength
- High relative permittivity

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D. Tan and P. Irwin (2011)
Types of composites

Commercial applications are mainly based on **2-2 and 1-3 composites**

- Fabrication and shaping may be complex (e.g. dice & fill)

**0-3 composites** allow a cost effective polymer-like processing and shaping

R.E. Newnham (1978)
The challenge of 0-3 composites

Fabrication of fluoropolymer based composites with high inorganic particles volume fractions and/or high aspect ratios:

- great **surface energy difference** between matrix and filler
- **complex morphology** due to coexistence of several phases

P(VDF-TrFe)/BaTiO$_3$ composite ($\Phi=0.6$)
Fluoropolymer composites: process – structure – property analyses
PVDF based polymers

\[
\begin{align*}
\text{PVDF} & \quad - \quad \left[ \begin{array}{ccc}
H & F \\
\text{C} & \text{C} \\
H & F \\
\end{array} \right]_n \\
\text{P(VDF-TrFE)} & \quad - \quad \left[ \begin{array}{ccc}
H & F \\
\text{C} & \text{C} \\
H & F \\
\end{array} \right]_n \left[ \begin{array}{ccc}
F & H \\
\text{C} & \text{C} \\
F & F \\
\end{array} \right]_m
\end{align*}
\]

Relative permittivity \( \varepsilon_r = 10 \)

\[ d_{33} = -30 \text{ pC/N} \]

\[ E_c = 500 \text{ kV/cm} \]

\[ T_C = 126 ^\circ \text{C} \]

\[ T > T_C \beta \rightarrow \alpha \]

Paraelectric

Piezoelectric
Functional (nano)particles

**Barium Titanate (BT)**
Spherical particles, d = 200 nm
Lead-free perovskite

![Diagram of Barium Titanate](image)

- A = Ba
- B = Ti

Relative permittivity $\varepsilon_r = 2000$

- $d_{33} = 100 - 350$ pC/N
- $T_C = 120 \, ^\circ C$

1Takahashi H et al. (2008)

**Layered silicates (clay)**
Cloisite 15A (organically modified montmorillonite)

![Diagram of Layered Silicates](image)

Cation: 2M2HT

Gas barrier enhancement:

- Conventional composites
- “Tortuous path” in layered silicate nanocomposites

In a recent study, Zhu et al. [98] reported the fire retardant properties of PS/MMT nanocomposites, which were prepared using three different types of new organically modified MMT (see Fig. 25). They initially used phosphonium salt for the modification of clay, and then examined the differences between organo ammonium and phosphonium salt treatments of clay fillers in nanocomposites towards thermal stability. The peak HRR for PS and the three nanocomposites is also shown graphically in Fig. 96.

As mentioned above, the suggested mechanism by which clay nanocomposites function involves the formation of a char that serves as a barrier to both mass and energy transport [17]. As the fraction of clay increases, the amount of char that can be formed increases, and the rate at which heat is released decreases. One of these nanocomposites, OH-16, is mostly intercalated. This yields a slight reduction in the rate of heat release compared with the other two systems, which contain a significant exfoliated fraction. This observation again supports the suggestion that an intercalated material is more effective than an exfoliated material in fire retardance [433].

In contrast, the decrease in the rate of heat release corresponds to (1) a decrease in mass loss rate and the amount of energy released by the time PS has ceased burning, and (2) a modest increase in the time at which the peak heat release is reached. The production of a char barrier must serve to retain some of the PS, and thus both the energy released and the mass loss rate decrease. The amount of smoke evolved and specific extinction area also decrease with the formation of the nanocomposites. There is some variability in the smoke production. Although it is observed that the formation of the nanocomposites reduces smoke production, the presence of additional clay does not continue this smoke reduction.

**4.5. Gas barrier properties**

Clays are believed to increase the barrier properties by creating a maze or ‘tortuous path’ (see Fig. 97) that retards the progress of the gas molecules through the matrix resin. The direct benefit of the formation of such a path is clearly observed in polyimide/clay nanocomposites by dramatically improved barrier properties, with a simultaneous decrease in the thermal expansion coefficient [11,255,257]. The polyimide/layered silicate nanocomposites with a small fraction of OMLS exhibited reduction in the permeability of small gases, e.g. $O_2$, $H_2O$, He, $CO_2$, and ethylacetate vapors [11]. For example, at 2 wt% clay loading, the permeability coefficient of water vapor was decreased ten-fold with synthetic mica relative to pristine polyimide. By comparing nanocomposites made with layered silicates of various aspect ratios, the permeability was seen to decrease with increasing aspect ratio.

Oxygen gas permeability has been measured for near to exfoliated PLA/synthetic mica nanocomposites prepared by Sinha Ray et al. [383]. The relative permeability coefficient value, i.e. $P_{PLACN}=P_{PLA}$ where $P_{PLACN}$ and $P_{PLA}$ are the nanocomposite and pure PLA permeability coefficient, respectively, is plotted as a function of the wt% of OMLS in Fig. 98. The data are analyzed with the Nielsen theoretical expression [436], allowing prediction of...
**Process**

**Solvent based**

- Dispersing and homogenizing in solution
- Casting, drying and annealing

**Melt process**

- Compounding in twin screw extruder
- Injection or compression molding

DSM microextruder
**P(VDF-TrFE)/BaTiO$_3$ composites ($\phi_p = 60\%$): morphology**

Scanning electron microscopy of freeze fractured surfaces
Porosity $\phi_v$ estimated gravimetrically

- **P(VDF-TrFE)+BT** $\phi_v = 25\%$
- **P(VDF-TrFE)+BT-A** $\phi_v = 16\%$
- **P(VDF-TrFE)+BT** $\phi_v = 15\%$
- **P(VDF-TrFE)+BT-A** $\phi_v = 11\%$
- **P(VDF-TrFE)+BT-TF** $\phi_v = 9\%$

**Silane coupling agents:**
- Aminosilane
- Fluorosilane

**Process optimization**

**Interface modification**
**Differential Scanning Calorimetry**

Melting enthalpy of P(VDF-TrFE)/BaTiO$_3$ composites

- Theor
- Untreated
- APTES
- TFPTMS

$\Delta H_f$ scales with BaTiO$_3$ wt%: the degree of crystallinity of the polymer does not change with addition of BaTiO$_3$.

**Dynamic mechanical analysis**

Hydrogen bonding between the aminosilane and P(VDF-TrFE) enhances thermomechanical stability.
Dielectric and piezoelectric properties

Relative permittivity and loss factor of P(VDF-TrFE)/BaTiO$_3$ composites

- Untreated
- APTES
- TFPTMS
- Bruggeman$^3$
- Jayasundere$^4$

$\varepsilon_r$ vs $\phi$ [vol%]

$\tan\delta$ vs $f$ [Hz]

$d_{33}$ of composites poled with $E_p = 100$ kV/cm

Composite with gold electrodes

6 mm
Piezoelectric composites with 60 vol% well dispersed submicron sized ceramic particles:

- Storage modulus: 7x increase with respect to P(VDF-TrFE)
- Relative permittivity: 8x increase with respect to P(VDF-TrFE)
- Piezoelectric coefficient: 5x increase with respect to P(VDF-TrFE) with poling field of 100 kV/cm
- Particle surface modification increased thermomechanical stability and decreased dielectric loss factor at low frequency

Research is ongoing to further increase dielectric and piezoelectric properties for practical applications
Morphology of P(VDF-TrFE)/clay composites

Images of P(VDF-TrFE)/clay films

0.5 vol% clay: exfoliation

0 vol% Clay
0.5 vol% Clay
1.0 vol% Clay
4.0 vol% Clay

Non exfoliated clay
Exfoliated clay

4 vol% clay non-exfoliation
The degree of crystallinity has a maximum for $\phi_{\text{clay}} = 0.5$.
Annealing increases $\beta$ phase.
Gas barrier and piezoelectric properties can be enhanced optimizing annealing time and clay concentration.
Self-sensing high pressure $\text{H}_2$ storage vessel
Self-sensing high pressure H$_2$ storage vessel

4 kg H$_2$ needed to drive a fuel cell car 400 km (45 m$^3$ at ambient $\rightarrow$ 0.11 m$^3$ at 400 bar)

Commercial H$_2$ storage vessels (thick polymer liner + metal + carbon fiber composites) are expensive and present a risk of H$_2$ embrittlement

- High barrier properties
  $\rightarrow$ Low permeability material
- Health monitoring and sensing (safety)
  $\rightarrow$ “smart structure”
- High pressure to reduce volume
  $\rightarrow$ High strength without embrittlement

Nanocomposite of PVDF-TrFE (polyvinylidene fluoride trifluoroethylene copolymer) with surface modified clay platelet particles + High strength carbon fiber reinforced composite
Collaboration EPFL-CSEM on process-structure-property relations in piezoelectric polymer materials

- The Greenpower project combines for the first time a self-sensing liner with a cost-effective composite production process
- Proportion of piezoelectric $\beta$-phase in modified P(VDF-TrFE): 95%
- 30% increase in piezoelectric coefficient
- 10x reduction of gas permeation

In-situ XRD analysis of P(VDF-TrFE)

Oxygen permeability of modified P(VDF-TrFE)

Oliveira F, et al. (2014)
Self-sensing high pressure H₂ storage vessel

- Silver electrode
- Composite shell
- PA12 Liner
- piezo sensor

1 liter, 100 bars demonstrator
Conclusions and outlook

• Fluoropolymer based 0-3 composites offer a unique combination of properties and design flexibility for sensing and actuating applications
• Their structure and properties are highly dependent on processing conditions

Practical applications have now become possible…
…and research is still ongoing to improve their properties and scale up processes
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References