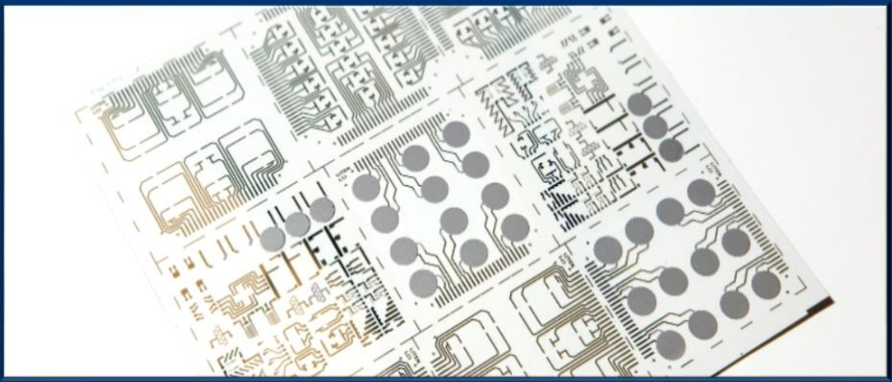
TDS PIEZOTECH® FC

For Printed Organic Electronics,
Smart Textiles and Plastronics



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I. Introduction

Piezotech® FC is a range of P(VDF-TrFE) printable electroactive polymers. After processing (deposition, annealing, poling etc…), they exhibit **pyroelectric**, **piezoelectric**, and **ferroelectric** properties. Typical applications are:

- printed sensors (Pressure, temperature, Ultrasound, Infra-red),
- printed keyboards,
- printed speakers,
- printed memories,
- printed actuators …

For many purposes, these polymers are used under thin film forms, obtained *via* printing processes with coated electrodes.

Piezotech® FC polymers are ferroelectric polymers. Figure 1 shows the typical hysteresis loop of polarization *vs* applied electric field of a Ferroelectric Copolymer (FC). Piezotech® FC copolymers exhibit a remnant polarization (P_r) when no electric field is applied. This remnant polarization can be reversed by an electric field above the coercive field ($|E| > E_c$).

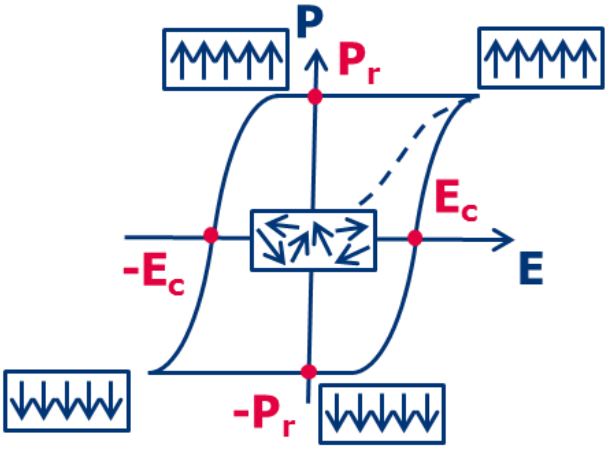


Figure 1. Typical Piezotech® FC hysteresis curve.

Piezotech® FC copolymers undergo a ferroelectric to paraelectric transition at the Curie temperature (T_{Curie}). This temperature varies with copolymer composition (see Figure 2) and governs the thermal stability of the piezoelectric properties. After poling, the copolymers exhibit piezoelectric, pyroelectric, and ferroelectric properties. Typical properties for the Piezotech® FC range are given in Annex 1.

Figure 2. P(VDF-TrFE) phase diagram

II. Processing

II.1 Ink Formulation

Piezotech® FC copolymers are soluble in different solvents given in Annex 2. The concentration of the polymer in the solvent has to be adjusted in order to get the appropriate viscosity corresponding to the printing process used. The actual ink formulation can be obtained by progressively adding the polymer into the solvent under heating. In order to get homogeneous films with high electrical breakdown a filtering step of the solution is required (ideally 1 µm or less). This will remove impurities and prevent the formation of gel particles. Standard commercial filtering processes using filtering cartridges or filtering syringes are commonly used.

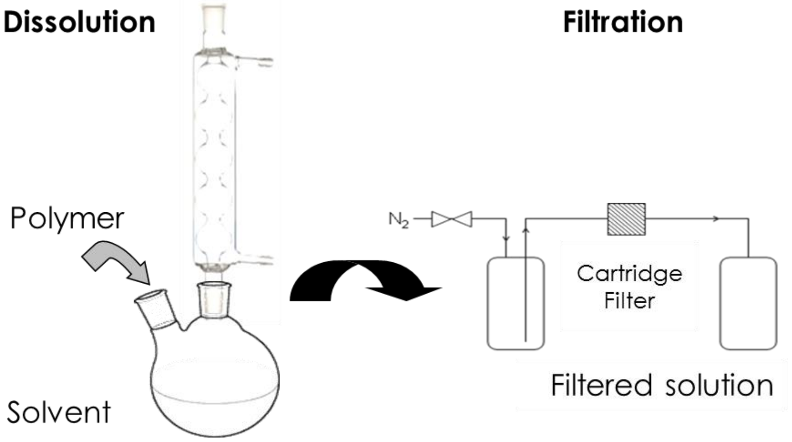


Figure 3. Ink formulation processing

II.2 Processing Steps: printing and post-treatments

The ink formulation (polymer solution) can be coated *via* different printing processes (solvent cast, screen printing, spin-coating, ink-jet, gravure …) on a given substrate (PET, PEN, PC, glass…) under a clean atmosphere, until an homogeneous and dry film is formed.

In order to avoid bubbles in the film, it is important not to use syringes during the printing process.

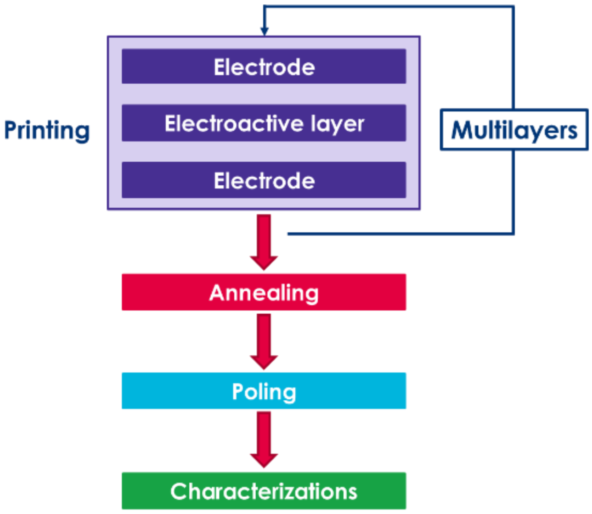


Figure 4. Processing steps from the ink

II.2.1 Solvent Evaporation

In order to get rid of any residual solvent and enhance film properties, a solvent evaporation step under atmospheric pressure or under vacuum can be carried out below the solvent boiling-point temperature.

II.2.2 Annealing

Annealing is a critical step to obtain the films with the best properties. It will control crystallization of the material and enhance electrical as well as mechanical properties. For this purpose, films may need to be annealed at a temperature between the Curie temperature and the onset of crystallization during a few minutes (typically 5-15 minutes at 135-140 °C). A rapid annealing may be obtained on thin films using infrared or flash annealing.

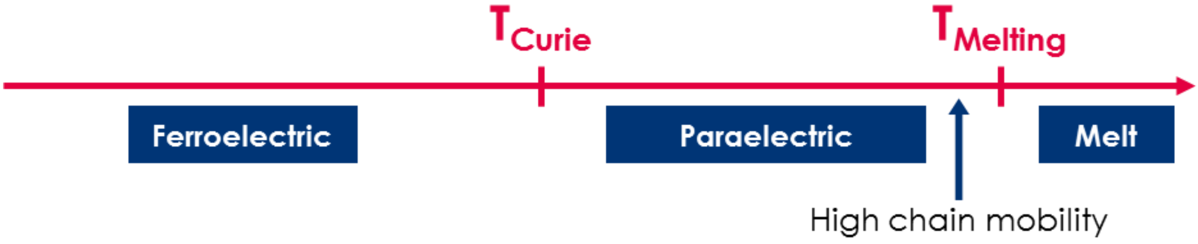


Figure 5. Thermal transitions.

II.2.3 Poling

In order to activate the piezoelectric properties of a copolymer film, a poling step is necessary to align the C-F dipoles. Using an increasing low-frequency voltage, an electric field above the coercive field value (*i.e.* 50 V/µm) has to be applied. Depending on the film thickness, its surface, and the response precision needed, different methods can be used.

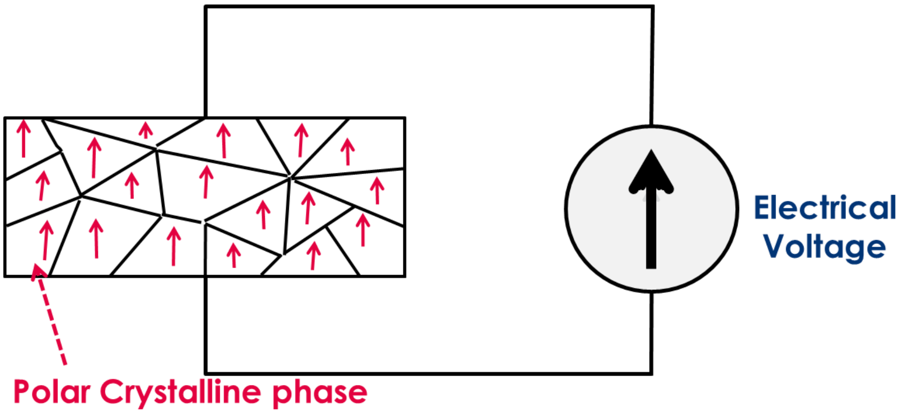


Figure 6. Activation of the piezoelectric properties by poling and the orientation of dipoles in the crystals.

The application of the electric field and the hysteresis curve characterization can be performed using one of the following:

- A direct application of the electric field through the electrodes with a voltage generator (in this case there is no measurement of the induced electrical polarization (charge displacement))
- A Sawyer-Tower circuit (electrical charges measurement, hysteresis curve)
- A ferroelectric tester (*i.e.*, *Precision MultiFerroelectric Radiant Technology*) with an external amplifier if a high electric field is needed (depending on the film thickness)

For example: the electric field can be applied according to the following parameters:

- Number of cycles to reach E_{max}: 15
- Frequency: 0.05 Hz (higher is possible)
- Signal: sinusoidal
- $E_{max} > 2*E_c$
- Typically E_{max} = 100 V/µm

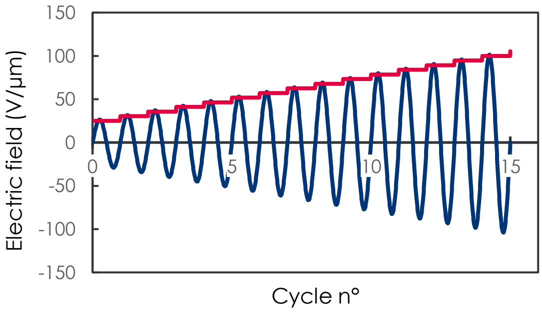


Figure 7. Typical poling process used for Piezotech® FC.

Many poling process can be possible with different voltage increase profiles.
For printed devices (mainly thin layers), the poling electric field can be applied directly through the film electrodes by using a direct probes contact system (Figure 8). For non-printed films (thick layers), poling can be done through contacting and pressing the film between two electrodes (Figure 9). For large surfaces, a non-contact Corona poling can be used because deposition of the top electrode.

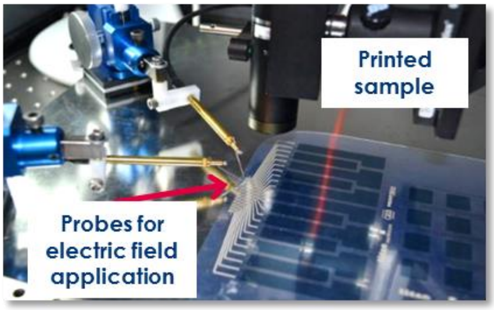


Figure 8. Direct probes poling process.

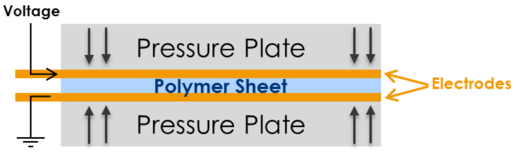


Figure 9. Contact poling process.

II.2.4 Clean-up

The product can be cleaned up with ketones solvents (MEK (methyl ethyl ketone), Cyclopentanone …)

III. Driving & Measurements

III.1 Deformation under an electric field

The deformation caused by the applied electric field can be defined by the simple formula:

$$S_i = d_{3i}E \qquad \text{I = 1;2;3}$$

Where

- $S_i = \Delta x_i / x_i = \Delta L / L$ represents the strain (relative deformation) of the sample in the x_i direction
- d_{3i} is the piezoelectric strain constant (in a perpendicular direction with respect to that of the applied electric field)

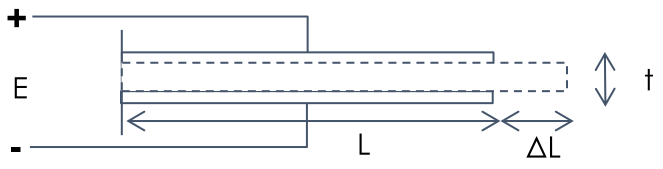
Example of an element with the following characteristics:

Length: l = 1 cm
Width: w = 2 mm
Thickness: t = 9 µm
Applied voltage: V = 200 V → E (electric field) = V/t
(d_{31}, d_{32}, d_{33}) = (11, 10, -30) pC/N

The piezo strain constant d is given by:

$$d = \frac{strain\ developed}{applied\ field} = \frac{S}{E}$$

$$\Delta L = d_{31} * \frac{V}{t} * L = 11.10^{-12}\frac{200}{9.10^{-9}}1.10^{-2} = 2.44\ \mu m$$



III.2 Sensors: Orders of Magnitude, Voltage Generation

The electric field output (E) caused by an applied force can be defined by:

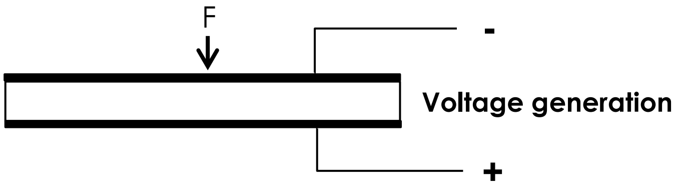
$$E = g_{ij}\sigma_i$$

Where:

- σ_i is the applied mechanical stress (N/m²)
- g_{ij} is the piezoelectric voltage constant (Vm/Nm²)

$$g = \frac{electrical\,field\,developed}{applied\,mechanical\,stress} = \frac{E}{\sigma}$$

$$g = \frac{d}{\varepsilon} = \frac{d}{\varepsilon_0 \varepsilon_r}$$



Example of an element with the following characteristics:

Length: l = 2 cm
Width: w =2 cm
Thickness: t = 100 µm
Compression 0.1 Bar → $\sigma = -10000\ \mathrm{N.m^{-2}}$
$(g_{31}, g_{32}, g_{33}) = (216, 19, -339) * 10^{-3}$ - Vm/Nm²

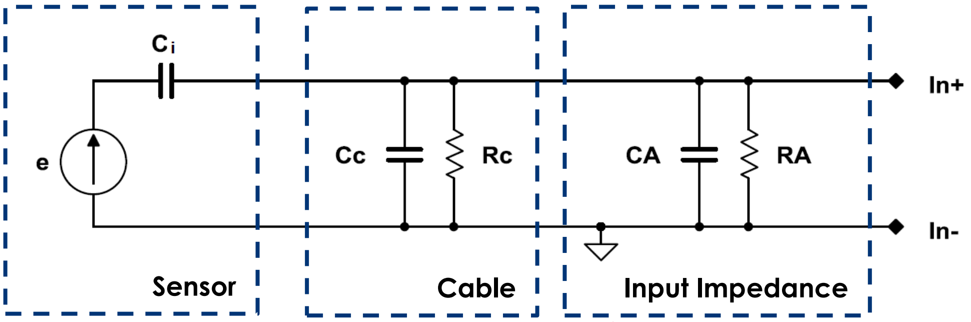
$$E = \frac{V_0}{t} = g_{33}\sigma_3$$

$$V_0 = g_{33}\sigma_3 t = 339mV$$

III.3 Signal Measurement

The piezo sensor is stimulated with a given mechanical stress and frequency (f) which generates charges (q). The voltage read (v_t) can likewise be proportional to the stress. The limit between the proportional and derivative modes is delimited by the cut-off frequency (f_c). By directly connecting a sensor to a DAC (Data Acquisition Card), Oscilloscope, the measurements are dependent of external impedances (sensor capacity, cable losses, oscilloscope probe…) but their influence can be minimized by using a charge amplifier.

Direct connection



Impedance combination:

$$C_{eq} = C_C + C_A$$

$$R_{eq} = R_C // R_A$$

$$f_C = \frac{1}{2\pi \cdot R_{eq} \cdot (C_{eq} + C_i)}$$

Derivative mode

$$f \ll f_C$$

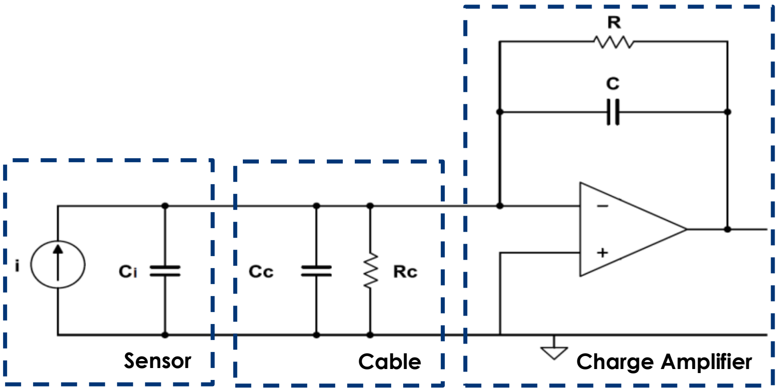
$$v_{(t)} = R_{eq} \cdot \frac{dq_{(t)}}{dt}$$

Proportional mode

$$f \gg f_C$$

$$v_{(t)} = -\frac{q_{(t)}}{C_{eq} + C_i}$$

Use of a Charge amplifier:



$$f_C = \frac{1}{2\pi RC}$$

Derivative mode

$$f \ll f_C$$

$$v_{(t)} = -R \cdot \frac{dq_{(t)}}{dt}$$

Proportional mode

$$f \gg f_C$$

$$v_{(t)} = -\frac{q_{(t)}}{C}$$

Annex 1. Piezotech® Polymer Range

		Piezoelectric				Electrostrictive and High-k	
Product name	**Method**	**Piezotech® FC**				**Piezotech® RT**	
Polymer base		**P(VDF-TrFE) Copolymer**				**P(VDF-TrFE-CTFE/CFE) Terpolymer**	
Grade		**FC 20**	**FC 25**	**FC 30**	**FC 45**	**RT-TS**	**RT-FS**
		Composition (mol%)					
		% TrFE				% CTFE	% CFE
	^{1}H & ^{19}F NMR	20	25	30	45	Standard Composition	
		Indicative Thermal Properties					
Melting Point (°C)	Second heating by DSC ASTM D3418	150	150	151	158	122	127
Curie Transition (°C)		136	115	100	60	-	-
		Indicative Molar Mass					
Mw (kg.mol^{-1})	SEC in DMSO PMMA eq	450				500	
MFI	ASTM D1238 230°C under 10 kg	1-6					
		Indicative Dielectric Properties					
ε_r	Capacity measurement at 1 kHz	9 - 12		10 - 14		40	55
Saturation Polarization (mC.m^{-2})	At 150 V.µm^{-1}	-	-	-	-	55	60
Remnant Polarization (mC.m^{-2})		80	70	65	45	-	-
Coercive Field (V.µm^{-1})		45	50	50	55	-	-
		Indicative Piezoelectric / Pyroelectric Properties					
d_{33} (pC.N^{-1})	Piezotest PM300 1 N, 110 Hz	-24 to -30		-18 to -22		-	-
Typical P3 (µC/m^2/K)	Literature	-30		-50		-	-
		Indicative Mechanical Properties					
Storage Modulus E' (GPa)	ASTM D638	0.8 – 2.8				0.2 - 0.4	
		Indicative Optical Properties					
Transmittance (%)	ASTM D1003	>96%				>99%	

Specific product composition or MFI are available on demand. Do not hesitate to ask us.

Typical properties are only given as indicative values, not specifications.
Electroactive performances strongly depend on processing and operating conditions.

Annex 2. Possible Solvents for Piezotech® Polymers

Indicative list of solvents that can be used to dissolve & formulate Piezotech FC® and Piezotech® RT polymers.

	Boiling Point (°C)	Flash Point (°C)
Acetone	56	-18
Tetrahydrofuran	65	-17
Methyl EThyl Ketone	80	-6
Methyl Isobutyl Ketone	118	23
Glycol Ethers	118	40
Glycol Ether Esters	120	30
N-Butyl Acetate	135	24
Dimethyl formamide	153	67
Cyclohexanone	157	54
Dimethyl acetamide	166	70
Diaceton Alcool	167	61
Diisobutyl Ketone	169	49
Tetramethyl urea	177	65
Ethyl Aceto Acetate	180	84
Dimethyl Sulfoxide	189	35
Trimethyl phosphate	195	107
N-Methyl-2-Pyrrolidone	202	95
Butyrolactone	204	98
Isophorone	215	96
Triethyl phosphate	215	116
Carbitol Acetate	217	110
Propylene Carbonate	242	132
Glyceryl triacetate	258	146
Dimethyl Phtalate	258	149

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