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Enhancement of pyroelectricity in gravure printed PVDF-TrFE films through corona poling: preliminary results

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Introduction

Pyroelectric energy harvesting is one of the more recent and promising approaches to directly convert temperature fluctuations into electric energy. As recently explored [1], the physical characteristics of pyroelectric devices make them compatible with conventional industrial thin-film-based printing technologies, offering several possible advantages such as low-cost, low-temperature processing, high-throughput, the use of flexible substrates and pattering/shaping at the same time as deposition. Such benefits make printing technologies very attractive for ever-increasing device flexibility and customization demand. Nevertheless, solution-based printing techniques miss fine control of film-forming microstructure, necessary to achieve a significant level of electric polarization. Therefore, to enable the use of printing for the fabrication of performing pyroelectric devices, a poling process must be applied to printed films for orienting its electric dipoles in a preferential direction.

Work purpose

Here, the corona treatment, already widely used in industry for improving the printing substrate wettability, is proposed as a poling method particularly suitable for printing processes, since it is fast, contact-less and does not require the deposition of metal electrodes. In this work, the first promising results obtained by post-treating Polyvinylidene fluoride–trifluoroethylene (PVDF-TrFE) gravure printed films are presented. Among the printing techniques, gravure is considered the most attractive since its ability to couple high quality, high throughput and because it is widely utilized in industry [2].

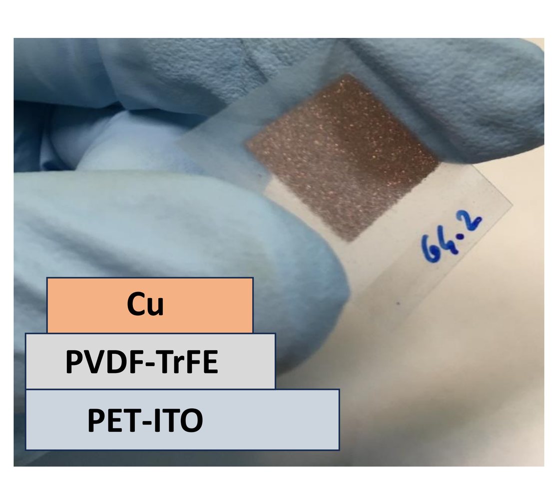
Pyroelectric device manufacturing

PVDF-TrFE *DMSO/Acetone* *Ink*

Gravure printing

PVDF-TrFE film

Corona poling



Pyroelectric device

Ink formulation

The first step was to develop a PVDF-TrFE-based gravure printable fluid (ink). To be properly deposited by gravure ink must have a viscosity < 100 mPa*s and a surface tension < 42 mN/m.
Inks suitable for gravure printing were prepared by dissolving PVDF-TrFE 80/20 mol% powder in a 50/50% w/w% of dimethyl sulfoxide (DMSO)/Acetone mixture at 60°C for 1h.

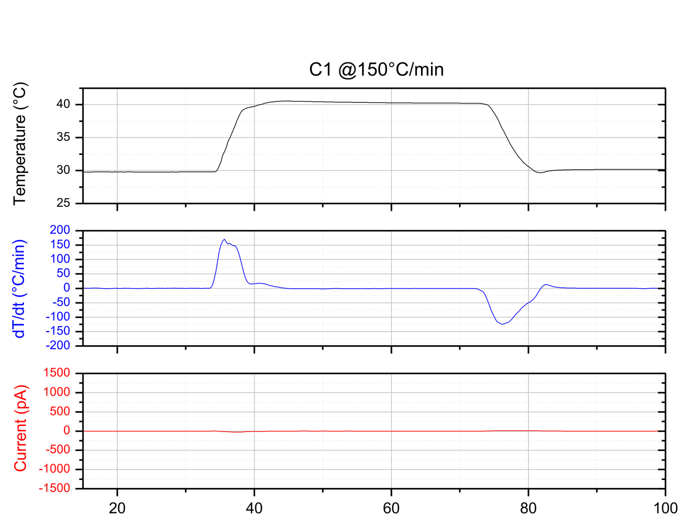
Gravure printing

Inks were gravure printed onto ITO (Indium Tin Oxide) coated PET (Polyethylene terephthalate) film, representing the lower contact of the devices.
To achieve the best macroscopic printing quality, ink and process parameters were adjusted to have $Ca = U\eta/\gamma < 1$ (where U is the printing speed, η and γ are the viscosity and the surface tension of the ink).
To avoid possible micro-short circuits occurring in the device due to pinholes in the printed film, multilayer printing was performed.
Inks were superimposed with decreasing PVDF-TrFE concentration (from 12 to 8 wt%) as the number of layers increased, stacking up to 5 layers at the same printing conditions (printing force of to 500 N and speed of 12 m/min).

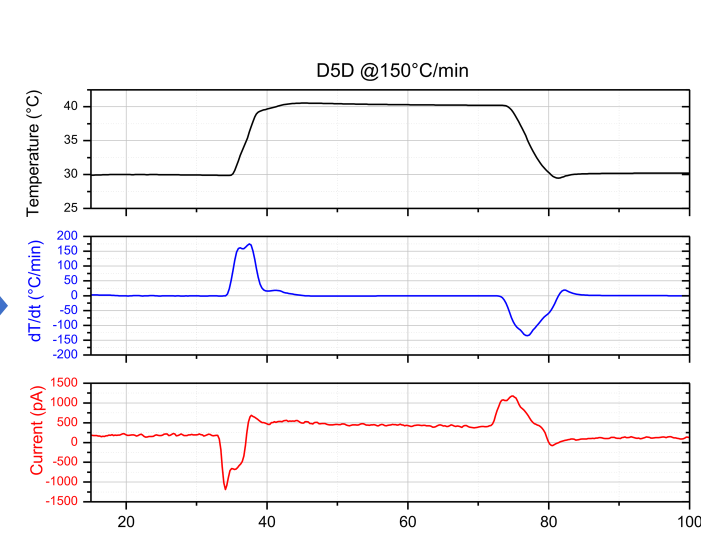
Corona poling

Printed samples were first thermal annealed at 120°C for 1h to increase the degree of crystallinity of the film.
The annealed printed films were corona poled as the voltage increases (up to 8kV) at a fixed treatment time of 1 min and 30°C.
Capacitive device samples were finally prepared by spraying a Cu-based varnish for making the upper contact on the printed films.

Pyroelectric characterization



As-is



Corona-poled w/ V > 7.5kV

Pyroelectric characteristics of the prepared samples were investigated imposing controlled thermal ramp at 2.5 K/s nominal rate between 30 and 40°C setpoints and measuring the short-circuit current.
Once a threshold poling voltage was exceeded (> 7.5 kV), the pyroelectric current increased (from $-2{,}4\ 10^{-2}$ nA to -1,3 nA) as the corona voltage increased (from 0 to 8kV), demonstrating that corona is an effective method to align electric dipoles in the polymer, dramatically enhancing the pyroelectric response of gravure printed films.

Future work

Other corona conditions (voltage > 8kV, time < 1 min) will be tried for enabling corona to be integrated into rapid and low-temperature mass production of printed pyroelectric devices.

References

[1] G. Sico, M. Montanino, F. Loffredo, C. Borriello, R. Miscioscia, “Gravure Printing for PVDF Thin-Film Pyroelectric Device Manufacture”, Coatings, 12 (2022), pp. 1020.

[2] G. Sico, M. Montanino, C. T. Prontera, A. De Girolamo Del Mauro, C. Minarini, "Gravure printing for thin film ceramics manufacturing from nanoparticles", Ceramics International, 44 (2018), pp. 19526–19534.

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