

# Supplementary Materials: Gravure Printing for PVDF Thin-Film Pyroelectric Device Manufacture

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**Citation:** Sico, G.; Montanino, M.; Loffredo, F.; Borriello, C.; Miscioscia, R. Gravure Printing for PVDF Thin-Film Pyroelectric Device Manufacture. *Coatings* **2022**, *12*, 1020. <https://doi.org/10.3390/coatings12071020>

Academic Editor: Aomar Hadjadj

Received: 30 June 2022

Accepted: 17 July 2022

Published: 19 July 2022

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**Table S1.** Raman bands assignment identified for the PVDF.

Raman Bands	Specific Vibration Assignment
485	$\alpha$ -CF <sub>2</sub> rocking [68], $\gamma$ -vibration [70]
514	$\beta$ -CF <sub>2</sub> bending [68,69]
605	$\alpha$ -CF <sub>2</sub> scissoring/CCC scissoring [68–71]
799	$\alpha$ -CH <sub>2</sub> rocking [67–71]
812	$\gamma$ -CH <sub>2</sub> wagging [67,70]
840	$\beta$ -CH <sub>2</sub> rocking/CF <sub>2</sub> antisymmetric stretching [67,69,70]
881	$\alpha$ e $\beta$ -antisymmetric stretching CC, $\alpha$ symmetric stretching CF <sub>2</sub> ns [67,69,71]

**Table S2.** Results of surface tension measurements carried out on PVDF diluted in DMSO/Acetone solutions.

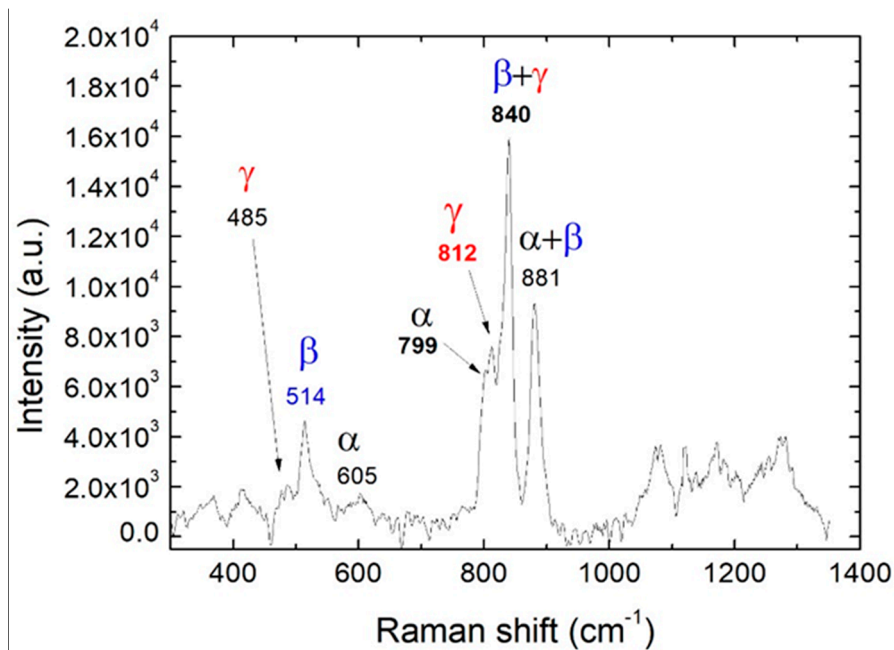
DMSO/Acetone (%w/w)	PVDF (wt%)	Surface Tension (mN/m)
100/0	0	44
50/50	0	29
50/50	8	29
50/50	10	29
50/50	12	28
0/100	0	25

**Table S3.** Preliminary printing tests results changing PVDF ink concentration, printing speed and force (ranking: ++ = Best quality/high resolution; + = Medium quality/acceptable resolution; - = Low quality/low resolution; X = Poor quality/layer defects). The printing results were the same for both Aluminum foil and PET-ITO substrates.

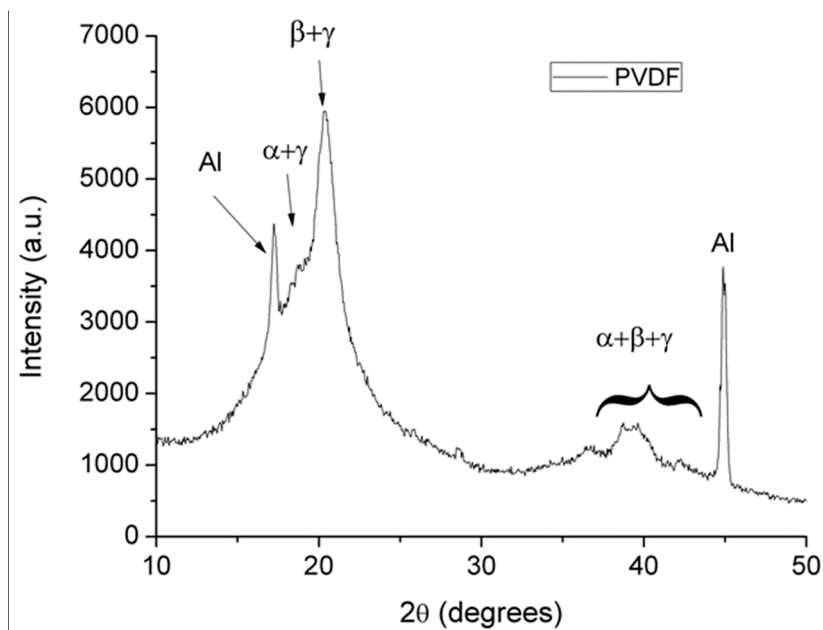
Ink Concentration (wt% of PVDF)	Ink Viscosity (mPa s)	Ink Surface Tension (mN/m)	Printing Speed (m/min)	Printing Force (N)	Ca	Printing Quality
15	68	27	12	300	0.5	-
				500	0.5	-
				700	0.5	-
			36	300	1.5	X
				500	1.5	X
				700	1.5	X
			60	300	2.5	X
				500	2.5	X
				700	2.5	X
12	45	28	12	300	0.3	-
				500	0.3	-
				700	0.3	-
			36	300	1.0	+
				500	1.0	+
				700	1.0	+
			60	300	1.6	-
				500	1.6	-
				700	1.6	-
10	36	29	12	300	0.2	-
				500	0.2	-
				700	0.2	-
			36	300	0.7	+
				500	0.7	++
				700	0.7	+
			60	300	1.2	-
				500	1.2	+
				700	1.2	+
8	30	29	12	300	0.2	-
				500	0.2	-
				700	0.2	-
			36	300	0.6	-
				500	0.6	+
				700	0.6	+
			60	300	1.0	-
				500	1.0	+
				700	1.0	+

**Table S4.** Layer characteristics of the gravure printed PVDF on Aluminum foil and PET-ITO substrates.

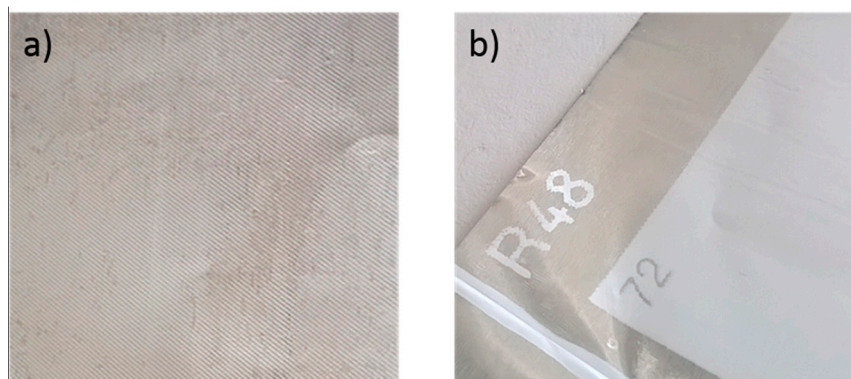
Printing Substrate	Number of Overlapped Printed Layers	Ink Concentration Profile	Printing Conditions (force; speed)	Printed Layer Thickness ( $\mu\text{m}$ )	Surface Roughness (Sq) ( $\mu\text{m}$ )
Aluminum foil	-	-	-	-	$0.20 \pm 0.02$
PET-ITO	-	-	-	-	$0.010 \pm 0.004$
Aluminum foil	1	10 wt% of PVDF	500 N; 36 m/min	$0.51 \pm 0.11$	$0.18 \pm 0.05$
PET-ITO	1	10 wt% of PVDF	500 N; 36 m/min	$0.41 \pm 0.04$	$0.05 \pm 0.01$
PET-ITO	5	Fixed (10 wt% of PVDF)	500 N; 36 m/min	$1.88 \pm 0.25$	$0.19 \pm 0.07$
PET-ITO	5	Decreasing (12, 11, 10, 9 and 8 wt% of PVDF)	500 N; 36 m/min	$1.68 \pm 0.12$	$0.10 \pm 0.03$



**Figure S1.** Typical Raman spectrum of a PVDF film deposited on Aluminum foil by wire-bar coating.



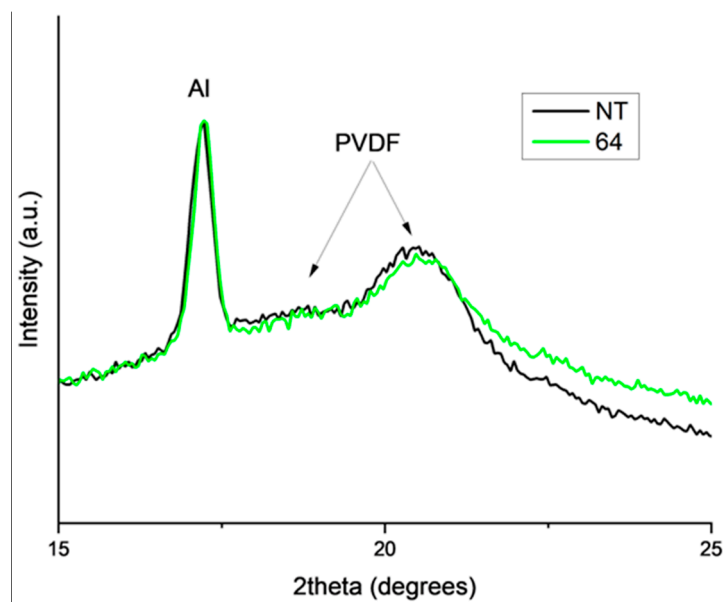
**Figure S2.** X-rays data of PVDF film obtained by depositing PVDF (15 wt%) dissolved in a mixture of 50/50 (%w/w) DMSO/acetone on Aluminum foil.



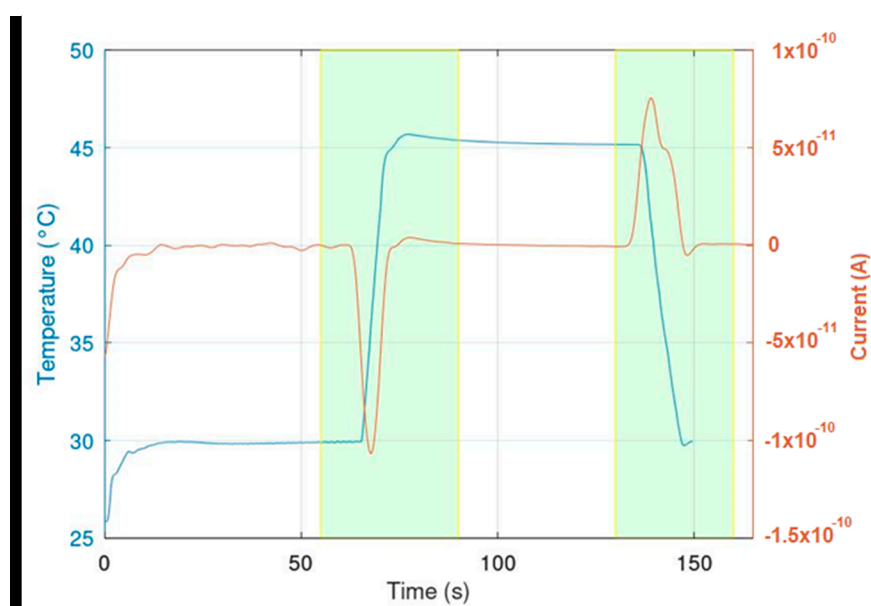
**Figure S3.** Examples of preliminary printing tests on Aluminum foil: defects obtained using 15 wt% PVDF ink (a); high printing quality using 10 wt% PVDF ink (b).



**Figure S4.** Example of gravure printed PVDF on PET-ITO substrate pre-treated by Corona at a power of 50 W.



**Figure S5.** X-ray diffraction patterns (Cu K $\alpha$ ) of a gravure printed multilayer PVDF film (5 layers) on Aluminum foil: pristine (NT) and treated by corona at the nominal power of 120 W for 64 s (64).



**Figure S6.** Temperature and electric current vs time for a multilayer PVDF device printed on a PET-ITO substrate treated by Corona at a nominal power of 120 W for 64 s.