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PVDF Piezoelectric Sensors on 3D low-Melting Point Substrates: a Preliminary Study on Paper

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Abstract—Polyvinylidene difluoride (PVDF) piezoelectric sensors were manufactured on a paper-based substrate using Aerosol Jet Printing to print silver interdigitated electrodes and the photopolymer NOA 81 to obtain restraining walls for PVDF. Silver traces were sintered thanks to Flash Lamp Annealing, a low-thermal exposure process to avoid damages to paper substrate. The samples were printed on a 3D cellulose-based substrate. Electrical capacitance measurements showed a mean value of 2.58 pF after Ag printing, to a mean value of 4.07 pF after PVDF deposition and poling. Different masses were employed, ranging from 50 to 500 g, during tests assessing a linear behavior of the sensors when loaded. A voltage peak value of 11.9 V was reached at a mass of 500 g. These preliminary results appear to be promising for the realization of a complete paper-based impact/force sensor to be applied in packaging.

Keywords—aerosol jet printing, flash lamp annealing, printed electronics, piezoelectric polymer, PVDF

I. INTRODUCTION

Nowadays one of the trend topics in sensors development is the possibility to realize them directly on 3D complex surfaces. In the near future this fact will allow to manufacture sensors and circuits embedded into objects, with the possibility to make them “smart” [1]. On the other hand, the ecological aspect and the environmental impact of the materials used is of increasing importance, privileging the usage of support materials like paper-based ones or polymers [2]. Piezoelectric sensors are of great interest in many application fields, but conventional piezoelectric ceramics (PZT, BaTiO₃) present process requirements in contrast with the above-mentioned substrates, like sintering/annealing temperatures and Curie temperatures. The need of low temperature piezoelectric materials opens up the usage of piezoelectric polymers like polyvinylidene difluoride (PVDF). This polymer presents good mechanical properties like resistance to fatigue, creep and sunlight, high mechanical strength, flexibility, chemical inertness. PVDF also shows fast response and high sensitivity [3]. Pressure sensing is a typical application of piezoelectric materials, in fact PVDF films were manufactured to develop a multifunctional pressure sensor measuring electrical capacitance, ultrasonic propagation time, vibration and temperature changes [4]. PVDF have also found application in the automotive field, thanks to a dynamic

normal pressure sensor between tire and ground [5]. This polymer was employed for structural health monitoring as a propellant embedded sensor to monitor the ageing of the propellant in solid rocket motors [6]. Once more, PVDF is also a lead-free material, a key requirement to be compliant with RoHS standard and to be used in the biomedical field [7], [8]. Unobtrusive monitoring system of cardiorespiratory signals was developed thanks to PVDF sensor obtaining accurate detection of respiration and heart rate if compared to gold standards polysomnography and electrocardiography [9]. An array pulse detecting tactile sensor was realized for artery pulse measurements evidencing both the central strong pulse, and also the transfer effect of the pulse to the surroundings which is an important aspect for artery pulse wave analysis [10].

In this manufacturing context, printed electronics (PE) technologies fit very well, being a sub-set of Additive Manufacturing with many useful features and characteristics like flexibility, reduced production cost, variety of materials to be used, capability to realize miniaturized custom sensors and circuits [11], [12]. Above all PE techniques, Aerosol Jet Printing (AJP) seems to be the best solution because of its greatest advantage of 3D direct printing on any kind of surface without masks. AJP physics consists in an aerodynamic focusing of liquid particles allows to print geometrical features in the range of 10-3000 µm in width with tens of micrometers as maximum thickness, and to overcome common PE issues like nozzle clogging and coffee-ring effect. AJP is also characterized by a wide range of printable inks like biological materials, metals, insulators, semiconductors and also piezoelectric inks [13]–[15].

A mandatory step in PE manufacturing is represented by the sintering/curing process, in which functional materials reach their final properties. In the above-mentioned context, it is not possible to employ conventional technologies, so low thermal point exposure processes are required. Flash Lamp Annealing (FLA) falls in this category: xenon flash lamps irradiate a light pulse absorbed by the printed features. Respect to traditional oven sintering, this technology is able to heat a printed thin film to high temperature on a low-melting point substrate (plastics, fabrics, paper-based materials, etc.) without damage and unwanted effects and in a millisecond

process, removing solvents and additives to reach the best performance in terms of adhesion and electrical properties [16]. The combination of PE technologies with such a curing/sintering process allows manufacturing of intelligent pieces and components for industrial field with embedded sensors, spreading the realization of smart objects

In light of this, the aim of this work is to present the first piezoelectric sensor made of PVDF, completely manufactured by means of AJP and FLA. The combination of these two techniques will allow the manufacture of piezoelectric sensors on 3D low melting point substrates. Section II will present materials and methods followed in the manufacturing steps and during testing. Section III will present and discuss the preliminary experimental results.

II. MATERIALS AND METHODS

In this section, sensors manufacturing process is explained considering materials involved and sensors layout (Section II-A and B), together with the manufacturing process (Section II-C), geometrical and electrical evaluation will be considered in Section II-D, while poling step will be defined in Section II-E.

A. Materials

At first, a photopaper tube was selected as 3D substrate material which was cleaned with ethanol and placed on the heating plate of the printer. Once selected the support material, inks choice was made as a consequence. HPS 108-AE1 (Novacentrix, Austin, TX, USA) is the conductive ink to print electrodes. It is an aqueous suspension of silver flakes, specifically formulated for AJP, containing a polymeric additive to strengthen the adhesion to substrates. FC 20 Ink I is the selected PVDF-TrFe Copolymer material (Piezotech, France). This formulation was selected because of its declared viscosity which fits well with AJP allowed viscosity range. This material presents a content of 20% of functional material and a viscosity of 16 cP. The typical dry content declared by the manufacturer is about 0.6 wt%. NOA-81 (Norland Products, Cranbury, NJ, USA) is a biocompatible photopolymer ink used to realize a restraining pool for PVDF ink.

B. Sensors design

AutoCAD was the devoted software for electrodes design. An interdigitated layout, dedicated to shear force sensing, was selected as preliminary geometry to test PVDF inks properties and to speed up the manufacturing process avoiding possible perforations of the functional layer. The electrodes were designed with a finger width and finger gap both of 300 μm ; single electrode length was about 11.9 mm, while single electrode width was about 4 mm. The total encumbrance of one sensor was 15 x 4.5 mm. In light of this, printing process parameters were tuned in order to obtain the described geometrical performances.

C. Manufacturing process

Figure 1 presents the block diagram of the manufacturing process. An AJ300 model (Optomec, Albuquerque, NM, USA) was the aerosol jet printer machine involved in this work. Silver layer was the first printed, considering as process parameters the ones reported in Table 1. Process pressures are expressed in standard centimeter cube per minute (SCCM). After curing this ink, the photopolymer was printed and UV-cured during printing. The UV Curing System is the Light Emitting Diode (LED) Spot-type Panasonic ANUJ6180

series, model 6423 (Panasonic, Kadoma, Osaka, Japan) characterized by a spot diameter of 3 mm, wavelength of 365 nm in correspondence of the peak and a peak intensity of 17200 mW x cm² at the distance of 8 mm. The selected power was 10% of the peak intensity. A total number of five samples was manufactured. After Ag printing step, Pulseforge 1300 (Novacentrix, Austin, TX, USA) is the FLA-employed machine for the curing phase. 540 V and duration of 1400 μs were the parameters considered, following a previous study performed in [17]. In presence of the pads, wires were connected with a conductive silver epoxy (CW2400, Chemtronics) mixing the two parts in equal amounts and performing a curing step in the oven at 70°C for 30 minutes. The final prototype can be seen in Figure 2, with a magnification captured through an optical microscope by Orma Scientific NB50T (trinocular zoom 0.8x–5x–LED), with its devoted HDMI MDH5 camera model, was used to acquire the images (Orma Scientific, Sesto San Giovanni, Milan, Italy).

The piezoelectric layer of the sensor in PVDF was obtained manually depositing an amount of ink about 10 μl through a micropipette. The procedure was repeated ten times, and each deposition was interleaved by a curing in a vacuum oven 10 minutes at 75 °C to achieve a first solvent evaporation and by a second curing for 10 minutes at 110 °C to fix the polymeric material. A third step was performed only after ten depositions, a final curing step for 5 minutes at 135 °C.

D. Geometrical and electrical evaluation

Silver interdigitated electrodes were tested after printing in terms of geometrical stability and electrical properties, for the total number of ten sensors manufactured. Resistance measurements were performed by means of the digital bench-top multimeter Hewlett-Packard 34401a considering the longest geometrical element. A mean resistance of 1.77 Ω was achieved, with a standard deviation about 5%. The geometrical analysis was then performed on cellulose samples owing to Filmetrics Profilim 3D optical profilometer (Filmetrics Inc., 10655 Roselle St., San Diego, CA, USA), to evaluate the shape of the printed lines. It is based on state-of-the-art white light interferometry (WLI), a non-contact optical method for surface height measurements on 3-D structures, to measure surface profiles and roughness down to 0.05 μm . The instrument works in the range of 50 nm–10 mm with substrates and materials characterized by a reflectance between 0.05–100%. The system implements a 5MP camera, the Nikon CF IC Epi Plan 20x model (field-of-view: 1.0 mm x 0.85 mm). The samples were measured in three different areas along the total length in order to state the stability of the thickness. The parameters evaluated in this phase are the total thickness, calculated as the difference between the maximum height and 1% of this value, and line width, calculated as difference between two consecutive 1% values on the two sides of the maximum height. As for Ag ink, a thickness of 16 μm and a line width of 306.6 μm were achieved, respectively with a relative standard deviation of 4.4% and 6.7%. Once evaluated these geometrical parameters, a resistivity of 48.2 $\mu\Omega$ x cm was calculated, which is in agreement with data declared by the manufacturer from 14 to 44 $\mu\Omega$ x cm, depending on deposition and curing parameters. Considering NOA-81, a thickness of 31.2 μm and a line width of 413.6 μm were achieved, respectively with a relative standard deviation of 2% and 7%. Figure 3 shows the results of the profilometer analysis.

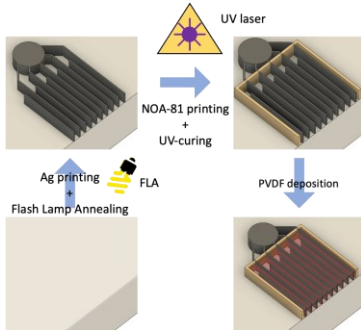


Fig. 1. Block diagram of the manufacturing process.

TABLE I. PRINTING PROCESS PARAMETERS

Parameter	Printed material	
	HPS 108-AE1	NOA-81
Sheath gas flow (SCCM)	500	1000
Atomizer gas flow (SCCM)	1150	1600
Exhaust gas flow (SCCM)	1100	700
Plate Temperature (°C)	40	0
Printing speed (mm/s)	2	1
Depositions number	2	1

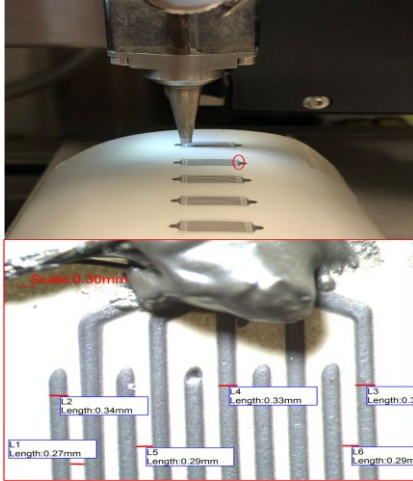


Fig. 2. Sensors during printing phase (top); microscope magnification highlighting geometrical features (bottom) after wire contacting.

E. Poling step

After the complete manufacturing of the sensors, a proper polarization must be performed. The piezoelectric layers were polarized to orient the ferroelectric domains and thus increase the piezoelectric effect of the films. A voltage of 1000 V was

applied across the samples with the sensors placed in an oven at a temperature of about 130 °C for 30 minutes in the Curie range of (128-132) °C. Then the oven was switched off and cooled down while the polarizing voltage is maintained for 30 minutes more to impose the direction of the ferroelectric domain. Furthermore, one sample was unable to withstand such a high voltage, so it was kept around 850 V during poling. On the other side, one sensor was poled at the highest voltage possible about 1150 V.

III. EXPERIMENTAL SETUP

The impedance analyzer HP 4194A (Hewlett-Packard, Palo Alto, California, USA) was used to perform capacitance measurements on printed electrodes before PVDF deposition and before and after poling step. After this analysis, impact tests were performed on our sensors, stressed by applying masses that were dropped on them to replicate impacts. For this purpose, standardized masses have been employed starting from 50 g and reaching 500 g in step of 50 g. The samples were therefore tested using a customized structure that provided a vertical drop for each weight with a fixed stroke of 0.03 m. Each sensor has been evaluated with triple tests in the presence of each mass. During tests, the samples were placed inside a metal shielding box to avoid possible environmental noise. Impact data were recorded using a digital storage oscilloscope model InfiniiVision DSOX2012A purchased from Keysight Technologies. A charge amplifier Kiag Swiss model 5001 was used as charge to voltage converter permitting to acquire the output generated by the sensors during impact tests. BNC connectors were used to connect the different parts of the experimental setup. Figure 4 presents the block diagram which explains the experimental set up described above.

IV. PRELIMINARY RESULTS

A. Electrical capacitance measurements

Electrical capacitance measurements evidenced a mean value about 2.58 pF (relative standard deviation of 10%) in case of only electrodes analyzed. After PVDF deposition and curing, the mean capacitance value registered on the samples was about 2.98 pF (relative standard deviation of 7%). The last examined situation regarded PVDF-coated electrodes after poling step, a mean value of 4.07 pF (relative standard deviation of 11%), evidencing the effect inducted in the functional layer by the poling step.

B. Force-dependent behavior

Since the PVDF layer has been manufactured thanks to a manual deposition, it is not possible to perform an aggregate comparison between sensors. At the same time, some considerations can be provided. Figure 5 reports mean peak-peak voltages for each sensor as function of increasing mass. All the sensors manufactured presented a linear behavior in presence of an increasing mass applied to them. More in details, sensors S2, S3 and S5 (red, grey and green in the picture, respectively) showed a similar behavior in presence of an applied force, reaching a maximum voltage of 7.28, 8.03 and 7.22 V respectively. S1 was the sensor which reaches the highest level of the batch with a maximum value of 11.91 V in presence of a mass of 500 g. This fact can be addressed to a higher poling voltage applied to this sensor about 1150 V. On the other side, S4 characterized by a poling voltage of 850 V reached the lowest peak value of the batch in presence of a mass of 500 g which is 5.06 V. Table II resumes the main

results obtained with our PVDF piezoelectric sensors. It can be noted that it is not possible to evidence a proportional increase of voltage at each mass increase. In fact, some points of the curve of the same sensor are confusable with each other. This effect can be caused by a non-homogeneously deposited PVDF layer inside the NOA-81 containing wall, which leads to imbalances in the distribution of electrical dipoles. In continuing the work, AJP will be employed also to deposit PVDF layer, thus with dedicated process parameters a more homogeneous deposition will be carried out for each developed sensor.

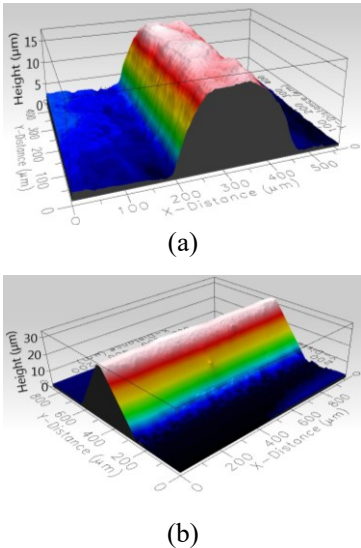


Fig. 3. Profilometer scan results for silver ink (a) and NOA-81 (b).

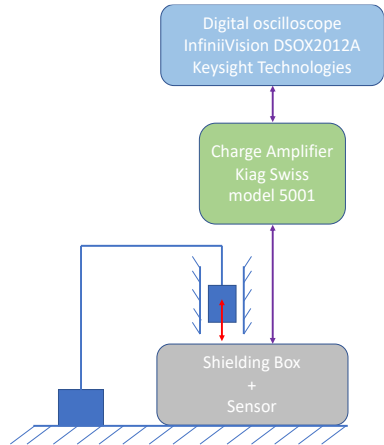


Fig. 4. Block diagram of the experimental setup.

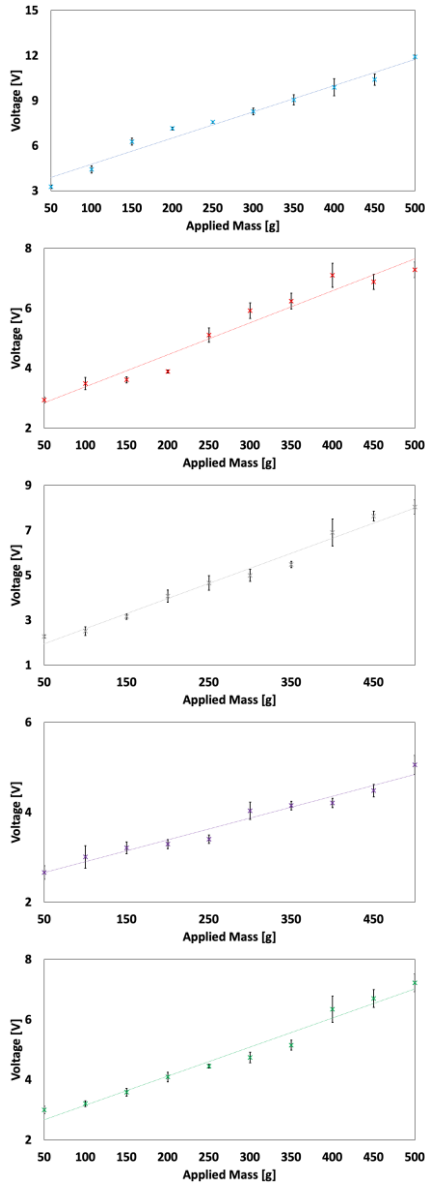


Fig. 5. Voltage vs. Applied Mass each sensor with error bars. Color legend: S1 plotted in blue, S2 in orange, S3 in grey, S4 in violet, S5 in green.

TABLE II. RESUMING PROPERTIES OF THE TESTED SENSORS.

	S1	S2	S3	S4	S5
Poling Voltage [V]	1150	1000	1000	850	1000
Mean Voltage at 500 g [V]	11.91	7.28	8.93	5.06	7.22
Voltage St. Deviation at 500 g [V]	0.15	0.26	0.32	0.21	0.29
Mean Voltage at 50 g [V]	3.27	2.94	2.27	2.66	2.99
Voltage St. Deviation at 50 g [V]	0.11	0.09	0.07	0.15	0.13

V. DISCUSSION AND CONCLUSIONS

PE technologies have all the characteristics to be part of the ones that will change in the near future many areas of human life, thanks to the possibility to realize customized sensors and circuits on every surface and material. In this preliminary study, interdigitated electrodes have been produced by Aerosol Jet Printing using a conductive ink and manually depositing a piezoelectric polymeric ink on them. Thus, the obtained sensors were characterized in impact tests in which increasing masses were impacted on the samples. The latter showed a linear behavior as a function of increasing mass, highlighting differences due to variations in the poling voltage. In addition, the piezoelectric functional material was not deposited in a repeatable manner and therefore the layer surrounding the electrodes cannot be homogeneous, introducing a second disturbing element.

Starting from these first aspects, future developments of this work will concern the definition and optimization of the printing process also for PVDF ink in order to obtain a homogeneous and compact layer of functional material. An internal analysis of PVDF material in terms of electrical dipoles distribution will be performed. In addition, a dynamic frequency characterization will be considered in order to fully determine the piezoelectric coefficient that characterizes these devices. Finally, a possible variation of the geometry will be evaluated in order to be able to consider sensors able to detect both axial and shear impact forces.

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