PRINTING AND ENCAPSULATION OF ELECTRICAL CONDUCTORS ON POLYLACTIC ACID (PLA) FOR SENSING APPLICATIONS

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ABSTRACT

This paper presents the printing of resistive and interdigitated (IDE) capacitive devices for temperature and humidity sensing applications, respectively, on biodegradable polylactic acid (PLA) substrates. Inkjet and gravure printing were evaluated to transfer silver-based nanoparticles inks. Flash photonic ink sintering methodologies were employed to maintain the PLA mechanical integrity due to its low glass transition temperature (58 °C). Between the two printing techniques investigated, gravure-printed devices on 200 µm-thick PLA sheets were shown to have better resolution and higher sensitivities to temperature and humidity (1100 ppmK^{-1} and 5.6 fF/%RH). Additionally, we demonstrated the inkjet printing of IDE onto thin (25 µm) dissolved-PLA spin-coated substrates, to enhance the mechanical flexibility and to reduce the response time to humidity (from 238 s to 70 s). Finally, a low temperature encapsulation is proposed by embedding the printed structures within PLA sheets.

INTRODUCTION

Nowadays, there is a high interest to have electrically conductive materials on biodegradable substrates, mainly for biomedical and smart packaging applications. Such structures would allow the design of environmental transducers to track and monitor ambient or body parameters (e.g. temperature and humidity). Additionally, the disposal of such devices could be done at composting sites due to the biodegradable nature of the substrate and the low quantity of conductive material deposited. Polylactic acid (PLA) is preferred among other bio-plastics due to its inherent renewable source (maize starch) and production cycle.

Recently, global production capacity of PLA has increased specially in technical housing and packing due to its characteristics as bio-compatible, bio-degradable and bio-compostable. Some groups have already reported the sputtering and hot embossing of zinc [1], the lamination of copper [2] and the soldering at low temperatures [3] on PLA. However, the direct printing and sintering of electrical conductors on PLA has not been explored yet, due to its challenging low glass transition temperature (T_g: 58 °C).

In this study the sintering of printed silver-based inks on PLA by means of photonic techniques (near infrared– NIR wavelength: 500-1500 nm) is demonstrated. The latter are effective thanks to the low PLA absorption of NIR wavelengths which only heat the surface of the printed lines, maintaining the substrate integrity.

These printed and conductive lines were implemented and characterized as resistive temperature and capacitive humidity sensors. For the latter, the PLA substrate is also used as humidity sensing layer. Performances of the devices printed by both techniques on commercially available 200 µm-thick PLA sheets and 25 µm-thick spin-coated PLA films were compared and optimized. Finally, an encapsulation technique is proposed to fully embed the conductive structures within PLA sheets at low temperatures (< 60 °C). The printing, the sintering, as well as the encapsulation procedures are compatible with foil-level and large area fabrication methods.

FABRICATION

The conductive structures were fabricated using two different printing techniques, namely inkjet and gravure printing, onto two types of PLA substrates. The first one was the transparent 200 µm-thick film Bioclear® from the company Sodinor. The second one was a custom-made film obtained by spin-coating dissolved PLA beads (Ingeo 4032D), from the company NatureWorks. The dissolution was performed by mixing the PLA pellets with dioxane (from Sigma-Aldrich) at 40 °C with mechanical stirring. In order to decrease the dissolution time the pellets were added to the solvent after a vortex was created by the mechanical stirring. The solution (PLA/dioxane) was spin-coated onto 4'' silicon carrier wafers. Different concentrations and spin-coating speeds were used to obtain different film thicknesses. For this work a volume concentration of 15 % (7.5 g of PLA within 50 mL of dioxane) and a speed of 1000 rpm for 60 s were used as solution and spin-coating conditions. This combination was proven to give a homogenous film with a thickness of 24.5±0.1 µm.

After an oxygen plasma surface treatment (15 s), inkjet printing was performed on both types of PLA at room temperature. The non-contact technique was performed with a Dimatix® - DMP2800 printer using the silver-based nanoparticles ink SunTronic® JetEMD506 from SunChemical. The gravure printing technique was done onto the 200 µm-thick PLA with a TeslaColor-171® machine from Schläfli at 15 m/min using the silver-based nanoparticles ink TC-PR-020 from InkTec.

The sintering process was performed using near infrared (NIR) photonic tools, namely, NIR-120® from Adphos and PulseForge®-1200 from Novacentrix, referred as NIR and NIR-pulsed, respectively, in the document. The PLA films are mostly transparent to the NIR wavelength [4-5] but not the silver-based inks. Leading to an increment of temperature just at the surface causing ink sintering and protecting the film integrity (T_g: 58 °C). Figure 1 presents the PLA transmittance compared to a typical NIR energy source, showing a relatively high transmittance between 500 nm and 1500 nm. Inkjet-printed devices were sintered using 3 passes with an intensity of 55 % (≈ 1650 W) at 0.12 m/s with the NIR-120 machine. Gravure-printed devices used 5 flash-pulses of 808 mJ/cm^2 with the PulseForge machine.

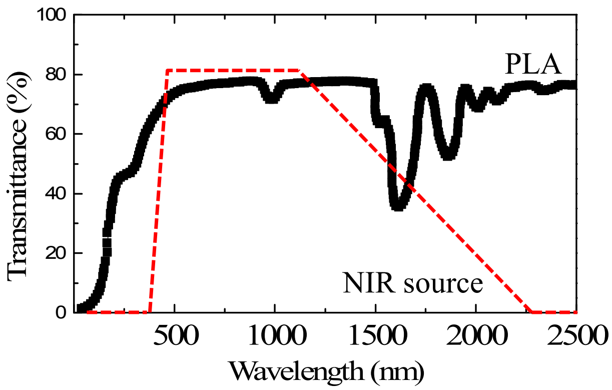

Figure 1: Transmittance profile of PLA (black-continuous line) compared to a NIR energy source (red-dotted line).

Following the procedure described above, two types of structures were designed and fabricated: resistors and IDE capacitors, used as temperature and humidity sensors, respectively. Figure 2 shows the optimal images of the inkjet- and gravure-printed devices on 200 µm-thick PLA film. The gap and pitch obtained were: 70µm/220µm and 30µm/160µm, respectively.

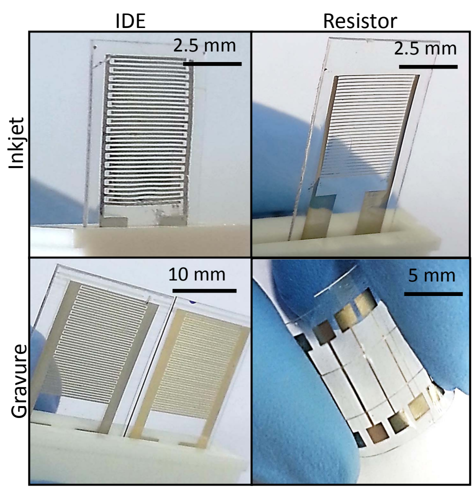

Figure 2: Optical images of the inkjet- and gravure-printed capacitive and resistive devices on PLA substrates (200 µm-thick).

CHARACTERIZATION

Photonic sintering process

The photonic sintering of inkjet-printed devices was performed with the NIR-120 (NIR) system (Figure 3a), which has as parameters the energy and speed under the lamp. Both variables need to be optimized depending on the type and thickness of the ink and substrate. It was observed that the PLA substrate was deformed plastically when energies too elevated were used. Additionally, the electrodes were damaged at the interface with the pads when the exposure took too long, as shown in Figure 3b. An optimal intensity and speed of 55 % (1650 W) and 0.12 m/s, respectively, were found optimal for this case.

The photonic sintering of gravure-printed devices was performed with the PulseForge (NIR-pulsed) system (Figure 3c), which has the energy dose as main parameter. It was observed that the PLA substrate started to deform and more interesting the ink started to crack above 830 mJ/cm^2, as shown in Figure 3d. For this reason several pulses at lower doses (808 mJ/cm^2) were found as optimal.

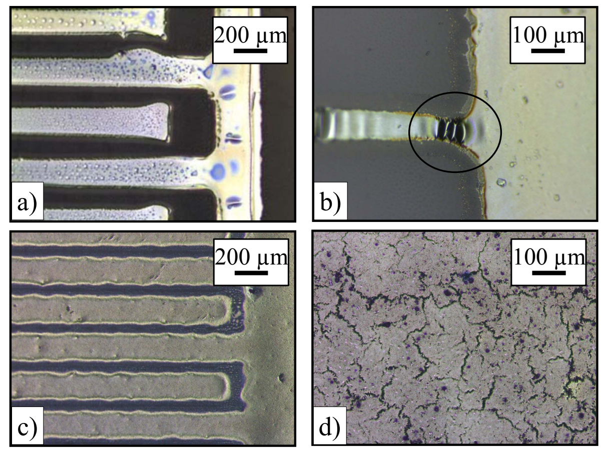

Figure 3: Optical images of inkjet-printed IDE sintered with: a) optimal speed, b) too low speed. Gravure-printed IDE sintered with: c) optimal dose, d) too high dose.

Electric properties

The resistivity of the sintered inks was calculated using their geometry parameters and measured resistances (4-points technique). Gravure + NIR-pulsed ink was shown to have 1/2 of the inkjet + NIR ink's resistivity, while the printed layers after curing had the same thickness (Table 1).

Table 1: Measured thicknesses (white light interferometer) and calculated resistivity for the inkjet- and gravure-printed structures.

Technique	**Thickness (nm)**	**Resistivity (µΩ·cm)**
Inkjet + NIR	700 ± 40	43.2 ± 2.1
Gravure + NIR-pulsed	700 ± 30	16.2 ± 0.3

The temperature coefficient of resistance (TCR) for the printed resistive structures was measured from -10 °C to 40 °C at 40 %RH. Figure 4 presents the up- and down-sweep curves showing a TCR value of 800 ppm·K^{-1} and 1130 ppm·K^{-1} for the inkjet and gravure silver-based inks, respectively.

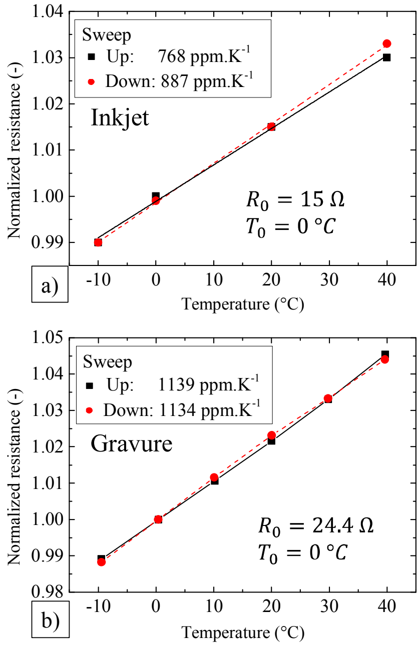

Figure 4: Temperature coefficient of resistance for a) inkjet + NIR ink and b) gravure + NIR-pulsed ink.

Humidity response

Using the demonstrated printing and sintering techniques, IDE capacitive structures were fabricated as humidity sensors with the PLA as sensing layer. Additionally, the sensor configuration (i.e. printing resolution and substrate thickness) was optimized

The devices were exposed to a humid environment in a climatic chamber with cycles from 30 %RH to 70 %RH of one hour at 25 °C. Figure 5a and 5b presents the curves for the inkjet- and gravure-printed devices on 200 µm-thick PLA, showing a sensitivity of 3.4 fF/%RH and 5.6 fF/%RH, respectively. Higher printing resolution of gravure IDE capacitors led to higher capacitance for the same area. The latter allowed higher absolute RH sensitivities (1.6 times better) and a better sensor performance. The dynamic behavior to relative humidity was measured in a climatic chamber using controlled RH steps from 10 % to 70 % at 25 °C. Figure 6a and 6b presents the curves for the inkjet and gravure devices on 200 µm-thick PLA, with response times of 238 s and 273 s (from 10 %RH to 30 %RH at τ = 63%.), respectively.

The same dynamic analysis was performed with the inkjet-printed devices on the spin-coated 25 µm-thick PLA films. The latter were printed and sintered using the Si wafer as a carrier substrate to maintain the planarity, and then cut and peeled-off, as shown in Figure 7. Since the rigidity is proportional to the cube of the thickness, it is interesting to point out that the 25 µm-thick film is about 500 times less rigid than its 200 µm-thick counterpart. This proportionates highly flexible and to some extend conformal films and printed structures.

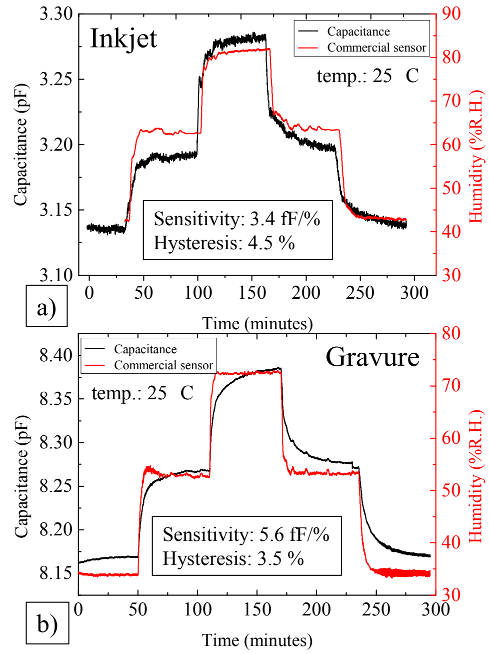

Figure 5: Response to humidity for a) inkjet- and b) gravure-printed IDE capacitors, showing the calculated-absolute sensitivity and hysteresis.

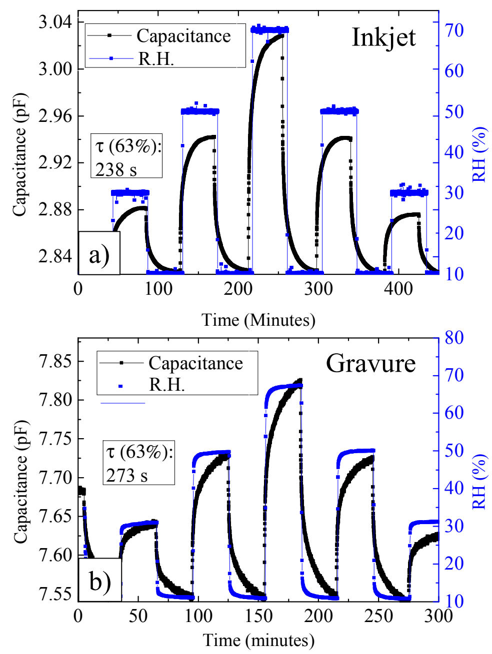

Figure 6: Response curves to RH steps for: a) inkjet- and b) gravure-printed IDE capacitors on 200 µm-thick PLA substrate, showing the response time (τ=63%).

Figure 8 shows the response to humidity of the 25 µm-thick PLA film at different RH levels (from 10 % to 70 % at 25 °C). It is noted that the device follows the input RH profile. However, its reversibility is hindered after a relatively high humidity exposure (70 %). The response time from 10 %RH to 30 %RH was found to be 70 s, which is 3.9 times faster than the devices on thick PLA.

The inset of Figure 8 shows the linear relationship between the capacitance and humidity, with a sensitivity of 0.2 fF/%RH, which is lower than the devices on thick PLA.

The improvement on the response time and the worsening of the sensitivity are due to the substantial reduction of the PLA thickness (8 times) keeping the same printing resolution (gap/pitch: 70 µm/220 µm). In order to maintain the fast response and increase the sensitivity, higher printing resolution and the deposition of an RH sensing layer (e.g. CAB, PLA, etc.) on top of the electrodes are required.

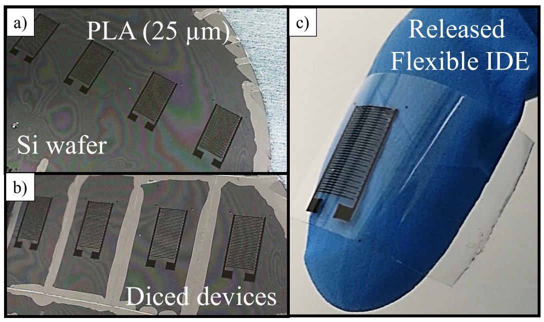

Figure 7: Photographs of: a) inkjet-printed devices on spin-coated PLA onto Si wafer, b) diced devices on Si wafer and c) released flexible device.

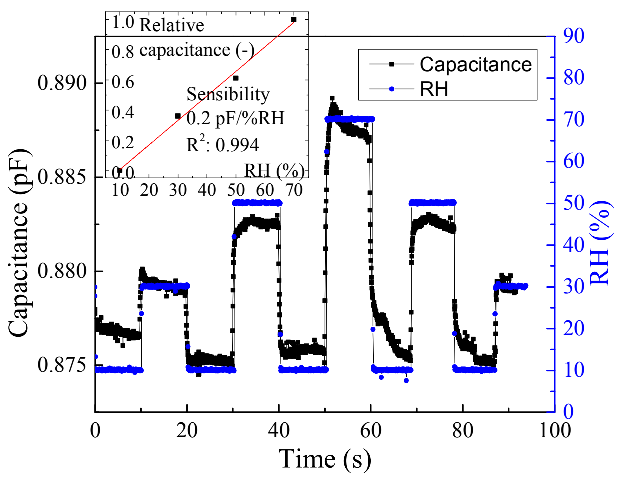

Figure 8: Response curve to RH steps for the inkjet-printed IDE capacitor on 25 µm-thick PLA substrate, showing the response time and the absolute sensitivity (inset).

ENCAPSULATION

A flexible encapsulation method is proposed to fully embed the printed structures onto PLA films at low temperatures (< 60 °C). After the printing of the conductive devices onto the thin PLA substrate, a second spin-coated film was pressed together to the first stack at 58 °C and 40 kPa for 2 minutes. Finally, the complete multilayer stack is cut and released from the Si carrier wafers, as shown in Figure 9. The encapsulation is used to keep the ink adhesion to PLA when in contact with the compost environment in biodegradation tests.

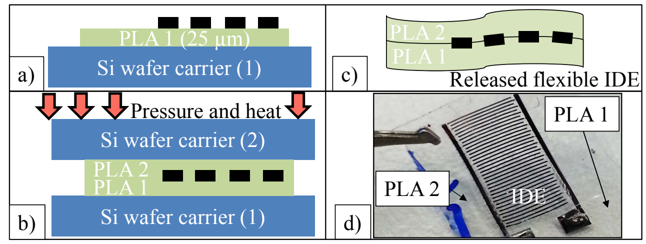

Figure 9: a-c) Schematics of PLA encapsulation process and d) photograph of an encapsulated IDE capacitor.

CONCLUSIONS

This paper presented the printing (inkjet and gravure) and photonic sintering of resistive and capacitive structures on polylactic acid (PLA). The procedures kept the integrity of the film which has a relatively low T_g (58 °C). Gravure-printed devices on 200 µm-thick PLA were shown to have higher sensitivity to temperature 1100 ppmK^{-1} and humidity 5.6 fF/%RH. Inkjet-printed devices on 25 µm-thick PLA were shown to have faster RH response time (70 s). Finally, the fully PLA encapsulation of printed devices was proposed at low temperatures. The latter are being tested for biodegradation in controlled compost environments.

ACKNOWLEDGEMENTS

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