Inkjettable, polydimethylsiloxane based soft electronics

Riikka Mikkonen Faculty of Information Technology and Communication Sciences Tampere University Tampere, Finland riikka.mikkonen@tuni.fi Matti Mäntysalo Faculty of Information Technology and Communication Sciences Tampere University Tampere, Finland matti.mantysalo@tuni.fi

Abstract— In this paper, we report our recent work with an inkjettable polydimethylsiloxane (PDMS) solution, which is intended for multilayer printing of soft electronics. Here, we present optimized printing parameters for the PDMS ink, and the surface treatment modification methods of PDMS for conductive track printing are discussed in further detail. In this paper, processing parameters are described for successful multilayer printing of soft electronics, such as sensors.

Keywords—PDMS, inkjet printing, soft electronics

I. INTRODUCTION

PDMS is known as an inexpensive, optically transparent and biocompatible soft elastomer. For these reasons, it is widely used in applications like tissue mimicking, electronic skin (e-skin) and microfluidics [1-3]. Unfortunately, the traditional manufacturing methods (lithography, mold casting) make PDMS fabrication both time-consuming and inconvenient. Therefore, approaches for additive manufacturing of PDMS have been presented in the recent years [4-6].

An example of additive manufacturing methods is inkjet printing. This digital technique is already utilized in the printed electronics fabrication, where it can be used to build soft, large area flexible and stretchable electronics, such as piezoelectric devices, and skin-conformable systems [7,8]. Combining inkjet printing of soft materials with other jettable materials would simplify building of these complex devices, when less process steps are required.

Earlier, we presented an approach for multilayer printing of PDMS based soft electronics [9]. This paper reports our recent work with the printed PDMS. In addition to PDMS jetting parameters, alternative surface modification methods of PDMS for silver printing were studied.

II. MATERIALS & METHODS

A. inkjettable PDMS

Here, a two-component PDMS (Sylgard 184, Dow) was used in a 1:10 ratio (catalyst to base). To create a jettable solution, it was mixed in a 1:3 ratio with octyl acetate. The details of the solvent selection have been discussed in [9]. The solution was stirred for 15 min at 1500 rpm before injecting it to an ink cartridge. A Dimatix DMP 2800 inkjet printer was used to print the PDMS ink solution, using 10 pl-volume liquid crystal polymer (LCP) cartridges. The ink was cured at 120 °C temperature for 25 min.

B. PDMS surface treatments

Spin coated (1600 rpm, 60 s), 20 μ m thick Sylgard 184 (1:10 ratio) layers were used as substrates for silver printing. The PDMS surface was treated before silver printing with several surface modification methods: First, with a flame-pyrolytic surface silicating method (NanoFlame, Polytec PT GmbH), where a thin silicon oxide layer is formed on the substrate surface. The precursor particles are separated thermally, dividing the tool's flame to a reducing inner part, and an oxidizing outer part.

Another method was a chemical modification with a (3mercaptopropyl)trimethoxysilane (MPTMS) solution that was spin coated on a plasma treated PDMS surface (1600 rpm, 2 min) and baked for 30 min at 120 °C. These methods were compared to the nitrogen plasma modification (Diener Atto, Diener Electronic GmbH) reported in [9].

C. Conductor printing

An inkjettable silver nanoparticle (Ag np) ink (Silverjet DGP-40LT-15C, Advanced Nano Products Co., Ltd.) was used to print the conductive tracks with the Dimatix printer. A 10 pl standard DMP cartridge was used. The cartridge temperature was 40 °C, and the substrate temperature was kept at 60 °C. After printing, all samples were cured at 120 °C for 30 minutes.

III. RESULTS

A. PDMS printing

As discussed already in [9], it is necessary to minimize the temperature during PDMS printing. Lower temperature will help to prevent elastomer crosslinking and thus, to increase the cartridge's shelf life. Here, we studied the printing parameters further.

It was concluded that a waveform, where a strong and long firing pulse is used, improved ink jetting significantly from the previous results. This waveform shape is typical for high viscosity inks, and it was clearly enhancing the jetting stability, when the cartridge was used on several days in a row, in comparison to other waveforms. The nozzles could be kept firing by simply elevating the cartridge temperature by a few degrees at the time. Thus, small temperature increments allow printing for several days, if the cartridge is stored in a refrigerator overnight. summary of the printing parameters for the PDMS ink is given in Table I.

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Test substrates with each surface treatment were prepared for Ag np inkjet printing. A summary of the optimized treatment parameters is given in Table II. The alternative treatments were studied and compared to the nitrogen plasma, as it has been reported that the plasma treatment may not provide a permanent surface modification of PDMS, causing it to recover its native hydrophobicity over time, even though differences between plasma gases have been reported [10].

Parameter	Value
Substrate temperature	60 °C
Cartridge temperature	30 °C (elevated over time)
Max. jetting frequency	2.0 kHz
Jetting pulse duration	69.76 μs
Firing voltage	24 V
Firing pulse level	100 %
Slew rate	0.54 (Rising and falling edge)
Non-jetting time	89.024 μs

TABLE II. SURFACE TREATMENT SPECIFICATIONS

Method	Specifications
Nitrogen plasma	Exposure power: 100 W, time: 1 min,
	chamber pressure 0.6 mbar, gas flow 700
	sccm [1]
MPTMS	A 6 % solution in ethanol, spin coat for 2
	min at 1600 rpm on plasma treated
	PDMS, bake for 30 min at 120 °C
Pyrolytic	Treat substrate with a steady back-and-
coating	forth movement for 4 times

B. Surface treatments and Ag np printing

Once the substrates had been prepared, the printing trials were started by drop matrix printing, to determine the suitable drop spacing for each ink-substrate combination. When the drop spacings were calculated from the droplet diameters, we tried line printing on each substrate. Smooth, well-defined lines could be printed on the nitrogen plasma-treated substrate (Fig 1b), whereas the line prints on both PDMS with pyrolytic coating, and MPTMS-coated PDMS had rougher edges (Fig. 1d & Fig. 1f).

The MPTMS-coated PDMS was observed to be rough, and it seems that the substrate's surface roughness affects the print quality on this substrate. Kirikova et al found in [11] that this treatment type is well suited as an ink primer for improved wetting and adhesion of screen printed silver patterns on PDMS. Since the inkjet printed lines tend to be an order of magnitude thinner than the screen printed lines, it is likely that the Ag np ink is more sensitive to the variations in the surface roughness.

In addition to the wetting experiments, we did a simple peeling test of the printed lines with each ink-substrate combination using a scotch tape. Some ink was removed from the nitrogen plasma- and MPTMS-treated samples, but the samples with the pyrolytic coating could withstand these peeling tests outstandingly (Fig. 2).

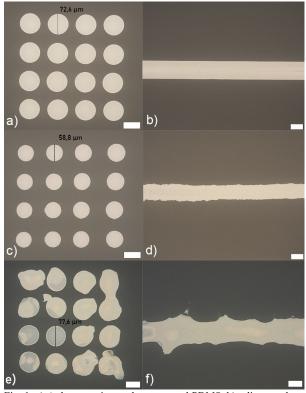


Fig. 1. a) A drop matrix on plasma treated PDMS, b) a line on plasma treated PDMS, c) A drop matrix on PDMS with pyrolytic coating, d) a line on PDMS with pyrolytic coating, d) a drop matrix on MPTMS-coated PDMS, d) A line on MPTMS-coated PDMS. Scale bar: 50 μ m.

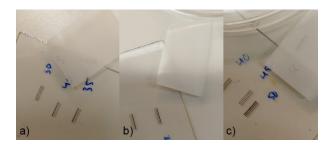


Fig. 2. Peeling test results of Ag np ink on a) plasma treated PDMS, b) PDMS with pyrolytic coating, c) MPTMS-coated PDMS.

Based on the results of line printing trials and peeling tests, the pyrolytic coating was selected for the multilayer printing experiments. The process flow for the multilayer printing is illustrated in Fig. 3. First, the PDMS substrate is modified with the chosen surface treatment method. Secondly, a layer of conductive tracks is printed with the Ag np ink, followed by the elastomeric dielectric printing. After that, the PDMS surface is modified again, including the printed elastomer. Then, the second layer of conductive tracks is printed. Each layer is cured after printing.

In comparison to the previously used, nitrogen plasmabased process, a pyrolytic coating process is both faster and simpler, since only a handheld tool and gas refill are required. On the other hand, since this treatment is more dependent on the user, it is harder to achieve a repeatable surface modification process. For example, the distance of the flame to the sample may vary between samples, and the treatment time is hard to control with the manual back-and-forth movement. However, we managed to fabricate similar 2-layer structures as before in [9] with the nitrogen plasma, as illustrated in Fig. 4. Furthermore, we observed that despite the challenges with the pyrolytic coating stability, less cracks and wrinkling of the conductive tracks were observed than before, when the treatment was successful (Fig. 4). This is assumed to be due to the silicon oxide layer that is formed on the PDMS surface, protecting the underlying elastomer from the chemical exposure and making it more stable during the thermal curing phase.

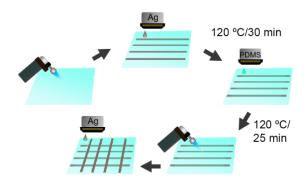


Fig. 3. Process flow of PDMS based multilayer printing.

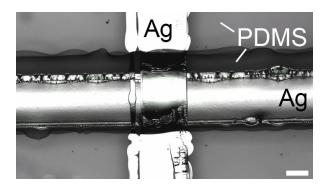


Fig. 4. A multilayer print on PDMS with pyrolytic coating, including two layers of conductive tracks, and a printed PDMS layer as a dielectric between them. Scale bar: $200 \ \mu m$.

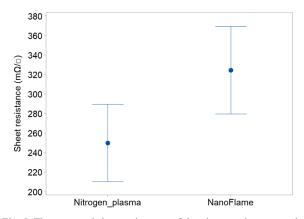


Fig. 5. The measured sheet resistances of the nitrogen plasma samples and the samples with pyrolytic coating (NanoFlame). 16 measurements, confidence interval for the mean is 95 %. The nitrogen plasma results are adapted from [9].

To compare the electrical properties of the samples with the previous results from [9], the sheet resistances of the samples were measured. The results are illustrated in Fig. 5. The measured sheet resistances of the samples with the pyrolytic coating were approximately 40 % higher than the previous results. Still, the sheet resistances are well below 0.5 Ω/\Box .

IV. CONCLUSIONS

In this paper, we reported our recent work towards all inkjet printed, PDMS based soft electronics. Here, PDMS jetting parameters were discussed, and alternative surface treatments for plasma were studied. The results show that a silicon oxide layer, which can be formed on the PDMS surface by a straightforward and fast, flame pyrolytic silicating method, improves the adhesion of the conductive inks significantly in comparison to the previously used plasma treatment.

Our process is designed for the widely used Dimatix material printers, and thus, the results are readily applicable. Therefore, these findings could be used in electronics manufacturing to build, for example, soft sensors and other complex devices, where multilayer printing of more than one material is required, in order to achieve the desired functionalities.

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REFERENCES

- J.-H. Kim, S.-R. Kim, H.-J. Kil, Y.-C. Kim, J.-W. Park, "Highly conformable, transparent electrodes for epidermal electronics", Nano Lett. 2018, vol. 18, pp. 4531–4540.
- [2] D. E. Backman, B. L. LeSavage, S. B. Shah, and J. Y. Wong, "A robust method to generate mechanically anisotropic vascular smooth muscle cell sheets for vascular tissue engineering", Macromol. Biosci., 2017, 17, 1600434.
- [3] M.P. Drupitha et al, "Morphology-induced physico-mechanical and biological characteristics of TPU–PDMS blend scaffolds for skin tissue engineering applications", J. Biomed. Mater. Res. Part B Appl. Biomater., 2019, 107, pp. 1634–1644.
- [4] C.S. O'Bryan, et al, "Self-assembled micro-organogels for 3D printing silicone structures", Sci. Adv. 2017, 3, e1602800.
- [5] V. Ozbolat, M. Dey, B. Ayan, A. Povilianskas, M. C. Demirel, and I. T. Ozbolat, "3D printing of PDMS improves its mechanical and cell adhesion properties", ACS Biomater. Sci. Eng. 2018, 4, pp. 682–693.
- [6] C. Sturgess, C. J. Tuck, I. A. Ashcroft, and R. D. Wildman, "3D reactive inkjet printing of polydimethylsiloxane", J. Mater. Chem. C., 2017, 5, pp. 9733–9745.
- [7] D. Thuau, K. Kallitsis, F. D. Dos Santos, and G. Hadziioannou, "All inkjet-printed piezoelectric electronic devices: energy generators, sensors and actuators" J. Mater. Chem. C., 2017, 5, pp. 9963–9966.
- [8] S. Wang et al, "Skin electronics from scalable fabrication of an intrinsically stretchable transistor array" Nature, 2018, vol. 555, 83.
- [9] R. Mikkonen, P. Puistola, I. Jönkkäri, and M. Mäntysalo, "Inkjet printable polydimethylsiloxane for all-inkjet-printed multilayered soft electrical applications", ACS Appl. Mater. Interfaces, 2020, vol. 12, pp. 11990-11997.
- [10] V. Jokinen, P. Suvanto, and S. Franssila, "Oxygen and nitrogen plasma hydrophilization and hydrophobic recovery of polymers", Biomicrofluidics, 2012, vol 6, 016501.
- [11] M. N. Kirikova et al, "Direct-write printing of reactive oligomericalkoxysilanes as an affordable and highly efficientroute for promoting local adhesion of silver inks polymer substrates", J. Mater. Chem. C., 2016, vol 4, pp. 2211-2218.