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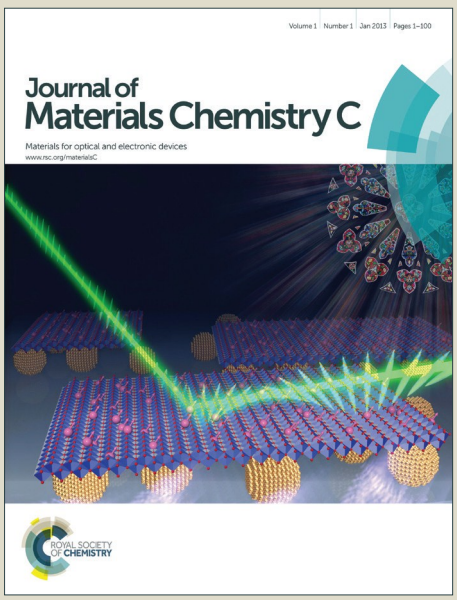

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ARTICLE

Direct-Write Printing of Reactive Oligomeric Alkoxysilanes as an Affordable and Highly Efficient Route for Promoting Local Adhesion of Silver Inks on Polymer Substrates

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A novel approach for improving printability and adhesion of silver inks on flexible and stretchable polymeric substrates is reported. The method is based on polymer surface functionalisation with an organosilicon interlayer by solution processing and, more specifically, the deposition of a self-assembled layer (SAL) from thiol-containing oligomeric alkoxysilanes prepared under active media conditions. We demonstrate the potential of SAL formation on polymer substrates by large-area uniform coating or by small features printing. The direct-writing method, which is also referred to as reactive inkjet printing, enables selective modification of polymer surfaces with functional thiol-containing interlayers, resulting in local adhesion enhancement of screen-printed silver nanoparticle inks. This study establishes that SALs printed from oligo(3-mercaptopropyl)(methoxy) siloxane (OMPMS) lead to significant adhesion improvements of both aqueous- and organic-based silver inks approaching approximately 100% for polyethylene naphthalate (PEN) and even polydimethylsiloxane (PDMS) substrates. Exceptional electrical and mechanical stabilities of the printed silver conductors under bending and stretching are demonstrated.

Introduction

To date, there has been a historical trend in the electronics manufacturing industry towards miniaturisation of components of electronic devices to furnish them with a broader range of functions whilst keeping the size and weight minimal. Basic constituents of traditional electronic circuits have become increasingly diminutive and compact and, therefore, a structure where such tiny elements could be mounted on a polymeric substrate enabling malleability of the whole device can be envisioned.[1] Such heterogeneous integration is typically viewed as a transitional step towards entirely printed and deformable electronics. Numerous devices including displays,[2] logic,[3] memory,[4] sensor systems[5] and solar cells[6] have already been shown to have a flexible form factor.

Conductive interconnects are at the core of flexible and printable electronics since they are intended to support reliable electrical contacts and routings across the device, which has likely a plastic substrate with low thermal stability. Significant efforts have been made towards the development of flexible interconnections in order to couple electrical conductivity with mechanical deformation. Different approaches have been suggested including lithographic patterning of serpentine metal structures,[7] embedding liquid metals,[8] metal nanowires and carbon-based nanocomposites;[9] amongst these, additive printing and solution-based methods have appealed for a decade mainly due to their low cost and high speed, together with the fact that these methods are better compatible with a large spectrum of plastics than the conventional vacuum techniques.[10]

Metal nanoparticles in solution, such as silver, copper and nickel, are recognised as the most promising printable materials for building interconnects due to their high conductivity,[11] however, these possess reduced adhesion to plastic substrates. Auxiliary substances and additives constituting the ink may help to improve adhesive strength and mechanical properties of metal structures by means of meticulous and complex design of the ink composition,[12] yet this is ultimately achieved at the cost of decreased conductivity.

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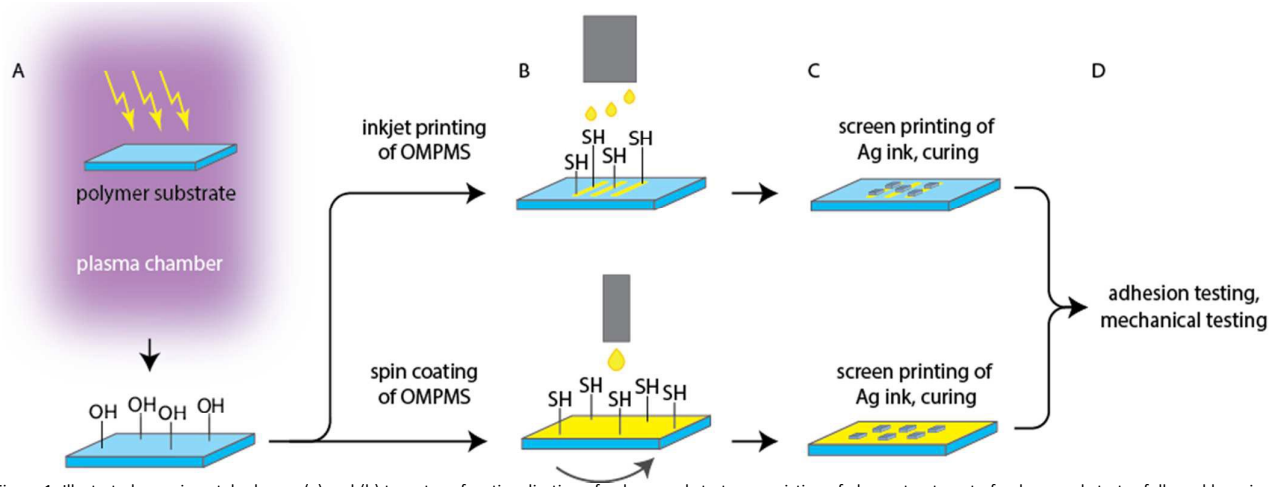

Figure 1. Illustrated experimental scheme. (a) and (b) two-stage functionalisation of polymer substrates, consisting of plasma treatment of polymer substrates followed by spin coating or inkjet printing of OMPMS (c) deposition of silver ink by screen printing (d) adhesion and mechanical testing of printed silver structures.

A complimentary approach relying on substrate surface pre-treatment and modification could also meet the performance requirements of the metallic ink provided for commercially viable electronic devices. Thus, to enhance wetting ability of the media and adhesion of the metal nanoparticles to an inherently inert polymeric substrate, chemical bonding or physical (mechanical) anchoring are typically considered, although commonly a combination of both is used. The most reported treatment methods include ultraviolet ozone (UVO), oxygen plasma,[13] microstructuring and nanopatterning,[14] roughening by plasma or etching[15] and a variety of chemical methods[16] such as self-assembled monolayer (SAM) deposition.[17] With its rich chemistry,[18] SAM results in the formation of functional groups on the polymer surface (oxygen-, nitrogen- or sulphur-containing), which serve as the anchors to bind metal particles to the polymer. These chemical bonds remain after curing of the ink and provide improved adhesion and better retention of conductive layers during bending, twisting or other mechanical deformations and, moreover, the electrical characteristics of the bulk material are kept intact. However, there are still a number of practical complications associated with the short lifetimes of UVO/plasma modified surfaces and rather slow SAM deposition processes, making these techniques incompatible with high-speed roll-to-roll (R2R) production and large-scale manufacturing. In addition, the challenges of local adhesion promotion, which allow binding of a certain pattern selectively, remain. Therefore, a new affordable method of surface functionalisation using the direct write capability is in high demand, especially due to its potential local applicability.

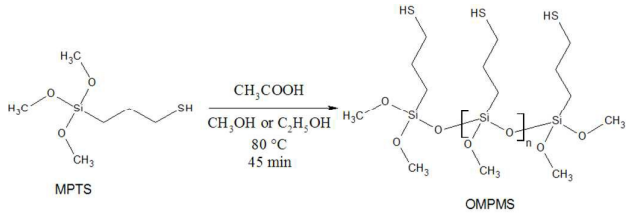

Figure 2. Synthesis of oligo(3-mercaptopropyl)(methoxy)siloxane (OMPMS) under active media conditions.

This work demonstrates a novel technique for local chemical modification of flexible polymer surfaces aimed at improving the printability and adhesion of silver inks through novel thiol and organosilicon chemistry, whilst minimising roughness contribution (Figure 1). The silver nanoparticle ink is selected for the purposes of this study, as it is the most reported interconnect material in printed electronics. The procedure involved oligomerisation of (3-mercaptopropyl)trimethoxysilane (MPTS) under active media conditions (Figure 2) resulting in the formation of oligo(3-mercaptopropyl)(methoxy) siloxane (OMPMS) and the subsequent deposition of this functional organosilicon oligomer to form the self-assembled layer (SAL) on a beforehand plasma treated substrate. Unlike SAMs, SALs are thicker layers that generally have better coverage of the surface[19] and, importantly, deposition of SAL is a long-term modification in contrast to conventionally applied plasma or UVO treatments that persist for comparatively shorter periods of time. Additionally, usage of spin coating allows large-area substrates to be modified with the functional oligomer developed. Coupling the method proposed with printing technologies, here we demonstrate that alcohol solutions of OMPMS, as opposed to the initial MTPS, can be effectively used as the inks for inkjet printing, functioning as a direct-write reactive process, which supports a local deposition of the adhesion promoter on polymer surfaces. In order to illustrate versatility of SAL functionalisation, which could potentially be applied for a broad range of printable materials and polymer substrates, we report the improved printability and adhesion enhancement of aqueous and organic-based silver inks on flexible PEN and stretchable PDMS substrates. The screen-printed silver structures on SAL functionalised surfaces possess improved electrical conductivity and reliable mechanical flexibility.

Results and discussion

Overview of the proposed approach

We recently reported vapour phase modification of polymer substrates by SALs of functional alkoxysilanes (mercapto- or aminopropyl).[19] Correspondingly to this study, the method of silver ink adhesion enhancement proposed previously consisted of several steps including plasma treatment, silanisation of the treated substrate from the vapour phase, silver ink printing and curing of the deposited structures. However, in contrast to the solution process, the main disadvantages of vapour phase modification are long treatment times required for SAL formation (2 to 72 hours) and the complexity involved in depositing such alkoxysilanes on the substrate as structured SALs of predetermined shapes. Consequently, we have developed a new material and method for surface modification through the introduction of a solution-processable SAL. The surface-modifying substance represents an MPTS-based oligomer called OMPMS, which is synthesised under active media conditions[20] (Figure 2). OMPMS has varying molecular weights and is provided in a liquid solution making it suitable for wet deposition on polymer surfaces using spin coating, inkjet printing or other suitable techniques.

Solution-processed functionalisation with OMPMS is a simple two-stage approach that involves surface pre-treatment and subsequent SAL formation (Figure 1). The first step, consisting of surface activation, is essential for effective SAL bonding and appears to be universal to conventional SAM deposition methods too.[21] We have used oxygen plasma although any appropriate procedure that would result in increased amount of hydroxyl surface groups could be utilized at this stage, for example, UVO treatment. Subsequently, the OMPMS solution is deposited on the treated surface either by spin coating or by inkjet printing. The SAL is further dried at 100-120 °C in order to accomplish complete polymerisation of the alkoxysilane groups of OMPMS and form a dense cross-linked thiol-reach organosiloxane layer. Ultimately, silver inks are printed over the SAL and cured at elevated temperatures following which adhesion evaluation and mechanical tests are performed.

During the crucial step, OMPMS molecules react with the hydroxyl-containing surface groups resulting in the formation of multiple covalent bonds between the remaining reactive Si-OCH_3 groups of OMPMS and the polymer surface. It is necessary to note that the silanisation process follows two concurrent reactions: (1) a fraction of the methoxysilane groups react with hydroxyl functions on the substrate and (2) the remaining groups cross-link each other resulting in three-dimensional polymerisation and growth of the organosiloxane layer. Presumably, terminal thiol groups protrude from the surface of this layer, the thickness of which can exceed tens of nanometers, constituting coupling sites for metal nanoparticles during the next step in which silver inks are deposited. These interactions determine strong adhesion between the layer of conductive inks and the polymer film. In the next sections we describe in more detail the experimental steps of SAL-functionalisation and, furthermore, silver binding through thiol chemistry.

Surface conditioning

Polymer preconditioning is necessary to increase the amount of OH-containing groups on the surface and, thus, to improve reactive capability of inherently chemically inert polymer surfaces. Hence, PDMS and PEN substrates were treated by direct-current discharge plasma at specifically selected conditions for each polymer.[19] Water contact angle (WCA) measurements confirmed activation of the surface indicating an enhanced surface wettability. Both hydrophobic PDMS (WCA = 118°) and slightly hydrophilic PEN (WCA = 80°) polymers were converted into superhydrophilic substrates (WCAs almost zero) by the plasma treatment. Immediate SAL deposition following plasma treatment is fundamental due to the interim effects of this process. Once OMPMS is deposited on the surface, the SAL-modified substrates are functional for at least 6 months.

Spin coating of SAL

In comparison to the slow and potentially dangerous vapour phase deposition of SALs,[19] whereby a substrate is placed in a closed atmosphere saturated with the vapours of reactive organosilane, liquid processing may be considered more rapid and practical from a manufacturing perspective. To demonstrate compatibility with wet coating technologies, the SALs have been deposited via spin coating, which is a widely used method with the ability to precisely control film thickness and uniformity. Moreover, spin coating reduces the SAL deposition time from hours to minutes producing similar

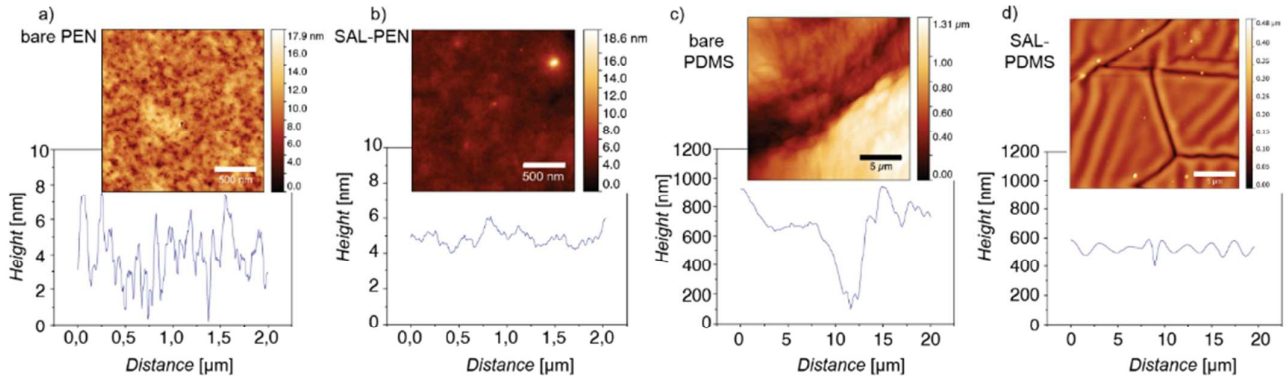

Figure 3. (a) AFM profiles and morphology of bare PEN (b) versus SAL-functionalised PEN. (c) Bare PDMS (d) versus SAL-functionalised PDMS. The SAL is deposited by spin coating of 6% OMPMS in MeOH.

multilayer structures as previously reported for the vapour-assisted approach.[19] However, commercially available alkoxysilanes are limitedly compatible with liquid-processing SAL formation due to their low boiling temperatures, low viscosity and high volatility; therefore, we opted for synthesising a MPTS-based oligomer with a higher molecular weight.

OMPMS was synthesised by means of partial condensation of methoxysilyl groups of MPTS in the presence of acetic acid in ethanol (EtOH) or methanol (MeOH) solutions (Figure 2). The molecular weight of the resulting oligomer was varied depending on the reaction conditions and appeared to be approximately 500-1000. These solutions were used for SAL deposition on PEN or PDMS substrates without any purification. Polymer substrate surfaces were modified by spin coating 30% (directly after the reaction) or 6% (5 times diluted) solutions of OMPMS.

Unlike surface modifications with a molecular SAM, SALs prepared from OMPMS have a number of advantages, such as stronger links to the surface due to numerous bonds of the anchoring methoxysilane groups and, consequently, the ability to form a denser and uniform layer with functional thiol groups located atop. This facilitates the reaction between the SAL and silver nanoparticles, which bind to the multiple thiol (SH) groups with increased efficiency.

According to atomic force microscopy (AFM) investigation of the surface morphology, a bare PEN substrate demonstrates a low root mean square (RMS) roughness of approximately 2–5 nm (Figure 3a). The surface was relatively smooth and homogeneous as confirmed by a series of AFM images taken at different locations. The samples showed similar morphology whether treated with 6% or 30% solutions of OMPMS, whereby a uniform functional organosilicon layer covered the whole polymer surface without any visible holes or cracks (Figure 3b). The SAL thickness was estimated to be at least 15 nm by AFM measurements (see Figure S2 in ESI), and the roughness was very close to that of bare PEN, varying from 1 to 2 nm. Given that the length of an OMPMS molecule is ca. 5 nm, the SAL in fact corresponds to a multilayer coating.

Figures 3c and 3d illustrate the morphology of a PDMS substrate before and after SAL-functionalisation, respectively. The local height variation of a bare PDMS surface was found to be 0.8 µm. After silanisation, this appeared completely covered with the SAL and, remarkably, more uniform producing an RMS of 35 nm and a height deviation of 150 nm. This finding indicates that the SAL smooths the polymer surface by filling any defects. We also note that this effect may contribute to the targeted adhesion improvement of the silver inks. Nevertheless, the inherent elasticity of PDMS polymers means that they can form surface microwrinkles during the course of substrate manipulations despite being covered with the SAL (Figure 3d).

Silver ink adhesion

To demonstrate enhanced reactivity of the surface, water-based and organic-based silver inks were screen printed over the SAL. It is assumed that the superficial thiol groups of the coupling layer interact with silver nanoparticles, which constitute the main body of the ink (PSI-211) and displace stabilising surfactants on the surface. Further sintering of the silver layer facilitated covalent bonds formation between –SH groups and silver atoms, which occurred simultaneously with solvent evaporation. In addition, we report that the silver ink with microparticles embedded in a polymer matrix (CRSN2442) can also benefit from the SAL interlayer, demonstrating significant adhesion improvement. Therefore, SAL modification of polymers appears to be compatible with a range of silver inks, independently of the size of silver (Ag) particles and the surrounding aqueous or organic media.

Binding of metal nanoparticle inks to PEN substrates is achievable by surface pre-treatment or by specific ink formulation in a relatively uncomplicated manner;[12] however, enhancement of metal adhesion to PDMS at a molecular level has rarely been reported as a result of the complexities involved in activating a surface with an extremely low surface free energy of about 20 mN/m.[22] Previously, we demonstrated modification of PDMS substrates with SALs using vapour deposition,[19] which enabled us to reach 85-95% adhesion of the silver inks. This notable result, however, was gained at the cost of a 2 hour deposition time, following which, over 70 hours were required to achieve approximately 100% adhesion. Herein we show that solution processes can enable the same

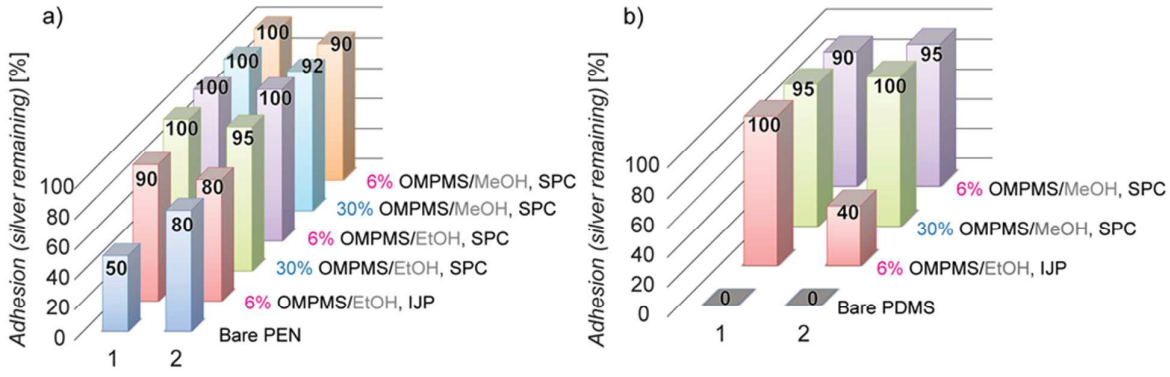

Figure 4. Evaluation of adhesion by tape test (0% - no adhesion, 100% - excellent adhesion) for aqueous (1) and organic-based (2) silver inks on (a) PEN and (b) PDMS substrates modified with inkjet printed (IJP) or spin coated (SPC) OMPMS self-assembled layers.

binding effect at significantly shorter times.

According to non-contact profile measurements, the thickness of aqueous and organic-based ink layers was 1.5±0.2 µm and 15.0±1.0 µm, respectively. In accordance with the standard crosshatch tape test, we observed an adhesion enhancement for both PEN and PDMS substrates after curing the ink. It was shown that modification of these polymers with SALs by spin coating increased the adhesion of both types of the silver inks by up to 90-100% (the remaining silver area after a tape test) compared to 50-80% for non-treated PEN and 0% for non-treated PDMS (Figure 4). On the other hand, a solvent present in the OMPMS ink did not have any impact on the final values of ink adhesion. Thus, the SALs spin coated from ethanol or methanol solutions exhibited almost equal adhesion improvements of up to 90-100% and, likewise, variations of the oligomer concentration in the solution (6% vs. 30%) produced similar results.

Inkjet printing of SAL

The formulation of inks used for inkjet printing typically presents a challenging task since this technique must adhere to and be compatible with the rheological requirements and chemical properties of the printing material. Thus, the most frequent setback associated with inkjet printing is the obstruction of micrometer head nozzles by solid components in the ink. Besides complying with the demands of the printing process itself, the ink composition must support necessary wetting, easy drying and curing of the printed structure, resulting in a uniform and continuous layer. Deposited on a flexible substrate, the ink should have appropriate mechanical properties to sustain large strain stress amongst other types of deformation without detaching off the substrate. All these aspects define performance characteristics of a printed functional layer.

As an alternative to conventional inkjet printing, wherein the material is typically deposited from nanoparticles dispersed in a solvent, reactive inkjet printing (RIJ) generates a product in situ on the substrate with components of the reaction digitally deposited in the desired pattern.[23] This relatively new approach has supported reactive printing of various functional materials such as silver,[24] copper[25] nickel,[26] gold nanoparticles,[27] PEDOT:PSS,[28] polyurethanes[29] and electroactive polymers.[30]

Here, we introduce reactive deposition of a thiol-rich organosilicon SAL aimed at functionalising polymer surfaces. Alcohol solutions of OMPMS possess appropriate characteristics for application as reactive inks in inkjet printing. Measured viscosities of 6% and 30% OMPMS solutions were 1.22±0.02 mPa·s and 1.14±0.02 mPa·s, respectively. Measured liquid surface tension of 6% and 30% OMPMS solutions was 22.7±0.2 mN/m and 26.4±0.2 mN/m, respectively, which is in the vicinity of the recommended upper range for inkjet inks. Nonetheless, printing was only attainable with a 6% OMPMS alcohol solution and all efforts to utilise a 30% solution were unsuccessful, most likely due to the limited setting capabilities of the print heads used. The Z number of ethanol inks estimated by Fromm formula[31] was established to be 25.15 for

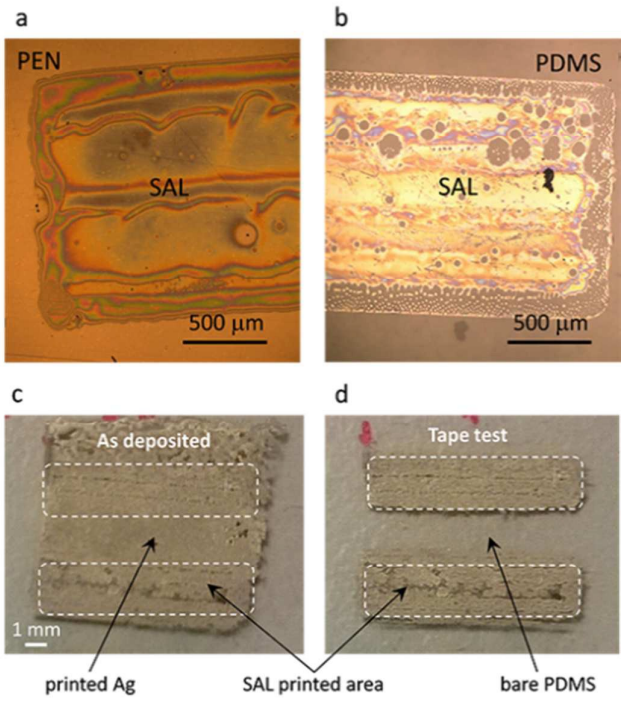

Figure 5. Optical images of inkjet printed SAL (using 6% OMPMS in ethanol) on (a) PEN and (b) PDMS substrates. The thickness of printed SAL is 250±50 nm. Screen-printing of aqueous silver ink over the SAL pattern on PDMS results in controlled local adhesion as shown (c) before and (d) after the tape test. The overall thickness of silver/SAL film is 1.3 ± 0.1 µm.

6% and 30.2 for 30% solutions, taking into account their densities of 827±2 kg/m^3 and 904±2 kg/m^3, respectively. Thus, the Z number of a 6% solution (25.15) was nearer to the optimal range for inkjet printing (Z = 2 – 14), as opposed to the 30% solution (30.2), accounting for the differences in printing success. Deposition of 6% solution of OMPMS in ethanol on plasma treated PEN and PDMS resulted in structures with sufficient uniformity and pattern fidelity (Figure 5). The printability on PEN is evidently better than that on a PDMS substrate, most likely owing to a higher content of hydroxyl groups on the surface rather than the property of the solution. The observed defects and mediocre uniformity of the SAL on PDMS (Figure 5b) can be attributed to a more challenging surface activation of siloxanes due to their high chemical stability.

Similar to spin coating, inkjet printing with a 6% OMPMS solution lead to noticeable adhesion enhancement of the silver ink screen printed over the SAL. For both aqueous and organic inks, adhesion reached 80-90% of the remaining silver in the case of PEN substrate and 100% in the case of PDMS for aqueous silver ink. The printed structure was highly conductive with a consistent resistivity of 20±5 mΩ·cm even after the tape test. A visual demonstration of the difference between silver ink retention on the functionalised and non-functionalised PDMS surface is presented in Figures 5c and 5d. The regions covered with SAL were able to retain the silver coating, whilst

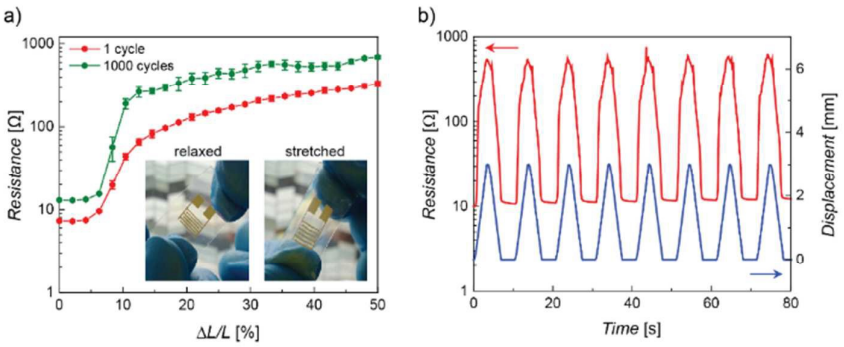

Figure 6. Resistance measurements of organic silver ink printed on SAL-modified PDMS upon (a) stretching before and after 1000 cycles of 30% elongation, and (b) repeated mechanical deformation at 30% of strain. The inset images show the printed silver structure on SAL-PDMS in the relaxed and stretched states.

the silver layer on the bare surface detached during the tape test.

Electrical and mechanical reliability

As previously discussed, the ability of conductors printed on polymer substrates to sustain mechanical deformations is a key property in the development of flexible devices. For practical implementation, printed structures should maintain their performance characteristics upon stretching, bending or twisting and possess strong adhesion to the substrate. Here we demonstrated that the silver patterns printed on SAL-modified substrates have a relatively low sheet resistance of 80±5 mΩ/sq for both ink types on the PEN substrate and 190±10 mΩ/sq for organic-based ink on the PDMS substrate, which is comparable to 100±20 mΩ/sq of the aqueous silver ink on the bare PEN substrate. Note that the adhesion of the inks on bare PDMS was negligible and the resistance was not recorded.

The printed structures on SAL-functionalised PEN have a reversible bending radius of 10 mm, which corresponds to approximately 0.6–0.7% of the tensile strain with less than 1.5% of the relative resistance change (see Figure S3 in ESI). Note that such deviations can be further reduced by using silver ink with enhanced mechanical properties. Furthermore, the silver structures on SAL-modified PDMS showed no increase in resistance at 6% of elongation as established by stretching studies and they were, additionally, able to conduct the current at a relatively high level at a greater elongation of 50% (Figure 6a). Furthermore, the silver tracks on PDMS exhibited excellent adhesion and were capable of sustaining multiple stretching cycles without apparent delamination (Figure 6b).

The resistance during repetitive stretching reproducibly follows the cycle run and returns to the base value in a relaxed state. Perhaps, an increase in resistance with stretching is caused by the formation of cracks in the silver layer, which is commonly observed on elastomer substrates.[32,14a] Owing to its predictable resistance alterations upon deformation, the conductive structures on SAL-PDMS can be potentially applied to circuits encountering a moderate mechanical stress.

Experimental Section

Materials. EtOH, MeOH and MPTS were purchased from Sigma-Aldrich and used according to the manufacturer's instructions. Oligomerisation of MPTS was performed in the presence of glacial acetic acid using the procedure described: a solution of MPTS (1.0 g, 5 mmol), acetic acid (0.3 g, 5 mmol) and 2 mL of methanol or ethanol was stirred at 80 °C in an oil bath for 45 minutes, following which, the oligomer was used without any purification as a 30 wt% solution or diluted to 6% with the corresponding alcohol. According to the gel permeation chromatography (GPC) data, the molecular weight of oligomers obtained was ~500 - 1000 Da. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 0.73 – 0.83 (m, 2H, Si-CH_2-CH_2-CH_2-SH), 1.30 – 1.42 (m, 1H, Si-CH_2-CH_2-CH_2-S*H*), 1.64 – 1.86 (m, 2H, Si-CH_2-CH_2-CH_2-SH), 2.48 – 2.65 (m, 2H, Si-CH_2-CH_2-CH_2-SH), 3.58 (s, 6H, Si-O-CH_3) – see Figure S1 in ESI. Ultrapure water obtained from an Akvilon deionizer D-301 system (Russia) was used for cleaning of the substrate. The flexible substrate was a 125 µm thick poly(ethylene naphthalate) foil (PEN, Teonex Q65FA, Teijin DuPont Films, Japan) and the stretchable substrate was a 1 mm thick polydimethylsiloxane (PDMS) layer obtained from a commercially available Sylgard 184 silicon elastomer kit (Dow Corning, USA), used as described by the manufacturer. The aqueous silver ink PSI-211 was supplied by PChem, USA and the organic-based silver ink CRSN2442 was purchased from Sun Chemical, USA.

Plasma modification. Oxygen plasma treatment of the polymer substrates was carried out using a direct-current discharge and vacuum set-up described elsewhere.[19] All samples were washed with deionised water immediately following plasma treatment to facilitate removal of electrical charge from the surface.

SAL deposition. Subsequent to plasma treatment, liquid-processed chemical modification of the polymer substrate surfaces was performed by spin coating for large areas and inkjet printing for local deposition. Spin coating of 6% and 30% OMPMS solutions in methanol or ethanol was performed using a Laurell WS-650Mz-8NPP Spin Processor at the speed of 2000 rpm for 2 minutes. Inkjet printing of 6% OMPMS solution in

ethanol was achieved using a Dimatix DMP2831 inkjet printer with a 10 pL print head on a hot plate at 60 ºC.

Silver deposition. The test structures for adhesion evaluation were screen printed using a EuroPrint hand screen printer, by means of a polyester screen mesh of 120 threads/cm with a thread diameter of 35 µm and a squeegee with a hardness of 75 Shore A. The wet inks were cured in a drying oven at 120 °C for 10 minutes (PSI-211) and at 150 °C for 30 minutes (CRSN2442).

Characterization. ^{1}H NMR spectra were recorded on a Bruker WP 250 SY spectrometer (250.13 MHz). GPC analysis was carried out using an Akvilon Staier liquid chromatograph on Phenomenex columns (USA). These were filled with Phenogel sorbent consisting of a pore size of 500 Å and tetrahydrofuran (THF) was used as the eluent. The molecular weight was determined using calibration according to linear polystyrene standards. Static WCA measurements were performed using a Kruss EasyDrop drop shape analyzser (Germany). AFM studies were performed with a NT-MDT Solver NEXT instrument (Russia) in a semi contact mode under ambient conditions. Commercially available standard silicon probes Brücker FESPA with resonance frequency of 70 kHz were used. The printed samples were inspected by optical microscopy using a Carl Zeiss AxioImager A2m. The thickness was measured by means of a white-light interferometer KLA-Tencor MicroXAM-100. The adhesion was evaluated by scratch and tape tests based on the standard BS 3900/ASTM D-3359/DIN 53151/ISO 2409. The electrical resistance values were calculated based on two-point probe measurements using an Agilent 34410A digital multimeter.

Conclusions and outlook

In conclusion, this study reports a simple and versatile method for the improvement of silver ink printability and adhesion on different polymer substrates by building a thiol-reach organosilicon SAL on the surface of flexible PEN or stretchable PDMS substrates by means of solution processing. For this purpose, a novel functional MPTS-based oligomer (OMPMS) was prepared under active media conditions. Spin coating of OMPMS was demonstrated to cover large areas and produce uniform coatings, whereas inkjet printing of 6% OMPMS ethanol inks enabled a direct-write deposition of the required pattern. With its active surface rich in SH groups, SAL decoration of polymer substrates resulted in significant adhesion enhancements for both aqueous and organic-based silver inks, approximating 100% for both polymer substrates studied. Investigations of the resistance changes under mechanical deformations, such as bending or stretching, confirmed advanced stability of the printed silver conductors on the polymer substrates. Taking into account that not only silver but many other metals such as gold, copper and nickel are able to react with thiols, we predict that such SAL modifications may be useful for printing of the other metal inks as well. Overall, the printability of functional SALs demonstrated in this report offers the potential for scaling-up and R2R manufacturing advantages, paving the way towards mechanically reliable all-printed electronic devices.

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