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Ryspayeva, Assel; Jones, Dr Thomas D.A.; Khan, Sadeque Reza; Esfahani, Mohammadreza Nekouie; Shuttleworth, Matthew P.; Harris, Russell A.

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Selective Metallization of 3D Printable Thermoplastic Polyurethanes

ASSEL RYSPAYEVA¹, THOMAS DAVID ARTHUR JONES², SADEQUE REZA KHAN¹,
MOHAMMADREZA NEKOUIE ESFAHANI³, MATTHEW P. SHUTTLEWORTH³,
RUSSELL A. HARRIS³, ROBERT W. KAY³, MARC P. Y. DESMULLIEZ¹, (Senior Member, IEEE),
AND JOSE MARQUES-HUESO¹

¹School of Engineering and Physical Sciences, Nature Inspired Manufacturing Centre (NIMC), Heriot-Watt University, Edinburgh EH14 4AS, U.K.

²School of Science and Engineering, University of Dundee, Dundee DD1 4HN, U.K.

³Future Manufacturing Processes Research Group, School of Mechanical Engineering, University of Leeds, Leeds LS2 9JT, U.K.

Corresponding author: Jose Marques-Hueso (j.marques@hw.ac.uk)

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ABSTRACT This paper presents a selective metallization method for the newly developed 3D printable thermoplastic polyurethane elastomers (TPU): FilaFlex[®], SemiFlex[™], PolyFlex[™], and NinjaFlex[®]. Silver nanoparticles were fabricated *in-situ* by photo-reduction on the surface of TPUs and acted as catalysts for copper ion adsorption. This method demonstrates the successful fabrication of copper patterns on flexible TPU filaments. Furthermore, Polyflex[™] and acrylonitrile butadiene styrene (ABS) filaments printed in the same part have been used to enable selective electroless plating directly on Polyflex[™] material. Electroless copper deposited onto Polyflex[™] has a sheet resistance of $(139.4 \pm 7.2) \text{ m } \Omega / \square$ and a copper conductivity of $(1.1 \pm 0.1) \times 10^7 \text{ S/m}$ that is comparable with bulk copper. Copper-plated Polyflex[™] interconnects were fabricated as a proof of concept demonstrators.

INDEX TERMS Thermoplastic polyurethane elastomers (TPU), fused filament fabrication (FFF), 3D printing, additive manufacturing (AM), hybrid-AM, silver nanoparticles (Ag NPs), electroless copper plating, FilaFlex[®], SemiFlex[™], PolyFlex[™], NinjaFlex[®].

I. INTRODUCTION

Digitally printed electronics using additive manufacturing (AM) has been steadily developing over the last three decades towards the manufacture of electronics components, devices and systems [1], [2]. AM such as 3D printing does not require high vacuum, high voltage deposition processes and multi-stage photolithography to produce conformable electronics [3], [4]. With the development of flexible electronics, metallized polymer films have gained an increased interest from the microelectronic packaging, computer technology and biomedical engineering community [5], [6]. Whilst a number of printing techniques, including ink-jet [7] and screen printing [8], have been adapted to print interconnects and circuitry on flexible substrates, fused filament fabrication (FFF) is currently one of the most commonly applied methods for printing plastic parts such as flexible polymeric

substrates [4]. FFF printing works by the controlled extrusion of thermoplastic filaments onto a build platform using a layer-by-layer motion [9]. Although FFF is an attractive, simple and affordable manufacturing method to produce plastic parts and structures at relatively high speed [10], it is mostly limited to a certain number of thermoplastic filaments such as polycarbonate (PC), acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) [4], [9]. Nevertheless, new materials with superior flexible properties are constantly being researched, which include thermoplastic polyurethane elastomers (TPU). TPUs are multi-phase block copolymer that consists of rigid hard segments, diisocyanate and short chain extenders, and rubbery soft segments, commonly polyester or polyether-based, which are linked by hydrogen bonds [11]. These filaments mainly consist of polyurethane and additives to aid the printing process. Polyurethanes are attractive materials for flexible and stretchable electronics due to their outstanding elongation capacity, chemical resistance, thermal stability and versatility in applications [12]. Due to its wide

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mechanical and chemical properties, polyurethane finds applications in rigid and flexible substrates, adhesives, flame retardants, automobiles and biomedical applications [12]. These new TPUs still have to be tested for performance and behavior during the printing process [13].

Whilst thermoplastic conductive filaments are continuously being developed for FFF printers [14], the electrical conductivity of these thermoplastic composite filaments remain generally low compared to their bulk metal counterparts [15]. In the pursuit of achieving 3D printing of multifunctional materials, hybrid-AM has therefore become one of the approaches to introduce metal parts on plastics by applying post-processing techniques [16], [17]. These include electroless plating and electroplating of 3D printed parts produced by stereolithography, laser sintering and FFF printers [18], [19]. Whilst electroplating requires a deposition of an additional metal layer on non-conductive surfaces, electroless plating allows metallization of 3D geometries with simpler equipment, reducing costs and increasing throughput [3], [20]. Therefore, post-processing of the TPUs may open new opportunities to create a bespoke circuitry and interconnects onto non-conductive flexible surfaces. Circuit structuring of the flexible polymers can be performed by using a laser direct structuring (LDS) [21] or laser-induced selective activation (LISA) [22]. However, these techniques frequently use expensive activators which include palladium [22], [23].

This article demonstrates the development of a direct and selective metallization method for TPU filaments and 3D printed TPU parts through surface treatment and electroless copper plating. This method does not require expensive vacuum processing, complex equipment and allows metallization of flexible substrates. Copper patterns could be formed directly on the 3D printed plastic structures with a good selectivity. Moreover, conductive segments could be realized on insulators, by printing multiple materials and plating them selectively with reduced number of steps. We study four recently developed TPU filaments: FilaFlex[®] (Recreus), SemiFlex[™] (Ninjatek), PolyFlex[™] (Polymaker) and NinjaFlex[®] (Ninjatek). The method involves the formation of photosensitive AgCl and photo-reduction of Ag ions to Ag nanoparticles (NPs) on the surface of the polyurethane material. These Ag NPs are shown to act as a catalysts for copper ion adsorption during the electroless copper plating [24]. Conductivity of the resulting metal films is comparable to values obtained in bulk metal.

II. MATERIALS AND METHODS

In this study, four flexible 1.75 mm diameter TPU filaments were tested: FilaFlex[®] (Recreus), SemiFlex[™] (Ninjatek), PolyFlex[™] (Polymaker) and NinjaFlex[®] (Ninjatek). TPU filaments have outstanding elongation properties as shown in Table 1. A test scale for Shore hardness is A, which corresponds to a scale used for soft plastics in ISO 7619-1 [25]. Selective metallization method was applied

TABLE 1. Material properties.

	FilaFlex [®]	SemiFlex [™]	PolyFlex [™]	NinjaFlex [®]
Material	Polyether-poly-urethane	Poly-urethane	Poly-urethane	Poly-urethane
Shore hardness	82A	98A	95A	85A
Elongation (%)	665	600	330	660

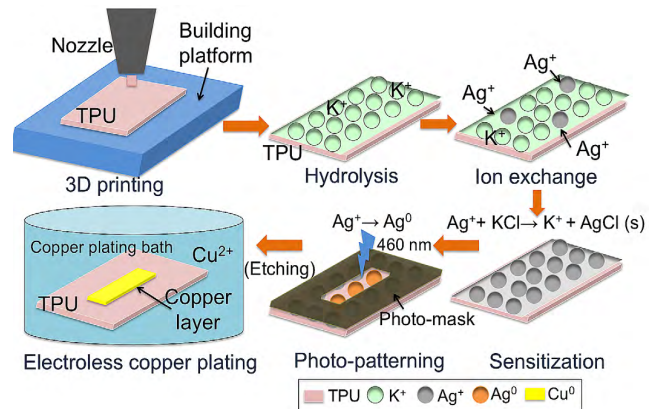


FIGURE 1. Schematic steps of selective metallization of TPU material. Clockwise: 3D printing of the required structure, hydrolysis, ion exchange, sensitization, photo-patterning and electroless copper plating.

directly to TPU filaments as well as to the 3D printed parts. Fig. 1 shows the process used to achieve a metal pattern on the TPU surface. 3D parts were also produced from the PolyFlex[™] filament.

A. AG NPs SYNTHESIS AND PHOTO-PATTERNING

TPU filaments were cleaned in D.I. water using ultrasonic bath for 2 minutes. Samples were then immersed into a 15 M potassium hydroxide (KOH, Fisher Scientific, UK) solution at 50°C for 2 hours with stirring. After rinsing with D.I. water, samples were immersed into 0.1 M silver nitrate (AgNO₃, Fisher Scientific, UK) solution for 20 minutes at room temperature (RT). TPU samples were then rinsed with D.I. water and dried. Prior to the photo-patterning step, samples were immersed into a solution of 0.01 M potassium chloride (KCl, Fisher Scientific, UK) for 1 minute.

Photo-patterning was performed using a 3-minute LED exposure with a high-power (1 W) LED at 460 nm having a light intensity of 12 W/cm². A chromium on glass mask was used to selectively pattern TPU samples. The removal of the unexposed and unwanted Ag ions was performed through a wet etching with 18% ammonia solution (NH₃, Fisher Scientific, UK) for 3 minutes following by 5% sulfuric acid (H₂SO₄, Fisher Scientific, UK) for 1 minute with a D.I. rinse between each etching step. The application of etchants to the entire substrate surface removes unprocessed Ag ions weakly bound to the substrate with little removal of the Ag metal [24]–[26] and, therefore, allow successful selective electroless copper plating.

B. ELECTROLESS COPPER PLATING

Electroless copper solution was prepared by dissolving 6 g of copper sulfate (98%, Sigma Aldrich), 8 g of sodium hydroxide (98.5%, Acros Organics), and 28 g of potassium tartrate (99%, Fisher Scientific) into 200 ml of DI water. Before electroless plating, 12 mL of the concentrated solution was diluted with DI water in the ratio of 1:1 and 2 ml of formaldehyde (37 %, Acros Organics) was added. TPU samples were immersed into electroless copper bath and plated at 30°C for 20 minutes.

C. CHARACTERIZATION

Fourier-transform infrared spectroscopy (FTIR) was obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrometer operated in attenuated total reflection mode. Optical images were obtained with LEICA CTR 6500 microscope. Scanning electron microscopy (SEM) was performed with a Quanta 3-D FEG. Ag NPs and copper grains average sizes (diameters) were measured using the Fiji (based on ImageJ) open source image processing software. Resistance was measured with SIGNATONE S-1160 two-point probe station. Sheet resistance measurement was performed on metallized PolyFlex™ TPU square samples (20 mm × 20 mm) using a Jandel Model RM3000 four-point probe station (England). The conductivity was calculated as the inverse of the resistivity, ρ which was found from the product of sheet resistance, R_s and the copper thickness, t :

$$\rho = R_s \times t \quad (1)$$

Copper thickness was measured using Dektak³ Stylus profilometer. The quality of the metal plating adhesion was tested using the IPC-TM-650 scotch-tape test on the square samples [27]. Pressure sensitive tape was pressed across the metallized PolyFlex™ TPU square samples of 20 mm × 20 mm size. The tape was pulled rapidly and visually examined for any material removal from the specimen. The test was performed three times on three different samples. The percentage of the removed copper from the PolyFlex™ substrate was evaluated using digital image processing. Digital images of the scotch-tape with the removed copper were converted to 8-bit type, and segmented by thresholding to locate the regions of the removed copper using Fiji. Black and white (BW) images were evaluated in MATLAB (The Math-Works Inc.) by counting all the dark pixels and calculating the percentages of the removed copper.

D. PRINTING OF 3D PARTS

Production of 3D parts was performed using a MakerBot Replicator 2X (MakerBot Industries, LLC, Brooklyn, NY). The building platform was covered with a painter's tape (Scotch Blue 2093EL tape, 3M) for adhesion. The thickness of the individual layer was set to 0.2 mm with 100 % infill. A PolyFlex™ substrate was printed with an extrusion temperature of 230 °C and a bed temperature of 60 °C.

3D structure of a PolyFlex™ part on ABS substrate was printed with an extrusion temperature of 230 °C and 100 °C bed temperature.

III. RESULTS AND DISCUSSIONS

A. SURFACE TREATMENT

The general chemical structure of the polyurethane is shown in Fig.2a, which consists of the hard and soft segments linked through the –NH-(C = O)-O- urethane group [28]. The surface of the TPU filaments is expected to be modified by the highly alkaline KOH solution, as demonstrated in [24], [26] by FTIR measurements of polymer substrates. For this reason, FTIR scans have been applied here for the four TPU filaments at different stages of processing, as shown in Fig. 2. Spectra of the TPU materials were taken for untreated samples, samples treated with KOH and samples treated with AgNO₃. The exact chemical composition of the filament is unknown, however, it is known that Filaflex is a polyether-polyurethane [29]. Since the FTIR spectra in Fig. 2 d-f are similar to the Filaflex spectrum in Fig. 2c, it is presumed that TPU filaments exhibit polyether-based polyurethanes characteristics. Polyether-polyurethanes are highly resistant to hydrolysis and bacteria and, therefore, are desirable for medical applications [30]. However, under severe conditions such as strong alkali treatment, polyether polyurethane can undergo hydrolysis, which occurs at urethane linkage [31], [32]. Urethane is a derivative of the amide and, therefore, undergoes the same hydrolysis mechanism as for amides, Fig.2b [33]. Samples treated with silver nitrate have similar peaks as samples after hydrolysis since potassium ions exchanged with silver ions (Fig. 2b) do not lead to changes in FTIR spectra [24].

The absorption band at around 1725 cm⁻¹ is due to a stretching vibration of amide band (– C = O) of urethane [34]. Secondary urethanes absorb strongly at 1525 cm⁻¹ due to –CNH- group vibration [35]. The vibration band at 1700 cm⁻¹ is attributed to hydrogen bond between N-H and C=O groups in the hard segment [36], [37]. Esters, ethers and carboxylic groups absorb strongly in the range between 1300 cm⁻¹ and 1000 cm⁻¹ due to C-O stretching vibrations [34]. The peak at 1725 cm⁻¹ (amide band) that is present in the untreated samples is attenuated for all treated samples, indicating that the urethane linkage is broken due to hydrolysis [30], [38]. Moreover, peaks at 1162 cm⁻¹ (C-O) and 1139 cm⁻¹ (C-O) are also attenuated, which indicates that hydrolysis may also take place in the various functional groups of the soft segments (e.g hydrolysis of esters) in the polyurethane structure [32], [38]. The complete cleavage of the above mentioned peaks is observed in SemiFlex™ and PolyFlex™ (Fig. 2 d, e), which suggests that these TPU filaments are more susceptible to alkaline attack.

Prior to light exposure, a sensitization step was utilized to accelerate formation of Ag NPs during the photo-reduction step. Silver treated filaments were immersed into solution of 0.01 M KCl in ethanol:water (3:1) to form highly photosensitive AgCl. This sensitization step was successfully demonstrated and discussed in previously published work [24], [26].

The distribution of NPs across a surface influences the quality of the further processing by electroless copper [24], [26]. The NP dispersion is a figure of merit that can

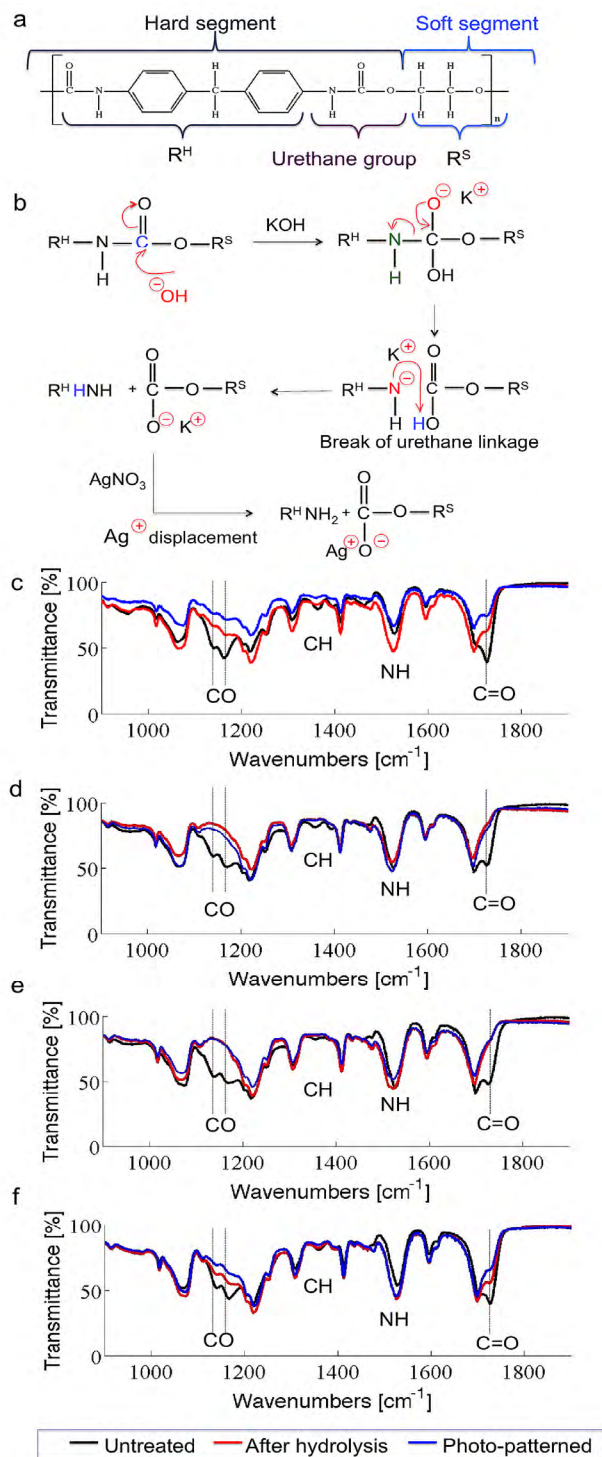


FIGURE 2. a) A schematic of a polyurethane structure that consists of hard and soft segments, (b) a schematic for hydrolysis and ion exchange mechanism, where potassium ions are displaced with silver ions. R^H and R^S stand for functional groups of the hard and soft segments of the polyurethane, respectively. FTIR spectra measured for filaments: c) FilaFlex[®], d) SemiFlex[™], e) PolyFlex[™] and f) NinjaFlex[®] at different process stages.

characterize NP treatment performance and can be evaluated from SEM images of Ag treated surfaces [26]. Fig. 3 shows SEM images of the photo-reduced Ag NPs on TPU surfaces

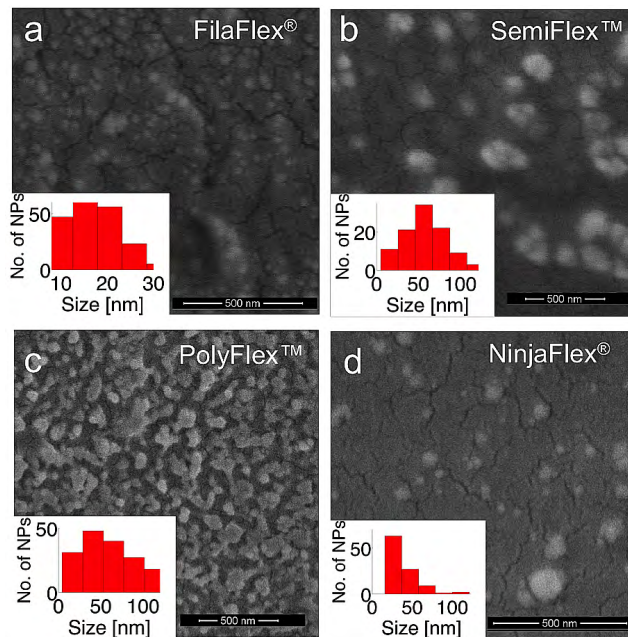


FIGURE 3. SEM micrographs showing photo-reduced Ag NPs on TPU filaments: a) FilaFlex[®], b) SemiFlex[™], c) PolyFlex[™], d) NinjaFlex[®]. The insets show size distribution of Ag NPs.

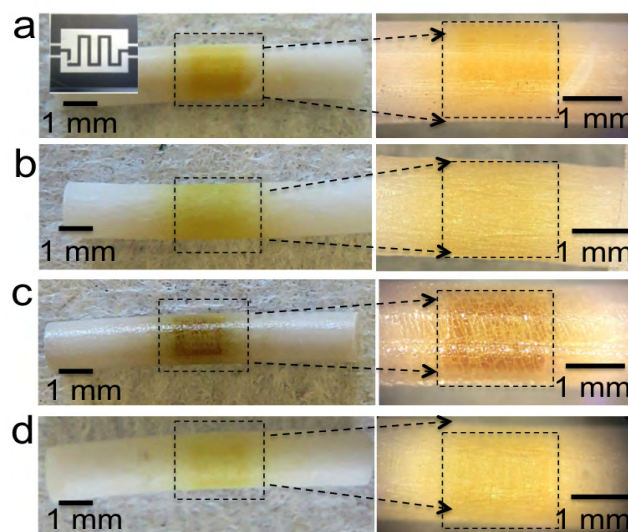


FIGURE 4. Images of TPU filaments after photo-reduction: a) FilaFlex[®], b) SemiFlex[™], c) PolyFlex[™] and d) NinjaFlex[®]. The inset shows the photo-mask used during the LED exposure.

with the insets displaying the histogram plots of Ag NPs size distribution. The average size of Ag NPs reduced on FilaFlex[™] (label a Fig. 3) is 17 nm ± 5 nm. Ag NPs are monodisperse with a polydispersity index of 0.29, covering the polymer surface uniformly.

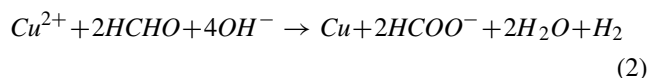
The average sizes of Ag NPs formed on Semiflex[™], PolyFlex[™] and NinjaFlex[®] filaments (label b, c, d in Fig. 3) are 58 nm ± 27 nm, 68 nm ± 41 nm and 38 nm ± 20 nm, respectively. Ag NPs appear spherical in shape forming agglomerates. The nanoparticles have a broad size distribution with polydispersity indices of 0.47, 0.6 and 0.52,

respectively. Ag NPs photo-reduced on PolyFlex™ are more densely packed as compared to nanoparticles formed on Semiflex™ and NinjaFlex®. High nanoparticle densities provide higher surface coverage and therefore, are favorable for uniform and successful electroless copper deposition [26].

Fig. 4 shows images of the photo-reduced patterns produced on TPU filaments where silver ions were successfully reduced on all four TPU filaments. The photo-reduced Ag NPs appear yellow in color in FilaFlex®, Semiflex™ and NinjaFlex® samples. The pattern on PolyFlex™ shows a brown color which indicates the formation of a high concentration of Ag NPs [39], [40]. This could be due to a more successful hydrolysis, which resulted in a large Ag ions density. Therefore, the pattern on PolyFlex™ is more well defined compared to the patterns on others filaments.

B. ELECTROLESS COPPER METALLIZATION OF TPU FILAMENTS

After the photo-reduction step, the TPU filaments were immersed into electroless copper bath. Ag NPs act as catalytic centers for copper ions adsorption [41]. Electron transfer to the adsorbed copper ions on the silver seeds results in the deposition of copper metal on the catalytic substrate. Equation (2) shows an overall reaction for the electroless copper deposition with formaldehyde (HCHO) as a reducing agent [42], [43]:



The deposited copper metal then serves as a seed layer for subsequent copper ion adsorption and process repeats [44].

Fig. 5 shows SEM images of copper layers deposited onto TPU filaments and insets depicting the average grain size distribution. Copper layers have a granular structure covering TPU surfaces uniformly. The average sizes of the copper grains are $0.6 \mu\text{m} \pm 0.4 \mu\text{m}$, $0.3 \mu\text{m} \pm 0.1 \mu\text{m}$, $0.2 \mu\text{m} \pm 0.1 \mu\text{m}$, $0.4 \mu\text{m} \pm 0.1 \mu\text{m}$ for FilaFlex™, SemiFlex™, PolyFlex™ and NinjaFlex®, respectively. Copper layers on all samples are shown to have voids between the grains. These voids may form due to hydrogen release during the simultaneous reduction of copper and hydrogen [45], which results in trapping of hydrogen gas bubbles in copper grains forming voids [46]. Copper layer formed on PolyFlex™ has small grains that packed more densely than other copper depositions. Its higher density stems from the high amount of Ag NPs in the PolyFlex™ polymer, see Fig. 3, which creates more sites for copper ion adsorption.

Fig. 6 shows images of TPU filaments after electroless copper plating. The patterns on FilaFlex®, SemiFlex™ and NinjaFlex® filaments are less defined than on the PolyFlex™ filament. The copper pattern on PolyFlex™ resulted in a better-defined structure with a resistance of $34 \pm 9 \Omega$, while the resistances of the metal layers on the other filaments ranged in the kΩ. Therefore, PolyFlex™ was the most suitable material choice for

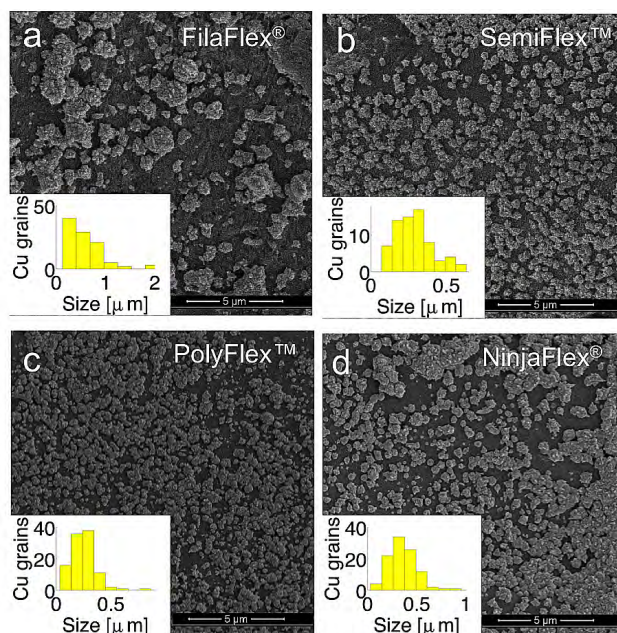


FIGURE 5. SEM micrographs showing electroless copper layer on TPU filaments: a) FilaFlex®, b) SemiFlex™, c) PolyFlex™, d) NinjaFlex®. The insets show size distribution of Cu grains.

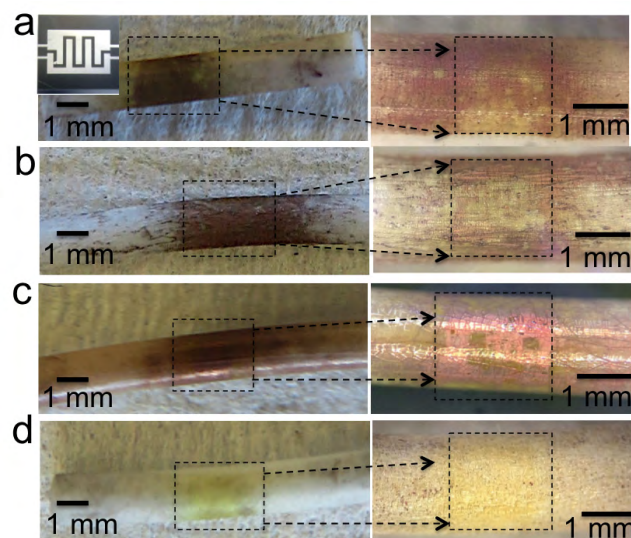


FIGURE 6. Images of TPU filaments after electroless copper plating: a) FilaFlex®, b) SemiFlex™, c) PolyFlex™ and d) NinjaFlex®. The inset shows photo-mask used during the LED exposure.

selective metallization of 3D printed parts, presented in the section C.

C. SELECTIVE METALLIZATION OF 3D PRINTED PARTS

A sheet resistance of $139.4 \pm 7.2 \text{ m}\Omega/\square$ was measured for the metallized 3D printed PolyFlex™ square samples, which is in agreement with previously reported values [3], [47]. Copper conductivity is calculated as $(1.1 \pm 0.1) \times 10^7 \text{ S/m}$ for grown thickness $(0.6 \pm 0.1) \mu\text{m}$, which is comparable to bulk copper values ($5.9 \times 10^7 \text{ S/m}$). Fig. 7 a, b shows

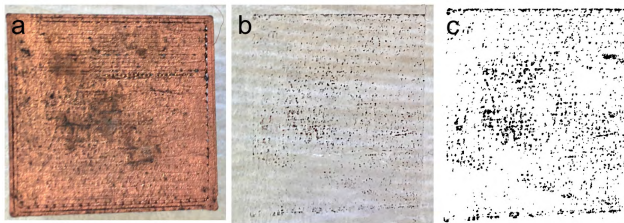


FIGURE 7. Images of a) the metallized PolyFlex™ after IPC-TM-650 scotch-tape test, b) tape with the removed copper, c) conversion of the tape image to the BW binary image. Black color indicates the removed copper by the scotch-tape.

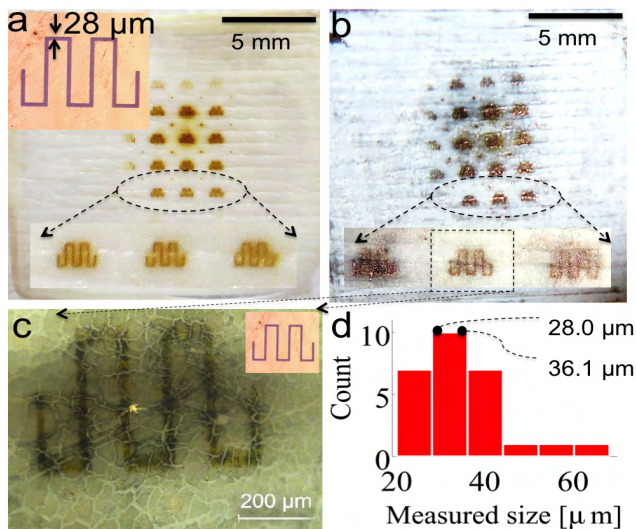


FIGURE 8. Images of the 3D printed PolyFlex™ substrate with features: a) after photo-patterning and b) after electroless copper plating, c) a feature under the optical microscope; and d) a distribution of the measured pattern size. The insets show the photo-mask with the $28\ \mu\text{m}$ feature size.

optical images of the metallized PolyFlex™ square sample after a scotch-tape test and a tape with the removed copper. Fig. 7c shows a BW binary image of the tape image. The black color indicates the removed copper from the surface of the metallized Polyflex™. The average percentage of the copper removed by the tape for the three tested samples is 7.3% from the surface area of $20\ \text{mm} \times 20\ \text{mm}$.

Fig. 8 shows images of the patterns fabricated on the 3D printed substrates made from the PolyFlex™ filament. The results show selective metallization where electroless copper plates on the catalyzed surfaces. Fig 8d shows a distribution of the measured feature sizes. The majority of the measured feature sizes are between $28\ \mu\text{m}$ and $36.1\ \mu\text{m}$, whereas the actual feature size on the photo-mask is $28\ \mu\text{m}$. The smallest and largest sizes measured were $20\ \mu\text{m}$ and $64\ \mu\text{m}$, respectively which highlights that some downsizing and enlarging of the feature size may occur.

The metallization selectivity was further studied and Fig. 9 shows images of the photo-patterned and copper metallized features on the Polyflex™ substrate. Fig. 9 (d) shows the magnified copper patterns, in which a relatively well-defined boundary between the copper and the

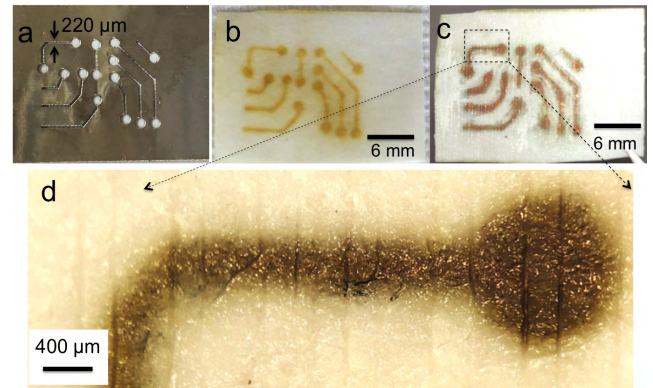


FIGURE 9. Images of a) a laboratory-made photo-mask, b) PolyFlex™ substrate with features after photo-patterning and c) after electroless copper plating, d) a feature under the optical microscope.

polymer is revealed. However, the resultant copper feature size ($\approx 449.2\ \mu\text{m}$) has enlarged more than twice the size of the photo-mask feature ($220\ \mu\text{m}$).

Conductive segments could be realized on insulators, by printing multiple materials. As a demonstration, Fig. 10a shows images of the 3D printed PolyFlex™ pattern onto an ABS substrate after the LED exposure. ABS undergoes the same treatment as PolyFlex™, however, due to the lack of Ag ion exchange with ABS, the etching step to remove unwanted silver ions is not required. Therefore, by submerging the photoreduced Ag-Polyflex™-ABS 3D structure into the electroless copper bath, copper plated selectively on the PolyFlex™ part only with a resistance $5 \pm 1\ \Omega$, leaving ABS unaffected, Fig. 10b. Hence, plating could be performed selectively between the two polymer materials.

Fig. 10d shows PolyFlex™ pattern printed on the ABS, which is copper plated directly after silver nitrate treatment, but without a prior LED exposure. Therefore, it is possible to metallize PolyFlex™ on ABS directly in a more environmentally friendly process that negates harmful etchants and with fewer numbers of steps.

D. COPPER-PLATED POLYFLEX™ INTERCONNECTIONS

As a demonstration, copper-plated PolyFlex™ parts were adhered using a glue to a hand prototype, which was printed from PolyFlex™ filament, and acted as interconnections between a motor and a motor driving circuit (label a, b Fig. 11). The wires from the motor driving circuit were connected with the PolyFlex™ interconnects by scotch tape. Arduino Nano 3.0 (ATmega328) microcontroller is used to control the rotation of the DC motor (Q4SL2BQ280001), which is connected to a finger of the hand. The pulse width modulation (PWM) feature of the microcontroller is used to regulate the motor speed. Furthermore, a totem pole structure using PMF370XN N-channel MOSFET is adopted to control the bidirectional rotation of the DC motor. Therefore, when the motor rotates upwards it drives the finger in the same direction and, when the motor rotates downwards it will then drive the finger down. Fig. 11 c, d shows the movement of

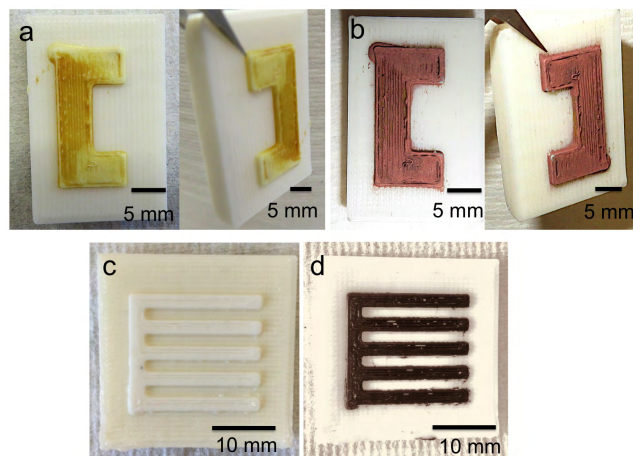


FIGURE 10. Selective metallization of 3D printed structure of PolyFlex™ pattern printed on the ABS substrate: a) after LED exposure and b) after electroless copper plating. Images of PolyFlex™ pattern on ABS substrate plated without prior LED exposure c) initial sample and d) after electroless copper plating.

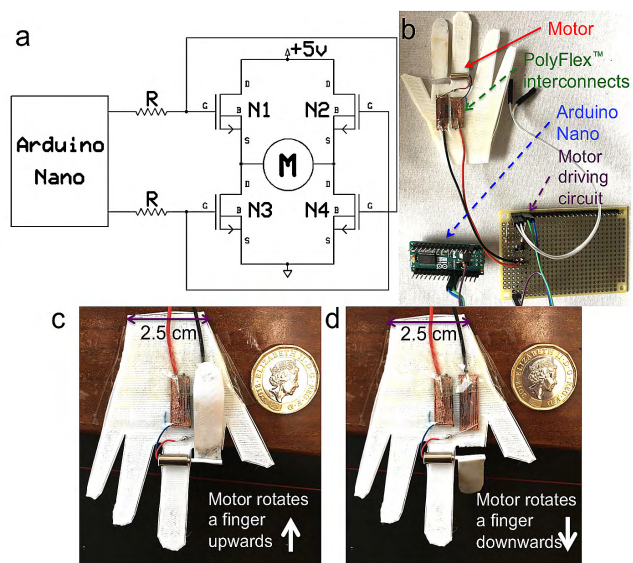


FIGURE 11. A hand demonstrator with the copper-plated PolyFlex™ interconnects connecting a motor attached to a finger with a motor driver circuit: a) schematic of the motor driver circuit, b) a set-up of the printed hand with a motor connected through copper-plated PolyFlex™ interconnects, c) motor rotates a finger upwards, d) motor rotates a finger downwards.

the finger in upward and downward directions as a result of the motor rotation. Therefore, with this demonstration, copper-plated PolyFlex™ parts are proved to function as interconnections in the electronic circuit.

IV. CONCLUSION

Four flexible TPU filaments were selectively metallized using a novel electroless copper metallization method. This method allows the fabrication of conductive patterns onto 3D printed flexible substrates. Furthermore, it is possible to fabricate conductive segments on non-conductive substrates by direct electroless plating of the 3D printed structure by submerging the whole structure at once. The electroless copper displayed

a sheet resistance of $(139.4 \pm 7.2) \text{ m}\Omega/\square$ and a conductivity of $(1.1 \pm 0.1) \times 10^7 \text{ S/m}$ which is comparable to bulk values. This work could be further improved by obtaining better-defined patterns on the TPU substrates by applying photo-reduction at a shorter wavelength.

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ASSEL RYSPAYEVA received the B.Eng. degree in electronics majoring in nanotechnology from Multimedia University, Malaysia, in 2012, and the Joint International M.Sc. degree (Hons.) in smart system integration from Heriot-Watt University, U.K., the University of South-Eastern Norway, and the Budapest University of Technology and Economics, in 2016. She is currently pursuing the Ph.D. degree in electrical engineering with Heriot-Watt University.



THOMAS DAVID ARTHUR JONES received the B.Sc. degree in nanoscience from Heriot-Watt University, in 2011, the M.Sc. degree in nanoelectronics from the University of Sheffield, in 2012, and the D.Eng. degree in photonics and optics technologies from Heriot-Watt University, in 2017. He is currently a KTP Associate with the University of Dundee. His research interests include materials science, specifically nanoparticle formation on polymers for microelectronics, and metal casting processing for electric automotive and power industries.



SADEQUE REZA KHAN received the B.Sc. degree in electronics and telecommunication engineering from the University of Liberal Arts Bangladesh, in 2010, and the M.Tech. degree in VLSI design from the National Institute of Technology Karnataka, India, in 2014. He is currently pursuing the Ph.D. degree in electrical engineering with Heriot-Watt University, U.K.



MOHAMMADREZA NEKOUIE ESFAHANI received the B.Sc. degree in mechanical engineering and the M.Sc. degree in advanced manufacturing technologies from the University of Manchester, in 2011, and the Ph.D. degree in laser material processing from Loughborough University, Loughborough, U.K., in 2015. He is currently a Research Fellow with the University of Leeds. His research interest includes advanced manufacturing processes in particular laser-based

hybrid additive manufacturing technologies. He is also experienced in Laser Materials Processing Inc., laser welding, laser polishing, and laser surface texturing.



ROBERT W. KAY received the Ph.D. degree in microsystems engineering from Heriot-Watt University, U.K., in 2008. He is currently an Associate Professor in advanced manufacturing with the University of Leeds. He has conducted advanced manufacturing research, both in academia and industry, since 2001. He has published over 50 publications in refereed journal papers and international conferences. His research interest includes primarily focus around processes for the manufacture of

more functional devices with his research increasingly driven by high value devices in a variety of applications.



MATTHEW P. SHUTTLEWORTH received the M.Eng. degree in aeronautical engineering from Loughborough University, U.K., in 2016. He is currently pursuing the Ph.D. degree in mechanical engineering with the University of Leeds, U.K. He has accepted an offer for the role of Research Fellow in the manufacture of sensors for experimental biomechanical simulations at the University of Leeds.



MARC P. Y. DESMULLIEZ (M'08–SM'12) was born in Lille, France, in 1963. He received the degree from the École Supérieure d'Électricité of Paris, Paris, France, in 1987, the dual Diploma degrees in microwave and modern optics, and theoretical physics from University College London, London, U.K., and the University of Cambridge, Cambridge, U.K., in 1987 and 1989, respectively, and the Ph.D. degree in optoelectronics from Heriot-Watt University, Edinburgh, U.K., in 1995.

He is currently the Deputy Head of the Research Institute of Signals, Sensors, and Systems with the School of Engineering and Physical Sciences, Heriot-Watt University, where he has been the Director of the Microsystems Engineering Centre, since 1999. He is also a Chartered Engineer and a Chartered Physicist of the Institute of Physics, U.K. He has coauthored 476 publications. He is also a Fellow of the Institute of Engineering and Technology and the Institute of Physics.



RUSSELL A. HARRIS has been specialized in the field of advanced manufacturing research, since 1997, primarily in academia, but also with significant links to industry. He has presented and published over 100 research papers, including such prestigious publications as Proceedings of the Royal Society, The Lancet, Procedia CIRP, and the American Society of Mechanical Engineers. His research portfolio has particularly focused on high-value manufacturing across a range of appli-

cations. He is characterized by its collaborative interdisciplinary nature and industrial links. He has received grant awards as the Principal Investigator from the EPSRC, a EC Framework Programme, and the Department of Health, alongside industry funding. The value and impact of his manufacturing research has been recognized in the award of the 2013 Queen's Anniversary Prize for High-Value Manufacturing.



JOSE MARQUES-HUESO received the M.Sc. degree in physics from the University of Valencia, Spain, and the Ph.D. degree with the Optoelectronic Materials and Devices Group, Materials Institute, University of Valencia, in 2011, where he completed the PG Cert. on photonics, in 2006. From 2002 to 2005, he was with the Soft-Matter Group, Johannes Gutenberg Universität Mainz, Germany. In 2011, he joined Heriot-Watt University, Edinburgh, U.K., as a Research Associate to

apply photon-managing technologies on materials for solar cells. In 2015, he commenced a position as a Research Fellow on the use of metallic nanocomposite materials in additive manufacturing. Since 2017, he has been a Lecturer with the Institute of Sensors, Signals and Systems, Heriot-Watt University. He has published over 60 journals and conferences papers, two book chapters, and an international patent on nanofabrication. He has more than 50 participations in conferences and scientific events, including symposium and conference organization and several invited oral presentations. His research interests in the use of functional materials for optoelectronic devices, sensors, and additive manufacturing.

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