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Atmospheric plasma sources for surface modifications in 3d printed scaffolds

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Abstract: In this work we investigate the coating of 3D-printed polymer structures with a robotic atmospheric pressure plasma jet with (3-aminopropyl)tri-methoxysilane. In particular, we investigated how deeply the coatings penetrate into the porous polymer structures and whether the nucleophilic groups are preserved. The influence of other process parameters (duty cycle, temperature, angle of the plasma jet to the substrate surface) is also discussed.

I. Introduction

Influencing the adhesion and the surface chemistry are important issues for 3D printing. On the one hand, sufficiently high adhesion to the build plate is necessary for extrusion-based printing processes, and on the other hand, it must also be possible to detach it again. The adhesion of the individual printed polymer layers determines the mechanical stability of the printed component in the z-direction. Post-processing by welding, gluing or coating also requires sufficient adhesion on the surface on the printed part. Furthermore, in medical applications tissue cells behave differently on different surfaces, so that the ingrowth behaviour of implants, for example, can be controlled by suitable surface chemistry.

Atmospheric pressure plasmas are an effective method of chemically modifying surfaces. These can be generated by high electric fields in suitable setups. Depending on the process gases used, oxidation and reduction processes, chemical functionalisation and coating processes are possible. In this way, the surface energy can be varied over a wide range to create or reduce adhesion. The growth conditions of adherent cells on implant structures can also be modified by plasma treatment. For example, plasma-polymerised (3-aminopropyl)tri-methoxysilane (pp-APTMS) is known to provide good cell adhesion [1]. There are different setups for atmospheric plasma sources. In addition to planar and linear sources, there are also so-called plasma jets. These are gas jets in which a plasma is generated inside a tube and forced outwards as a plasma flame by the gas flow. Such plasma jets can be built relatively small and are suitable for integration into extrusion-based 3D printing systems.

II. Material and methods

To investigate the influence of plasma jet coatings on porous printed polymer structures, a robot-guided plasma jet (from Nadir S.r.l.) mounted on a dispensing robot "I&J 7100" from Fisnar® was used (Fig. 1). The plasma jet is powered by a combination of radio frequency (15 W at 27 Mhz) and HV power (16 kHz). The jet consists of 3 concentric tubes. The inner tube contains a layer-forming precursor with a carrier gas (2 slm argon), the middle tube contains the process gas for igniting the gas discharge (10 slm argon) and the outer tube transports a non-reactive protective and cooling gas (15 slm nitrogen). The purity of the used argon and the nitrogen gas was 99.999%. The precursor used was (3-aminopropyl)trimethoxysilane with 97% purity from abcr GmbH.
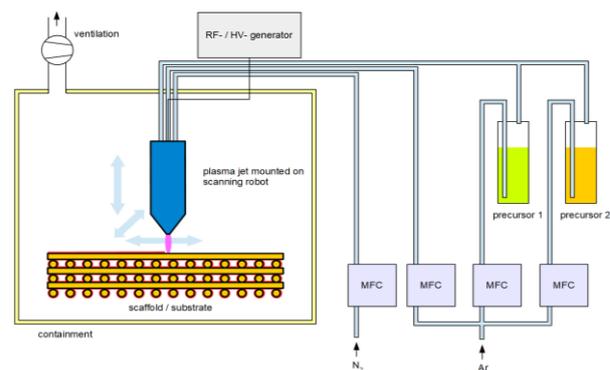

Figure 1: Used deposition setup with a plasma jet mounted on a scanning robot

The scanning robot moved the plasma jet at 1 mm/s with a line pattern (1mm line spacing) and a nozzle-to-substrate distance of 1 mm. 3D-printed polymer scaffolds (20 x 20 x 10 mm³) with 250 µm fibres and 1 mm fibre spacing made of polyethylene oxide terephthalate-polybutylene terephthalate copolymer and polypropylene were used to characterise the penetration depth of the plasma jet coating into the scaffolds (Fig. 2).
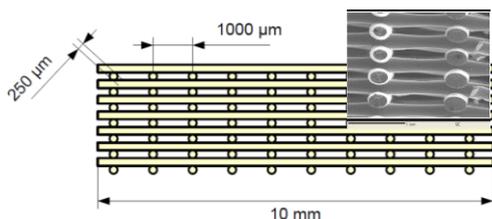
Figure 2: As substrate used 3D-printed polymer scaffold structures

To determine the nucleophilic group density, the coated substrates were derivatised for 2 h with 4-(trifluoromethyl)benzaldehyde vapours, which bind to the nucleophilic groups of the APTMS layers [2, 3]. The amount of silicon and fluorine was determined with electron probe micro analysis. The amount of silicon is a measure of the thickness of the pp-APTMS layers and the amount of fluorine is a measure of the density of the nucleophilic groups.

III. Results and discussion

It was observed that the pp-APTMS layers completely penetrate the approx. 1 cm thick scaffold structure. Almost the same amount of silicon as well as fluorine (and thus also layer thickness and nucleophilic group density) could be determined measured over the entire scaffold depth (Fig. 3 and 4). A plausible explanation for the deep penetration is that the activated molecules condense and evaporate several times and can thus reach deeper structures.
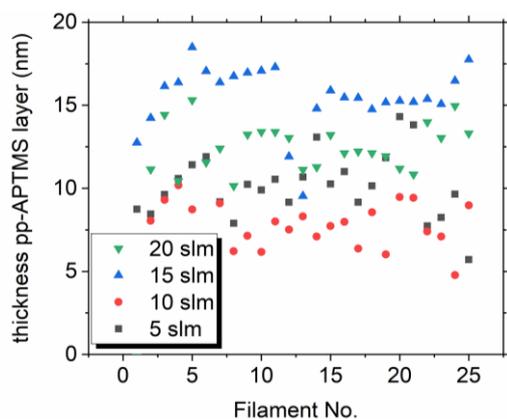

Figure 3: Thickness of the pp-APTMS layers as a function of the filament number of the scaffold structure
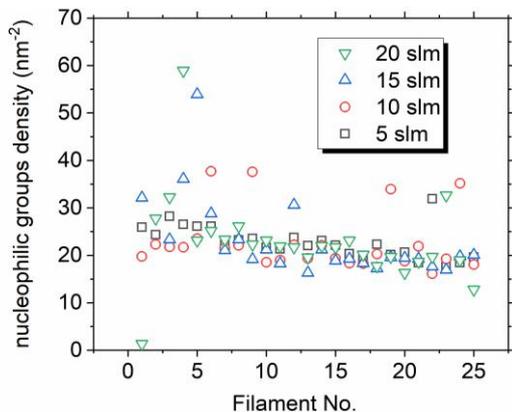

Figure 4: Density of nucleophilic groups of the pp-APTMS layers as a function of the filament number of the scaffold

It was also found that the penetration depth of the coatings also depends on the following factors: the duty cycle of the plasma, the substrate temperature, the density of the scaffold structures and the angle at which the plasma jet is oriented to the substrate. A low duty cycle promotes the structural preservation of the precursor molecule during deposition, so that functional groups such as NH_2 are also preserved better [3]. However, the deposition rate decreases. Higher deposition temperatures (adjustable via the ratio of purge gas to electrical power) also lead to an increase in the density of the functional groups, since more fractionated molecules have a shorter residence time and thus a lower deposition probability on the substrate surface. Higher densities of the framework structures and non-vertical inflow of the plasma clearly hinder the layer deposition (Fig. 5).
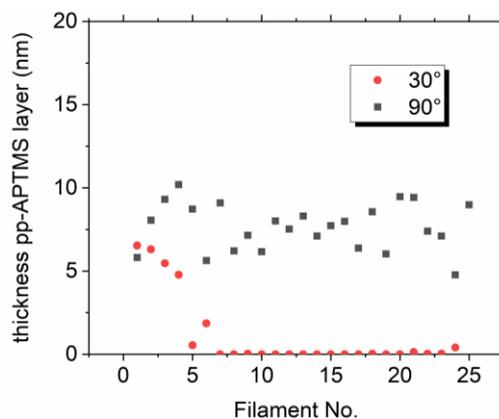

Figure 5: Thickness of the pp-APTMS layers as a function of the filament number for different plasma jet angles

IV. Conclusions and Outlook

In this work, we have shown that plasma jet coatings can be a suitable tool for coating porous 3D-printed polymer structures with functional chemical groups. Currently, we are working on the miniaturisation and integration of the atmospheric pressure plasma source into extrusion-based 3D printers to modify the printed polymer in-situ or to achieve a higher resolution of surface functionalisation.

AUTHOR'S STATEMENT
Conflict of interest: Authors state no conflict of interest. Informed consent: Informed consent has been obtained from all individuals included in this study. Ethical approval: The research related to human use complies with all the relevant national regulations, institutional policies and was performed in accordance with the tenets of the Helsinki Declaration, and has been approved by the authors' institutional review board or equivalent committee.

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