Influence of the substrate temperature on the layer properties made by an atmospheric plasma jet using different precursors

T. Neubert[1], K. Lachmann[1], V. Zeren[1], F. Schlüter[2], P. Scopece[3], A. Patelli[4], M. Thomas[1]

[1]*Fraunhofer Institute for Surface Engineering and Thin Films IST, Braunschweig, Germany*
[2]*Fraunhofer Institute for Wood Research Wilhelm-Klauditz-Institut WKI, Braunschweig, Germany*
[3]*Nadir S.r.l., Venezia, Italy*
[4]*Dept. of Physics and Astronomy - University of Padova, Padova, Italy*

Abstract: In this work the surface temperature of porous polymer scaffolds treated with an atmospheric plasma jet was determined by theoretical estimations and infrared measurements. Based on these results the scaffolds were coated with functional plasma polymer layers using this plasma jet and different precursors. The influence of the substrate temperature on the plasma polymer layer properties like thickness and chemical reactivity was investigated.

Keywords: plasma jet, deposition, substrate temperature

1. Introduction

3D printing of polymer scaffolds using extrusion based techniques like fused deposition modelling (FDM) is a very interesting new approach for the treatment of missing bone fragments [1, 2]. Suitable materials are copolymers of thermoplastic and biodegradable polyethyleneoxide-terephthalate-polybutylene-terephthalate copolymer (PEOT-PBT) [2]. For better cell adhesion and cell proliferation it is necessary to coat the polymer scaffolds with a plasma polymer layer using an atmospheric PECVD process during the 3D printing process [3]. These plasma polymer layers can provide certain functional groups like nucleophilic amines or electrophilic carboxyl groups to influence the cell growth [4, 5]. To generate the plasma polymer layers parallel to the 3D printing process an extruder based 3D-printer for the PEOT-PBT was combined with an atmospheric plasma jet. Since temperature plays an important role in the 3D printing and in the gas phase deposition processes we have investigated its influence on the layer properties using a plasma jet.

2. Experimental

2.1 Materials and plasma set-up

For the experiments an atmospheric plasma jet provided by Nadir S.r.l. was mounted on a dispensing robot "I&J 7100" from Fisnar®. Thus the plasma jet can be moved well defined above the substrates to generate uniform coatings. The plasma jet consists of three coaxial tubes for the precursor gas (up to 2 l min^{-1} STP 99.999% argon enriched with different precursor vapours), the process gas (10 l min^{-1} STP 99.999% argon) and the shielding and cooling gas (15 l min^{-1} STP 99.999% N_2) (Fig. 1). The main features of the plasma jet are, that it is simultaneously powered by a high-voltage (HV) generator and a radio-frequency (RF) generator and that both generators can be pulsed simultaneously [6].

2.2. Determination of the substrate temperature

To determine the surface temperature on polymer scaffold structures theoretical estimations were made. First, it was assumed that the RF power P_H of the plasma jet of approx. 15 W is completely thermalized by the argon gas flow of Φ_{Ar} = 10 l min^{-1} STP and no mixing with the nitrogen takes place. Knowing the ambient gas temperature T_0, the specific heat of the argon c_{Ar} and its density ρ_{Ar} the gas temperature and the maximum surface temperature can be estimated by equation 1.

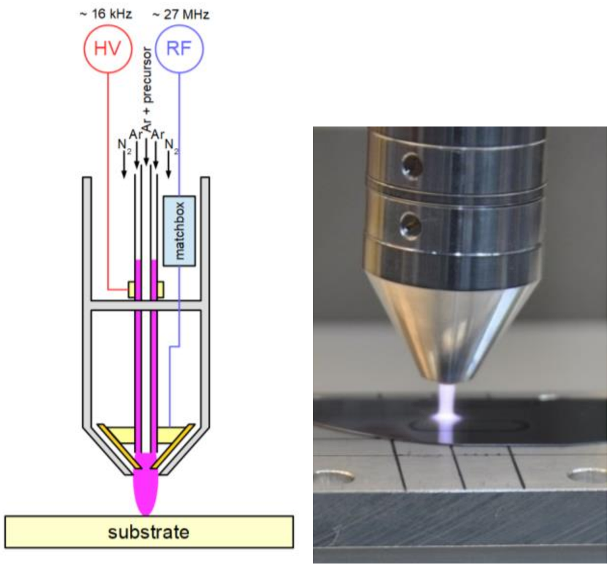

Fig. 1. Used plasma jet setup from Nadir S.r.l.

$$T = T_0 + \frac{P_H}{c_{Ar} \cdot \varrho_{Ar} \cdot \Phi_{Ar}} = 117\,°C \quad (1)$$

If we assume that there is a complete mixture of the hot argon flow and the cool nitrogen flow than the maximum surface temperature T can be calculated according equation 2 knowing the average heat capacity <c> and the average mass density <ρ> of the total gas flow $\Phi_{tot} = \Phi_{Ar} + \Phi_{N2}$.

$$T = T_0 + \frac{P_H}{<c> \cdot <\varrho> \cdot \Phi_{tot}} = 50\,°C \quad (2)$$

To verify these results, measurements with an IR camera system "Geminis 327 k ML Pro" from IRCAM GmbH were performed. The IR camera was first calibrated with a heated black body with known temperature. After this, the working plasma jet was focussed on a PEOT-PBT scaffold structure (20 x 20 x 10 mm^3) with 250 µm fibres and 1 mm fibre distance (Fig 2) using different nozzle to surface distances between 1 and 16 mm.

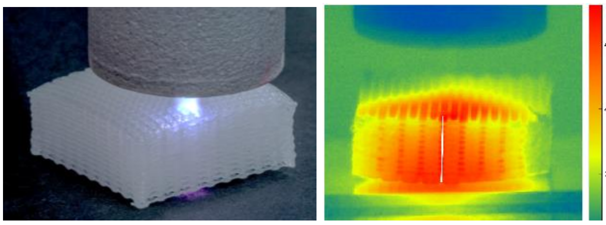

Fig. 2. Plasma jet focussed on a polymer scaffold (left: photo / right: thermal image)

2.3 Film deposition at different substrate temperatures

Based on the results of the thermal imaging coating experiments with the plasma jet on heated planar polyethylene (PE) substrates and glass slides with a 100 nm thick sputtered niobium oxide layer were performed with the following precursors:

- (3-aminopropyl)trimethoxysilane (APTMS) with 97% purity from abcr GmbH
- Mixture of 1 part maleic anhydride (MAA) with 99% purity from VWR International GmbH and 12 parts vinyltrimethoxysilane (VTMOS) with 98% purity from Sigma Aldrich Chemie GmbH
- hexamethyldisiloxane (HMDSO) with 98% purity from Sigma Aldrich Chemie GmbH
- and tetramethylysilane (TMS) with 99.9% purity from abcr GmbH

To study the influence of the substrate temperature the substrates were placed on a heating plate and heated to various temperatures between 25°C and 95°C (Fig. 3) 10 min before and during the deposition process. For the film deposition process the plasma jet was moved with a speed of 1 mm/s in a line pattern with 1 mm line distance and 1 mm distance between the plasma jet nozzle and the substrate surface. The amount of precursor was controlled by the amount of argon led through the precursor bubbler. For the MAA-VTMOS precursor gas mixture two separate bubblers were used.

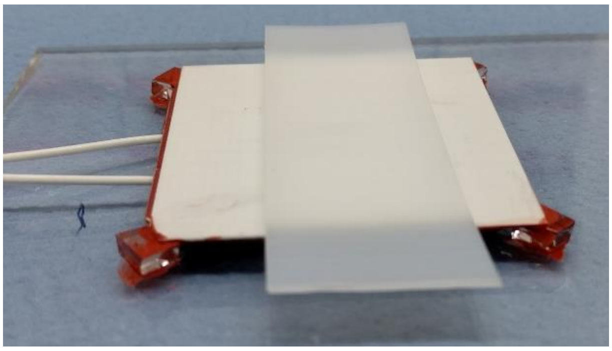

Fig. 3. PE substrate placed on heating plate

The coated layers were analysed using a spectroscopic ellipsometer "SE 850 DUV" from Sentech Instruments GmbH on the niobium oxide coated glass slides to determine the film thickness. The high refractive niobium oxide layers is necessary since the refractive indices of the glass slides and the plasma polymer layers are too similar.

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The density of nucleophilic groups onto the pp-APTMS layers was analysed directly after the deposition process by chemical derivatisation with 4-(trifluoromethyl)-benzaldehyde (TFBA) (98% from Sigma Aldrich Chemie GmbH) according to Neubert et al. [5]. ATR-FTIR spectra, taken with a "Nicolet is10" FTIR spectrometer from Thermo Scientific, were used to determine the density of nucleophilic groups from the area of the C-CF_3-vibration at 1325 cm^{-1} according to Klages et al. [7, 8].

In addition, the chemical activity of the electrophilic pp-MAA-VTMOS layers was proven by dipping the coated PE samples for 0.5 h in methylene blue solution (0.5 g / 500 ml H_2O).

3. Results and Discussion

The results for the thermal imaging have confirmed the theoretical estimations (Fig. 4). Using a 1 mm nozzle to substrate distance maximum surface temperatures of the scaffold structure of approx. 90 °C after approx. 25 s were observed (estimation: 117 °C). While increasing the nozzle to a distance of 16 mm a maximum surface temperatures of 46°C after approx. 3 s (estimation: 50 °C) was measured.

From these results, one can conclude that lower nozzle to substrate distances avoid a mixing of the hot argon flow and the cool nitrogen flow, while at larger distances there is more time for the gas stream to mix and thus to reduce the substrate heating.

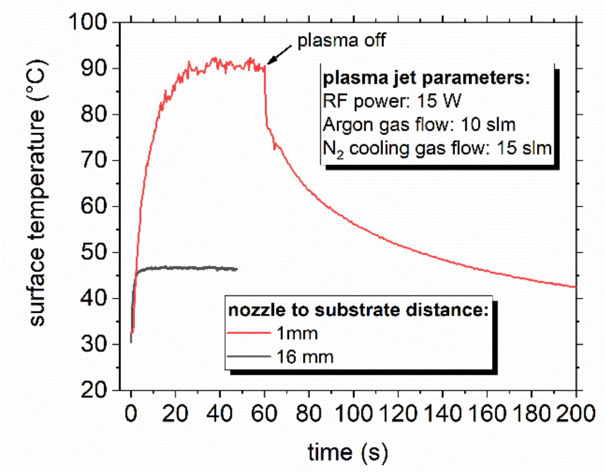

Fig. 4. Measured scaffold temperatures for different nozzle to substrate distances

Knowing the range of expectable temperatures, coating experiments with the plasma jet were performed. For the precursors HMDSO, MAA+VTMOS and APTMS a significant decrease of the layer thickness with higher substrate temperatures was observed (Fig. 5). This can be explained by higher desorption rates of the precursor molecules at higher substrate temperatures. However, the same experiment for TMS shows a significant increase of the layer thickness with increasing substrate temperatures (Fig. 5). This effect seems to correlate with the vapour pressure, which is relatively high for TMS (Fig. 6).

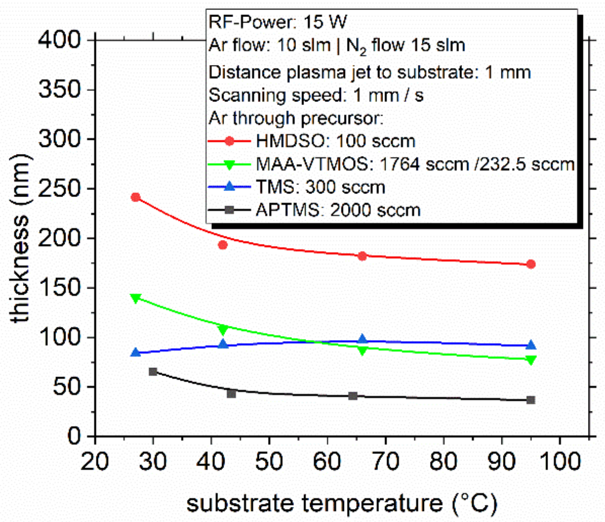

Fig. 5. Layer thickness as a function of substrate temperature for pp-HMDSO, pp-MAA-VTMOS, pp-TMS and pp-APTMS layers

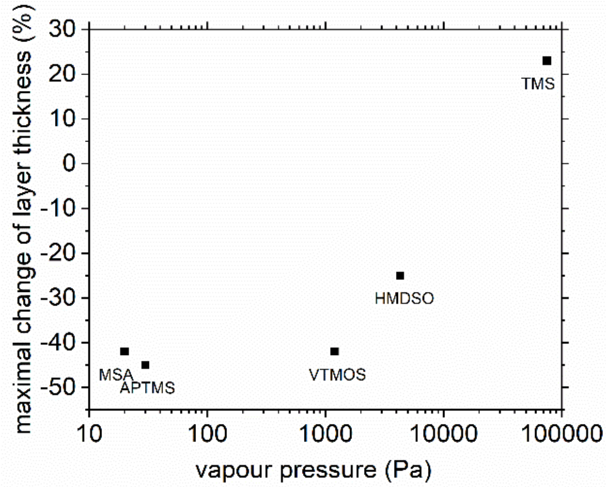

Fig. 6. Correlation between precursor vapour pressure and change of layer thickness

To investigate the influence of the substrate temperature on the chemical reactivity the pp-APTMS layers were analysed by derivatisation with TFBA. It was observed that the density of the nucleophilic groups trippled by increasing the substrate temperature from 25 °C to 70°C (Fig. 7) during the film deposition. A possible explanation for this effect is that smaller APTMS fragments with damaged or missing amino group generally should have a higher desorption rate. This reduces their retention time at the substrate surface and their probability to be part of the layer deposition process. At substrate temperatures above 70 °C the density of nucleophilic groups decreases again, possibly due to thermal degradation.

Staining tests of the pp-MAA-VTMOS samples indicate that their electrophilicity is also preserved at higher substrate temperatures (Fig. 8). A slight decrease in colour intensity can be explained by lower deposition rates.

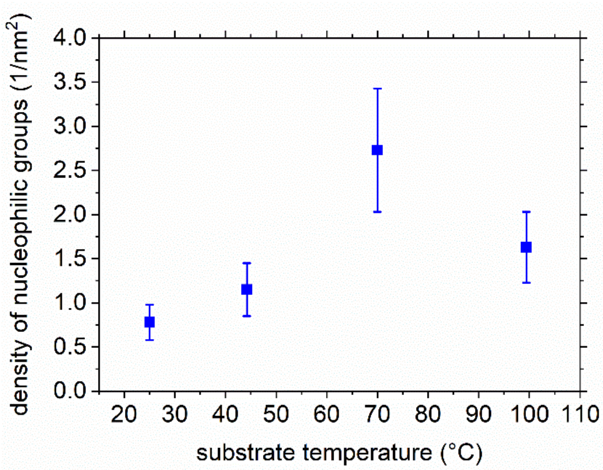

Fig. 7. Density of nucleophilic groups of pp-APTMS layers made with different substrate temperatures

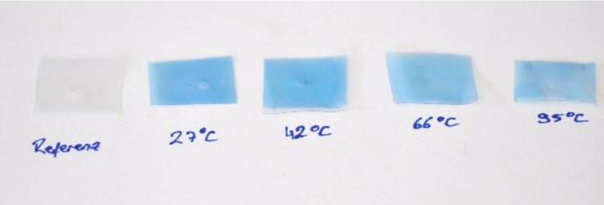

Fig. 8. pp-MAA-VTMOS layers coated at different substrate temperatures stained with methylene blue

4. Conclusion and Outlook

In this work the temperature of polymer scaffold structures heated by an atmospheric plasma jet was calculated and confirmed by measurements with an IR camera. Furthermore, the influence of the substrate temperature on the deposition process of plasma polymer layers made with the plasma jet using different precursors was investigated. We found that for precursors with low vapour pressures (below approx. 10 kPa) the layer thickness decreases with increasing substrate temperature. The effect can be explained by higher desorption rates of the precursor molecules on the hot substrate surface. However, for precursors with relatively high vapour pressures above 10 kPa (like TMS) the mechanism seems to be different. Here a slightly increasing trend for the layer thickness to higher substrates temperatures was observed. It was also found, that elevated substrate temperatures have a positive effect on the nucleophilic group density of pp-APTMS layers. The activity of electrophilic pp-MAA-VTMOS layers is not considerably affected by the substrate temperature.

A FDM 3D printer prototype combined with the investigated plasma jet is currently used for the investigation of the manufacturing of plasma polymer coated scaffolds with biological cell growth and in vivo implantation tests.

5. Acknowledgements

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6. References

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