

Single-step deposition of surface chemical gradients with a corona jet at atmospheric pressure

H. Malekzad¹, T. Gallingani², F. Barletta², M. Gherardi^{2,3}, V. Colombo^{2,3}, and D. Duday¹

¹*Department of Material Research and Technology, Luxembourg Institute of Science and Technology, Belvaux, Luxembourg*

²*Department of Industrial Engineering (DIN), Alma Mater Studiorum-Università di Bologna, Bologna, Italy*

³*Advanced Mechanics and Materials, Interdepartmental Center for Industrial Research (AMMICIR), Alma Mater Studiorum-Università di Bologna, Bologna, Italy*

Abstract: Interactions between nanostructured surfaces and biological media are still obscure due to the many cues (chemical, etc) that can play independent or synergetic roles. Generating surface gradients of these cues on a single device could be a promising approach to improve their understanding. In this work, a plasma jet controlled by a 3-axes robot was used to generate surface chemical gradients on polymer substrates; plasma power and O₂ content were varied linearly during the movement of the plasma jet to control the properties (i.e. cues) of the coating.

Keywords: Chemical gradient, plasma jet, HMDSO, polyethylene, AFM, FTIR, WCA.

1. Introduction

As surface gradient enables systematic study of the impact of gradually varying experimental parameters by conducting single experiment and using only a single surface and keeping conditions identical [1], it is highly preferential for developing high performance biosensing platforms or surfaces for cell guidance. Nevertheless, to fully benefit from the advantages of gradient, the ideal is to develop gradients under less-complicated operational systems for high throughput possibility of upscaling and with linear change of the variable over distance (for better prediction of the correlation between two) to fully benefit from the advantages of gradient. Among numerous techniques for making surface gradients, plasma polymerization techniques offer many advantages. Controlling plasma parameters, it is possible to tailor mechanical properties, topography or chemistry of the polymer coatings. There are two possible ways of generating gradients by plasma, one called surface activation is based on passing a reactive gas over a surface and activating functional groups of the substrate, and the other one is based on deposition and polymerization of a precursor over a substrate. There are few reports on using plasma polymerization for generation of chemistry or wettability gradients by deposition [2-4]. However, part of the plasma-generated gradient studies reported so far are based on the activation of surface in the absence of precursor and does not generate stable chemical properties [5]. The approach reported in this study is maskless and combines automated procedure with deposition of the precursor for generation of plasma polymer coating with wettability and chemistry gradient and since it is one-step simple approach, it is advantageous over previously reported similar plasma generated chemical gradient approaches. Herein, we report the generation of plasma-enabled deposited chemical gradients by using HMDSO as precursor and by varying O₂ flow rate and power input. The main motivation of adding O₂ while polymerizing the precursor is to achieve broad wettability gradient as

a result of gradual destruction of CH_x groups and simultaneous formation of silica bonds and silanol groups.

2. Experimental

All the experiments were performed using a fully automated system (AlmaPLUS, AlmaPlasma srl) equipped with a CNC pantograph and a remotely controlled high voltage pulsed generator (AlmaPULSE, Almaplasma srl). The system also includes a remotely controlled liquid and gas console composed of four mass flow controllers (EL-FLOW, Bronkhorst), a liquid flow meter (miniCORI flow, Bronkhorst) and a controlled evaporation mixer (CEM, Bronkhorst). The plasma source, fixed on the head of the CNC system, is a single high-voltage electrode corona jet (AlmaJET), previously described in [6], well suited for localized plasma treatments and deposition of complex three-dimensional coatings. The primary gas introduced in the plasma discharge region from the upper part of the source consisted of 2 slpm of argon (Ar) and 0.2 g/h of hexamethyldisiloxane (HMDSO, Sigma Aldrich); different oxygen percentages (0–16%) are added to the primary flow. A secondary gas (3 slpm of Ar) was injected through a diffuser in the region downstream the high-voltage electrode tip. A shroud gas (3 slpm of nitrogen, N₂) was injected at the outlet of the plasma source using a further gas diffuser specifically designed to confine the plasma discharge from the surrounding environment. The distance between the tip of the plasma jet and the substrate was kept constant at 15 mm. The treatment speed was 15 mm/min. The deposition of polymer films was performed on polyethylene films (thickness 500 µm). FTIR measurements were performed on polymer films by means of an Agilent Cary 660 FTIR spectrometer in ATR mode, performing 32 scans with a scan resolution of 4 cm⁻¹. Deconvolution was performed on the wide peak occurring at 1000-1250 cm⁻¹ in all spectra based on Gaussian curve fitting. Static contact angle (WCA) measurements were performed by

means of drop shape analyser (DSA30, KRUSS): a distilled water drop (2 μ l) was deposited on the sample substrate and the contact angle was measured using the Young-Laplace method. For each sample, the contact angle was measured both in the central point and at the edge of the deposited spot. AFM analysis was performed with an Innova microscope (Bruker, Santa Barbara) and images were acquired in air in AC mode at scan rates between 0.5 and 1 Hz. semi-contact silicon cantilever (RTESP; Bruker) with a spring constant of 40 Nm^{-1} were employed. Surface topography of filaments and cells were acquired by maintaining the first resonance amplitude of the tip constant. Images were processed with the manual tilt correction of the software SPIP (ImageMet).

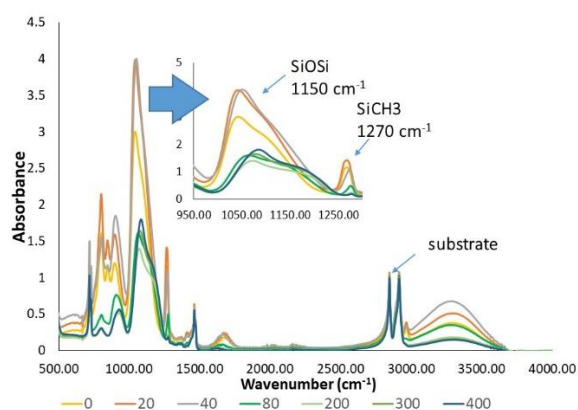


Fig. 1. Normalised FTIR spectra for chemical gradient of HMDSO film with increasing O_2 content (0 to 400 ml/min O_2 corresponding to 0-16% O_2 in plasma gas) after baseline correction.

3. Results and discussion

FTIR spectra of the different regions of the surface gradient generated by the Corona plasma jet on a polyethylene foil are presented on Figure 1. It is shown that two different regimes of deposition are generated by varying the O_2 content in the discharge. For low O_2 contents (< 40 ml/min i.e. 4% O_2), deposition rates are around twice higher (higher intensity of the SiOSi peak) than ones with higher O_2 contents. This phenomenon is related to the formation of coatings richer in CH_x groups at lower oxygen content with less decomposition of the HMDSO precursors by reactive species. Looking at the SiOSi peak evolution on Figure 1 indicates a fast transition between organic PDMS-like to hybrid $\text{SiCH}_3/\text{SiO}_2$ coatings (around 40 ml/min O_2) with the increase of oxygen in the plasma gas. It is also shown on Figure 2 where the ratio of SiCH_3 peak/SiOSi peak is given versus the oxygen content in the plasma gas. After this fast transition, a slower decrease of the ratio of SiCH_3 peak/SiOSi peak is observed until reaching coating's chemistry close to silica ones for O_2 contents higher than 200 ml/min. From 40 to 300 ml/min, the

decrease of organic character is quite constant and linear as shown on Figure 2. It means that surface energy or mechanical properties of the coatings may also vary significantly and linearly along the plasma surface gradient of HMDSO. The water contact angles (WCA) were measured all along the plasma surface gradient (10 cm long) and the resulting curve is shown on Figure 2 (upper curve). As expected, the WCA evolution with O_2 content in the gas phase is quite similar to the chemical evolution measured by FTIR. When no O_2 is added, the WCA is quite high (110°) due to the high content of CH_x chemical groups.

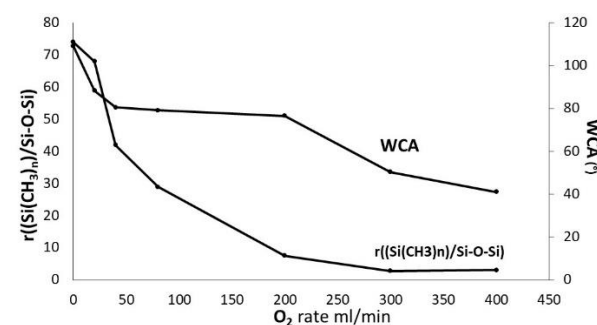


Fig. 2. The bottom curve shows the evolution of ratio of area under organic peak to area under inorganic peak $r(\text{aSi}(\text{CH}_3)_n/\text{aSiOSi})$ for surface gradient versus oxygen flow rate in plasma gas. On the upper curve, the corresponding WCA ($^\circ$) evolution on the plasma gradient versus oxygen flow rate in plasma gas.

Then, a rapid decrease of WCA down to 80° is observed up to 40 ml/min O_2 due to the increased decomposition of the precursor with higher densities of reactive oxygen species. For higher O_2 contents, the WCA decreases slowly from 80° to 40° , with the full decomposition of the precursor and the increasing amount of Si-O-Si and silanol groups in the coating. A surface energy gradient has been generated at the same time as the chemical gradient on a length of 10 cm, which is the first step to devices allowing a better understanding of interaction between nanostructured surfaces and biological objects. In order to see if the evolution of the WCA with the O_2 content in the gas phase was also influenced by the coating roughness, the topography of the different areas of the coatings has been characterized by atomic force microscopy. The results are shown on Figure 3 with the bottom curve. The roughness is lower on the areas deposited with a lower amount of O_2 in the gas phase with values lower than 20 nm. Then, the roughness of the surface gradient increases quite rapidly 40 nm with the increase of O_2 in the gas phase, when the decomposition of the precursor in the gas phase increases. This increase of roughness may be explained by an increase of the polymerization rate of polymer clusters in the gas phase. These polymer clusters generate this increase roughness when depositing on the surface, and further coalesce on the surface to form a rougher coating. As previously

observed with the other parameters, the increase of roughness is then increasing more slowly up to a flow of 200 ml/min of O₂. The maximum roughness observed is around 65 nm. For higher flows of O₂, the surface gradient roughness stays relatively constant around the maximum roughness. This phenomenon of constant roughness when a critical value of O₂ in the gas phase is reached could be linked to a maximum decomposition of the precursor in the gas phase that is limiting the growth of the polymer clusters in the gas phase. It indicates that reactive species generated by the plasma are in excess compared with the molecules of monomer. The evolution of the roughness does not seem to influence the evolution of the WCA when using polyethylene foils as a substrate, but it is clearly shown here that roughness is varying quite significantly with the O₂ content in the gas phase. The increase of roughness from 10 to 65 nm could affect the interaction of cells with the surface [7].

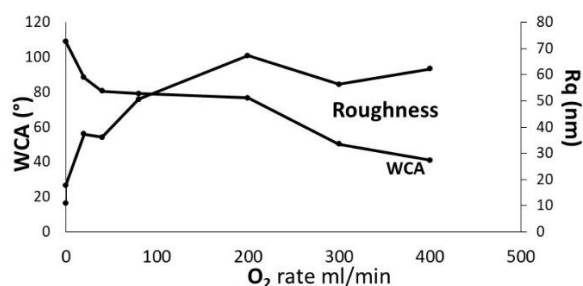


Fig. 3. The bottom curve shows the evolution of surface plasma gradient roughness (nm) versus oxygen flow rate in plasma gas. On the upper curve, the corresponding WCA (°) evolution on the plasma gradient versus oxygen flow rate in plasma gas.

4. Conclusion

Plasma surface gradients have been generated on thermally sensitive polymer films by using a single step and a single precursor atmospheric plasma jet. Plasma surface gradients varying continuously from a PDMS-like to a silica-like coating on a length of 10 cm were obtained by varying the amount of O₂ in the plasma gas phase simultaneously to the displacement of the plasma jet. The variation of the WCA all along the surface gradient was quite large from 40 to 120°. However, the variation of WCA was linked with a variation of the roughness, which can also affect interaction of the surface gradient with cells or biomolecules. Next steps are to optimize the deposition parameters to obtain more linear variations of WCA and chemistry with lower variations of roughness. This maskless approach for generating chemical and WCA surface gradients is very promising and will certainly lead to a new generation of devices for biomedical and sensing applications.

5. Acknowledgements

The authors want to thank the Fonds National de la Recherche du Luxembourg for the funding of this work

through the MASSENA PRIDE program. Patrick Gryan from LIST-MRT is also thanked for his support for AFM characterizations.

6. References

- [1] Kim, M.S., G. Khang, and H.B. Lee, *Progress in polymer science*, **33**, 138 (2008).
- [2] Yang, J., et al., *Advanced Materials*, **21**, 300 (2009).
- [3] Harding, F.J., et al., *Acta biomaterialia*, **8**, 1739 (2012).
- [4] Menzies, D.J., et al., *Langmuir*, **26**, 13987 (2010).
- [5] Lee, H.-B., et al., *Polymer Korea*, **29**, 423 (2005).
- [6] Barletta, F., et al., *Materials Letters*, **214**, 76 (2018).
- [7] Dobbenga, S., et al., *Acta Biomaterialia*, **46**, 3 (2016).