

Water intrusion in nanometer-thick plasma polymer films affecting surface properties

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Abstract: Application of plasma polymer films in aqueous environments requires special consideration of water-surface interaction and intrusion of water molecules into nanometer-thick films. Water penetrates both into hydrophilic and hydrophobic coatings yielding restructuring, hydrolysis, leaching, and water accumulation in the near-surface region. While stabilization of functional plasma polymer films is thus of great interest, such effects can also be used to control antibacterial efficacy and protein adsorption.

Keywords: water interaction, aging, crosslinking, functional group density, silver release.

1. General

Material's surfaces are frequently exposed to aqueous environments, whereby water molecules might not only adsorb on the surface but can also react with the surface material or penetrate into it. This interaction might be detrimental yielding oxidation and degradation reactions, but it is also substantial e.g. for the interaction with biomolecules [1]. The latter typically considers only the water-surface interaction directly at the surface showing different arrangements of water molecules depending on the surface wettability [2]. The diffusivity of water molecules on hydrophobic surfaces is thus enhanced favouring for example the denaturation of proteins [3,4].

Water molecules, however, also penetrate polymeric surfaces as well as (nano)porous materials. Water intrusion in hydrophilic materials proceeds with a flat front, whereas a ramified, finger-like intrusion is observed for hydrophobic materials as schematically shown in **Figure 1** [5].

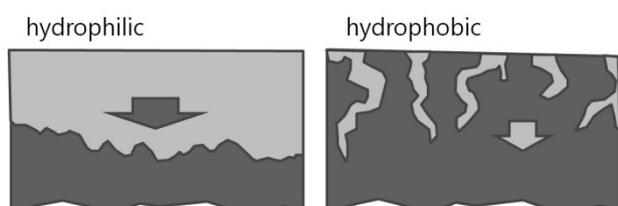


Fig. 1. Intrusion of water into porous materials, left: hydrophilic (flat front), right: hydrophobic (finger-like).

For functional plasma polymer films (PPFs) with polar, i.e. hydrophilic, groups, the consideration of water interaction is thus crucial. Restructuring and hydrolysis effects might distinctly alter surface properties strongly affecting their application in aqueous environments such as e.g. biosensors [6]. Hence, strategies to stabilize functional PPFs are of great interest [7]. Therefore, we are investigating the deposition of functional plasma polymer films at varying deposition conditions during film growth

to achieve a vertical chemical gradient towards the surface of the PPF. Most of all, the degree of crosslinking was found to determine the PPF stability [8]. Higher crosslinked base layers are terminated by 1-2 nm thick highly functional cover layers to minimize restructuring, migration and water intrusion [9,10]. The potential of this concept is discussed for oxygen- and nitrogen-containing functional surface groups with respect to stability in water.

Hydrophobic cover layers, on the other hand, are suited to control the intrusion of water [11,12], which is investigated regarding protein adsorption on hydrophobic-to-hydrophilic vertical gradient PPFs and antibacterial efficacy by covering Ag-containing layers.

2. Experimental

Lab-scale, pilot-scale and industrial reactors were used to deposit plasma polymer films, silver islands by sputtering as well as parylene C films at low pressure conditions. The investigated bilayer and vertical gradient structures are listed in **Table 1**.

Table 1. Investigated coating structures.

Base layer	Cover layer
crosslinked CHO PPF	functional CHO PPF (1-2 nm)
crosslinked CHN PPF	functional CHN PPF (1-2 nm)
crosslinked CHO PPF	functional CHN PPF (1-3 nm)
nanoporous SiO _x PPF	hydrophobic ppHMDSO (2-12 nm)
Polystyrene + Ag layer	hydrophobic ppHMDSO (100 nm)
PET + Ag layer	CHO PPF (30-180 nm)
PET + Ag layer	hydrophobic a-C:H PPF (6-150 nm)
Parylene C + Ag layer	hydrophobic parylene C (40-120 nm)

The coatings were investigated after immersion in water for hours, days and weeks using water contact angle, XPS, ToF-SIMS, ICP-OES, FIB-SEM, FTIR, and TInAS to characterize chemical structure, film loss, functionality, and leaching.

3. Results and discussion

At first, plasma polymerization conditions were optimized to deposit crosslinked PPFs that allow a simple change of plasma deposition conditions by varying $\text{CO}_2/\text{C}_2\text{H}_4$ or $\text{NH}_3/\text{C}_2\text{H}_4$ gas ratio and power input. A hydrophilic functional cover layer is thus deposited with an optimized thickness of 1-2 nm to restrict aging effects. The surface functional group density can thus be retained by storage in water as schematically indicated in **Figure 2**. Moreover, protein adsorption was found to be affected by the cover layer thickness and related water intrusion, which is an important finding for all biomaterials.

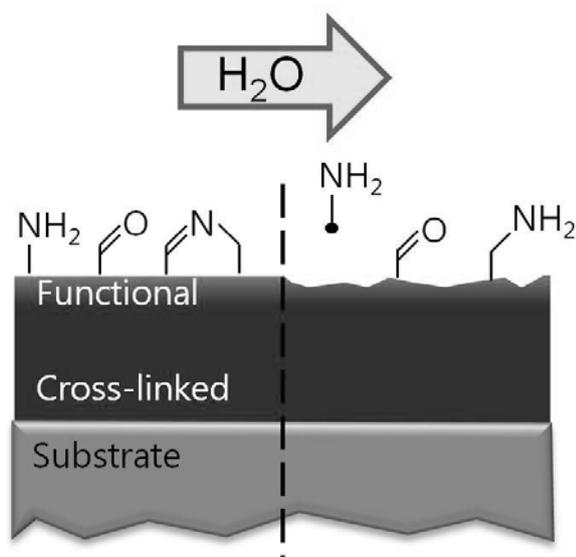


Fig. 2. The cross-linked base layer restricts surface restructuring and water intrusion retaining the surface functional group density when immersed in water.

Finally, hydrophilic and hydrophobic cover layers ranging from 6 to 180 nm in thickness were deposited on Ag layers to investigate the Ag ion release kinetics. Mainly hydrophobic cover layers (a-C:H, ppHMDSO and parylene C) are suited to enable a steady release rate that can be adjusted over the timescale of months. This finding is ascribed to the finger-like water intrusion in hydrophobic coatings forming nanochannels for limited Ag ion diffusion through the cover layer and release. Furthermore, morphological changes of the deposited Ag layer due to strong Ag migration effects were analysed by FIB-SEM (**Figure 3**).

4. Conclusions

As water interaction with material surfaces plays a crucial role in many technical and biomedical applications, its effect on the outermost surface chemistry and structure as well as water intrusion into the material surfaces needs to be investigated in detail. Understanding the interaction enables to stabilize material surfaces comprising functional groups, to control protein adsorption and to modulate Ag ion release.

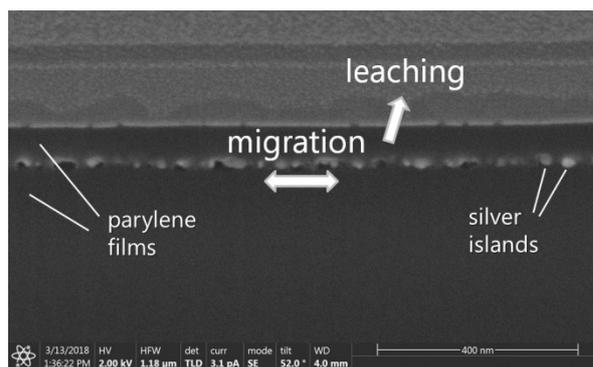


Fig. 3. FIB-SEM image of parylene C-covered (~100 nm) Ag layer (forming islands) indicating Ag ion migration and leaching.

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6. References

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