Deposition of a biodegradable inorganic-organic hybrid precursor via aerosol injection in the afterglow of a cold atmospheric pressure plasma jet

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Abstract: Using aerosol-assisted plasma deposition an inorganic-organic hybrid precursor was deposited on aluminum and silicon wafer using the after glow of a plasma jet. Very high deposition rates between 1-4 μ m m min⁻¹ were achieved. Chemical properties and effectiveness for corrosion protection of the plasma coating were compared with a process where the precursor was applied and cured as a typical paint system.

Keywords: aerosol-assisted, atmospheric plasma polymerization, bioORMOCER®

1. Introduction

For thin film deposition with cold atmospheric pressure plasmas the precursor can be fed as vapor (gas) or as liquid droplets inside the plasma. The latter method is also called aerosol-assisted plasma deposition (AAPD) [1]. An additional parameter is the location of precursor injection, which can occur directly into the plasma excitation volume or in the afterglow part of the plasma.

A key motivation to supply the precursor as an aerosol is to achieve a soft fragmentation to realize a high degree of structural retention in the deposited plasma polymer. Another advantage of this technology is that precursors that cannot (easily) be vaporized become available for plasma deposition, e.g. precursors with low vapor pressure or with high (> 300 u) molecular weight, e.g. biomolecules, nanocomposites, or prepolymers [2].

A special class of inorganic-organic hybrid polymers are so called ORMOCER[®]s, which consist of an inorganic silica network backbone, with organic cross linking units and functional moieties. Due to their high molecular weight and their prepolymeric nature, they are typically applied by conventional paint coating technology (doctor blade or rollers followed by thermal or radiation curing). Applications of ORMOCER[®]s include scratch resistant transparent coatings, barrier layers for food packaging, or protective coatings. A new development for this class of biodegradable hvbrid polymers are so-called bioORMOCER®s that are based on a comparable system but where non-degradable components are substituted by biodegradable constituents.

Today thin (< 500 nm) coatings are rarely considered in the evaluation of recycling and biodegradation performance of coated products, although they can have a significant effect on recyclability/biodegradability [3,4]. Therefore, we believe, the deposition of biodegradable coatings will become more important in the future.

Here we report on the deposition of a biodegradable precursor via AAPD in the afterglow of a commercial atmospheric pressure plasma jet (APPJ) using a pulsed arc-like (spark) excitation scheme. Paulussen et al. reported before on the use of inorganic-organic hybrid precursors [5]. In contrast to this study, in [5] a DBD was used, the precursor was fed directly into the plasma excitation zone between the electrodes, and the precursor was not biodegradable.

Our process has the advantage that it runs completely at open atmosphere, does not require the use of rare gases for plasma operation and aerosol injection, and is also largely insensitive to the amount of gas impurities in the plasma in comparison to most DBDs. Next to soft fragmentation, a key motivation for this study was to achieve a high deposition rate and fast curing time (compared to conventional paint application) for thin film deposition of hybrid polymers for commercial applications, e.g. for corrosion protection.

2. Experimental

A commercial plasma jet of type RD1004 from Plasmatreat GmbH (Steinhagen, Germany) was used. The jet was operated with air using a FG5001 generator from the same company. For plasma excitation the centre electrode is driven by an excitation frequency between 17 and 22 kHz, with pulse peak heights of approx. 2-5 kV. The flow rate of the compressed air gas for plasma operation was 29 slm. Generator settings for (intermediate) voltage were 300 V and 100% for PCT (so called plasma cycle time). Typical conditions for the dynamic deposition process were a plasma jet - substrate distance of 15 mm and a relative speed of 2-4 m/min.



Fig. 1. Representative structure of the hybrid precursor.

The precursor was of the bioORMOCER[®] class (Fig. 1) with an average molecular weight of approx. 600 u and was used as a 50% wt solution in water [6]. The precursor was injected as a liquid droplet spray in the afterglow of the plasma jet [7]. For the injection a Meinhard nebulizer (from Meinhard, Golden, USA) was employed. The nebulizer was operated with nitrogen. Precursor flow rate was not specifically measured or controlled, but we estimate that the flow rate was in the range of 2-10 g/h. The typical distance between plasma plume and exit of nebulizer was 10 mm and the nebulizer exit was directed towards the center of the visible plasma plume (Fig. 2).



Fig. 2. Injection of precursor aerosol in the afterglow of the plasma jet.

As substrates, we used Aluminum 99.5, Aluminum 2024, or polished Si-Wafers. They were rinsed with isopropanol before use. For electron microscopy a Zeiss GeminiSEM was used. FT-IR spectra were recorded in IRRAS mode with a Bruker Vertex 80. Salt spray testing was performed in close agreement to DIN EN ISO 9227.

3. Results and Discussion

Fig. 3 displays the coating with a thickness of approximately 1000 nm deposited on a silicon wafer that we achieved using the setup for AAPD as outlined above.

We estimate from the thickness of the coating, that using the aerosol injection with this precursor we achieve an extremely high deposition rate in the order of 1-4 μ m m min⁻¹. This is even higher than the deposition rate we achieve using HMDSO as precursor with the same plasma source (but via precursor vaporization) which is already very high with approx. 0.5 μ m m min⁻¹ [8]. This high deposition rate is partly attributed to the prepolymeric nature of the precursor that facilitates cross-linking and also to its different chemical structure&reactivity in comparison to HMDSO. In addition, the close proximity of precursor molecules in the individual droplets could also increase probability towards polymerization reactions in general.



Fig. 3. Electron microscopic image (side view) of the coating using an inorganic-organic precursor. To observe the side of the coating masking with tape was applied to the silicon wafer while coating.

The coating in Fig. 3 appears to be relatively smooth and homogeneous and we did not observe powder formation. However, occasionally we also observed areas with a non-regular structure, as shown in Fig. 4. We attribute these features with dimensions of several microns most likely to an irregular aerosol generation where very large droplets were injected into the afterglow or hit directly the substrate surface.



Fig. 4. Electron microscopic image of the coating (side view) with irregular structures.

Fig. 5 compares the IR spectra of the coatings with the precursor deposited by the AAPD process in comparison to conventional paint application and thermal curing (2h at 130 °C). We do not observe significant differences between the spectra. This indicates that the final polymerized product is similar with both methods. We attribute this to soft fragmentation patterns in the AAPD process that seem not to deteriorate the functional groups

of the precursor significantly. This shows that similar coating properties can be realized with the plasma process as with the conventional wet chemical approach, but at much higher process speed.



Fig. 5. IR spectra of APPD coating and coating deposited as a typical paint with thermal curing.

To check the corrosion protective properties the coating was deposited on two different aluminum alloys, Al 99.5 and Al 2024, using the AAPD process. For reference, the hybrid polymer was also applied by a doctor knife and thermally cured with an approximate thickness of 5 μ m. The coated samples were exposed for 72h to a neutral salt spray test. Three samples for each variant were analyzed. Figs. 6 and 7 display the samples made of Al 99.5 and Al 2024 after testing, respectively.







Fig. 7. Al 2024 specimens after 72h of salt spray testing.

From both figures it can be seen, that the plasma coated samples improve resistance towards corrosion significantly in comparison to the control sample. The plasma deposited systems show identical (if not better) performance than the conventionally cured hybrid polymer systems. This indicates that the plasma deposited coating has comparable properties for corrosion protection as the conventional paint coating, even at lower thickness.

Another key advantage of the AAPD process over the paint application process is process speed. The process time for application and curing is reduced from two hours to seconds. In addition, the energy for curing is saved and the hardware for thermal curing can be eliminated for the production process. The influence on biodegradability is currently studied.

In summary, a coating could be deposited with a highmolecular weight hybrid precursor using the AAPD process at a very high deposition rate. The coating shows similar properties as the conventional wet chemical paint process, but has the advantage of a higher process speed and lower energy consumption.

4. References

[1] F. Massines, C. Sarra-Bournet, F. Fanelli, N. Naude,

N. Gherardi, Plasma Process. Polym., 8, 1041 (2012).

[2] F. Fanelli, F. Fracassi, Plasma Chem Plasma Process, **34**, 473 (2014).

[3] P.Tian, X. Liu Regenerative Biomaterials **2**, 135 (2015).

[4] K. Kaiser, M. Schmid, M. Schlummer, Recycling **3**, 1 (2018).

[5] S. Paulussen, R. Rego, O. Goossens, D.

Vangeneugden, K. Rose, J. Phys. D: Appl. Phys., **38**, 568 (2005).

[6] S. Amberg-Schwab, p. 3295-3315 in *Handbook of Sol-Gel Science and Technology*, eds. Lisa Klein, Mario Aparicio and Andrei Jitianu, Springer, 2016.

[7] Patent EP 2 279 801 B1.

[8] U. Lommatzsch, J. Ihde, Plasma Process. Polym. 6, 642 (2009).

5. Acknowledgement

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