PLASMA-ASSISTED VAPOUR THERMAL DEPOSITION WITH CONTINUOUS MATERIAL FEED

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Abstract

The Plasma-Assisted Vapour Thermal Deposition (PAVTD) is thin-film deposition technique utilizing a classical polymer as a source of material. The polymer is heated to fragmentation/evaporation under low pressure. The released fragments (effective a "monomer") with molar mass of 10^2 to 10^3 g/mol are then repolymerized in the rf plasma. The high molar mass of the film building blocks offers an opportunity to tune the structure and properties of the films in an exceptionally broad range for a plasma polymer, effectively bridging the gap between classical polymers and PECVD films.

Currently, the PAVTD method has several drawbacks compared with PECVD. The deposition must be done as a batch process, governed by the capacity of the crucible. The thermal release of the precursor fragments is highly temperature-and history- sensitive. The resulting fluctuations in deposition rate make retaining good reproducibility of the process rather tricky. To overcome these technical limitations, a modification of the setup utilizing a filament for FDM 3D-printing fed into a modified filament heater/extruder was made.

In this paper, overview of the possibilities of PAVTD using PLA as the source material will is given along with the first results obtained using an improved deposition setup with continuous material feed. Significant improvements in deposition rate and control of stability of the deposition are presented.

Keywords: Plasma polymer, plasma assisted vapour thermal deposition, continuous process, polylactic acid

1. INTRODUCTION

Plasma polymerization (PECVD) is well-established method for the preparation of organic highly crosslinked thin films [1,2] for applications such as protective or barrier coatings [3,4], in packaging, wettability control [5,6] or in the biomedical field [7-9].

Typical plasma polymerization methods utilize volatile precursor, which is fragmented and repolymerized in the plasma zone. Necessity of volatile precursors limits PECVD to use only low molar mass monomers. As the result of fragmentation and subsequent repolymerization are semi-random structures, the final molecular structure if the film is typically quite different from the original precursor [10-14]. This significantly limits the ability of PECVD to prepare chemically complex materials. To overcome this issue, plasma-assisted vapour thermal deposition (PAVTD) has been developed [15].

Since heavy molecules have low volatility, PAVTD uses high molar mass oligomers obtained in-situ from thermal degradation/evaporation from a solid polymer as a precursor. The subsequent process of plasma polymerization is the same as for classical PECVD. As the evaporated fragments are typically much larger than single monomeric unit of the original precursor the resulting product of plasma polymerization preserves much better the original chemical structure of the precursor, while still being crosslinked. Recently, as model case of the molecular structure, polylactic acid (PLA) was chosen, since it exhibits interesting properties dependent on its molecular structure, like biodegradability and hydrolyzability [16-18]. Using PAVTD, it was clearly demonstrated that the PLA structure can be retained in a plasma polymer thin film and controllably modified, allowing for control of the film properties in an usually broad range [19,20].

The main advantage of PAVTD (usage of high molecular precursor) is also the main disadvantage of the process as it brings the complexity of polymer evaporation into consideration. The macromolecules do not have well-defined boiling point and vapour pressure. The evaporation process of polymers is rather driven by the thermal decomposition of the large macromolecules into shorter fragments that are volatile. Due to the changing parameters inside of the evaporation crucible (temperature, actual amount material, process history, etc.), it is quite challenging to stabilize the deposition process. Unstable deposition rate leads to low reproducibility [21] as the product of the process is mostly dependent on power to precursor mass flow ratio i.e. Yasuda scaling law [22,23].

To overcome this issue, we propose a modification of the original batch PAVTD process into a process with a continuous feed of the material into the evaporation crucible. Having all the time only a small amount of material in the crucible is expected to improve the control over the process.

2. EXPERIMENTAL

The continuous feed version of PAVTD setup was strongly influenced by the Fused Deposition Modelling (FDM) 3D printing technology, both in used components and polymer material form. Since PLA is one of the most common 3D printing materials, it was possible to compare the films prepared using older batch (powder-filled) and a new continuous feed (filament-fed) setup.

2.1. Deposition setup

The original batch PAVTD setup was already described elsewhere [15,19]. The difference between batch and continuous feed setups is schematically shown in the **Figure 1**. The main difference is the feed system itself. It utilizes mostly off-the-shelf FDM 3D printer components with zero or minimal modifications (heater/heating block, heat break, extruder, stepper motor), the water-cooling being the main difference from the common 3D printing parts. The system is controlled by a proprietary Arduino-based circuitry.

The crucible had diameter of 20 mm and height of 30 mm. The centre of the circular (diameter 60 mm) rf electrode was 40 mm and the sample plane (with vacuum load-lock system) was 120 mm above the top of the crucible. The whole PAVTD setup was placed in a steel vacuum chamber with 500 mm height and 330 mm diameter with diffusion pump backed by a rotary pump.

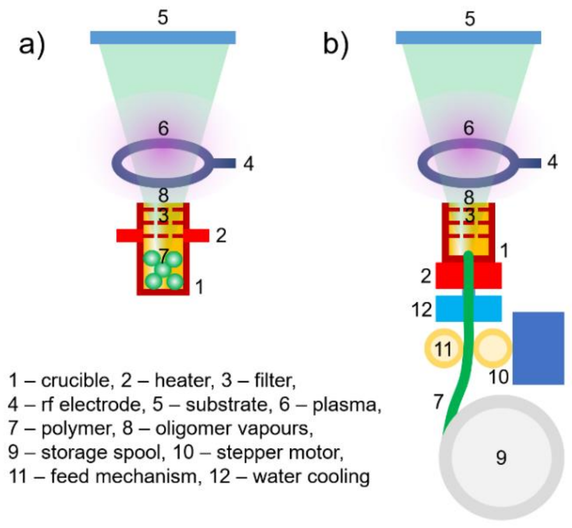

Figure 1 Scheme of the experimental setup for PAVTD a) batch setup b) continuous feed setup

2.2. Materials

As a source of the material, PLA printing filament (“natural”, Gembird) with standard 1.75 mm diameter was used. As substrates, glass, one-side polished silicon and gold-coated glass were used. Argon was used as a carrier gas.

2.3. Deposition conditions

The heater (65 W) temperature for PLA filament was kept in the range of 320-350 °C, where the deposition rate can be controlled directly by the feed rate from the storage spool (10-50 g of the PLA filament). During testing of the setup, the filament material feed rate was varied between 0.3 g/h and 15 g/h. The sample series prepared to demonstrate the discharge power dependence of the film composition was prepared at the filament feed rate of 7 g/h. The chamber was fed with argon gas flow of 4.5 cm^3_{STP}/min to maintain working pressure 0.35 Pa. The discharge power (rf, 13.56 MHz) was varied from 0 W (pure thermal deposition) to 16 W.

2.4. Characterisation of the process and thin films

The deposition rate of the film was monitored by quartz crystal microbalance (QCM) sensor placed 60 mm above the substrate. In-situ QCM measurements in Hz/s were calibrated to nm/s by ex-situ film thickness obtained with spectroscopic ellipsometry (J. A. Woollam M-2000 DI). Chemical composition of the films was characterized using infrared spectroscopy (FTIR, Bruker Equinox 55 in reflection-absorption mode on gold-coated glass substrates) and X-ray photoelectron spectroscopy (XPS, Specs Phoibos 100).

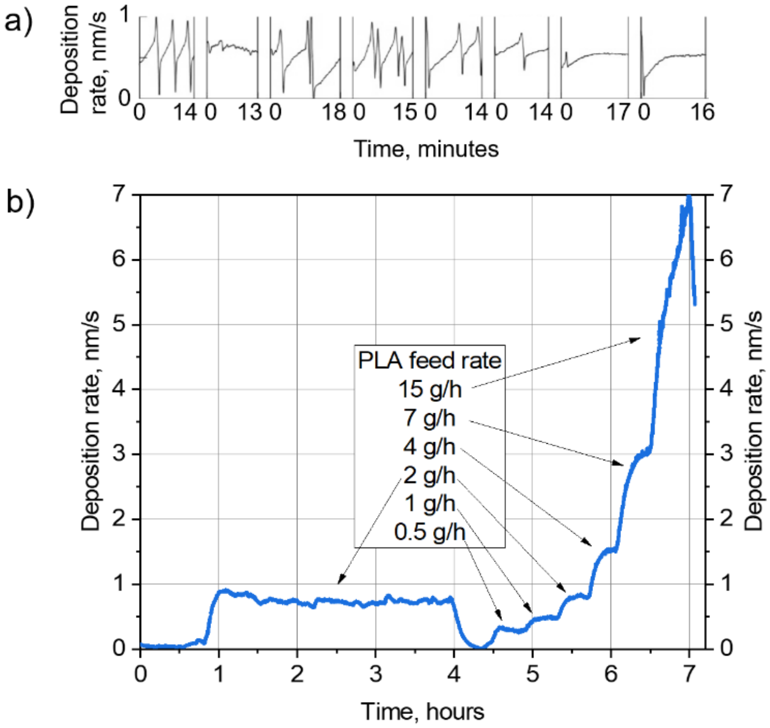

Figure 2 Comparison of deposition stability and duration of PAVTD process measured by QCM in a) batch in high-deposition rate mode (data: Z. Krtous, thesis, 2020) b) continuous feed variant.

3. RESULTS AND DISCUSSION

3.1. Stability of the deposition

The stability of deposition was studied both in terms of the short- and long-term fluctuations.

Repeated experiments did not reveal any fundamental limitation in the deposition length. Several experiments with run time of over 6 hours were performed. The deposition time was limited only by the amount of filament stored inside the vacuum chamber, which can be easily upgraded. Since the PAVTD operates at about 100 °C temperature higher than a 3D printer for the same material, limits of the deposition rate were found to be mostly caused by blockages of the feed system both at low and high end of deposition rate ranges (caused by heat creep and material overflow, respectively). The deposition rate inside these limits was found to be proportional to the feed rate. This makes the control much simpler than in the case of the batch process, where the fluctuations of over 50 % of the mean value were observed at high deposition rates (**Figure 2a**), so in most experiments, deposition rates had to be kept below 0.08 nm/s. The continuous feed setup was possible to operate at nearly 10 times higher value (**Figure 2b**). The stability at deposition rate levels comparable to those of the batch setup is also significantly better.

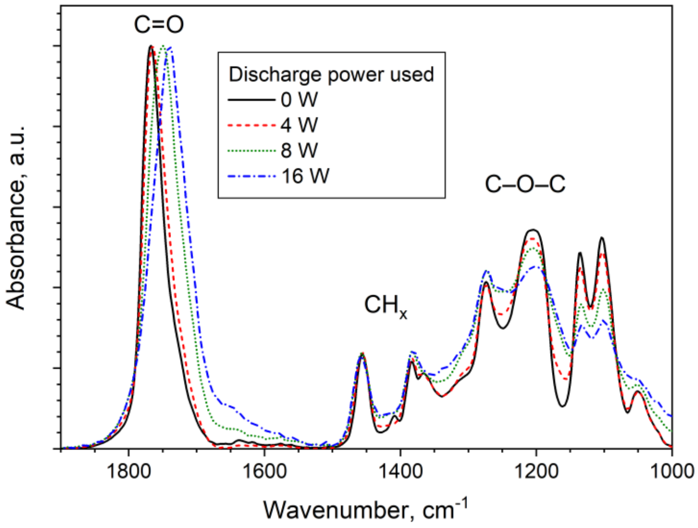

Figure 3 FTIR spectra (normalized to C=O peak) of PLA-like films prepared using PAVTD at the deposition rate of 7 g/h at varying discharge power

3.2. Chemical composition of the deposited thin films

The chemical composition of the film was found to be very similar to the films prepared previously using batch setup [19-21], as expected.

The infrared spectra of the films correspond well to the PLA structure. With increasing discharge power, the spectra show signs of slightly more disordered/fragmented structure of the films, exhibited by broadened peaks. The shift and shape change of the carbonyl peak (~1750 cm^{-1}) can be explained by the presence of more carbonaceous moieties (like C=C, ~1650 cm^{-1}). This is supported by the XPS data, where a significant decrease of the O/C ratio was observed in film prepared at higher discharge powers. This effect was also observed previously in the films prepared in the batch setup.

Table 1 Changes in the elemental composition of PAVTD PLA-like films with the discharge power (note: O/C ratio of original PLA is 0.66)

Discharge power (W)	**C (XPS at. %)**	**O (XPS at. %)**	**O/C ratio**
0	62.5	37.5	0.60
4	64.6	35.4	0.55
8	67.7	32.3	0.48
16	71.1	28.9	0.41

4. CONCLUSION

The plasma-assisted vapour thermal deposition setup with a continuous material was developed. The chemical properties of the PLA-like films prepared in this setup correspond well to the films prepared in the earlier batch variant of the method. The good control of the properties of the films is reproduced in the continuous process.

The continuous feed setup allowed to increase the deposition rate more then by one order of magnitude. At the same time, the total running time of over 7 hours was demonstrated (limited only by the filament storage) while maintaining much better deposition rate stability. This makes the continuous-feed PAVTD both an interesting tool to study classical polymer – plasma polymer transition and a practical deposition method.

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