

# Tunable classical-plasma polymer hybrid thin films prepared using plasma-assisted vapour thermal deposition

J. Kousal<sup>1</sup>, Z. Krtouš<sup>1</sup>, P. Solar<sup>1</sup>, I. Křivka<sup>1</sup>, I. Krakovský<sup>1</sup>, S. Ali-Ogly<sup>1</sup>, L. Hanyková<sup>1</sup>

<sup>1</sup> Department of Macromolecular Physics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

**Abstract:** Plasma Polymerization technique is well-established way to deposit organic thin films. However, the molecular structure complexity of these films is limited compared to classical chemistry. In order to overcome this limitation, Plasma-Assisted Vapour Thermal Deposition (PAVTD) is utilized. Using a classical polymer as a source of material for plasma polymerization, hybrid classical-plasma polymer thin films with tunable properties can be prepared. Recently, continuous-feed PAVTD has been developed.

**Keywords:** Plasma polymer, plasma-assisted vapour thermal deposition, continuous process

## 1. Introduction

Plasma polymerization/Plasma-Enhanced Chemical Vapour Deposition (PECVD) serves well for the preparation of organic thin films with high crosslinking [1, 2] for deposition of protective or barrier coatings [3, 4], films for packaging and wettability control [5, 6] or in the biomedical field [7-9].

Plasma polymerization mostly works with a volatile precursor, fragmented and repolymerized in the plasma zone. The requirement for the volatility of the precursor limits its molar mass and, in this way, its chemical structure complexity. Additionally, due to fragmentation and subsequent repolymerization into semi-random structures, the final molecular structure of the film typically does not correspond directly to the molecular structure of the original precursor [10].

One of the ways how to overcome this limitation of plasma polymerization is to produce the “monomer” molecules in-situ. Using this idea, plasma-assisted vapour thermal deposition (PAVTD) has been developed [11]. PAVTD uses a classical polymer as a source of comparatively high molar mass oligomers ( $10^2$  to  $10^3$  g/mol) obtained from thermal degradation/evaporation from a solid polymer placed in a crucible. These oligomers are released in a (RF) plasma and re-polymerized into a thin film that can be considered a hybrid film between classical and plasma polymers.

Since the evaporated fragments are typically much larger than a single monomeric unit of the original precursor, the resulting product preserves well the original chemical structure of the precursor, even with plasma-induced fragmentation and crosslinking. In this way, PAVTD utilizes both top-down and bottom-up processes.

Poly(lactic acid) (PLA) is a good model material since its molecular structure promotes PLA properties like biodegradability and hydrolyzability [12-14]. In thin films prepared using PAVTD, retaining the PLA structure was clearly demonstrated, as well as the possibility to tune the film properties in a very broad range, bridging the gap between the classical and plasma polymers [15, 16].

## 2. Batch PAVTD

Currently, the PAVTD method has several drawbacks compared with PECVD/plasma polymerization. When the deposition is done as a batch process, the duration of the deposition (~2h) and the resulting film thickness ( $10^2$  nm) are governed by the capacity of the crucible. Additionally, the thermal release rate of the precursor fragments is highly temperature- and history-sensitive. Then, fluctuations in the deposition rate are hard to avoid, which complicates retaining good reproducibility of the process [17]. The product of the process is mostly dependent on power to precursor mass flow ratio, i.e. Yasuda scaling law [18, 19]. Therefore, a more stable release rate of oligomers is desired.

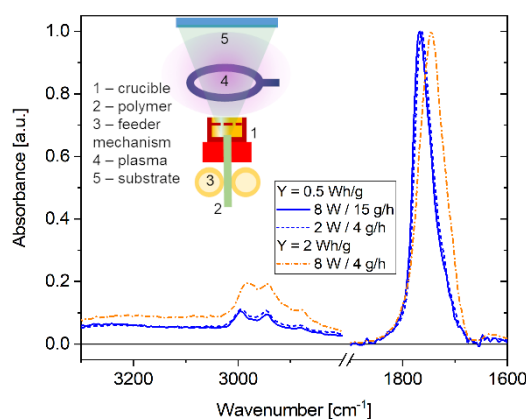


Fig. 1. Infrared spectra of PLA-like films prepared using PAVTD. Example of Yasuda-like scaling law utilizing better independent control of deposition rate and plasma power using continuous-feed PAVTD. (Inset: Simplified scheme of the PAVTD setup with continuous feed)

## 3. Continuous-feed PAVTD

To overcome the technical limitations of batch-PAVTD, a modification of the setup utilizing a commercial 1.75 mm diameter polymer filament for FDM 3D-printing fed into a modified off-the-shelf filament heater/extruder was made (Fig. 1, inset). Compared to 3D printing, the filament feed is much slower (several g/h), but this is a significant

material input for plasma polymerization. Plasma powers (RF, in argon at 0.4 Pa) between 0 and 32 W were utilized.

It was demonstrated that continuous feed of the material into the evaporation crucible significantly improves the stability of the deposition process [20]. The deposition rate could be increased by one order of magnitude (to several nm/s) at notably better deposition rate stability. The total running time of over 7 hours was demonstrated (limited only by the filament storage).

The improved stability of the process, together with an easier shift to lower energy-per-mass ratios, make PAVTD also a potential tool to study the plasma polymerization processes in a new way (Fig. 1, spectra). At the same time, PAVTD shows the potential to become a practical deposition method.

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