

# Solid coatings deposited from liquid methyl methacrylate via plasma polymerization

L. Wurlitzer<sup>1,2</sup>, S. Dahle<sup>1,2</sup> and W. Maus-Friedrichs<sup>1,2</sup>

<sup>1</sup>Clausthal Centre of Material Technology, Clausthal University of Technology, Agricolastraße 2, D-38678 Clausthal-Zellerfeld, Germany  
<sup>2</sup>Institute for Energy Research and Physical Technologies, Clausthal University of Technology, Leibnizstraße 4, D-38678 Clausthal-Zellerfeld, Germany

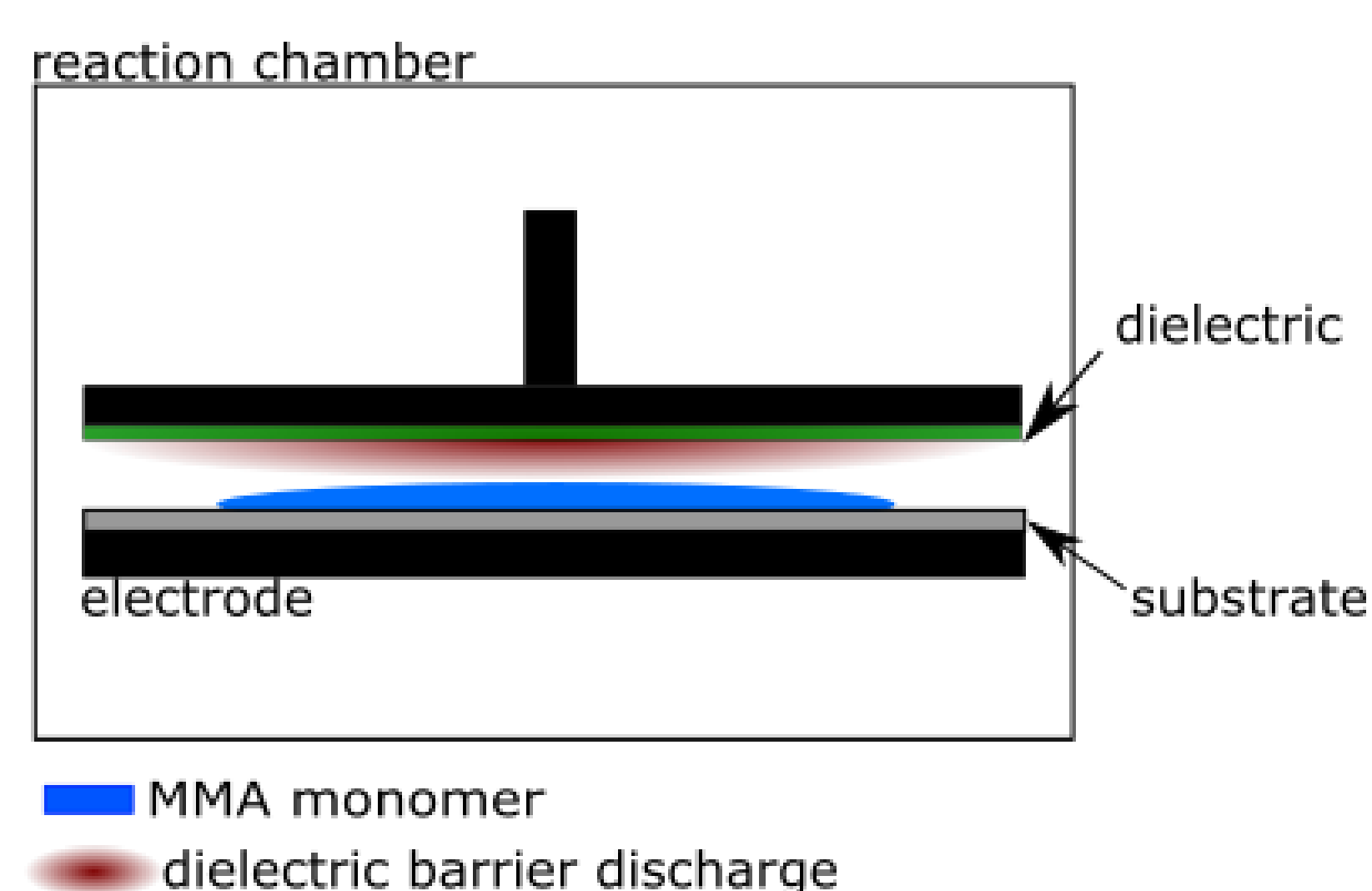


## Basic idea

Solid coatings usually are deposited via plasma enhanced chemical vapor deposition (PECVD), a well known technique in which the monomer that is used is in the liquid phase at room temperature. During the PECVD process, the monomer is transferred into the gas phase. On the one hand there is a phase transition in addition to a complex system for gas guiding but on the other hand the deposition does not take place on the substrate only. The whole reactor can catalyze the deposition reaction, so there is also deposition on the reactor walls. As a result, this leads to some higher costs.

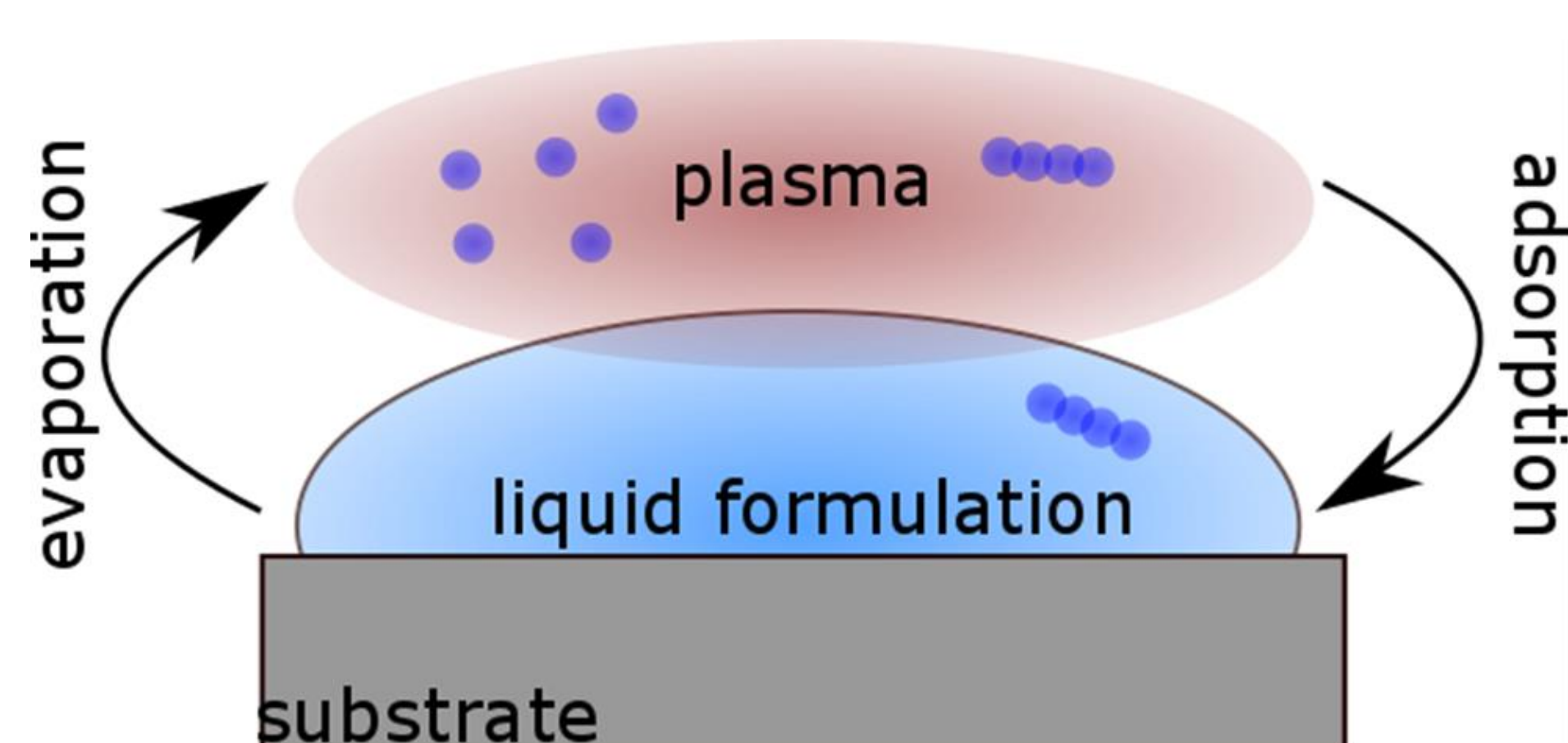
Using the monomer at room temperature in the liquid phase for the plasma enhanced deposition of solid coatings could be a better method. In this connection the monomer is directly applied to the substrate surface. In addition, this preparation method allows the inclusion of functional particles into the coating.

## Experimental setup



- Closed reaction chamber
- Discharge distance: 1 mm
- Atmospheric air
- Monomer on substrate: 1 ml
- HV short pulses; 13 kV peak voltage; 1.6 kHz repetition voltage; 0.6 μs pulse duration
- Plasma treatment time: 15 min

## PECSD mechanism



### Dynamic process:

- Evaporation of the monomer into the gas phase: formation of short oligomers
- Condensation: increasing oligomers chain length → polymer condensation

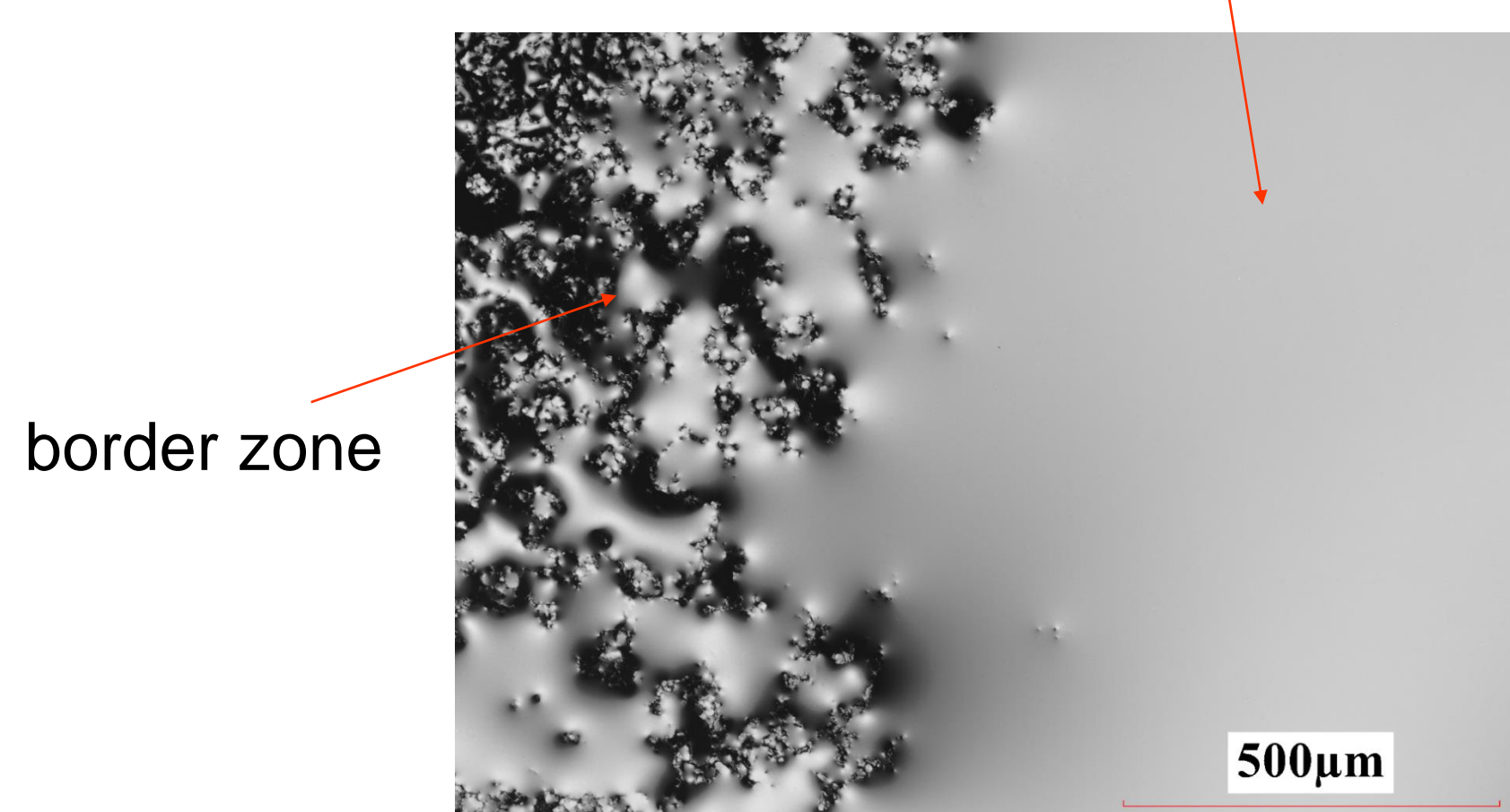
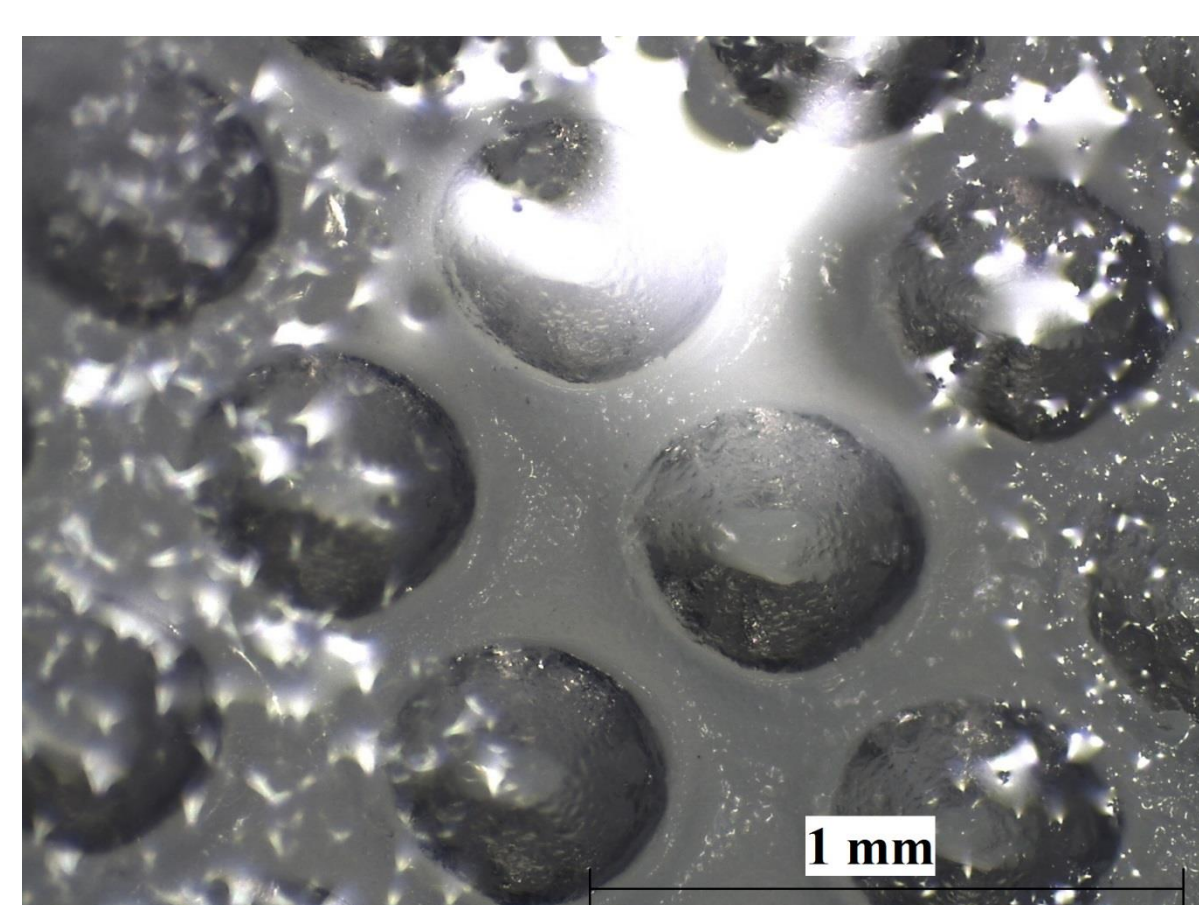
### 3 different reaction zones:

- Plasma phase: radicals initiate polymerization
- Liquid phase: polymerization of condensed oligomers continues
- Interphase: etching, chain scission, initiation of polymerization

## Analysis of coatings on polypropylene

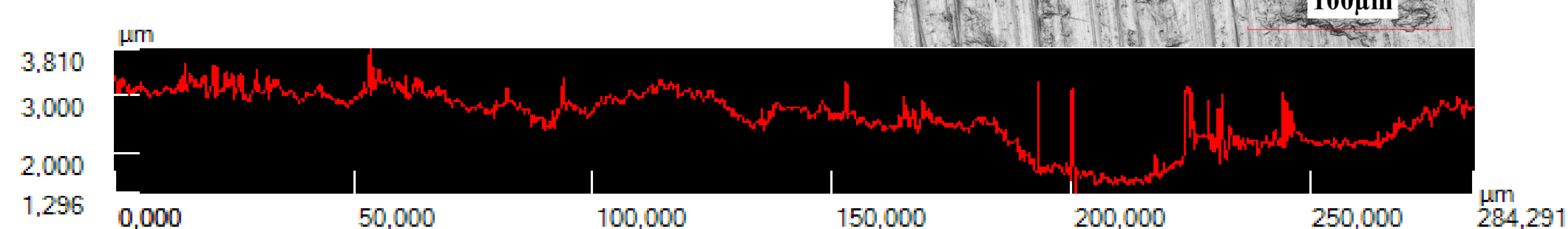
- Clear, colourless
- Firm coating
- Sticky

CLSM picture:  
➤ Coherent coating



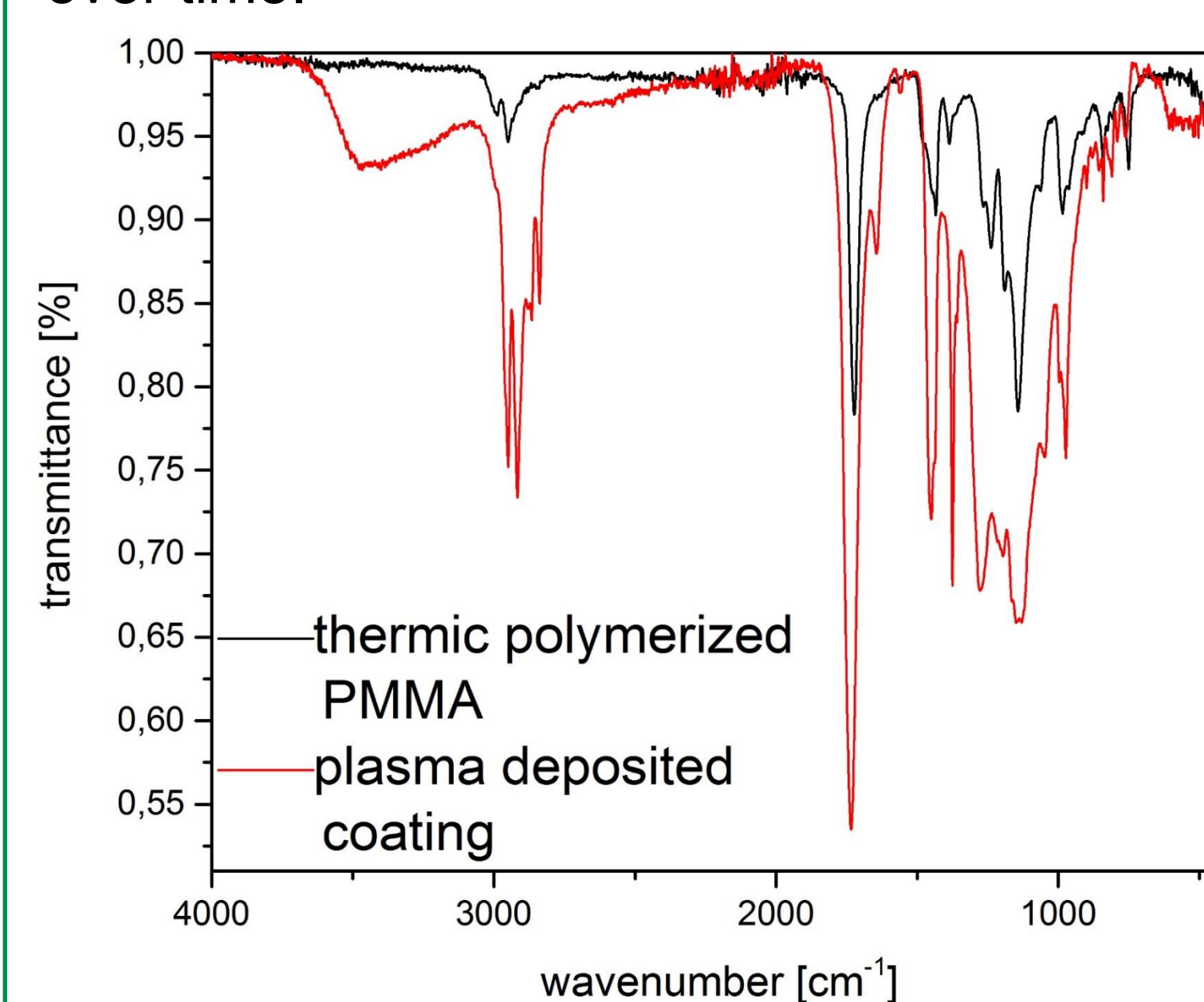
## Analysis of coatings on aluminum

- Surface profile of the solid coating on aluminum substrate
- 3 μm thick coating
  - No consistent thickness



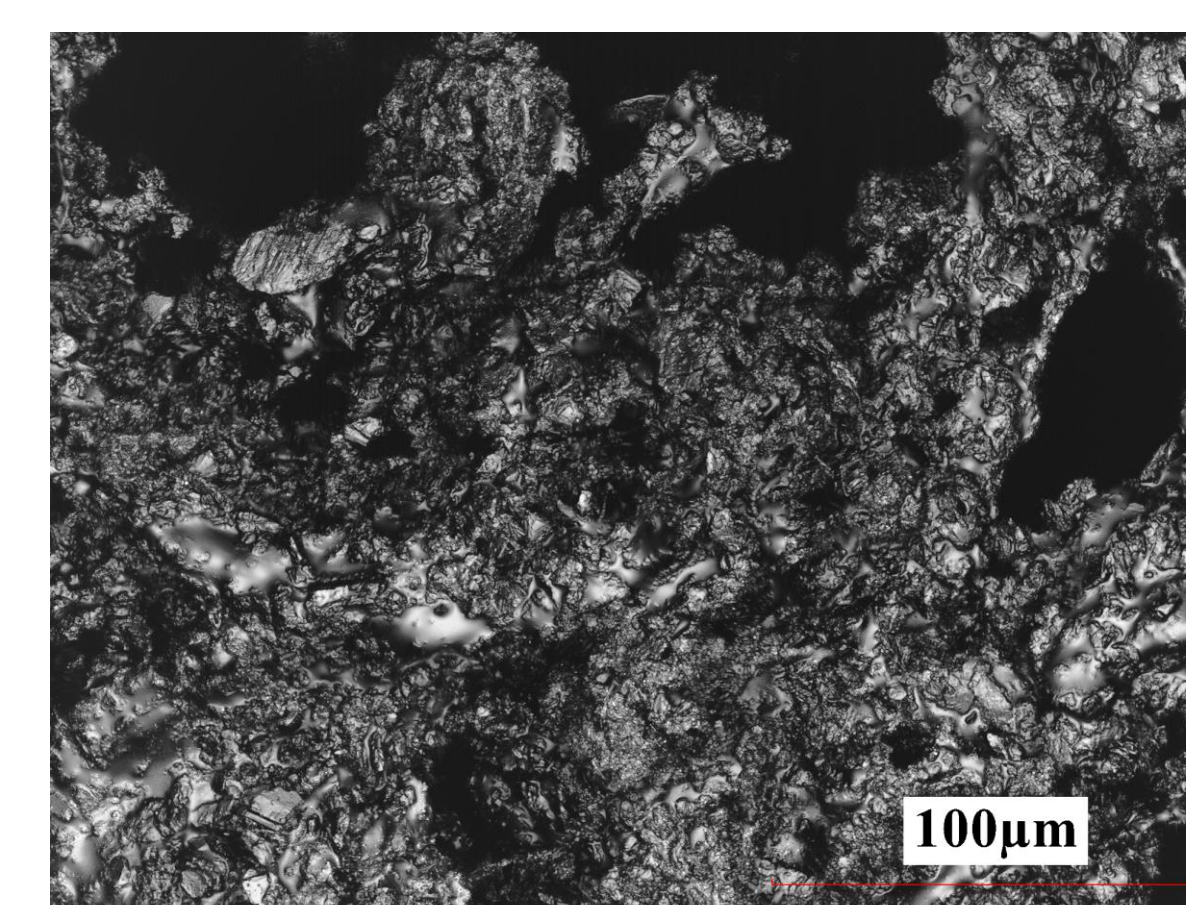
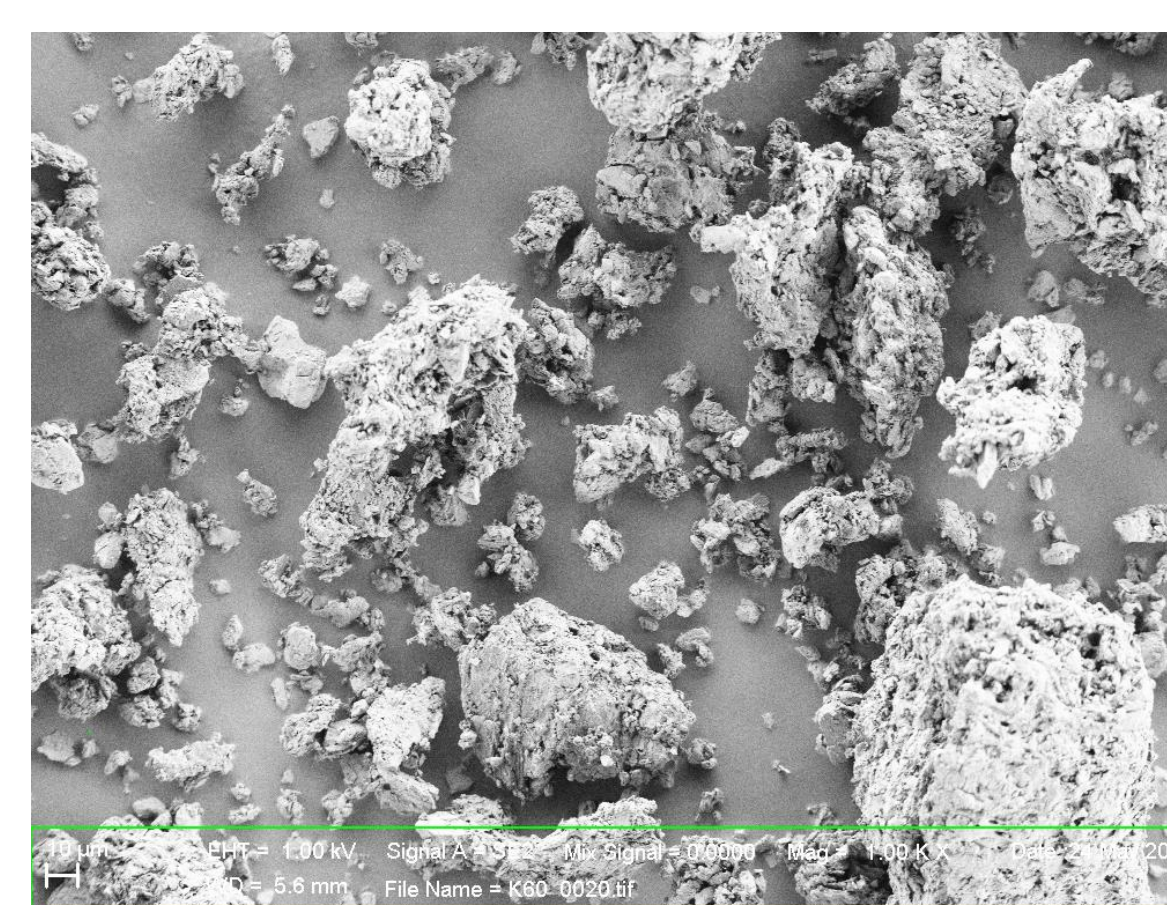
## Comparison to thermic polymerized PMMA

The plasma deposited coating is in ways different to thermic polymerized PMMA. For the plasma deposited coating peaks are seen directly from the monomer and on the contrary there are differences not depending on the appearance of the monomer. The plasma deposited coating comprised a large amount of water. However this can be removed by heating in a vacuum over 180°C and a scratch resistant coating will follow over time.



- Water peaks
- C=C double bond peaks from monomer
- CH<sub>2</sub> asymmetric and symmetric stretching vibrations and deformation peaks of the monomer
- Small amounts of monomer and water still remain in the coating
- Removable by heating

## Particle filled coatings

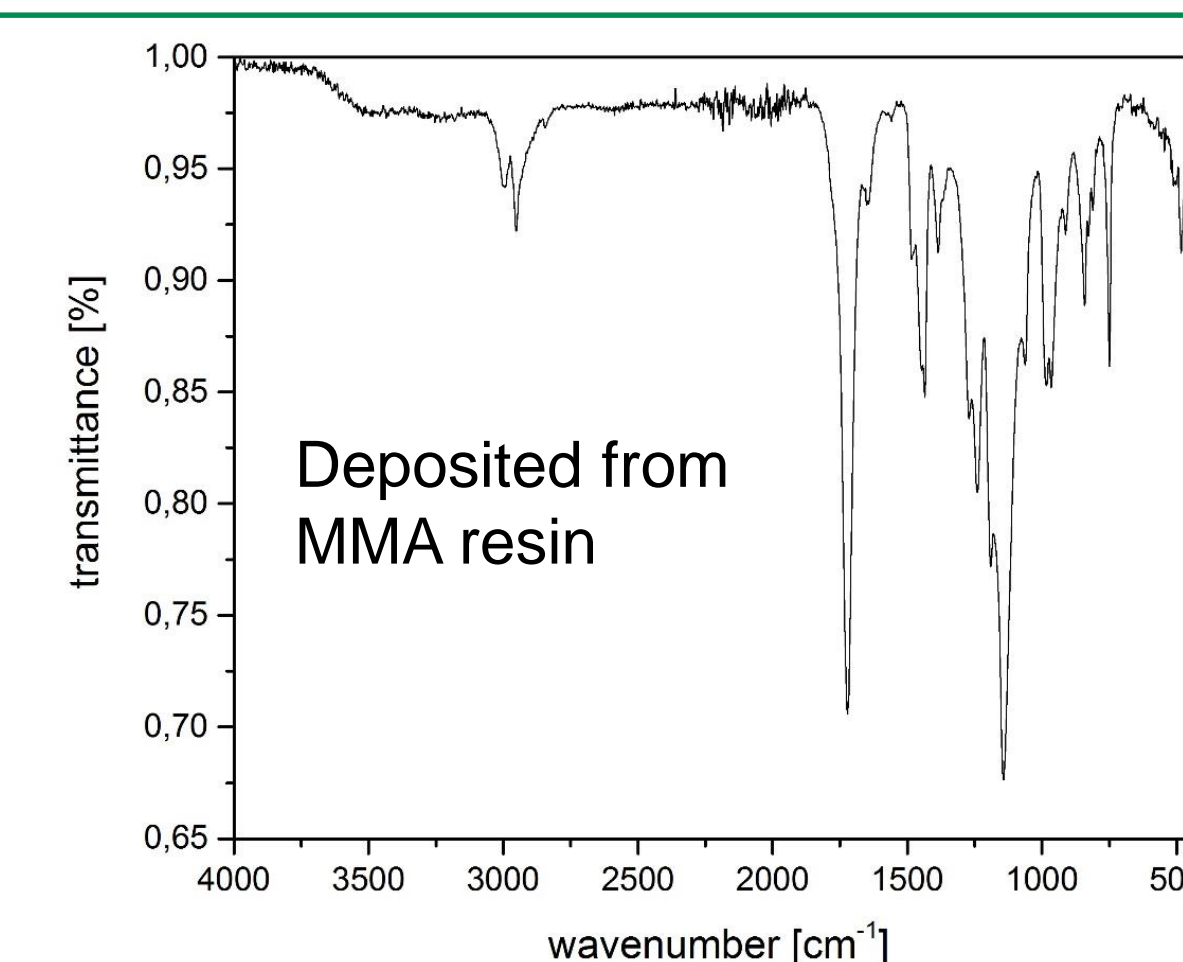


Filling material: aluminum hydroxide polymethyl methacrylate composite powder  
Preparation: swelling composite for 2hrs in MMA before application on the substrate

- Closed coating
- Powder is embedded into polymer coating
- Coating adheres to the substrate surface

## Summary/Outlook

- Firm, coherent coating which is at first sticky
- After heating process nearly scratch-resistant
- Method useful for deposition of particle filled films
- Using MMA as monomer is complicated: high evaporation rate, high loss
- MMA resin application: thicker coatings with low loss of monomer



## Acknowledgement

We are grateful for the use of the CLSM from Prof. Endres, Institute of Electrochemistry and for the use of the ATR-IR from Prof. Schmidt, Institute of Organic Chemistry, Clausthal University of Technology. We also thank KOLPA by courtesy of SEM measurements.