Functional coatings on wood-based materials using PVD and atmospheric plasma

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Overview

Part 1 – PVD coating

- Aim of the feasibility study
- PVD-Process / Magnetron Sputtering
- Materials & Methods
  - Substrates and coating materials
  - Thin film deposition using magnetron sputtering
- Results
  - PVD-coating on wood-based materials
  - Characterization of the thin films
  - Prototyping of an electrically conductive laminate board

Part 1 – Aim of the study

- To make wood-based products sustainable and future-oriented, the development of multifunctional, smart and even intelligent surfaces (interactive, electronic, self-analyzing) is more and more postulated.
- This requires wood and wood-based substrates to be provided with electrically conductive layers and structures.

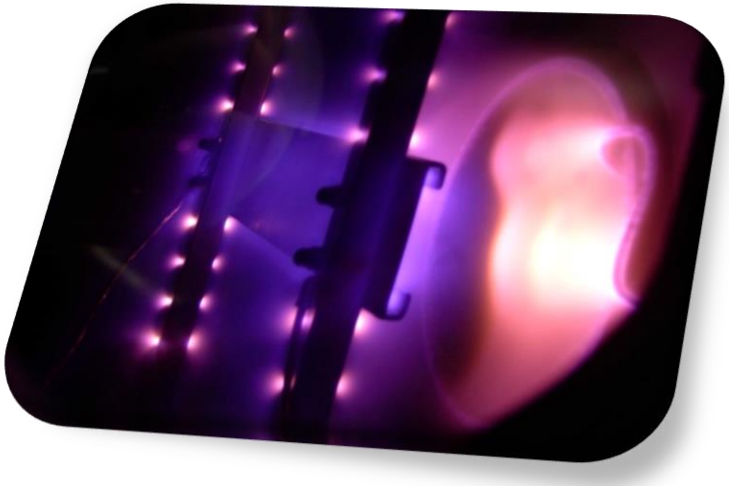
→ **Aim of the present feasibility study** was to generate an electrically conductive film on wood and wood-based materials using the PVD (physical vapor deposition) technology.

→ Application focus of the study was the integration of electronic features in wood-based furniture components.

Part 1 – PVD-Process

Modern PVD process technologies are used for the deposition of high quality films with different functional properties, like

- scratch- and wear-resistant
- easy-to-clean
- conductive
- antimicrobial
- hydrophilic / hydrophobic



Main basic PVD process technologies

- Evaporation
- Magnetron sputtering
- Arc source deposition

PVD processes are mostly plasma and/or ion assisted

→ to control and optimise the deposition process

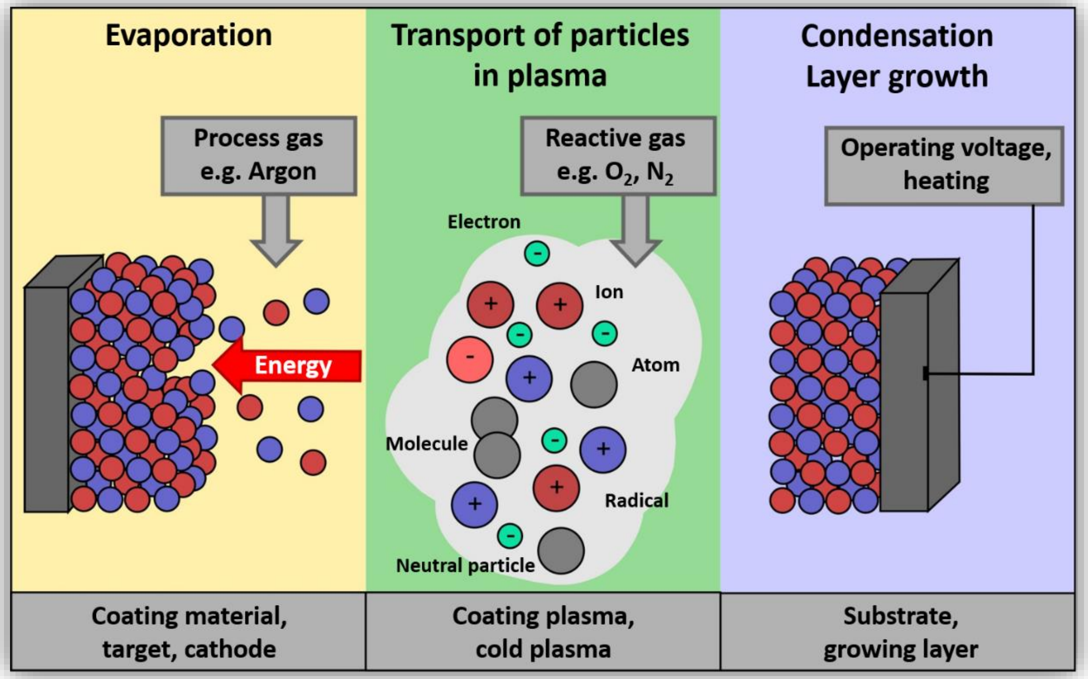
→ improve the properties of the obtained films, for e.g. good film adhesion, high film density and hardness and low surface roughness

Part 1 – Magnetron Sputtering

Magnetron sputter deposition is a non-thermal vaporization process, in which surface atoms and molecules of a target material (metal, alloy, oxide) are physically ejected from a solid surface by transfer via an energetic bombardment of gaseous ions from a plasma (usually argon).

The deposition of a thin film can be divided into three phases:

1. Generation of the coating species (atoms, molecules and clusters) by bringing energy into a target material
2. Transport of these particles from source to substrate (mostly plasma assisted)
3. Condensation and adsorption of the particles on the substrate and layer growth



Bewilogua K (2013) *PVD und CVD Verfahren*, OTTI Fachforum, Regensburg
Mattox DM (1998) Handbook of Physical Vapor Deposition (PVD) Processing, Noyes Publication

Part 1 – Magnetron Sputtering

Advantages of magnetron sputtering processes in comparison to conventional coating technologies for the deposition of metal films on wood-based materials

- Electrically conductive films can be applied directly onto the substrate, regardless of its surface roughness and the thickness of the substrate.
- Use of an almost unlimited number of different target materials (metals, alloys and oxides).
- Process temperature remains constantly low (below 50°C) → enormous advantages, especially for the temperature-sensitive wood-based materials.
- Process can be adapted to the geometry and size of the substrates; a full-area coating of the substrate can be achieved in one process step.
- “Dry” coating process: no solvents, liquid chemicals, etc. are used → avoid swelling of hydrophilic materials like wood, wood-based materials and paper.

Part 1 – Materials & Methods

Materials

- Substrates: MDF; European oak timber; WPC (70% wood flour, 30% PP); kraft paper (80g/m²)

Magnetron sputtering deposition

- Target material: molybdenum
- Process gas: argon
- Total pressure: 10^{-2} to 10^{-1}mbar
- Voltages: 200V to 400V
- Temperature: below 50°C
- Frequency: dc mode

Vacuum magnetron sputter deposition unit Auto 306 Vacuum Coater from Edwards (MCT – Material Center Tyrol, University of Innsbruck)

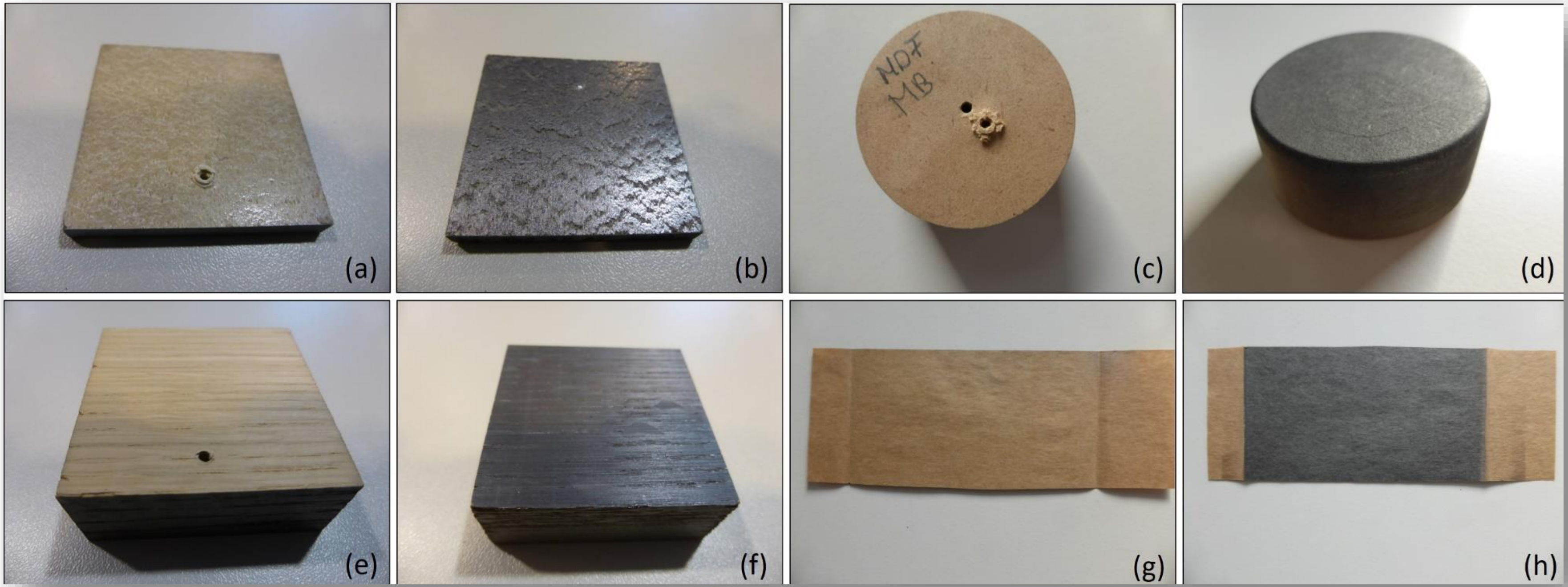
Part 1 – Results

PVD-coating trials / Characterization tests / Prototyping

Part 1 – PVD-coating

PVD-coating on wood and wood-based substrates

- Successful deposition of a homogenous molybdenum film with a thickness of approximately 300nm on all tested materials.
- Individual surface topographies maintain (e.g. "open-pore" structure of oak).



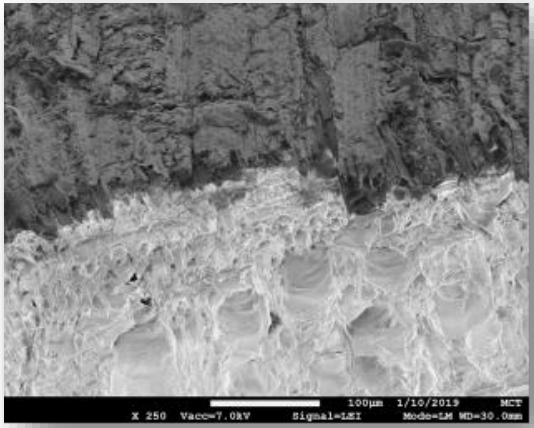
Images of the uncoated (a), (c), (e), (g) and PVD-coated specimens (b), (d), (f), (h)
WPC (a) and (b); MDF (c) and (d); oak timber (e) and (f); paper samples (g) and (h)

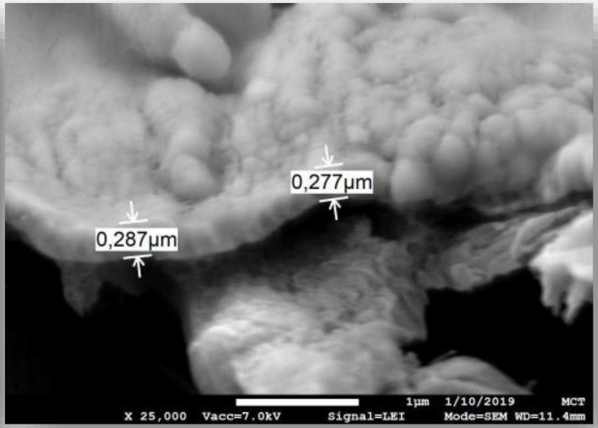
Part 1 – Characterization

- **Adhesion of the thin films**

Cross cut tests (manually) with 2 cuts in longitudinal and cross section; examination was carried out using a microscope.

Results: Good adhesion, no delamination





SEM-image of the molybdenum-coated oak sample
(a) 250-fold magnification and
(b) 25.000-fold magnification

- **Determination of film thickness**

Determination of the layer thickness from the images by means of a scanning electron microscope at a 25.000-fold magnification.

Results: On average, thicknesses of 300nm were measured

Part 1 – Characterization

- **Measurement of electrical conductivity of the thin films**

Electrical resistance measurements using a tera-ohmmeter (uncoated samples) and a multimeter (PVD-coated samples).

Results: The electrical resistance values of the PVD-coated samples are significantly lower by a factor of 10^6 (oak) to factor 10^{10} (WPC).

Resistance values of the uncoated and molybdenum-coated specimens

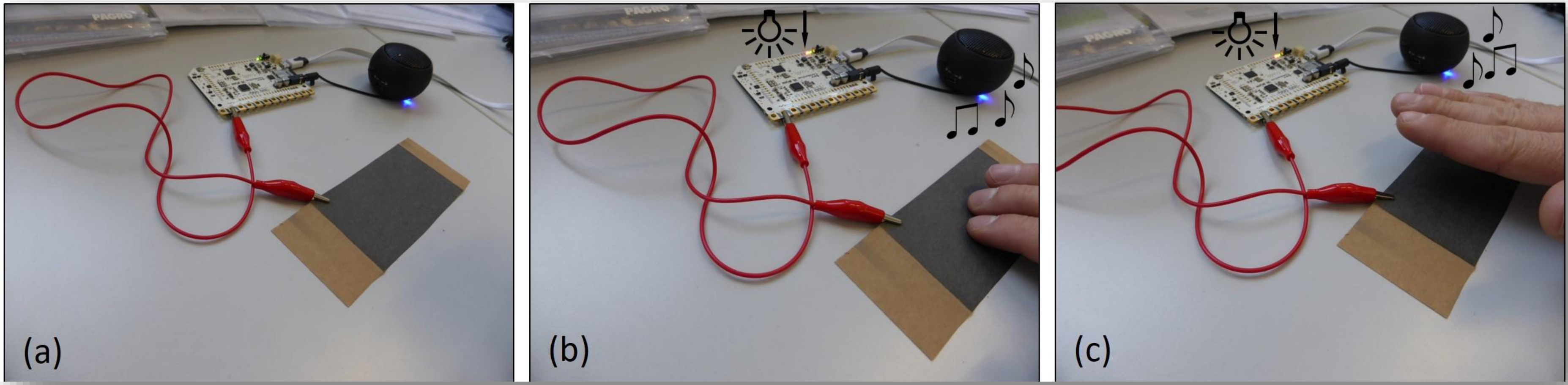
No.	Materials	Resistance [Ω] before PVD-coating	Resistance [Ω] after PVD-coating
1	WPC	$8 \cdot 10^{12}$	227 ± 21
2	MDF	$5 \cdot 10^{11}$	1010 ± 113
3	Oak	$3 \cdot 10^{9}$	1200 ± 173
4	Paper	$2 \cdot 10^{11}$	320 ± 17

Part 1 – Characterization

- **Investigation of electrical conductivity of the thin films**

Examination of effectiveness of the electrical conductivity of the thin layers was performed using a microcontroller board with loudspeaker.

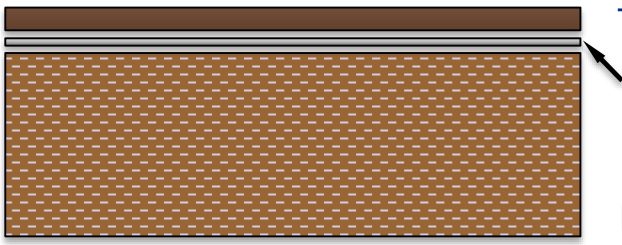
Results: For all tested materials the switching circuit was operating both in the touch and the capacitive proximity function.



Switching circuit due to the conductive molybdenum layer on the paper sample (a) in standby-mode, (b) operating via touch function and (c) via capacitive proximity function.
The switching function is indicated by an orange LED lamp lighting up and by an acoustic signal transmitted via loudspeaker.

Part 1 – Prototyping

Prototyping of an electrically conductive laminate board



Top layer: walnut veneer 0,6mm

Intermediate layer: molybdenum PVD-coated paper

Base plate: particle board 19mm

- Bonding: 2K-Epoxy system (amount = 140g/m²)
- Hydraulic pressing: $T = 100°C$; $t = 10min$; $p_{spec} = 3bar$

Results:

- Prototype of a wood-based laminate board with an integrated conductive layer
- After lamination, no significant increase of the electrical resistance of the PVD-layer was detected (has to be confirmed on large-scale specimens)
- The effectiveness was tested using the microcontroller board: the conductive laminate board worked both in the touch and capacitive proximity function

Part 1 - Conclusion & Outlook

- In the present feasibility study, molybdenum films with thicknesses of approx. 300nm were successfully deposited on wood-based materials (MDF, oak, WPC, paper).
- The thin films exhibit good adhesion to all substrates, a homogenous surface topography and distinguished electrically conductive properties.
- A prototype of a conductive laminate board with integrated molybdenum layer was successfully produced.

Further studies and experiments:

- Due to the outgassing of wood-based materials further optimization of the magnetron sputtering process and adaption of parameters (pressure, temperature, gas supply, sample holder, plasma conditions, chemical composition of gaseous phase) are required to deposit repeatable layer systems with desired film properties.
- Development and production of conductive laminates in full-scale components with different laminate structures according to customer demands.

Overview

Part 2 – Atmospheric plasma coating

- Aim of the feasibility study
- Atmospheric plasma coating
- Materials & Methods
  - Substrates and coating materials (precursors)
  - Thin film deposition using atmospheric plasma
- Results
  - Deposition of different functional coatings on wood-based materials
  - Characterization of the coated materials

Part 2 – Aim of the study

- Background was an increasing number of demands from customers, companies and interested stakeholders on the topic of hydrophobic coatings on paper, non-wovens and wood-based materials as well as on antimicrobial surface coatings and adhesion promoter layers.
- Therefore, the study should investigate whether plasma technologies can be used to develop such functional surface coatings that will be industrially feasible.

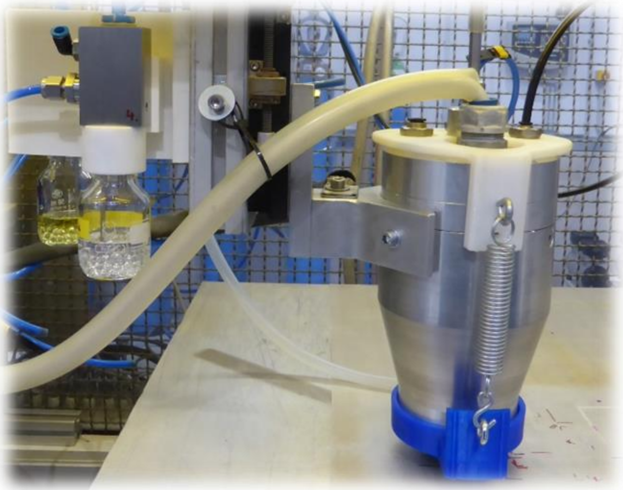
→ **Aim of the present feasibility study** was to deposit different functional and transparent films on wood-based materials using the atmospheric plasma technology.

→ Application focus of the study was to generate hydrophobic, antibacterial/antimicrobial and adhesion promoter layers for different applications in the packaging, wood and furniture industry.

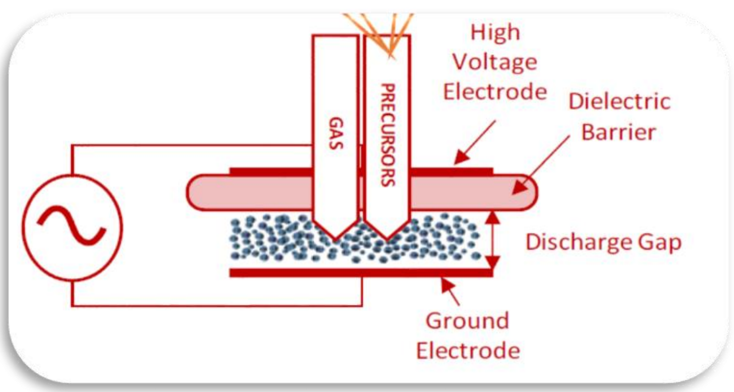
Part 2 – Atmospheric plasma coating

Molecular Plasma Technology (MPG - Molecular Plasma Group)

R&D equipment of MPG with a PlasmaSpot® (Source: MPG)



PlasmaSpot® in co-injection mode (Source: MPG)



Functional principle of the PlasmaSpot® from MPG (Source: MPG)

Part 2 – Atmospheric plasma coating

Molecular Plasma Technology

- Gas Type: no limitations
- Low-Energy Plasma: (non)-polymerizable H_2, CO_2, NH_3, C_2H_2,….+ liquid precursors
- Application: Permanent tailor-made surface functionalization

Advantages of Molecular Plasma

- Injection of liquid precursors (nanosized aerosols) → tailored grafting
- Mild plasma treatment:
  - Maintain integrity of precursor
  - No negative effect on bulk properties
  - Process remains at ambient temperature
  - Possibility to treat inert materials (PTFE, PVDF,..) as well as natural (wood, paper, wool,..) and biodegradable materials (PLA,..)
- No solvent emission, no drying step, no contaminated waste water

Part 2 – Materials & Methods

Materials

- Substrates: Birch plywood; non-woven fabric; WPC (70% wood flour, 30% PP) Standard and with carbon black additives; kraft paper (80g/m²)
- Precursor for the coating: APTES (Aminopropyltriethoxysilane); PFDTES (Perfluorodecyltriethoxysilane); GLYMA (Glycidylmethacrylate)

→ Generation of different functional, transparent nanofilms:

- Antibacterial coatings on plywood and paper (APTES)
- Hydrophobic coatings on plywood, paper and non-woven fabric (PFDTES)
- Adhesion promoter between WPC and an acrylic topcoat (GLYMA)

Part 2 – Materials & Methods

Atmospheric plasma coating

- Equipment: PlasmaSpot® from MPG
- Process gas: nitrogen
- Gap between nozzle and substrate: 1mm
- Line speed: 4m/min
- Step size of the nozzle: 50mm
- Ambient temperature
- Atmospheric pressure

Standard R&D equipment of MPG with a PlasmaSpot®

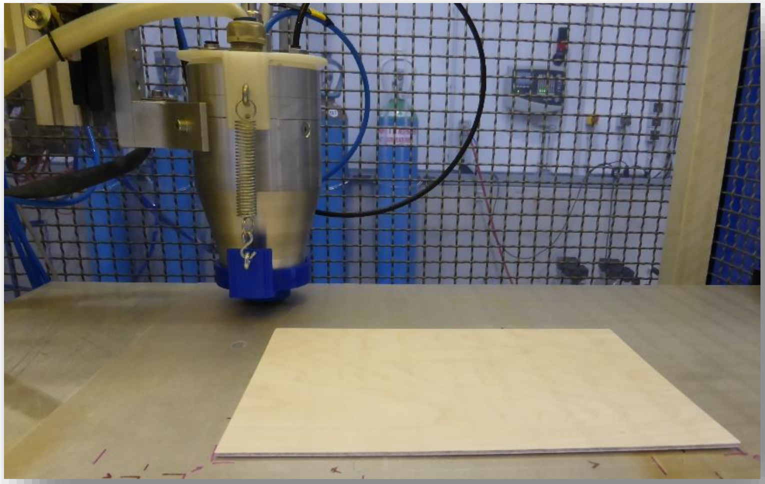
Part 2 – Results

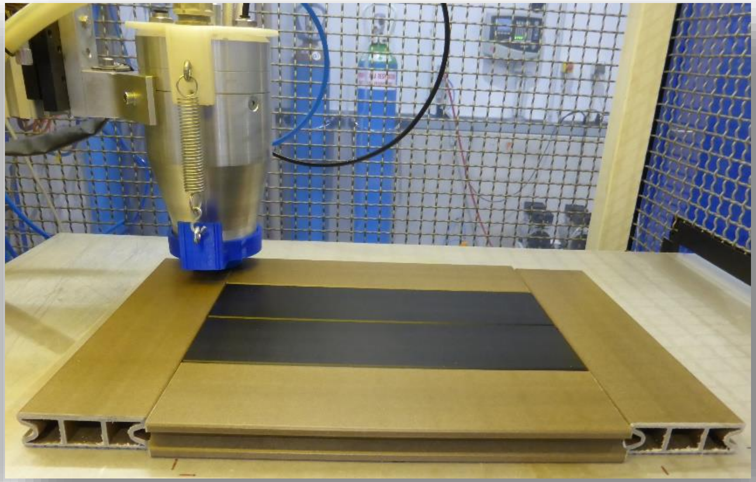
Atmospheric plasma coating trials / Characterization tests

Part 2 – Atmospheric plasma coating

Atmospheric plasma coating on wood-based substrates

- Successful deposition of functional, transparent coatings based on different precursor types on all the tested wood-based materials.





Above:
Plasma coating on plywood (left) and WPC samples (right)

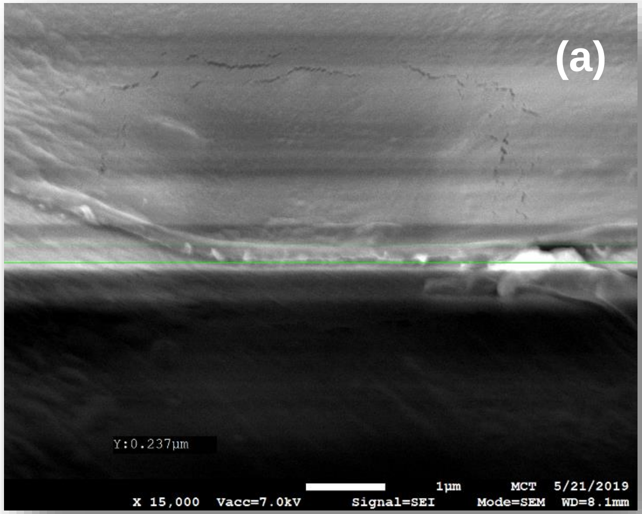
Below:
“Superhydrophobic” coating on a plywood sample

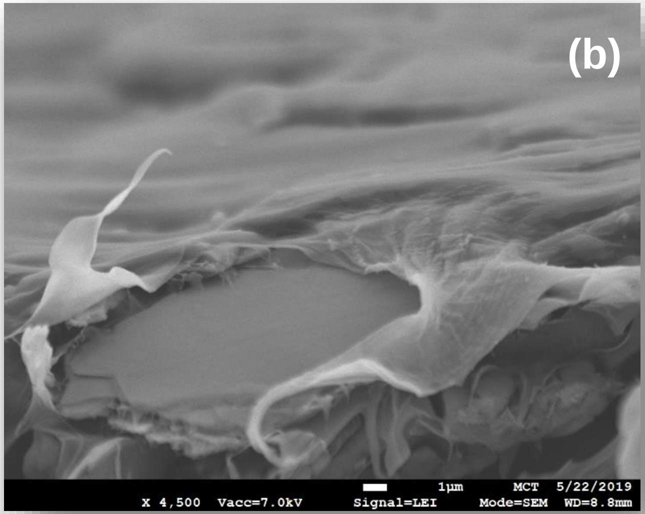
Part 2 – Characterization

- **Determination of film thickness**

Determination of the layer thickness from the images by means of a scanning electron microscope.

Results: On most samples, the fracture edge was too fissured to determine the layer thickness and to analyze the layer morphology → Exception: Fluorinated silane layer (PFDTES) on plywood (film thickness = 237nm). Detection of the layer was also possible on the WPC sample with the adhesion promoter coating (GLYMA) due to its elastic-plastic deformation.





(a) SEM-image of the PFDTES-coated plywood sample at 15.000-fold magnification

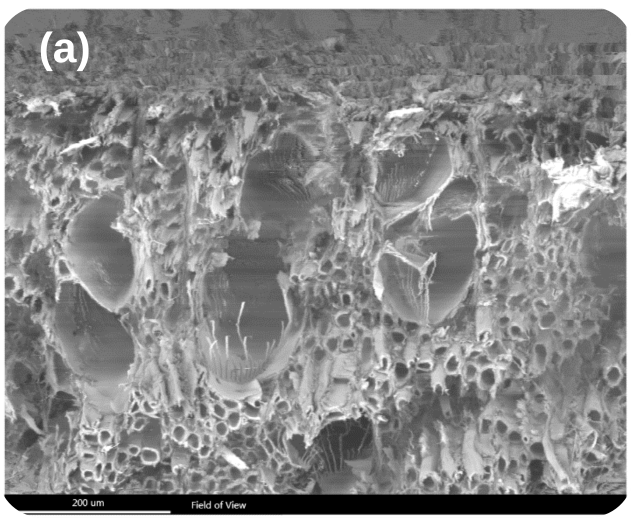
(b) SEM-image of the GLYMA-layer on the WPC sample at 4.500-fold magnification

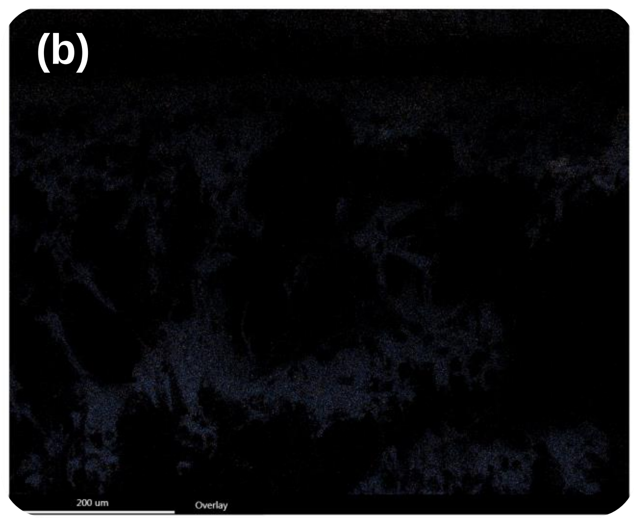
Part 2 – Characterization

- **Material analysis (“SEM-EDX Mapping”)**

In addition to the SEM images, a material analysis by means of energy-dispersive X-ray spectroscopy was carried out on the plywood with PFDTES layer with the aim of determining the penetration depth of the plasma layer.

Results: The analysis for the selected image section showed a distribution of the elements carbon : silicon : fluorine of 88% : 6% : 7%. The evaluation also showed that silicon and fluorine from the plasma coating penetrate into the plywood at least to a depth of 400µm.





(a) Selected image section for the material analysis of the plywood coated with PFDTES

(b) Graphic representation of the element analysis by means of EDX

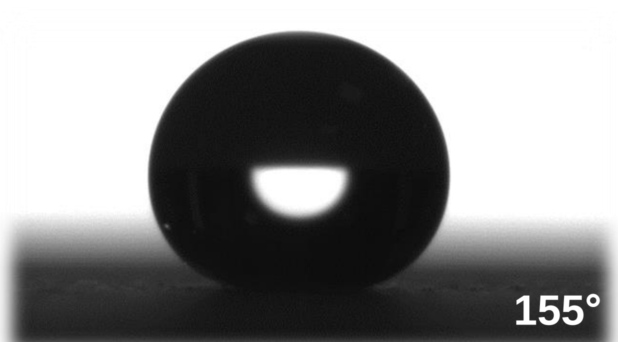
Part 2 – Characterization

- **Contact angle measurements**

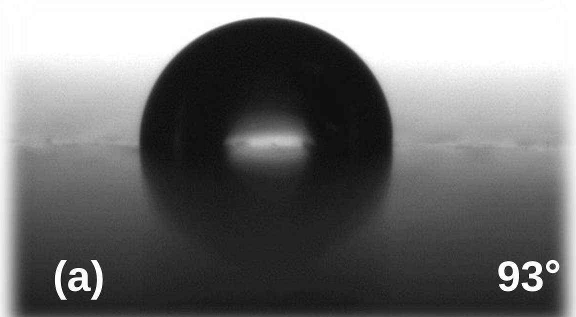
Investigation of changes in the surface energy behavior of wood-based materials after the deposition of different functional coatings.

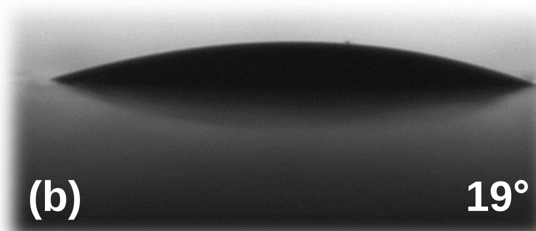
Results:

- Plywood, paper and non-woven materials: Due to the fluorinated silane layers (PFDTES) “superhydrophobic” properties with surface energy values **below 10mJ/m²** were achieved.
- WPC: Due to the adhesion promoter layer (GLYMA) an improved wettability of the unpolar WPC-surface was obtained (untreated WPC: 30mJ/m²; coated WPC: 65mJ/m²).



Water contact angle on plywood coated with PFDTES





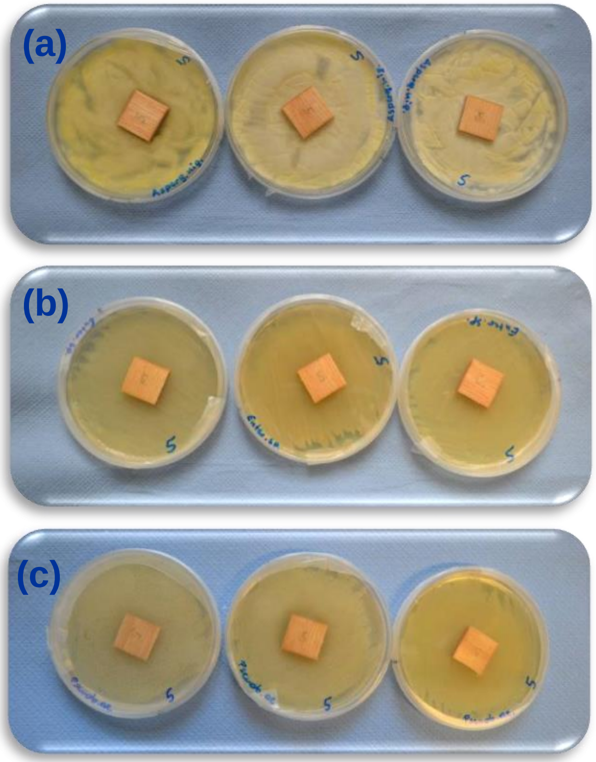
Water contact angle on (a) WPC uncoated and on (b) WPC coated with GLYMA

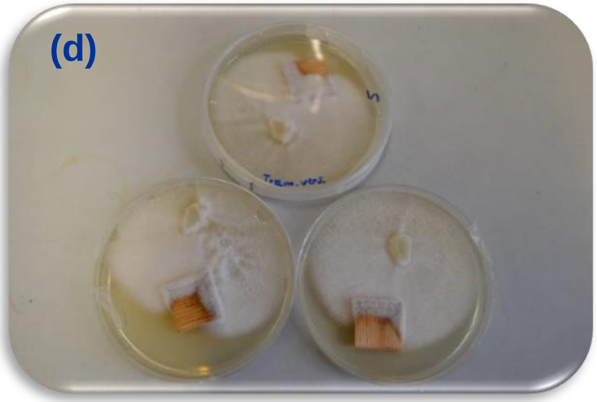
Part 2 – Characterization

- **Microbiological examination**

Plywood and paper samples with an APTES and PFDTES coating with silver nanoparticles were tested using 2 fungal strains (*aspergillus niger, trametes versicolor*) and 2 bacterial strains (*pseudomonas aeruginosa*, *enterobacter sp.*).

Results: Tests showed no inhibitory effect





Plywood with APTES-coating tested with
(a) *aspergillus niger*,
(b) *enterobacter sp*.
(c) *pseudomonas aeruginosa* and
(d) *trametes versicolor*

Possible reasons for the insufficient inhibition:

→ Precursor type

→ Amount of nanoparticles was too low

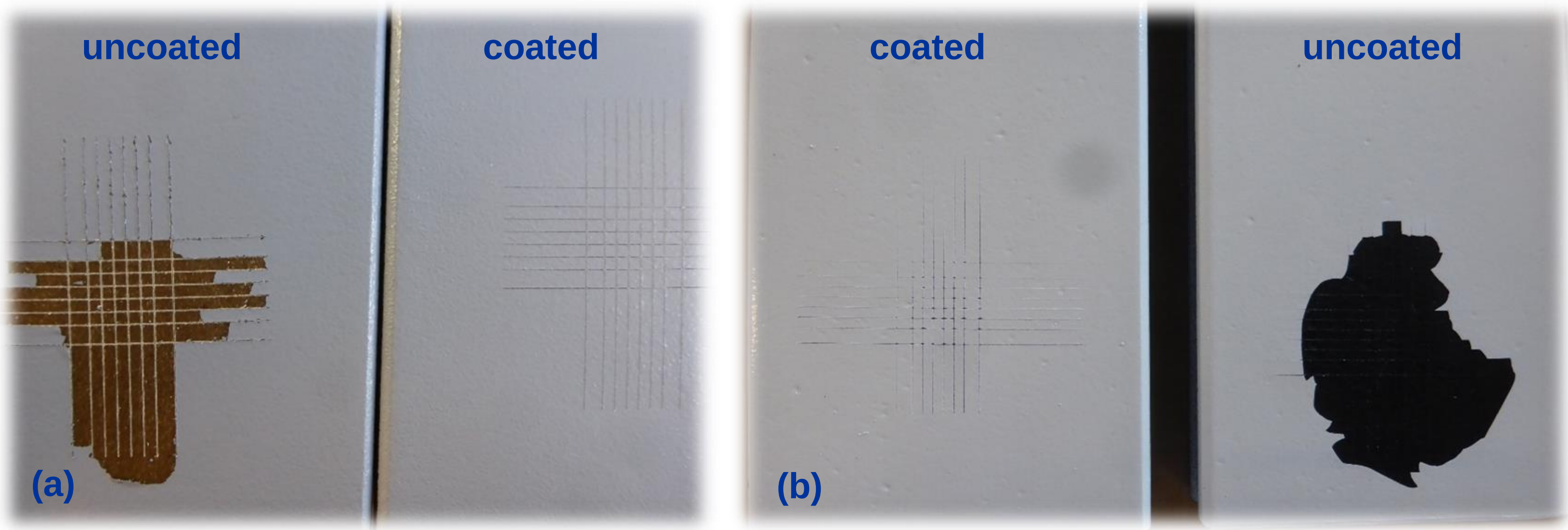
→ Layer thickness of a few 100nm was too small

Part 2 – Characterization

- **Test of adhesion between the GLYMA-coated WPC and acrylic topcoats**

WPC profiles with the adhesion promoter layer (GLYMA) were coated using an acrylic powder coating system and an acrylic wet paint. Afterwards, cross cut tests were performed.

Results: Very good adhesion between WPC and both acrylic topcoats



Cross cut tests on WPC profiles with an adhesion promoter layer (GLYMA) using (a) a wet acrylic paint and (b) an acrylic based powder coating

Part 2 - Conclusion & Outlook

- In the present study, functional coatings (hydrophobic, antibacterial, adhesion promoter) were successfully deposited on wood-based materials (plywood, non-woven fabric, paper, WPC) using the atmospheric plasma technology.
- Depending on the particular application, tailor-made surface properties could be achieved, i.a. “superhydrophobic" surfaces on plywood, paper and non-woven materials as well as adhesive layers on WPC-profiles that showed an excellent adhesion to subsequently applied powder coatings and wet paints.

Further studies and experiments:

- Optimization of the plasma deposition (use of further/alternative precursors, adaption of process parameters) is required to generate repeatable layer systems with desired film properties.

Thank you for your attention!

Acknowledgements

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