

# **Plasma treatment on biobased materials**

**Judith SINIC**

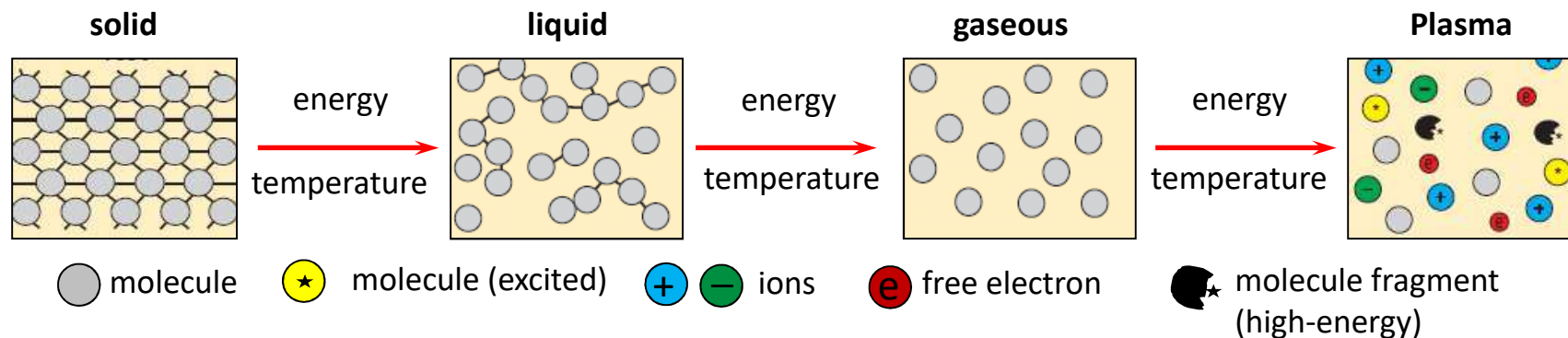
**Student Camp Biorefineries and Biobased Industrial Products**  
Linz, February 25-28, 2019

# Introduction

## Plasma

*"Over 99% of the matter in the universe is in the plasma or plasma-like state. When energy is added to solid matter, it becomes liquid and finally gaseous. If you continue to add energy, the gas will change to the plasma state in which atoms and molecules are in excited or ionized form. "[1]*

Plasma is therefore often called the 4th state of aggregation.



[1] A. Wolkenhauer et al. (2005): Haftungsverbesserung von Holzbeschichtungen durch Plasma-Vorbehandlung; Holztechnologie 46 (2005) 3, Carl Hanser Verlag München  
Chart: Plasmatrete GmbH Steinhagen (modified)

# Introduction

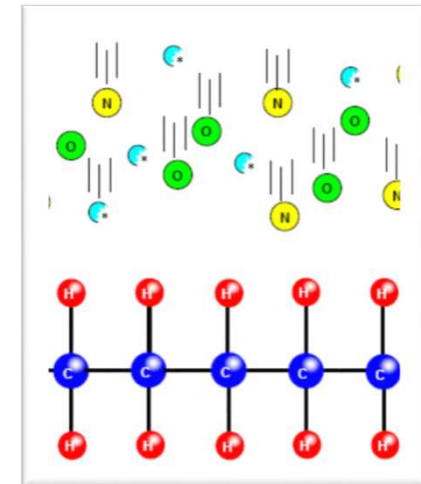
## Technical use of Plasma

Plasma activation: Activation of the surface by addition of functional groups. The surface energy of the substrate is increased. This is a prerequisite for good adhesion of paints, varnishes, inks, adhesives.

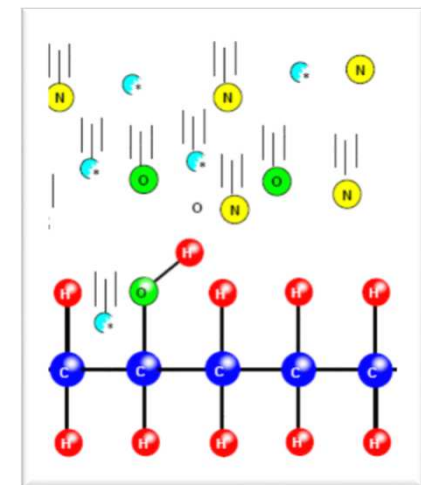
Plasma etching: Material removal of surfaces by plasma processes. The process gases convert the material to be etched into the gaseous state.

Plasma coating: Plasma-based processes in which substrates of all kinds are coated with thin layers of different materials, for example hydrophilic / hydrophobic layers, tribological and corrosion layers, antibacterial / antimicrobial layers, adhesion promoter layers ...)

Plasma cleaning: Removal of grease, oil or releasing agent residue; Mechanical cleaning by micro sand blasting with argon plasma; Reduction of oxide layers on metals



Surface activation  
via oxidation processes



# Introduction

## PECVD – Plasma Enhanced Chemical Vapour Deposition

In the low-pressure plasma technique, gas is excited in vacuum by supplying energy. High-energy ions and electrons are generated as well as other reactive particles that form the plasma. This allows surfaces to be effectively modified.

There are three different plasma effects:

- Micro sand blasting: The surface is removed by ion bombardment
- Chemical reaction: The ionized gas reacts chemically with the surface
- UV radiation: The UV radiation breaks long-chain carbon compounds



Low-pressure plasma system from Diener electronic (Certottica Srl)

Applications: packaging industry, automotive industry, furniture industry, medical engineering, sports equipment industry, textile industry

# Introduction

## Atmospheric pressure plasma (plasma jet)

As a result of a high voltage discharge, an electric arc is generated. Compressed air, which passes the electrodes, is transferred to the plasma state. Through the nozzle head, the plasma reaches the substrate to be treated (potential-free). Activation and fine cleaning of the surface are carried out by the reactive particles contained in the plasma jet. Loosely adhering particles on the surface are removed.



Atmospheric pressure plasma system from Plasmacreat (Wood K plus)

By varying the speed of treatment and the distance to the substrate surface, the treatment can be controlled.

### Applications:

Pretreatment of plastics, glasses, ceramics, wood-based materials for subsequent printing, coating and glueing processes; Activation and ultra-fine cleaning of metals before soldering or bonding; Sterilization treatments

# Introduction

## PVD – Physical Vapour Deposition

PVD technology is a process for producing metallic layers by generating a partially ionized vaporization of the metal, its reaction with certain gases, and the formation of a thin film on the substrate exhibiting a specific composition. The PVD process is carried out under high vacuum.

The most common methods:

- Sputtering: Evaporation is created by bombarding a metal target with high-energy gas ions.
- Cathodic arc discharge: Arc discharges in a vacuum that hit the metal target and vaporize the material.

### Applications:

Deposition of layers of carbides, nitrides and carbonitrides for cutting and forming tools, mechanical components, medical devices and products, etc. that benefit from the hardness of the coating.



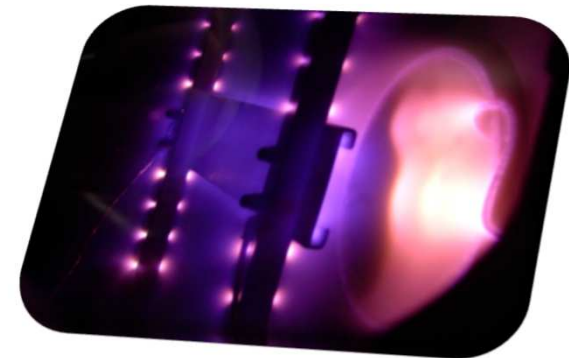
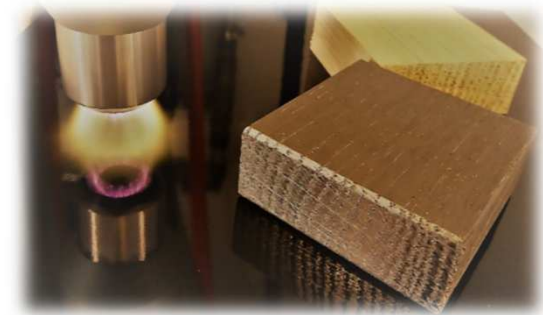
Vacuum magnetron sputtering system from Edwards (Material Center Tyrol)

# Plasma treatment on biobased materials

**Plasma treatments on wood, timber products and fibre material enable long-term stable and efficient coating and treatment processes**

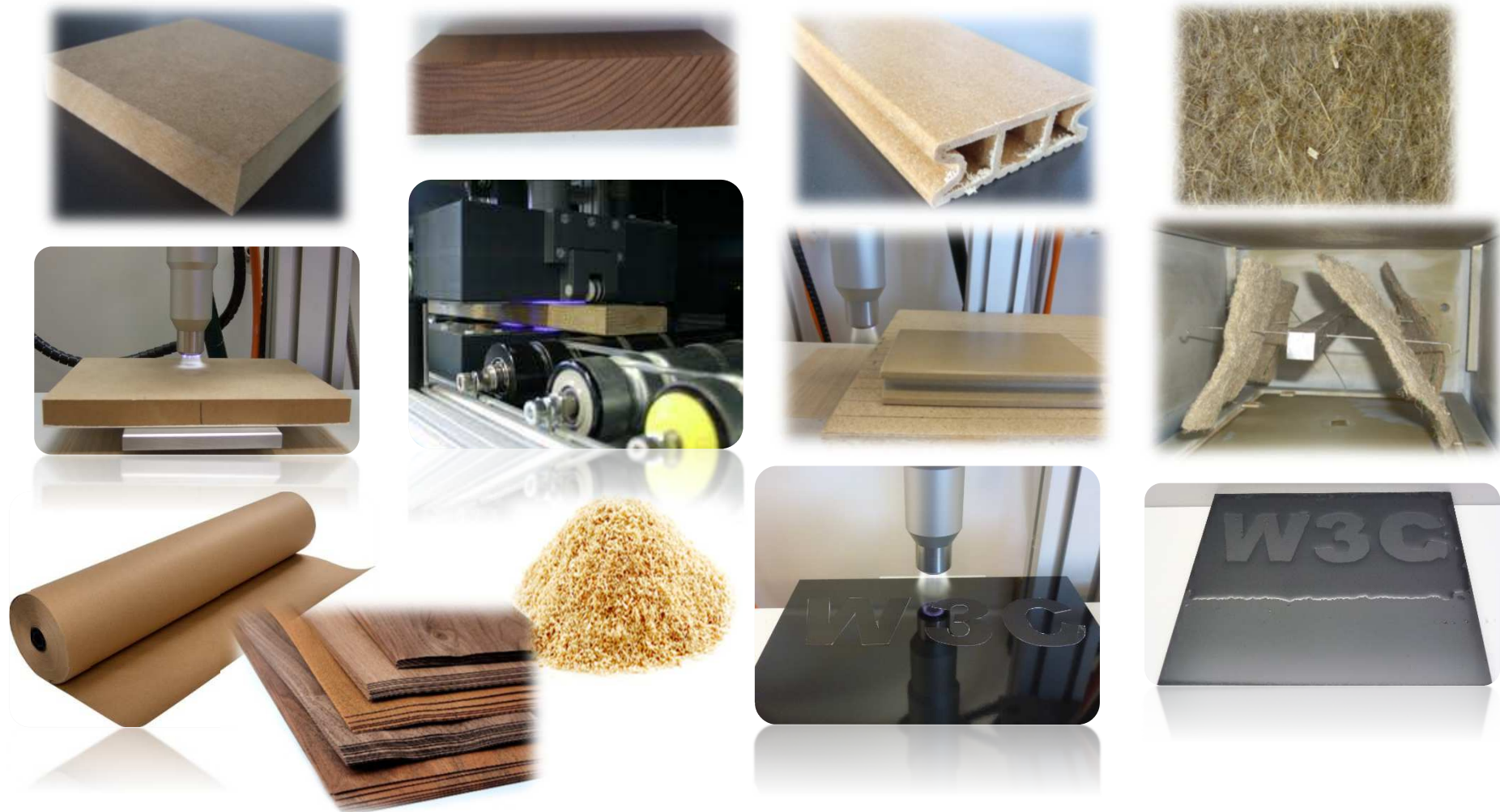
## Advantages of plasma treatments

- Homogenous distribution of liquid coatings on surfaces
- Improved penetration of resins and modification agents
- Increase in adhesion of coating systems and bonded joints
- Germ and spore reduction
- Plasma coating methods: generation of functional and decorative thin layers on surfaces



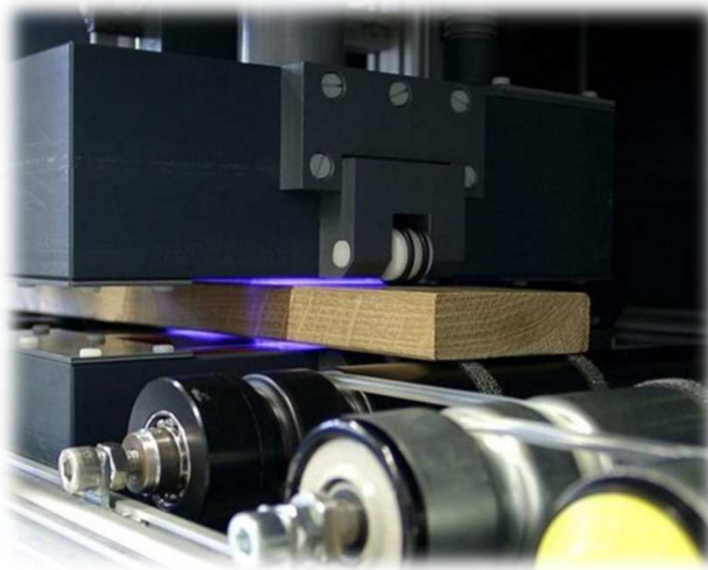
# Plasma treatment on biobased materials

## Areas of application



# Plasma activation

## Plasma treatment of wood



**Plasma equipment for the treatment of solid wood  
(up to 30mm thickness)**

Source: Anwendungszentrum für Plasma und  
Photonik des Fraunhofer-IST

### Industry-oriented prototype for an activation of wood and timber product surfaces

- Use of a dielectric barrier discharge (DBD) under atmospheric pressure
- Fast and extensive pretreatment of wood and timber products (no heating of the substrate)
- Pretreatment for subsequent coating with paints, varnishes and adhesives <sup>[1], [2]</sup>

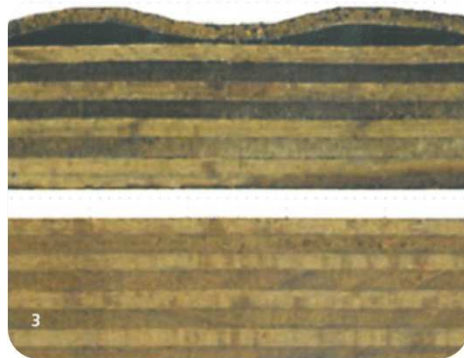
[1] A. Wolkenhauer et al. (2005): Haftungsverbesserung von Holzbeschichtungen durch Plasma-Vorbehandlung; Holztechnologie 46 (2005) 3, Carl Hanser Verlag München

[2] Georg Avramidis et al. (2010): Holzoberflächenmodifikation mittels Atmosphärendruckplasma; Vakuum in Forschung und Praxis, Vol.22 Nr.1, WILEY-VCH Verlag GmbH & Co.KGaa, Weinheim

# Plasma activation

## Plasma treatment on wood-based panels and chipped wood

Plywood panels of thermally modified beech wood veneers were plasma treated before bonding → No swelling of the veneer layers after artificial weathering.



**Plywood panels of thermally modified beech wood veneers after artificial weathering – untreated (above) and plasma treated (below)**

Source: Anwendungszentrum für Plasma und Photonik des Fraunhofer-IST



**Plasma treatment on wood strands for the production of oriented strand boards (OSB) (belt conveyor system)**

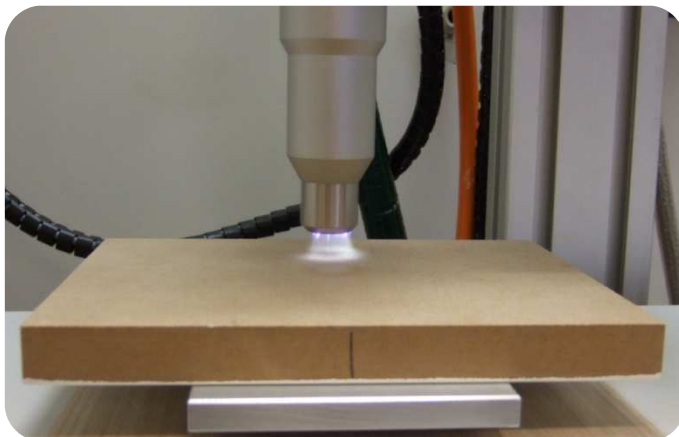
Source: Pressestelle der HAWK Hochschule für Angewandte Wissenschaft und Kunst

[http://www.hawk-hhg.de/aktuell/default\\_211593.php](http://www.hawk-hhg.de/aktuell/default_211593.php)

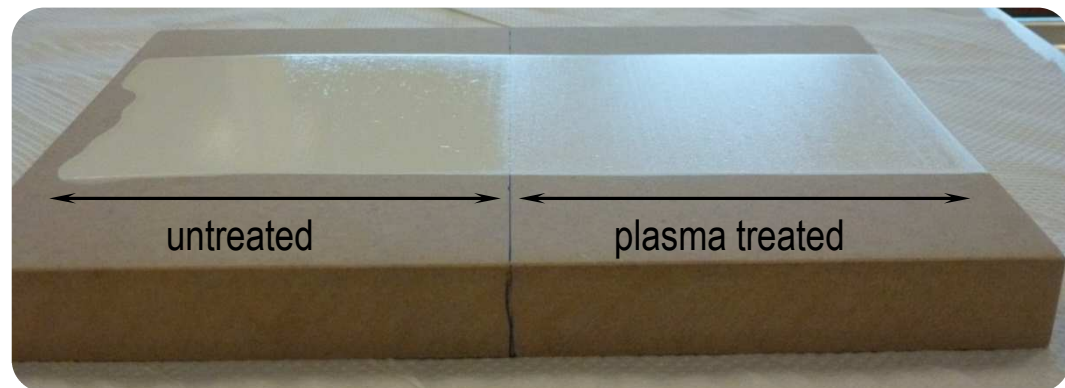
# Plasma activation

## Plasma treatment on Medium Density Fibre boards (MDF)

The plasma treatment on MDF panels increased the wettability of the surface. In coating trials with water based varnishes a faster surface drying was detected.



Plasma treatment on a MDF panel



Faster surface drying of the water based paint on the plasma treated part of the MDF panel

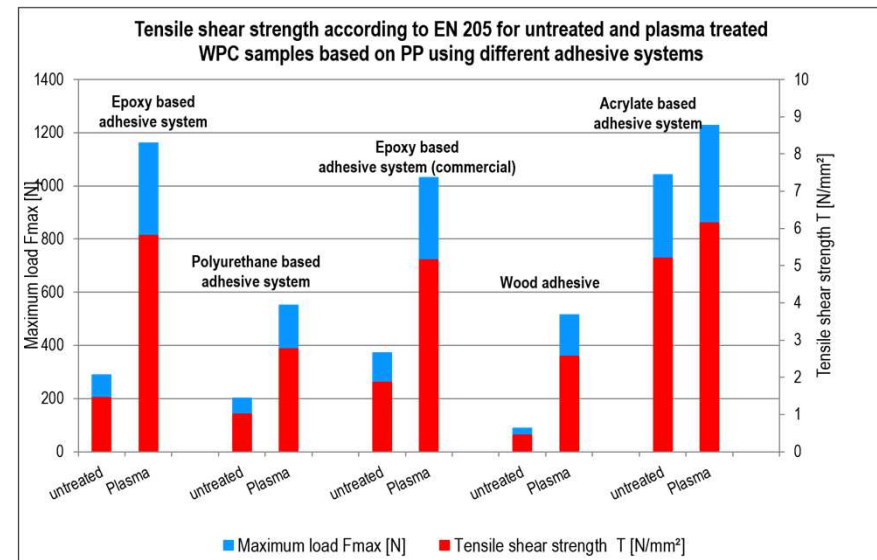
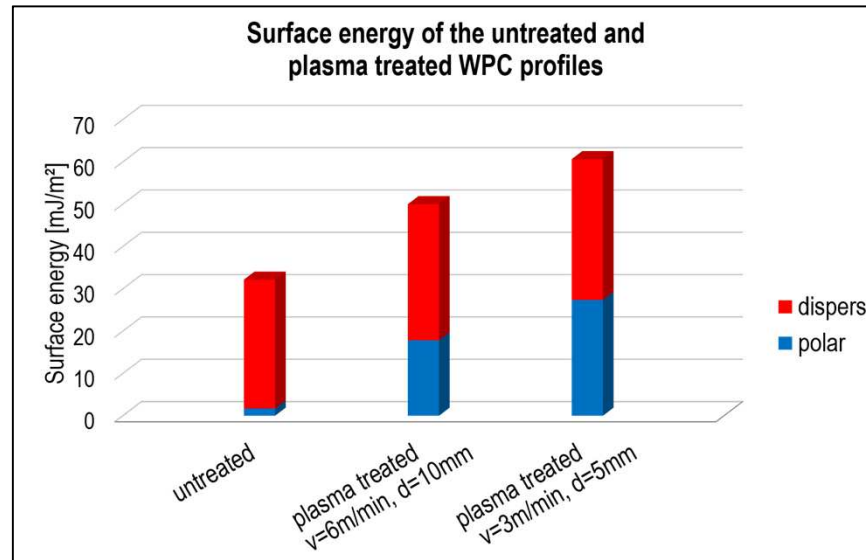
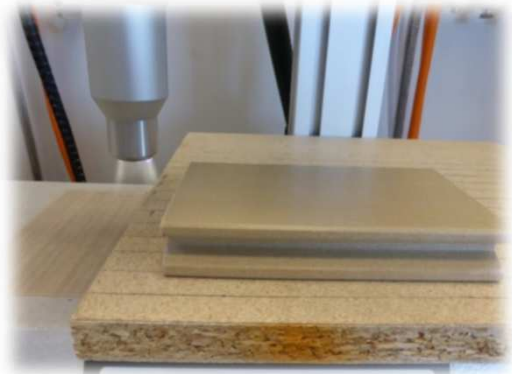
# Plasma activation

## Plasma treatment on Wood Plastic Composites (WPC)

WPC samples (60% spruce, 38% PP, 2% adhesion promoter) were treated using atmospheric plasma.

→ Increase of the surface energy (polar component) of the plasma treated samples due to a deposition of functional groups

→ Increase of the tensile shear strength after plasma treatment of the WPC samples using different adhesive systems



# Plasma activation

## Plasma treatment on flax fibre mats

By means of low-pressure plasma treatment flax fibre mats were pre-treated, afterwards impregnated by resin and finally pressed to a panel. The aim was to attain an increase of stiffness of the panel due to an improved adhesion between fibre and resin.



Untreated flax fibre mat

### Low-pressure plasma treatment

- The plasma treatment of the fibre mats was performed in a vacuum chamber of a low-pressure plasma equipment (Certottica Scrl).
- Different process gases (oxygen, air, argon/oxygen, and argon) and different treatment times (between 1min and 15min) were tested.



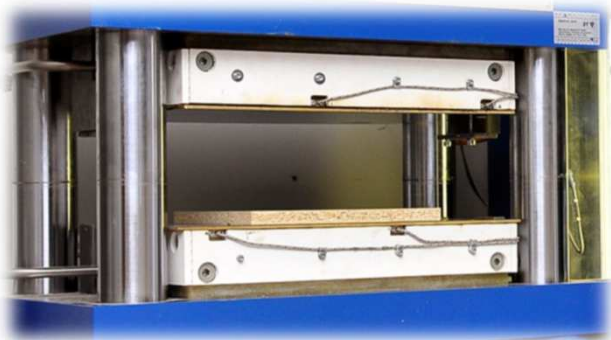
Plasma treatment of flax fibre mats by means of low-pressure plasma

# Plasma activation

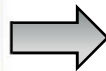
## Plasma treatment on flax fibre mats



**Impregnation with epoxidized linseed oil  
(30% resin, 70% fibres)**



**Pressing 180°C, 50bar, 15min**



**Untreated**



**Plasma treated**



**Max. bending strength [N/mm<sup>2</sup>]  
and max. flexural modulus  
[N/mm<sup>2</sup>] were achieved using  
oxygen as process gas with a  
treatment time of 5min**

**→ Increase of 20% in  
comparison to the untreated  
reference panel**

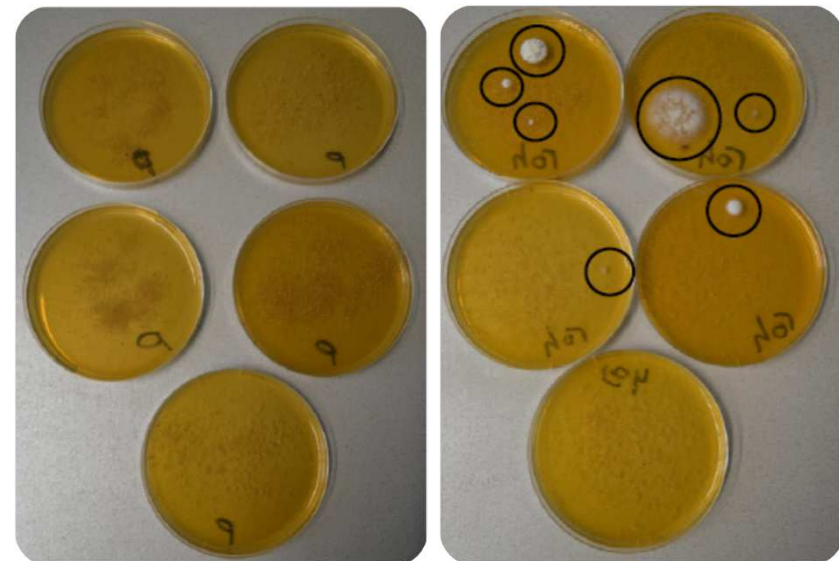
# Plasma activation

## Plasma treatment on wood flour

In a feasibility study wood flour samples were pre-treated using the low-pressure plasma technique and equipment (Diener GmbH). The aim of the plasma treatment of wood flour was to achieve a reduction of germ and spore in the wood, that could lead to mould and fungal attack.

→ In microbiological analysis no mould growth was detected in the plasma treated wood flour samples, whereas in the untreated samples sporadic growth was found (mould fungus of the species penicillium).

→ The plasma treatment had no influence on the moisture uptake of the wood flour samples.

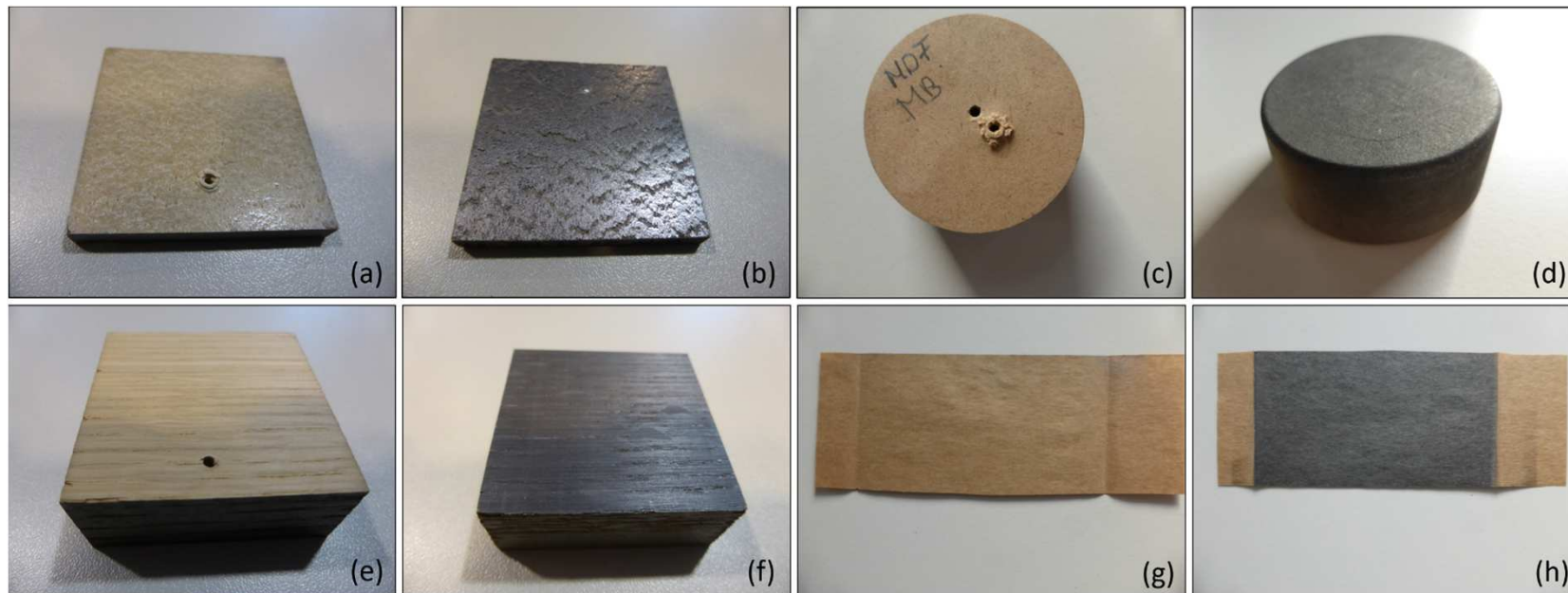


No mould growth on the test panels with plasma treated spruce wood flour (left);  
7 germ cells after 4 days incubation on test panels with untreated wood flour (right)

# Plasma coating

## Deposition of metallic thin layers on wood-based substrates using PVD

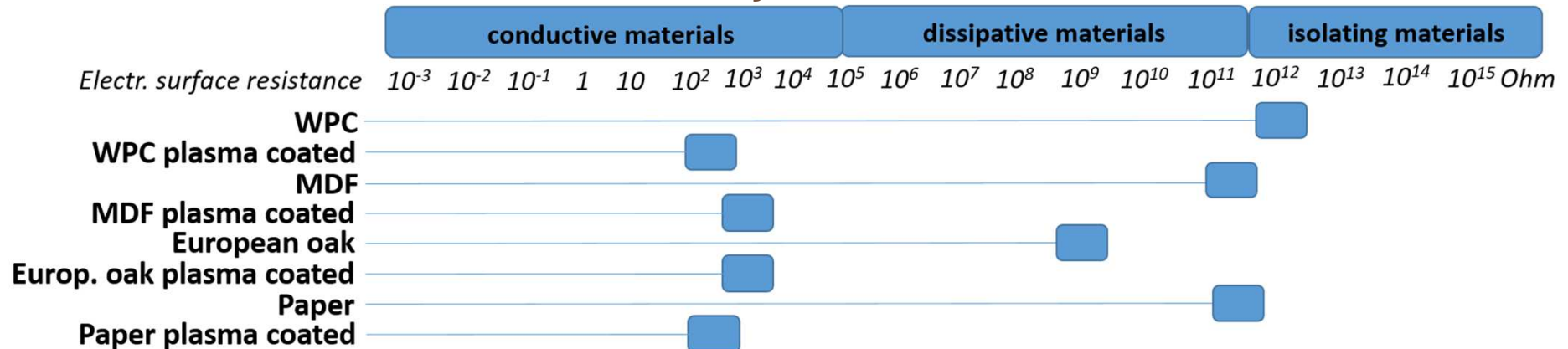
The aim of the feasibility study was to generate an electrically conductive film (thickness 300nm) with good adhesion on wood and wood-based materials using the PVD technology. The application focus was the integration of electronic features in wood-based furniture components.



(a) WPC untreated and (b) with molybdenum layer, (c) MDF untreated and (d) with molybdenum layer, (e) oak wood untreated and (f) with molybdenum layer, (g) paper untreated and (h) with molybdenum layer

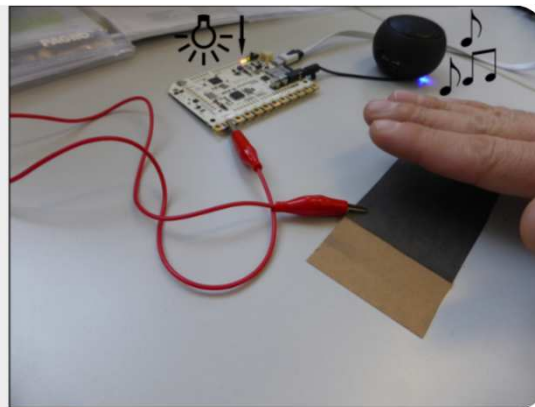
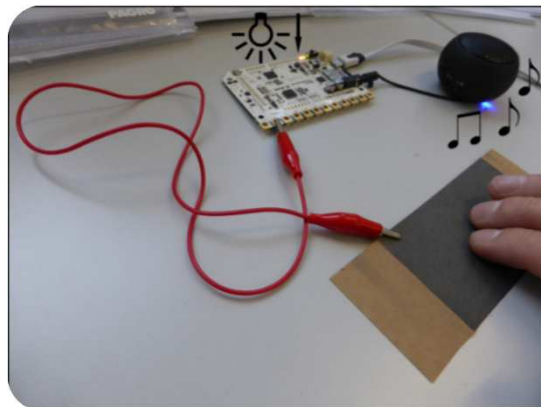
# Plasma coating

## Examination of electrical conductivity of the coated materials



## Microcontroller board with touch and capacitive proximity switching function

For all tested materials (WPC, MDF, oak, paper) the switching circuit was operating both in the touch and the capacitive proximity function.



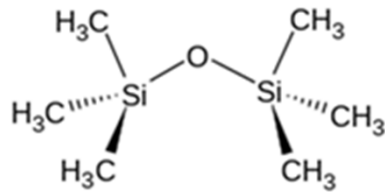
Due to the conductivity of the molybdenum layer on the paper the switching circuit was operating both in the (a) touch function and (b) proximity function → Orange LED lights up, signal tones can be heard via loudspeaker

# Plasma coating

## Deposition of a hydrophobic coating on natural fibre textiles and plywood

The aim of the feasibility study was to deposit a hydrophobic  $\text{SiO}_x$ -film on natural fibre textiles and birch plywood samples using CVD under vacuum conditions.

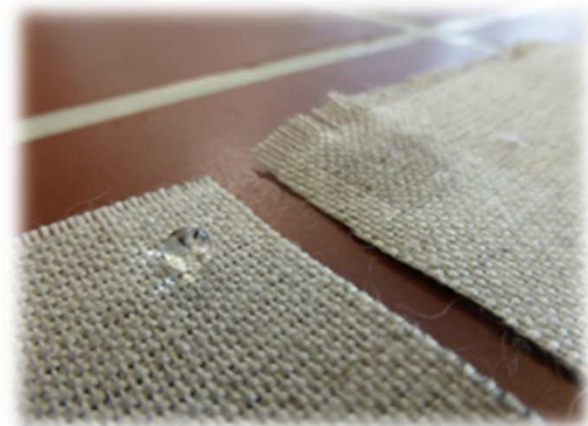
*Precursor for the CVD:*



Hexamethyldisiloxane (HMDSO)



Drop of water on the  $\text{SiO}_x$  coated birch plywood (left) and on the untreated birch plywood (right)



Drop of water on the  $\text{SiO}_x$  coated textile (left) and on the untreated textile (right)

→ Due to the  $\text{SiO}_x$  nanolayer hydrophobic properties on the surface of the samples could be generated.

→ A drop of water rolled off the surface of the textile sample (residue-free) and birch plywood (with minor moistening).

# Conclusion

## Plasma treatment on biobased materials

- Wood / veneers / wood strands: Due to a plasma treatment an improved wettability and accelerated impregnation for a subsequent coating with paints, varnishes, resins and glues could be achieved → Increased adhesion of varnishing and adhesive systems; Pre-treatment of wood strands/particles for an effective resin uptake
- Particle and fibre boards: Faster drying of water based glues and increase of stiffness of glued parts
- Wood/Plastic composite (WPC): Due to a plasma treatment the surface energy of WPC is increased significantly → Improvement of wettability and increase of bonding strength with printing, paint, varnishing and adhesive systems
- Natural fibres: The surface of fibres could be activated using plasma (hydrophilic resp. hydrophobic) → Superior fibre/matrix-adhesion in composite materials and higher strength values
- Wood flour: Germ and spore reduction to prevent mould and fungal attack
- Functionalization of wood-based materials: Deposition of metallic conductivity thin films, hydrophobic/hydrophilic films, antibacterial/antimicrobial films, adhesion promoter layers,...

**Thank you for your attention!**

## Acknowledgements

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