Applications of Plasma treatments on natural fibres
Outline

- Introduction
  - Objectives
  - Contact angle measurements for absorbing materials

- Experimental
  - Materials
  - Contact angle measurements - basic characterization of wettability for
    - Single natural fibres
    - Natural fibre preforms
  - Supplementary examinations
  - Pilot tests
    - Plasma treatment of flax fibre mats
    - Producing flax fibre boards with epoxidized linseed oil as binder
    - Bending tests

- Conclusion
Introduction

Objectives
Improvement of the adhesive strength between fibre and matrix in a composite due to the plasma activation of the single fibre respectively the natural fibre mats

Applications for plasma treated natural fibres
Pressing parts consisting of natural fibre mats
→ improvement of the impregnation of the natural fibre
→ improvement of the adhesion between fibre and resin matrix
Introduction – Contact angle measurements

The contact angle measurements are used for the identification of an improved wettability due to a plasma treatment and for the determination of the absorption time of a liquid / resin in a fibre material

Determination of the contact angle between water and a single fibre

- An automatical detection of the drop shape is not possible: use of a manual marked, curved base line (time-consuming calculation)
- Single outstanding fibres do not influence the calculation of the contact angle

→ but for natural fibres the Standard „Sessile Drop Method“ is not performable due to the fast absorption of the test liquid through the porous surface!
Introduction – Contact angle measurements

For porous materials an alternative method is the determination of contact angle/time curves. By means of a high speed camera the contact angle is recorded over the time („drop age“). The contact angle is calculated at the intersection point where the drop stabilized (no more change of the drop base diameter) and before the absorption occurred (contact angle at time $t = 0$).
Materials

- Fibres: Wood, hemp, flax, kenaf and coco (untreated, without binder)
- Flax fibre mats
- Test liquids for the contact angle measurements: water, epoxidized linseed oil, soy protein
Contact angle measurements of single fibres

Determination of the contact angle between water and the untreated single wood fibre
Calculation of high contact angle values and prolonged absorption times

<table>
<thead>
<tr>
<th>Drop dosing</th>
<th>Drop settling</th>
<th>Drop at time t: 0s</th>
<th>Contact angle: 95°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drop at time t: 10s</td>
<td>Contact angle: 88°</td>
<td>Drop at time t: 30s</td>
<td>Contact angle: 55°</td>
</tr>
<tr>
<td>Drop at time t: 50s</td>
<td>Contact angle: 0°</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Applications of Plasma treatments on natural fibres
Contact angle measurements of single fibres

Determination of the contact angle between water and the plasma treated wood fibre
Due to the plasma treatment the contact angle is significantly lower and the absorption time is definitely reduced

Drop dosing
Drop settling
Drop at time t: 0s Contact angle: 31°
Drop at time t: 1s Contact angle: 12°
Drop at time t: 2s Contact angle: 7°
Drop at time t: 4s Contact angle: 0°
Contact angle measurements of single fibres

Measurement direction transverse to the fibre

High Deviation → unsatisfactory results

Contact angle and absorption time of a untreated and plasma treated wood fibre
(test liquid: water)

plasma treated ... v = 3m/min; d = 10mm

Contact angle [°]

Absorption time [s]

untreated plasma treated
untreated plasma treated

Contact Angle  Absorption time
Preparing the natural fibre preforms for the contact angle measurements

Pooled fibres of wood, hemp, flax, kenaf and coco were used for preforming (fibre weight for the preforming sample: 60mg)

Natural fibre preforms with a plan surface (without a binder)

Preforming tool: manually operated hydraulic press (pressing power: 10 tons, pressing time: 2min)
Contact angle measurements of preforms

Determination of the contact angle between water and the untreated wood fibre preform

Drop at time $t$: 0s  
Contact angle: 73°

Drop at time $t$: 5s  
Contact angle: 0°
Contact angle measurements of preforms

Contact angle and absorption time of untreated and plasma treated fibres
(test liquid: water)

Contact angle [°]

Absorption time [s]

- wood
- flax
- hemp
- kenaf
- coco

Contact angle: untreated plasma treated 1...v = 3m/min; d = 10mm; plasma treated 2...v = 3m/min; d = 5mm

Applications of Plasma treatments on natural fibres
Contact angle measurements of preforms

Contact angle and absorption time of untreated and plasma treated fibres

Test liquid: epoxidized linseed oil / soy protein

Contact angle [°]

- wood / epox. linseed oil
- flax / epox. linseed oil
- hemp / epox. linseed oil
- kenaf / epox. linseed oil

Absorption time [s]

- untreated plasma treated
- untreated plasma treated
- untreated plasma treated
- untreated plasma treated
- untreated plasma treated

plasma treated ... v = 3m/min; d = 5mm
What is happening by the Atmospheric Plasma treatment?

Ra...average roughness of profile
Rt... total height of roughness of profile
Rz...average roughness of 5 measuring sections of profile

### Untreated flax fibre preform

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra</td>
<td>2.6 μm</td>
</tr>
<tr>
<td>Rt</td>
<td>20.4 μm</td>
</tr>
<tr>
<td>Rz</td>
<td>15.3 μm</td>
</tr>
</tbody>
</table>

### Plasma treated flax fibre preform

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra</td>
<td>10.6 μm</td>
</tr>
<tr>
<td>Rt</td>
<td>133.6 μm</td>
</tr>
<tr>
<td>Rz</td>
<td>69.6 μm</td>
</tr>
</tbody>
</table>
What is happening by the Atmospheric Plasma treatment?

**Wood fibre preform**
- untreated
- plasma treated

**Flax fibre preform**
- untreated
- plasma treated

**Results of the measurements:**
No differences in the spectra between untreated and plasma treated fibres were detected.
What is happening by the Atmospheric Plasma treatment?

above: untreated flax fibre (100-times magnified)

below: plasma treated flax fibre with local scorch marks (100-times magnified)

Olympus BX51 (max. 500-times magnified)

Results of the measurements:
After plasma treatment the flax sample showed local limited thermal damages on fibre parts

Applications of Plasma treatments on natural fibres
Pilot test – Producing flax fibre boards

Step 1: Raw flax fibre mat

Step 2: Plasma treatment of flax fibre mats

Step 3: Impregnation with epoxidized linseed oil (ratio: 30% binder, 70% fibre)

Step 4: Pressing 180°C, 50bar, 15min

Step 5: Flax fibre boards for bending tests
Pilot test – Plasma treatment of flax fibre mats

Atmospheric Plasma treatment

- Treatment with standard settings was not possible (hot plasma): due to the irregular mat surface the distance between nozzle and mat varied → burning occurred
- Use of the wide nozzle that induced a minor plasma intensity was necessary

but:
- Burning of fibre parts could not be excluded
- No improvement of impregnation was detectable

→ Atmospheric Plasma treated boards failed in bending tests!
Pilot test – Plasma treatment of flax fibre mats

Low Pressure Plasma treatment

- Plasma treatment of mats in the chamber of the Low Pressure device using a suspension attachment to provide a homogeneous treatment
- Different process gases (Argon, Oxygen, Argon/Oxygen and Air) and treatment times (between 1min and 15min) were used
After Low Pressure Plasma treatment the flax fibre mat showed an increased wettability (resin: epoxidized linseed oil).

Pilot test – Impregnation
Pilot test – Bending tests

Flexural modulus and flexural strength of plasma treated flax fibre boards with epoxidized linseed oil as binder (Low Pressure Plasma treatment)

Applications of Plasma treatments on natural fibres
Conclusion

• The contact angle measurement for the quantitative determination of an improved wettability due to a plasma treatment of natural fibres is principally suitable if the method of recording the contact angle/time curves is used. For repeatable contact angle values the method is limited to plan specimens (preforms). The determination of the contact angle is highly time-consuming because of the manual setting of the base line and drop shape → unsuitable method for high volume test series

• A better wettability and faster absorption due to the plasma treatment of single fibres and fibre preforms is veritably. Differences in the surface behaviour are found using different test liquids
  a) water: lower contact angles and faster absorption after plasma treatment
  b) soy protein: lower contact angles and no change in absorption behaviour after plasma treatment
  c) epoxid. linseed oil: faster absorption and slightly improved wettability after plasma treatment
→ surface behaviour of natural fibres due to plasma treatment strongly dependent on the matrix
Conclusion

• Plasma effect: primary via an increase of the roughness and micro-cleaning of the treated surface; no functionalization detectable by means of infrared spectroscopy

• Atmospheric Plasma treatment with a plasma spot (hot plasma): plasma intensity and therefor the heating is primary dependent on the distance between the plasma beam and the substrate; problem with the rough surface of natural fibres and fibre mats (scorch marks detected)

→ implementation of an Atmospheric Plasma spot device in a production line of natural single fibres, non wovens or natural fibre mats is unpredictable

• Using the Low Pressure Plasma, the treatment of raw flax fibre mats considering adjusted machine setting is possible; in bending tests the Plasma treated mats showed higher flexural strength and flexural modulus values (primarily with Oxygen as a process gas)

→ implementation of Low Pressure Plasma treatment in the production process of natural fibre products is supposable