Atmospheric and Low Pressure Plasma treatments: a comparison
Outline

- Introduction
  - What is Plasma?
  - Atmospheric Plasma and Low Pressure Plasma treatment

- Experimental
  - Results of contact angle measurements of plastic materials treated with Atmospheric and Low Pressure Plasma
  - Limitation of Plasma treatment
  - Proof of Plasma activated parts for different applications

- Conclusion
Introduction – What is Plasma?

**Definition:** Plasma is ionized gas in a highly unstable energy level and hence often determined as the 4. state of aggregation.

**Generation:** Due to an electric discharge, additional energy is transferred into a gaseous material. This excited state evokes the formation of free electrons, ions and molecule fragments = Plasma.

**Classification of Plasma according to the gas pressure:**
- Atmospheric Plasma – arc discharge („hot“ Plasma)
- Low Pressure Plasma – glow discharge
Introduction – Atmospheric Plasma treatment

Atmospheric Plasma treatment

Due to a high voltage discharge an electric arc is generated. The pressurized air passing the electrodes is transferred into the Plasma state. Through the nozzle the Plasma attains the substrate. To adjust the Plasma intensity, the distance between Plasma nozzle and substrate and/or the velocity of the movement device could be varied.

Standard treatment conditions for experiments

- Process gas: pressurized air
- Distance Plasma - sample: 5mm, 10mm
- Speed sample relative to Plasma: 50mm/s, 100mm/s

Plasmatreat Openair® RD1004, Generator FG3001
Introduction – Low Pressure Plasma treatment

Low Pressure Plasma treatment – process steps
1. Pumping down to a pressure lower than the operating pressure to evacuate the air gases
2. Gas flow of the gas (or the mixture) at the operating pressure to ensure the required conditions and stabilize the MFC (mass flow controller) delivery
3. Plasma process at the operating power and for the set time
4. Flushing/venting

Starting treatment conditions for grafting experiments
- Gases: Air, Argon, NH₃, H₂, C₂H₂, O₂, Ar/O₂, CO₂, N₂
- Time: 3min, 5min, 7min, 10min, 15min and 20min
- Pressure: 0.3mbar
- Power: 100%
Experimental - Contact angle measurements

Contact angle measurements
The contact angle measurements are used for the identification of an improved wettability and for the determination of an increased surface energy due to a Plasma treatment of a material.

Standard measurement conditions for experiments
- Method: Sessile Drop; Drop volume: 1.5µl
- Test liquids: Water, Ethylene glycol, Diiodomethane
- Surface energy is calculated using the OWENS, WENDT, RABEL and KAELBLE (OWRK) Equation.

DataPhysics OCA 35, Software version SCA 20

untreated

PA-film wetted with water

Plasma treated
Experimental - Materials & Treatment conditions

- **Low Pressure Plasma treatment**
  - Test materials: ABS/TPU, HDPE, PA12, PP (plastic films); Acetate, PA6.6 (Nylon), Propionate (plastic plate)
  - Process gases: Air, Argon, NH_3, H_2, C_2H_2, O_2, Ar/O_2, CO_2, N_2
  - Treatment times [min]: 3, 5, 7, 10, 15, 20

- **Atmospheric Plasma treatment**
  - Test materials: ABS/TPU, HDPE, PA12, (plastic films); Acetate, PA6.6 (Nylon), Propionate (plastic plate)
  - Distance between Plasma nozzle and substrate [mm]: 5, 10
  - Velocity of substrate relative to Plasma nozzle [mm/s]: 50, 100
Contact angle measurements after Low Pressure Plasma treatment

Atmospheric and Low Pressure Plasma treatments: a comparison

- **Best performance**: Ar, O\(_2\), Ar/O\(_2\)
- **No positive effect**: NH\(_3\), H\(_2\), C\(_2\)H\(_2\)
- **Exact adjustment of treatment time necessary to prohibit over-activation**

### Surface energy [mJ/m\(^2\)]

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Polar</th>
<th>Disp.</th>
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<tbody>
<tr>
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<td>Ar_15'</td>
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<tr>
<td>N(_2)_20'</td>
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</tr>
</tbody>
</table>
Contact angle measurements after Low Pressure Plasma treatment

Only a few process gases (Ar, O₂, Ar/O₂) lead to good results. Long-lasting treatments evoke higher activation.
Contact angle measurements after Atmospheric Plasma treatment

Atmospheric and Low Pressure Plasma treatments: a comparison

Surface energy [mJ/m²]

ABS/TPU
PA 12
HDPE
Acetate
PA 6.6
Propionate

Polar
Disp.

Atmospheric and Low Pressure Plasma treatments: a comparison
Material/Treatment-table for plastics

The best wettability respectively the highest increase of the surface energy was achieved using following plasma treatment parameters for the different plastic materials:

**Low Pressure Plasma treatment**

<table>
<thead>
<tr>
<th>Material</th>
<th>Gases</th>
<th>Gas and treatment time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ar</td>
</tr>
<tr>
<td>ABS/TPU</td>
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</tr>
<tr>
<td>HDPE</td>
<td>CO₂</td>
<td>10</td>
</tr>
<tr>
<td>PA</td>
<td>Ar/O₂</td>
<td>5</td>
</tr>
<tr>
<td>PP</td>
<td>Ar/O₂</td>
<td>5</td>
</tr>
<tr>
<td>Acetate</td>
<td>Ar</td>
<td>15</td>
</tr>
<tr>
<td>Nylon</td>
<td>O₂</td>
<td>20</td>
</tr>
<tr>
<td>Propionate</td>
<td>Ar/O₂</td>
<td>15</td>
</tr>
</tbody>
</table>

**Atmospheric Plasma treatment**

<table>
<thead>
<tr>
<th>Material</th>
<th>Distance [mm]</th>
<th>Velocity [mm/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS/TPU</td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>PA</td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>HDPE</td>
<td>5 / 10</td>
<td>50</td>
</tr>
<tr>
<td>Acetate trans</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>Nylon</td>
<td>5 / 10</td>
<td>50</td>
</tr>
<tr>
<td>Propionate</td>
<td>10</td>
<td>50</td>
</tr>
</tbody>
</table>

→ Material/Treatment-tables are only valid for the tested materials and not in general!
Limitation of Atmospheric Plasma treatment

Temporary dependence

- Faster decrease of surface energy respectively loss of plasma activation detected for PE

Custody of treated parts under normal storage conditions.
Limitation of Atmospheric Plasma treatment

Thermal influence

Storage of treated parts in a convection oven for 20 min and different temperatures.

- Gradually decrease of surface energy with increase of temperature
- No accelerated decrease of surface energy during storage due to the heating

Atmospheric and Low Pressure Plasma treatments: a comparison
Limitation of Atmospheric Plasma treatment

**Crack propagation and brand marks**

Due to an Atmospheric Plasma treatment of non-woven materials, cracks and brand marks occurred as a result of the heat impact. Similar results were detected treating natural fibres.

**PP-separator (non-woven material)**

**Thermal image of the separator surface during Atmospheric Plasma treatment**
Limitation of Low Pressure Plasma treatment

**Yellow discolouration**

Due to a Low Pressure Plasma treatment using the gases NH$_3$, H$_2$ and C$_2$H$_2$ a yellow discolouration of the plastic film samples was detected.
Areas of application

- **Bonding**

*Aluminium plates*

Due to a micro-cleaning via Plasma the aluminium surface should exhibit an improved adhesion to resin impregnated layers.

- **Results:**
  → A micro-cleaning of alu-plates was evident → production-related differences of the surface energy between top- and bottom-side of the plate were removed
  → No measurable improvement of adhesion in the Aluminium/resin layer-composite was found after cooking and water storage tests, drying chamber and climate testing.
Areas of application

- **Powder coating & Varnishing**

**PUR and WPC profiles**

Due to a Plasma treatment the adhesion of PUR profiles to a subsequent coating system was improved significantly. After the cross-hatch adhesion test the untreated profile showed a cross-hatch characteristic $G_t = 5$ (very bad adhesion) whereas the Plasma treated sample exhibited $G_t = 1$ (good adhesion).

Similar results were found testing Wood Plastic Composites (WPC).
Areas of application

- **Powder coating**

  *Metal and glass plates*
  
  Due to a Plasma treatment the adhesion to a subsequent coating should be improved.
  
  - **Results:**
    
    → A micro-cleaning of plates was evident → production-related differences of the surface energy between top- and bottom-side of the plates were removed
    
    → After tropical and climate tests no significant improvement of adhesion was detected

  *Medium Density Fibreboards (MDFs)*
  
  Due to a Plasma treatment an optimized technical surface for powder coating applications should be obtained.
  
  - **Results:**
    
    → Measurements of electrical resistance showed no improvement of the surface conductivity after plasma treatment
    
    → Powder coating experiments showed neither an improved distribution nor an enhanced levelling of the powder deposition.
Areas of application

- **Varnishing**

  **MDF boards**

  The Plasma treatment of MDF boards leads to an improvement of surface wettability. In varnishing experiments with water-based paint the surface drying of the paint accelerated distinctly.

  Plasma treatment of a MDF board

  Accelerated surface drying of the water-based paint on the Plasma treated side of the board
Areas of application

- **Anti-fogging**
In a grafting process using hydrogen and a mixture of nitrogen and acetylene, hard coated plastic lenses were treated to generate an anti-fogging behaviour. The treatment had a very high performance and effectiveness – contact angle measurements showed totally wetting even after 5 weeks.
Conclusion

- Atmospheric Plasma and Low Pressure Plasma treatment are suitable procedures for activation and micro-cleaning of different substrates for subsequent printing, bonding and coating processes.

- For plastic materials the activation due to a Plasma treatment is strongly dependent on the process gas, the treatment time and the type of polymer (structure, additives).

- Limitations of Plasma treatment:
  - Temporary dependence: decrease of surface energy of treated parts over the storage period; rate of decrease is dependent on the material.
  - Thermal influence: a) loss of Plasma activation of treated parts with higher temperature in a thermal process; b) hot plasma treatment could induce brand marks and cracks on thin and thermal sensitive materials.
  - Process gases could evoke discolouration.

- Due to a Plasma treatment plastic materials are activated (improvement of wettability) and hence suitable for printing, anti-fogging, powder coating and varnishing applications. For anorganic materials and fibre composites the Plasma treatment generates a micro-cleaning of the surface removing contaminations. A better wettability was determined but no significant improvement of adhesive properties in practical tests was detectable.