Low Pressure Plasma Technology
Outline

- About Europlasma
- What is Plasma?
- Plasma Processes + Case Studies
- Applications
- Plasma Equipment
- In-line Plasma Equipment
- Conclusions
About Europlasma
Mission Statement

- Europlasma designs, builds and sells turnkey vacuum plasma treatment equipment
- Europlasma develops and optimizes the plasma processes required to solve the material problems of its customers
- Europlasma helps its customers to produce better and/or cheaper products in an environment friendly way
Company History

- Founded in 1989 by Anthony Vanlandeghem
- Own engineering and construction under the Europlasma brand name since 1993
- Team of 20 specialized people
- World-wide marketing and after sales service
- More than 350 industrial systems running world-wide
- Reference list of blue chip companies
- ISO9001:2000
Company History

Up-scaling

Process complexity
Markets

- Activation and coating of plastic parts
- Activation and coating of industrial textiles, non-wovens or film
- Cleaning and etching of electronic parts
Positioning

- Leading supplier of vacuum plasma treatment equipment for plastic parts
- Custom designed equipment for high end electronic applications
- Unique line of reel-to-reel vacuum plasma systems
What is a plasma?

- ‘Fourth state of matter’
- A plasma is a mix of
  - Charged particles (ions, electrons)
  - Neutrals (atoms, radicals, molecules)
What is a plasma?

- Plasma is generated by an electromagnetical discharge in a gas at low pressure
Plasma processes for plastics
Plasma processes

- Removal of molecular contamination layers from a surface
- Etching of a surface (several nm up to 1 µm)
- Chemical activation of a surface
- Cross linking of chemical species on the surface
- Plasma polymerization on a surface
- Substrates can be plastics, metals or ceramics
Activation

- Surface modification of outer molecular layers
- Treatment depth limited to typically 0.3 – 1.5 nm!
- Process gas mixtures typically based upon $O_2$, $N_2$ or $Ar$
Activation of plastics

- High surface energy = low water contact angle = good wetting = good adhesion
Activation of polypropylene

Polypropylene BEFORE plasma treatment

Polypropylene AFTER $O_2$-plasma treatment: carbonyl-groups have been added
<table>
<thead>
<tr>
<th></th>
<th>Surface Energy</th>
<th>Water Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dynes/cm</td>
<td>before</td>
</tr>
<tr>
<td><strong>1. Hydrocarbons</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polypropylene</td>
<td>29</td>
<td>72</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>31</td>
<td>72</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>38</td>
<td>72</td>
</tr>
<tr>
<td>ABS</td>
<td>35</td>
<td>72</td>
</tr>
<tr>
<td>Polyester</td>
<td>41</td>
<td>72</td>
</tr>
<tr>
<td>Rigid PVC</td>
<td>39</td>
<td>72</td>
</tr>
<tr>
<td><strong>2. Fluorcarbons</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polytetrafluorethylene</td>
<td>37</td>
<td>72</td>
</tr>
<tr>
<td>polyethylene copolymer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorinated ethylene</td>
<td>22</td>
<td>72</td>
</tr>
<tr>
<td>propylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyvinylidene</td>
<td>25</td>
<td>72</td>
</tr>
<tr>
<td><strong>3. Elastomers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicone</td>
<td>24</td>
<td>72</td>
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<td><strong>4. Thermoplastics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pet</td>
<td>41</td>
<td>72</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>46</td>
<td>72</td>
</tr>
<tr>
<td>Polyamide</td>
<td>40</td>
<td>72</td>
</tr>
</tbody>
</table>
Activation applicable for:

- Painting
- Printing
- Gluing
- Flocking
- Electroplating
- Metallisation
Activation of plastic parts prior to painting

untreated

plasma treated
CASE STUDY 1 PAINTING

- Material: Schuladur® A GF30 Black (PBT)
- Primer: Eques 31848
- Topcoat: Eques 42102
CASE STUDY 1 PAINTING

For plasma treated parts: primer and/or paint applied 2 weeks after plasma treatment.

<table>
<thead>
<tr>
<th></th>
<th>No Primer/No plasma</th>
<th>Primer</th>
<th>Plasma + Primer</th>
<th>Plasma</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>GT=2</td>
<td>GT=0</td>
<td>GT=0</td>
<td>GT=0</td>
</tr>
<tr>
<td>2</td>
<td>GT=2</td>
<td>GT=0</td>
<td>GT=0</td>
<td>GT=0</td>
</tr>
<tr>
<td>3</td>
<td>GT=1</td>
<td>GT=0</td>
<td>GT=0</td>
<td>GT=0</td>
</tr>
<tr>
<td>4</td>
<td>GT=2</td>
<td>GT=0</td>
<td>GT=0</td>
<td>GT=0</td>
</tr>
<tr>
<td>5</td>
<td>GT=1</td>
<td>GT=0</td>
<td>GT=0</td>
<td>GT=0</td>
</tr>
</tbody>
</table>

PRIMER CAN BE ELIMINATED
CASE STUDY 1 PAINTING

- CD1000 PLC - kHz
- 504 parts/batch
- Proces gas: O₂
- Cycle time: 15 min

- Processing cost: 0,00037 EUR/part
- Material: Ureumformaldehyde (UF)
- Primer: Peter Lacke P 649048
- Topcoat: Peter Lacke P 68313
### CASE STUDY 2 PAINTING

- **Plasma + primer and painting after 2 days:** GT=0
- **Plasma + primer and painting after 2 weeks:** GT=0

<table>
<thead>
<tr>
<th></th>
<th>Primer + painting</th>
<th>Plasma + primer and painting after 2 days</th>
<th>Plasma + primer and painting after 2 weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GT=5</td>
<td>GT=0</td>
<td>GT=0</td>
</tr>
<tr>
<td>2</td>
<td>GT=5</td>
<td>GT=0</td>
<td>GT=0</td>
</tr>
<tr>
<td>3</td>
<td>GT=5</td>
<td>GT=0</td>
<td>GT=0</td>
</tr>
<tr>
<td>4</td>
<td>GT=5</td>
<td>GT=0</td>
<td>GT=0</td>
</tr>
<tr>
<td>5</td>
<td>GT=5</td>
<td>GT=0</td>
<td>GT=0</td>
</tr>
</tbody>
</table>

ONLY ADHESION WHEN PLASMA IS USED

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CASE STUDY 2 PAINTING

- CD1000 PLC - kHz
- 240 parts/batch
- Proces gas: O₂
- Cycle time: 15 min

- Processing cost: 0,00084 EUR/part
CASE STUDY 3 PAINTING

- Exterior part from AUDI Q7
- Material: Daplen KB 4436 PP EPDM M30
- Primer
- Topcoat
Plasma treated parts were painted after 1 week, 2 weeks, 4 weeks and 8 weeks.

Plasma treatment still effective after powerwash.

<table>
<thead>
<tr>
<th></th>
<th>Primer</th>
<th>Plasma</th>
<th>Cooking test</th>
<th>Condens test</th>
<th>Gloss</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GT=0</td>
<td>GT=0</td>
<td>OK</td>
<td>OK</td>
<td>12,1</td>
<td>1,06</td>
</tr>
<tr>
<td>2</td>
<td>GT=0</td>
<td>GT=0</td>
<td>OK</td>
<td>OK</td>
<td>11,9</td>
<td>1,05</td>
</tr>
<tr>
<td>3</td>
<td>GT=4</td>
<td>GT=0</td>
<td>OK</td>
<td>OK</td>
<td>12</td>
<td>1,06</td>
</tr>
<tr>
<td>4</td>
<td>GT=0</td>
<td>GT=0</td>
<td>OK</td>
<td>OK</td>
<td>11,8</td>
<td>1,02</td>
</tr>
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</table>

PRIMER CAN BE ELIMINATED

PLASMA GIVES BEST QUALITY GUARANTEE
EUROPLASMA NV

CASE STUDY 3 PAINTING

- CD2000 PLC - kHz
- Proces gas: O₂
- Cycle time: 10 min
- Processing cost: 0,20 EUR/batch
Activation of plastic parts prior to gluing
# Plasma as Pre-Treatment Prior to Gluing: Case 1 - Polymers

<table>
<thead>
<tr>
<th>TLSS-data</th>
<th>PE Untreated</th>
<th>PE Plasma treated</th>
<th>PP Untreated</th>
<th>PP Plasma treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>(MPa) ECCOBOND® 2332</td>
<td>0.63</td>
<td>&gt; 2.61</td>
<td>0.14</td>
<td>1.78</td>
</tr>
<tr>
<td>(MPa) ECCOBOND® 45 W 1</td>
<td>0.59</td>
<td>&gt; 2.66</td>
<td>0.12</td>
<td>1.82</td>
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<tr>
<td>Surface Energy (mN/m)</td>
<td>30</td>
<td>&gt; 68</td>
<td>33</td>
<td>&gt; 68</td>
</tr>
</tbody>
</table>

TLSS = Tensile Lap Shear Strength

Epoxy adhesives

Products supplied by: Emerson & Cuming

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(ECCOBOND® is a registered trademark of National Starch & Chemical)
**EUROPLASMA NV**

**PLASMA AS PRE-TREATMENT PRIOR TO GLUING: CASE 1 - POLYMERS**

<table>
<thead>
<tr>
<th>TLSS-data</th>
<th>ABS Untreated</th>
<th>ABS Plasma treated</th>
<th>PBT, 30 %GF Untreated</th>
<th>PBT, 30 %GF Plasma treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>(MPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ECCOBOND® 2332</td>
<td>-</td>
<td>-</td>
<td>7.02</td>
<td>12.62</td>
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<tr>
<td>ECCOBOND® 45 W 1</td>
<td>1.60</td>
<td>&gt; 4.92</td>
<td>2.34</td>
<td>7.92</td>
</tr>
<tr>
<td>Surface Energy (mN/m)</td>
<td>35</td>
<td>&gt; 68</td>
<td>35</td>
<td>&gt; 68</td>
</tr>
</tbody>
</table>

TLSS = Tensile Lap Shear Strength

Epoxy adhesives

Products supplied by: Emerson & Cuming
## PLASMA AS PRE-TREATMENT PRIOR TO GLUING: CASE 2 - METALS, Al

<table>
<thead>
<tr>
<th>TLSS (MPa)</th>
<th>Untreated</th>
<th>Plasma treated (physical cleaning, Ar/O₂)</th>
<th>Plasma treated (chemical cleaning, O₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECCOBOND® 2332</td>
<td>13.90</td>
<td>18.18</td>
<td>20.10</td>
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<tr>
<td>Surface Energy (mN/m)</td>
<td>35</td>
<td>&gt; 68</td>
<td>&gt; 68</td>
</tr>
</tbody>
</table>

TLSS = Tensile Lap Shear Strength

Epoxy adhesive

Products supplied by:

![Emerson & Cuming](https://example.com/emerson_cuming_logo.png)
Gluing of plasma activated PPS

- Smooth surface - no pre-treatment
- Plasma surface activation - 1
- Plasma surface activation - 2
- Physical surface roughening

Max break force, N
CASE STUDY 1 GLUING

- Interior part from RENAULT Laguna
- Material: PP + 20% talc (Borealis)
- Waterbased glue
- Flock
CASE STUDY 1 GLUING

- Without plasma → no adhesion of the glue on the PP
- Typical layer thickness glue: +/- 95µm
Activation of plastic parts prior to gluing/flocking
Electro pneumatic

- 3-D parts
- Flock flow adjustable
- Air flow adjustable
- High Voltage adjustable
Polymerization

- Reaction takes place on the substrate surface
- Permanent coatings with typical thickness of tens of nm
- Functionality determined by precursor gas(es):
  - Hydrocarbons (+ O₂): permanently hydrophilic coatings
  - Fluorocarbon mixtures: permanently hydrophobic and oleophobic coatings
Applicable for:

- Non-woven media for filtration
- Medical devices
- PCB
Oleophobic/Hydrophobic treatment filter media

Water absorption in % (soaking 22 hours + vertical dripping for X time)

- As received
- Plasma coated

<table>
<thead>
<tr>
<th>Weight increase in %</th>
<th>1: after 1 min; 2: after 1 h; 3: after 24 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
Etching

- Surface modification of outer molecular layers
- To remove parts of the material
- To remove a whole layer
- To obtain better adhesion
- To obtain roughening of the surface
- To avoid contamination
Etching
Etching

Figure 2-1: (a) visualization of the etching rate, (b) working principle of chemical etching, physical etching and combination of both
Plasma etching of POM and PTFE:
Applicable for:

- Medical devices
- Automotive windows
- PCB’s
- …
Applications
Automotive:

- Arm rest in car door
- Dashboard
- Gloveboxes
- Bumpers
- Windows
- Airfilters
- ...
Electronics:

- Multi layer boards (6-64 inner layers)
- Boards with high aspect ratio (via) holes
- PCB’s with micro-vias, buried vias, blind vias and laser formed vias
- PCB’s from Teflon-based materials
- Finished PCB (with components) before surface coating with protective resin (hybrids)
- Polyimide-based materials for multilayer flex and rigid-flex boards
Medical devices:

- Balloon catheters: activation of balloon before gluing to the stem
- Other catheters: activation before printing on the catheter hub or before gluing the metal part with the connector (PC)
- Syringes and dental needles: activation of needle hubs (PP) prior to gluing the needle
- Microtitre plates: activation for improved wetting and improved cell growth
- Stents:
  - Fine cleaning
  - Stents with membrane: activation for improved bonding quality
- Guide wire: fine cleaning of metal wire prior to hydrogel coating or Teflon® deposition
- Activation of medical parts in general prior to parylene coatings
Plasma treatment equipment
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Junior

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EUROPLASMA NV

CD400PLC

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EUROPLASMA NV

CD1000PLC
EUROPLASMA NV

CD1800

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Custom Design
EUROPLASMA NV

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Roll-to-roll plasma treatment system for nonwovens

EUROPLASMA NV

Vacuum chamber  Electrode system
Pump system
RF-Generator  Winding system
Proces control system
In-line plasma equipment
EUROPLASMA NV

Cycle: 6 bumpers in 6 minutes

Custom Design
EUROPLASMA NV

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In-line 2D treatment system
In-line 2D treatment system
In-line 2D treatment system
Conclusions
Advantages of vacuum plasma

- Effective treatment!
  - High surface energy levels
  - Good shelf life
- Uniform treatment of three dimensional parts
- Simple process control
- Low defect density
Advantages of vacuum plasma

- Low variable costs
- Dry and clean process
- Clean room compatible equipment
- Batch process easily integrated in production line