Coating Plasma Innovation

Optimization of atmospheric plasma for high speed industrial applications
Plasma

4\textsuperscript{th} state of matter: ionized gas
Cold atmospheric plasma

Cold:
\[ T_{\text{gas}} < 100 \, ^\circ C \]
\[ T_{\text{ions, neutrals}} < 100 \, ^\circ C \]
\[ T_{\text{electrons}} \approx 10,000 \, ^\circ C \]

Atmospheric:
Plasma gas is at atmospheric pressure
Open reactor, high density of particles

Hot:
\[ T_{\text{gas}} \approx T_{\text{ions, neutrals}} \approx T_{\text{electrons}} \]
\[ 10^4 < T < 10^8 \, ^\circ C \]

Energetic electrons ➔ chemistry
Corona

- Used for activation or cleaning
- Flat substrate
- Most of the time need to be used inline with other process
- Gas used: none (ambient air)

High Voltage

Ambient air
Filamentary discharge
Plasma jet (blown arc)

Gas injection (plasma gas + reactive gas or precursor)

- Used for activation or cleaning, deposition possible
- 3D substrate
- Gas used: Air, N₂, Ar, He
- Gas consumption: 30 - 60 l/min (10L/m² @ 100 m/min)

Post-discharge

Max. a few cm

Precursor

Controlled atmosphere

Uncontrolled/partially controlled atmosphere
Plasma DBD

Gas injection (plasma gas + reactive gas or precursor)

- Used for activation or cleaning, deposition possible
- Flat substrate
- Used online or offline
- Gas used: $N_2$, (Ar, He)
- Gas consumption (CPI tech) < 5L/m²
  (50 – 500 m/min)
Plasma vs Corona

**Corona**
- ✓ Very large web width
- ✓ Common technology
  - ✓ Cost
  - ✓ Cleaning
  - ✓ Activation
  - ✗ Grafting
  - ✗ Coating
- ✗ Uncontrolled atmosphere
- ✗ Aggressive chemistry
- ✗ Limited range of materials
- ✗ Inhomogeneous treatment
  - ✗ Pin holes
- ✗ Backside treatment
- ✗ Low efficiency
- ✗ Temporary effect

**Plasma**
- ✓ Large web width
- ✓ Controlled atmosphere
- ✓ Homogenous treatment
  - ✓ No surface damage
  - ✓ No backside treatment
- ✓ High performance treatment
  - ✓ **Long lasting effect**
    - ✓ Cleaning
    - ✓ Activation
    - ✓ Grafting
    - ✓ Coating
- ✓ Wide material range
- ✗ Common technology
  - ✗ Cost
Plasma vs Corona

Microscopy (AFM) image of BOPP film
1 µm x 1 µm images (Tapping)

Untreated

Plasma DBD

Corona

Es ≤ 30 mN/m
Es = 60 mN/m
Es = 38 mN/m

Identical discharge power

Controlled chemistry, homogenous discharge ➔ no surface damage
Plasma vs Corona

Surface energy measurements on BOPP film

Controlled chemistry ➔ Long lasting treatment, higher surface energy
DBD vs Jet/torch

**Torch/Jet**
- Localized treatment (max width ≈10 cm)
- Indirect plasma exposure (post discharge)
- Medium speed treatment (10’s m/min)
- 3D and complexes shape substrate
- Partially controlled atmosphere
- Cleaning, Activation, Grafting, Coating

**DBD**
- Up to several meters web width
- Direct plasma exposure
- High speed treatment (100’s of m/min)
- Thin flat substrate
- Controlled atmosphere
- Cleaning, Activation, Grafting, Coating
Cleaning - Grafting - Coating

Plasma

Contaminated surface

Surface contamination

CO₂↗, H₂O↗...

Cleaned sample

Torch, Corona, Plasma
Cleaning - Grafting - Coating

Grafting of nitrogen containing groups

Torch, Corona, Plasma
Specific molecules (precursor) are added to the plasma gas. Those molecules are activated by the plasma and react with the sample surface to form a thin film.

HMDSO precursor

SiO$_x$ hydrophilic

SiC$_y$O$_x$ hydrophobic
Conclusions

- Corona is adapted for basic treatment of low value materials. Limited performance regarding surface energy, durability of treatment and range of materials treatable.

- Plasma jet are adapted to localized treatment and 3D shaped objects. Cost and technical issues for large scale treatment.

- Plasma DBD is adapted to high performance applications and/or high performance materials. Not competitive if corona can achieve the same goal.
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Needed Improvement in atmospheric plasma technology

1st generation of atmospheric plasma issues:

- Treatment speed was too slow
- Gas consumption was too high
- Some materials could not be treated
- Coating was difficult
  ➔ Cost was too high in regard of the performances
Improvements in electrode design
• Homogenous plasma at high power density
• Longer exposure time with similar footprint

Improvements in gas dynamics:
• Controlled Chemistry even at high web speed
• Reduction in gas consumption

➢ High power density, longer exposure time:
  ✓ High speed treatment
  ✓ Inert material treatment such as fluorinated polymers

➢ Homogenous discharge, controlled chemistry:
  ✓ No hot spots, no damage of films (LMWOF)
  ✓ Stable atmosphere allow to add controlled amount of dopant gas (vapors)
  ✓ Treatment of sensitive or difficult materials (PTFE, ECTFE, PEEK, PLA...)
The plasma dosage (d) represents the amount of electrical energy applied to the material during the treatment.

\[
d = \frac{\text{Plasma power}}{\text{Web width} \times \text{Web speed}} = \frac{[W]}{[m] \times \left[\frac{m}{\text{min}}\right]} = \left[\frac{W \cdot \text{min}}{m^2}\right]
\]

Graph showing the relationship between plasma dosage, power, and web speed for constant power and constant dosage conditions.
Electrode design

High power density $\Rightarrow$ High Dosage at high speed
Electrode design

High Dosage without damage ➔ Long lasting treatment

Surface energy (mN/m)

Plasma Dosage (W.min/m²)

Corona limit

Day 0
Day 7
Day 14
Day 30
Controlled atmosphere - dopant

Dopant \( \rightarrow \) same performance at lower dosage
Gas dynamics

At high speed the film carries an air boundary layer in the plasma zone.

Air (Oxygen) is introduced in the plasma. Chemistry of the plasma is not controlled.

Air boundary layer must be removed:
- High N₂ flow rate
- Optimized gas diffusor geometry
- Low power corona
- Physical barrier
- ...
Gas dynamics - Controlled atmosphere

High O₂ concentration

- O₂ concentration [ppm]
- Web Speed [m/min]
- Flow rates: 5 m³/h, 10 m³/h, 15 m³/h, 20 m³/h, 30 m³/h, 40 m³/h, 50 m³/h
Electrode-gas diffusor assembly optimization \(\rightarrow\) running cost \(\downarrow\downarrow\)

Gas dynamics - Controlled atmosphere

N\(_2\) consumption per m\(^2\) of treated material

- Optimized
- Classical
Nitrogen grafting on BOPP (50m/min)

- **O$_2$ < 20 ppm**
- **O$_2$ ≥ 2000 ppm**

**Good inerting ➔ Higher surface energy**

**Surface Energy (mN/m)**

**Nitrogen flow rate (l/min)**

**% of grafted nitrogen**

**Corona**

**Plasma**
Coating by atmospheric plasma pressure was/is hindered by:

- Powder formation in the gas phase
  - low adherence to substrate
  - low quality powdery film
- Powder formation on the electrode
  - high maintenance

- Optimized electrode gas diffusor assembly solves those issues

Remaining issue: high density film at high speed

- Dense film at 10\textsuperscript{th} m/min \rightarrow slow for industrial use
- Deposition at 100\textsuperscript{th} m/min \rightarrow low density film
Conclusions

Improvements in electrode design and gas dynamics allowed to overcome most of the previous atmospheric plasma limitations.

• Treatment speed are very high (hundreds of m/min)
• Running cost are becoming competitive
• Chemistry of the plasma can be controlled

Plasma is adapted to high performance materials and/or high performance applications
Thank you