FLEXIBLE FILMS TREATMENT

ROLL TO ROLL
ATMOSPHERIC PRESSURE COLD PLASMA
- SURFACE CHEMICAL ACTIVATION & FUNCTIONNALIZATION
- DEPOSITION of NANO COATINGS At INDUSTRIALSCALE

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PRODUCTS AND SERVICES OF CPI

- **TREATED MATERIALS**
  - Polypropylene (BOPP, CPP, COPO)
  - Polyethylene (HDPE, BDPE, ...)
  - Polyester (PET, OPET), Polyamide (OPA)
  - Fluorinated polymers (PVF, PVDF, PTFE, ...)
  - Functional Poly olefins (EVOH, EVA, PVDC, ...)
  - Siloxanes (PDMS)
  - Printed polymer
  - Papers, textiles & fabrics
  - Metal foils & metallised films

- **SERVICES**
  - R&D
  - Industrial subcontracts
  - Trials
  - Manufactured products
APP TREATMENT UNIT

APP TREATMENT
Filamentary DBD CORONA like discharge

Flexible film

Slitting

Treated film
P600 Unit at CPI
SPECIFICATIONS

- **Conveying specifications**
  - Film width & thickness: 500 to 2000 mm wide & 5 to 600 µm thick
  - Reel max external diameter (Unwinding/winding) 1200 to 800 mm
  - Reel max external diameter (Unwinding/Winding) 900/400 kg
  - Core diameter: 76 or 152 m
  - Slitting ability just before winding (two winding axes)

- **APP reactor specifications**
  - Gaseous mixtures; pure N\textsubscript{2} (< 10 ppm O\textsubscript{2}) or with 500 ppm dopants (N\textsubscript{2}O / CO\textsubscript{2} / H\textsubscript{2} / C\textsubscript{2}H\textsubscript{2}(4) / SiH\textsubscript{4}, TEOS, HMDSO)
  - Frequency 45 kHz, Power 35 kW
  - Film speed: 40 to 300 m/min
  - APP Dosage: 5 to 300 W.min/m\textsuperscript{2}
  - Pre CORONA Dosage: 5 to 1000 W.min/m\textsuperscript{2}
  - Electrodes nature: Metal, ceramics
MAIN SURFACE PROPERTIES

- **APPLICATIONS**
  - Grafting and coating by chemical covalent bond
  - High level and stable surface energy
  - Permanent modification of the wettability
  - Improvement of adhesive & printing properties
  - Adjustable coefficient of friction
  - Anti-blocking effect

- **ADVANTAGES**
  - Suppression of adhesion primer & varnishing
  - High quality printing with all type of inks (water based, solvents, UV curable)
  - Film adhesion for lamination, metallization,...
Injection of Working gases:
- pure N₂, (< 10 ppm O₂)
- N₂ + dopants (200-2 000 ppm)
  (N₂O, CO₂, H₂, SiH₄, CₓHᵧ, TEOS, HMDSO)
$N_2(C^3\Pi_u)$  $v=3$ (13 ms) 11.1 eV

$N_2(A^3\Sigma_u)$  $v=2$ (1–3s) 6.2 eV

$N_2(X^1\Sigma_g)$  Ground state

$C(^3P) + N(^4S)$

Molecular $N_2$ 2nd positive system  CN violet system

$B^1\Sigma$  3.2 eV

$A^2\Pi$  $X^2\Sigma$
APP Dielectric Barrier Discharge (DBD) at Atmospheric Pressure

- High dielectric solid between electrodes
- Discharges in pure $\text{N}_2$ atmosphere (<10 ppm $\text{O}_2$)
- Avoid electric arcing, thermal & chemical degradation
- Filamentary - streamers (10 ns duration, 100 µm diameter)
- Distributed statistically over the treated surface
APP Chemical reactive species

$h \nu$ Electrons Ions Atoms Radicals Metastables

Atmospheric Pressure Plasma
→ only long life time neutral metastables (no ion)
→ surface activation by chemical grafting,
→ gradient in depth, different analytical data according to used techniques and inspection depth
SURFACE ENERGY BY CALIBRATED INKS

APP treated BOPP

✓ Untreated

$E_{\text{surface}} < 32 \text{ mN/m} (*)$

✓ APP – H2 - treated

$E_{\text{surface}} = 60 \text{ mN/m} (*)$

(*) ASTM D2578 – 99a test method / SOFTAL GmbH calibrated inks
Surface energy vs dosage for APP-H treated PET and PP

![Graph showing surface energy vs dosage for APP-H treated PET and PP](image)

- **PET**
- **Pure PP**

**Surface energy (mN/m)**

**APP dosage (W.min/m²)**

$t = 0$ j
PROCESS OPTIMIZATION

Surface energy vs dosage for APP -H treated PP

- Pure PP
- PP with additives

Surface energy (mN/m) vs APP dosage (W.min/m²) at t = 0 j
Surface energy ageing of APP -H treated PP

- Pure PP - 50 W.min/m²
- PP with additives - 100 W.min/m²
Surface energy ageing of APP treated Pure PP

Surf. energy (mN/m)

0 10 20 30 40 50 60 70 80 90 100

Shelf life (days)

APP-H2
APP-N2O
AIR CORONA
MORPHOLOGY BY AFM (*)

**TREATMENTS ON BOPP FILM**

- **Untreated**
  - $R_a = 0.52 \text{ nm}$

- **Air Corona**
  - $R_a = 0.36 \text{ nm}$

- **$N_2$**
  - $R_a = 0.41 \text{ nm}$

- **$N_2+N_2O$ (500ppm)**
  - $R_a = 0.46 \text{ nm}$

(*) AFM Tapping mode by BIOPHY RESEARCH
N & O Grafting on BOPP surface by APP

Untreated BOPP

APP treated BOPP

XPS analysis by BIOPHY RESEACH
N & O Grafting on BOPP surface by APP

YIELD of GRAFTING

Treatment parameters:
Gas: N2
Specific power: 30 - 70 W.min/m²
Speed: 50 m/min
Exposure time: 0.5 s

% Grafted N: In depth grafting reaction

% Grafted O: Surface adsorption by return to air (partially)
CHEMICAL COMPOSITION (XPS)

- **APP Treated BOPP:**
  Grafting controlled by reactant gas mixture composition

<table>
<thead>
<tr>
<th>GAS MIXTURES</th>
<th>% C</th>
<th>% O</th>
<th>% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIR CORONA</td>
<td>90.45</td>
<td>9.55</td>
<td>0.60</td>
</tr>
<tr>
<td>PURE N₂</td>
<td>82.21</td>
<td>4.03</td>
<td>8.76</td>
</tr>
<tr>
<td>N₂O (500 ppm)</td>
<td>84.30</td>
<td>10.45</td>
<td>4.95</td>
</tr>
<tr>
<td>CO₂ (500ppm)</td>
<td>88.15</td>
<td>5.40</td>
<td>6.45</td>
</tr>
<tr>
<td>H₂ (500ppm)</td>
<td>89.20</td>
<td>3.80</td>
<td>7.00</td>
</tr>
</tbody>
</table>
CHEMICAL FUNCTIONNALITIES GRAFTED ON PP BY APP

Treatment parameters:
Gas: pure N2
Specific power: 70 W.min/m²
Speed: 50 m/min
### CHEMICAL FUNCTIONNALITIES (XPS)

**APP treated PP:**

*Chemical functionalities controlled by reactant gas mixture composition*

<table>
<thead>
<tr>
<th>Gas mixtures</th>
<th>% Amine</th>
<th>% Amide</th>
<th>% Imide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure N₂</td>
<td>39.7</td>
<td>55.3</td>
<td>5.0</td>
</tr>
<tr>
<td>N₂ + N₂O</td>
<td>5.1</td>
<td>71.7</td>
<td>2.32</td>
</tr>
<tr>
<td>N₂ + CO₂</td>
<td>36.4</td>
<td>58.1</td>
<td>5.4</td>
</tr>
<tr>
<td>N₂ + H₂</td>
<td>49.3</td>
<td>48.6</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Percentages of total grafted N
SURFACE FUNCTIONNALIZATION: CHEMICAL GRAFTING

SPECIFIC CHEMISTRY
- Standard oxygen based surface chemistry
- New Amino, Amido and Imido based surface chemistry
AMINO and AMIDO/IMIDO chemistry features

- Amino and amido groups covalently linked to the surface providing:
  - PERMANENT SURFACE MODIFICATION
  - HIGH & STABLE SURFACE ENERGY
  - STRONG CHEMICAL REACTIVITY with:
    - Alkyds
    - Epoxydes
    - Isocyanates
    - Acids and Esters (e.g. acrylates)

CHARACTERISTICS
- Improved adhesion via hydrogen bonding or covalent bonding with binders
- Fast reaction kinetics leading to reduced curing time
ADHESION

PEELING TESTS ON TREATED BOPP

✓ Air Corona
Adhesion: 1/5 (*)

✓ APP – H2 treated
Adhesion: 5/5 (*)

(*) ASTM D3359 – 97 test method / AKZO blue water ink
0/5 : Total peeling of ink from the film to the tape (TESA 4104)
5/5 : No peeling
# Surface Energy and Adhesion

## APP treated BOPP

<table>
<thead>
<tr>
<th>RECIPE</th>
<th>SURFACE ENERGY (*)[mN/m (after 100 days)]</th>
<th>ADHESION (**)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNTREATED</td>
<td>&lt;30</td>
<td>0/5</td>
</tr>
<tr>
<td>AIR CORONA</td>
<td>34</td>
<td>1/5</td>
</tr>
<tr>
<td>ALDYNE™-P</td>
<td>52</td>
<td>1/5</td>
</tr>
<tr>
<td>ALDYNE™-C</td>
<td>58</td>
<td>3/5</td>
</tr>
<tr>
<td>ALDYNE™-H</td>
<td>60</td>
<td>4/5</td>
</tr>
</tbody>
</table>

(*) ASTM D2578 – 99a test method / SOFTAL GmbH calibrated inks

(**) ASTM D3359 – 97 test method / AKZO blue water ink

0/5 : Total peeling of ink from the film to the tape (TESA 4104)

5/5 : No peeling
Nanocoating

Silica nanocoating on BOPP

- Untreated: $\theta = 106^\circ$
- Silica nanocoating: $\theta \leq 20^\circ$

MODIFICATION OF SURFACE PROPERTIES
HYDROPHOBIC HYDROPHILIC
ANTI-FOG PROPERTIES

Silica nanocoating on BOPP

Untreated  Silica nanocoating
Nanocoating

Silica nanocoating on BOPP (AFM surface imaging)

Untreated BOPP

\[ Ra = 3.35 \pm 0.1 \text{ nm} \]

Silane treated BOPP

\[ Ra = 13.25 \pm 4 \text{ nm} \]

1 µm x 1 µm AFM images (Tapping)
Nanocoating

Silica nanocoating on BOPP (TEM section Imaging)

Low density layer (few tens nm thick)

Thin dense layer (few nm thick)

Dissolved agglomerate

Silane treated BOPP
Nanocoating

Silica nanocoating on BOPP (AFM surface imaging)

Untreated BOPP

Ra = 2.84 ±0.2 nm

TEOS treated BOPP

Ra = 1.42 ±0.2 nm

1 µm x 1 µm AFM images (Tapping)
**Nanocoating**

Silica nanocoating on BOPP (TEM section Imaging)

- Thin dense continuous layer (10 nm thick)
- Irregularities in the section

TEOS treated BOPP