Release – Adhesion enhancement of polymeric substrates using Atmospheric Plasma Technology

i-SUP 2008
22-25/04/2008

Marjorie Dubreuil, Erik Bongaers, Dirk Vangeneugden
Outline

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  - Conclusions
- Release coatings
  - Introduction
  - Characterization & Results
  - Conclusions
- General conclusions
INTRODUCTION
Surface modification using plasma technology

- Fragmentation
- Polymerisation
- Recombination
- Deposition

SUBSTRATE
Surface modification using plasma technology

- Cleaning, etching
- Activation, grafting
- Coating
Surface modification using plasma technology

Plasma assisted surface engineering
- Etching and cleaning (micro electronics, steel, glass, ...)
- Sterilization (biomedical, military, ...)
- Activation (plastics, textiles, steel, glass, paper, ...)
- Deposition of (multi) functional coatings (antimicrobial, scratch resistance, low friction, corrosion protection ...)

Advantages
- Environmental friendly
- Allows to deposit coatings with unique properties
- Flexible switching between process conditions
- Reliable operation
- Energy efficient
EQUIPMENT
PlasmaZone®

- Carrier gas: N₂, He, Ar, O₂, CO₂ (air), CF₄, SF₆,...
- Frequency range: 1-100kHz
- High voltage range: 1-100 kV
- Gaz consumption: 5-50L/min
- Power: 10-1000W
- Dissipated power: ≤ 1 W/cm²
- Temperature range: 25-250°C (~60-70°C)
- Gap ~ 2mm
PlasmaZone®

Semi-industrial roll-to-roll DBD plasma treatment

- Plasma treatment zone > 100 cm
- Width max.: 600 mm
- Speed: 1-200 m/min
- Power: 500 - 1000 W
PlasmaSpot® - PlasmaLine®

Indirect plasma (after glow)
ADHESION ENHANCEMENT
Introduction on Adhesion

- Present everywhere in the nature
- Among the oldest technologies
- 1st developments in chemistry in early 1900's

Today
- More than 1500 adhesives manufacturers
- Total consumption in 2005: 6.10^6 ton
Introduction on Adhesion

SUBSTRATE 1

ADHESIVE

SUBSTRATE 2

substrate 1

interface (adhesion)
adhesive (cohesion)

interface (adhesion)

substrate 2
Characterization & Results

Chemistry

\[
\begin{align*}
\text{ethyl acetate} & : \quad \text{CH}_3-\text{C}=\text{O}-\text{CH}_2\text{CH}_3 \\
\text{hydroxyethyl acrylate (HEA)} & : \quad \text{CH}_2=\text{C}=\text{O}-\text{CH}_2\text{CH}_2-\text{OH} \\
\text{allylamine (AAm)} & : \quad \text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}_2 \\
\text{acrylic acid (AA)} & : \quad \text{CH}_2=\text{CH}-\text{COOH} \\
\text{acetic acid} & : \quad \text{CH}_3-\text{COOH}
\end{align*}
\]
Characterization & Results

Surface tension parameters: 1 month after plasma treatment

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA H2O blanco</td>
<td>80</td>
</tr>
<tr>
<td>gpol blanco</td>
<td>70</td>
</tr>
<tr>
<td>SE blanco</td>
<td>60</td>
</tr>
<tr>
<td>CA H2O</td>
<td>50</td>
</tr>
<tr>
<td>gpol</td>
<td>40</td>
</tr>
<tr>
<td>SE</td>
<td>30</td>
</tr>
<tr>
<td>CA H2O</td>
<td>20</td>
</tr>
<tr>
<td>gpol</td>
<td>10</td>
</tr>
<tr>
<td>SE</td>
<td>0</td>
</tr>
</tbody>
</table>

Polyethylene (OW method)

Numerical values for various parameters:
- CA H2O blanco: 80
- gpol blanco: 70
- SE blanco: 60
- CA H2O: 50
- gpol: 40
- SE: 30
- CA H2O: 20
- gpol: 10
- SE: 0

Reference materials:
- gas activation
- HEA
- acetic acid
- ethyl acetate
- acrylic acid
- allylamine
Characterization & Results

Surface tension parameters: influence of treatment time

Polypropylene (acid-base method)
Characterization & Results

Structure analysis: labeling coupled XPS

- COOH, COOH, COOH coated substrate
- OH, NH, NH2 coated substrate
- (CF3CO)2O coated substrate
- SO2Cl2 coated substrate
- CF3CH2OH coated substrate
- NH2NHCH3 coated substrate
- C=O coated substrate

= N-NHCH3
Characterization & Results

Structure analysis: *labeling coupled XPS*

HEA-based plasma coating on Polypropylene

[OH], [NH$_2$] ~15%  
[COOH] ~2.6%  
[C=O] ~2.3%
Characterization & Results

Structure analysis: **ATR-IR**

EtAc-based plasma coating on Polypropylene

N-H in imines or amides

C=O in esters

C=O in amides

C-O-C in R$_1$COOR
Characterization & Results

Coating thickness & roughness: profilometry

plasma deposition mask removal
Conclusions

- Controlled and functional coating deposition via atmospheric pressure plasma

- Control of the surface tension parameters

- Re-organization of the precursor structure in the plasma → new functions created

- Applications:
  - Primer replacement
  - Enhancement of a substrate printability
  - Enhancement of the adhesion with a glue,
  - ...
RELEASE COATINGS
Introduction on Release coatings

Most important market: PSA
1st development in the XIXth century: surgical tape
Drastic development of PSA since beginning 1900’s
Applications: mold release (lubricants), masking tapes, PSA tapes, labels,...
Introduction on Release coatings

- wet chemical deposition, plasma-assisted chemical vapour deposition, gas fluorination, powder coating,...
- Cost issue
- Environmental issue
- ...

[Diagram showing layers: Release Coat, Backing, Primer Coat, Adhesive Mass]
Characterization & Results

Chemistry

Silicon free chemistry

\[ \text{Ethylhexyl acrylate (EHA)} \]

Silicon based chemistry

\[ \text{Hexamethyldisiloxane (HMDSO)} \]

Development in collaboration with Nitto Europe
Characterization & Results

Release properties: release tests

- **initial:**
  - tape brought at RT
  - removal after 2 hours

- **aged complex:**
  - tape brought at RT
  - ageing 24h or 1 week at 60°C
  - cooling down
  - removal
Characterization & Results

Release properties: release tests EHA

![Graph showing release values (cN/20mm) for different materials (PVC, PET, PP, PE) and conditions (sample initial, sample aged, reference aged)].

- PVC: Reference aged 1030, Sample initial 535
- PET: Reference aged 350
- PP: Sample initial 535
- PE: Sample initial 0
Characterization & Results

Release properties: release tests HMDSO

Release values (cN/20 mm)

- PVC
  - Reference aged: 1030
  - Sample initial: 0
  - Sample aged: 0

- PET
  - Reference aged: 535
  - Sample initial: 0
  - Sample aged: 0

- PP
  - Reference aged: 535
  - Sample initial: 0
  - Sample aged: 0

- PA
  - Reference aged: 535
  - Sample initial: 0
  - Sample aged: 0
Characterization & Results

Structure evaluation: ATR-IR - HMDSO

- No silicon transfer to the tape

Initial PP-coated sample
PP sample after ageing and tape removal
Characterization & Results

挂号 Thickness: SEM, profilometry

- 20-30nm
- 1.3µm
- 110nm

EHA

HMDSO
Conclusions

Controlled and functional coating deposition via atmospheric pressure plasma:
- Apolar silicon-free acrylate coatings
- Silicon-based coatings

Drastic improvement of the release properties

Applications:
- Release liner for pressure-sensitive adhesive tape
- Mold release
- Labels
- ...

May 6, 2008
GENERAL CONCLUSIONS
Conclusions

Atmospheric DBD plasma processes, based upon the same technology as current state of the art corona technology, offer new possibilities for sustainable dry surface engineering.

By controlling the gas atmosphere and the electrical conditions and by addition of reactive chemicals, one can increase the efficiency of the plasma surface treatment significantly and make the effects permanent.

The technology opens up new possibilities to deposit thin functional coatings in a continuous system at ambient pressure.

Efficient tuning of the final properties.
Questions ???

**STRANGE BREED** by Steve Langille

*Whatever happened to that guy from the 1980's Super Glue commercials?*