Coating and printing processes for the surface functionalization ... newest developments

Andrea Glawe, Frank Schäfer
KROENERT GmbH & Co KG
Schützenstr. 105 - 22761 Hamburg
Phone +49-40-85 393 172
Fax +49-40-85 393 171
info@kroenert.de - www.kroenert.de
Agenda

• Experience of KROENERT
• Self dosing versus pre dosing technologies
• Coating versus printing
• Coating line concepts
• Summary

Source: Modell region Hamburg for Electro mobility
Application for environmental protection

- Epoxy resin coating and impregnation for light construction materials
- Prepregs for glass, carbon and synthetic fiber composite materials
- Anodes, cathodes and separator film coatings for lithium ionic batteries
- Coating of anode, cathode and membranes for fuel cells
- Lamination for back-sheets and flexible solar cells
- Organic and printed electronics
- OPV, OLED, RFID technology
- Nano layers ≥ 50 nm on flexible materials for surface functionalization
- Membranes for water treatment and salt water desalination

Picture: Holst Centre
Applications

- Labels with information transfer by Near Field Communication (NFC)
- Electro luminescent layers
- Electro chrome layers like used for the window shades in the Dreamliner B787
- Foldable electronic magazines and displays
- Bighting wall paper
- Printed boards
- RFID-antenna
- Printed sensors
- Organic solar cells
Requirements for precise printing & coating

High performance of the coating necessary:
- Coating absent of defects
- Cross-Web Distribution less than +/-1%
- Wet thickness less than 1 µm – dry less than 100 nm
- Coating thickness must remain constant over 24h of production
- Printing texture with highest resolution
Self-dosing versus pre-dosing

⇒ **Self-Metered-Coating** means that the applied coating weight depends on the process => e.g. Dip-Coating, Roller-Coating, Knife-Edge-Coating

⇒ **Pre-Metered-Coating** means that the applied coating weight does **NOT** depend on the process => e.g. Slot-Die-Coating, Spray-Coating
Slot die technology in different setups

- Slot-die technology characterized by:
  - Capillary forces acting between slot-die and the substrate
  - Distances between slot die and substrate of less than 200µm
  - Very low wet film thicknesses (~ 1µm) is possible at substrate speeds of less than 50 m/min

- Web-Tension-Mode
- Extrusion-Coating-Mode
- Bead-Coating-Mode
- Short-Curtain-Coating-Mode
- Long-Curtain-Coating-Mode

Distance:
- \( d = 0 \)
- \( d < h \)
- \( d > 2 h \)
- \( d \text{ ca. } 1 \text{ cm} \)
- \( d > 1 \text{ cm} \)
The calculation of coating windows helps to control the process.

The following parameters are important:

- Fluid parameters (viscosity, surface tension)
- Process parameters (distance between slot die and substrate, wet film thickness, substrate velocity)
- Lip length of the slot-die

\[ \dot{m} = \rho \cdot U_w \cdot h \cdot B \]

- \( \dot{m} \) = Massflow
- \( U_w \) = Substrate Velocity
- \( B \) = Coating Width
- \( h \) = Wetfilm thickness
- \( \rho \) = Density
The coating window for a slot die operating in the short-curtain-coating-mode can be calculated in order to support the coating on the coating facility.
Applications – Printing and coating for Battery products

- Cathode
- Anode
- Separator
- Pouch or Coffee Bag

Prismatic Cell electrode Stack

Tabs
- Neg (-) Electrode
- Pos (+) Electrode

Separator

Wind power and electric car background image
Intermitted coating operation with slot die technology

- Slot die for full size or
- Slot die for stripes in length direction or pattern in cross direction
Intermittent coating operation with slot die technology

Technology transfer for intermittent slot die coating processes developed for battery electrodes to conductive layer application and OPV products

- **Edge accuracy**
- **Measurement of the surface topography**
- **Measurement of the rod movement with high speed camera**
Intermittent coating operation with slot die technology

General coating accuracy with slot die
- Gap adjustment slot die to substrate: 0,5 µm steps
- Running precision coating roller: 1 µm
- Precision of speed adjustment: +/- 1 %
- Tension: +/- 1 N
- Coating weight variation: +/- 1 %
- Coating thickness accuracy: +/- 0,5 µm
- Coating thickness adjustment: +/- 0,1 µm steps

Intermittent operation features
- Coating accuracy from one to the other side: +/- 0,1 mm
- Coating accuracy start and stop with intermittent coating: +/- 0,6 mm
- Tolerance of the coating length: +/- 0,5 mm
- Coating width: +/- 0,1 mm
Intermitted coating operation with slot die technology

Layers suitable with length and cross pattern for battery electrodes

- With shims realization of stripes in web cross direction.
- With the intermitted slot die intermitted application in web length direction.
Intermittent coating operation with slot die technology

Adhesive application for precise encapsulation of electronic devices

Tests with two different paste feeding systems.
- Pressure container
- Eccentric peristaltic pump

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Type</th>
<th>SC [%]</th>
<th>Solvent</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>45</td>
<td>Solvent</td>
<td>transparent</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>65</td>
<td>Water</td>
<td>white</td>
</tr>
</tbody>
</table>
Intermittent coating operation with slot die technology

Adhesive application for precise encapsulation of electronic devices

Results:

- A precise adhesive application is also possible
  - with very visco-elastic adhesives
  - with visco-elastic materials
Intermittent coating operation with slot die technology

Further activities

- Additional tests in preparation with conductive inks PEDOT-PSS for organic PV beside the stripe application in length direction
- Additional tests with low viscous lacquers for device encapsulation
Intermittent coating operation with slot die technology

Rotating bar-Technique

Valve-Technique
General coating operation with slot die technology

- die for full size
- die for stripes
- intermittent die
- combinations
Slot die technology for ceramic separator membranes

- New PE-based Evapore® process by film stretching developed from Brueckner Maschinenbau
- Cost-efficient production process for all types of lithium-ion batteries

Pilot Line
1.2 m

Production Line
4.2 m

For more information about the PE-membrane:
http://www.brueckner-maschinenbau.com/de/brueckner-maschinenbau/loesungen/spezialshyfolienanlagen/batterie-separatoren/
Slot die technology for ceramic separator membranes

- Tension very critical because of the sensitive semipermeable membrane.
- Corona treatment very important to improve the surface tension and with that adhesion.
- Substrate spreading quite critical to avoid curling.
- Thermal relaxing of the film for a better stability necessary.
- Critical slurry parameters because of the silicate mixture and sedimentation fear of the slurry.
Slot die technology for ceramic separator membranes

Ceramic coating development current status:

- Coating mixture / chemistry established.
- Coating trials with laboratory coating systems at KROENERT still running
  - Single side coating tested
  - Coating technology defined
  - Web handling optimized
  - Drying method defined
- Testing of properties of coated /impregnated membranes at Brueckner side.
- Evaluation of the reached target specification at Brueckner side.
- Upscaling of coating equipment done from 150 mm to 500 mm WW.
- Thermal relaxing of the film for a better stability qualified.
Roller application technology for printing & coating

Conventional gravure printing racle with oscillation

Gravure printing pan less pressure chamber system for direct coating and printing MPG 300

⇒ Printing – contact with the substrate

⇒ Coating – contact or contact less

T-chamber for gravure printing and coating in direct and reverse mode possible

Pan less pressure chamber system for reverse coating MPG 300
Gravure printing/coating technology

PRINTING TECHNOLOGY

- Engravure for min 2 pt textures
- Hexagonal cell engraving
- All kinds of line-engraving
- Structures engraving

- Hexagonal cell engraving
- All kinds of line-engraving
- Structures engraving

- Lines per centimeter
- Ratio
- Volume, ml/cm²
- Depth, µm
**Gravure printing/coating technology**

**Substrate:**
- Flex glass or PET-foils coated with conductive ITO as basis electrode

**Application of different functional layers:**
- Ion absorption layer P3HT-PCBM
- Hole (ion) transport layer PEDOT-PSS
- Silver paste as conductive grid

**Coating technology:**
- Slot die
- Engraved roller printing
- Rotary screen printing

---

P3HT = Poly(3-hexylthiophen)
PCBM = [6,6]-Phenyl-C61-butyric acid methyl ester
PEDOT = Poly-3,4-ethylenedioxy-thiophen
PSS = Polysulfonäure
Gravure printing for designed OPV from BeElectric

- Printing of OPV-cells with gravure roller technology from BeElectric
- Inverted solar cell
- Efficiency 3 – 4%
- Enough energy production to produce the energy of the German pavilion

Source of information: The solar trees of BeElectric – information exchange during the OE-A meeting in May 2015
Flexo printing technology

Laser engraved FLEXO PRINTING SLEEVES

- Defined flexo-printing technology with changeable printing sleeves.
- Precise coating material feeding with engraved rollers.
- Laser pattern of the sleeves for highest resolution.
Rotary screen printing technology

Precise printing processes
Compact pattern up to very fine and thin lines
Register steering

Layer 1 – engraved roller printing
Layer 2 – screen printing
Standard modules with individual setup

Coating Applications: Gravure, Slot-Die, Hot melt, Comma, Flexo-Printing
Coating-Weight (wet): 0,8 µm up to 500 µm
Coating Tolerances: +/- 5% (MD and TD)
Machine Speed: 0,1 up to 100 m/min
Register (longitudinal): +/- 0,02 mm
Register (lateral): +/- 0,02 mm
Register (double sided): +/- 0,50 mm
Floatation Drying: 40 up to 300 °C
Curing: up to 500°C
Comparison of the different technologies

<table>
<thead>
<tr>
<th></th>
<th>Screen</th>
<th>Flexo</th>
<th>Gravure</th>
<th>Offset</th>
<th>Inkjet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film thickness wet</td>
<td>µm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6-50</td>
<td>1-10</td>
<td>1-8</td>
<td>0.1-2</td>
<td>0.01-0.5</td>
</tr>
<tr>
<td>Minimal printable feature size</td>
<td>µm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>30</td>
<td>5</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Rheological limits</td>
<td>Pas</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5-50</td>
<td>0.1-1</td>
<td>0.05-0.2</td>
<td>5-100</td>
<td>0.001-0.04</td>
</tr>
<tr>
<td>Image carrier costs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td>-</td>
</tr>
</tbody>
</table>

Tim Claypole „Manufacturing methods and challenges for printed electronics“, LOPE-C 2014, Munich
Configuration for adhesive application

Hotmelt and wet coating process in one line
Configuration for battery electrode production
Configuration for OPV

5 coating units with register control – CSEM Brazil


David Wolin, Technical & Production Director bei CSEM Brasil, und Frank Schäfer, Sales Director bei KROENERT
Configuration for OPV

3 coating units with register control – Eight19
Configuration for printed sensors

Thinfilm Sweden

The Smart Bottle from Thinfilm
Test possibilities to define processes
Purpose of test centers

Purpose for customers:
- Test runs under production conditions with various coating methods
- Process optimization
- Process development

Purpose for the machinery supplier:
- Optimization of existing processes and development of new technologies
- Determination of guaranteed process specifications
- Development of process expertise (from know-how to know-why)
I’m pleased to answer to your questions.

Andrea Glawe
info@kroenert.de