Material printing – The new opportunities for printing industry

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Outline

- Interduction of R&D activities
- Challenges and aspects of printed/coated functionalities
- Materials
- Printing/Coating techniques perspective
- Case studies
- Conclusion

R&D activities, printing/coating techniques competency

- R&D of technology of preparation of functional structures
- R&D of ink formulation and benchmarking of commercial ink formulation
- Personally 400-800 mixed/tested ink formulations per year

- Screen printing
- Flexo
- Gravure
- Pad printing
- Offset
- DJ
- Negative patterning – lasers – UV/VIS, NIR, IR
- Lab2Fab experiences, Narrow web (410 mm), Widesweb production trials, pilot plant trials incl. high speed material printing (1.3 m, 320 m/min)
Why coating and printing technologies?

- The printing and coating techniques should provide cheap and fast production of low cost and low-end functionalities.
- Printed/coated functionalities are sometimes tens years behind to products made by traditional technologies in terms of their characteristics.

Printed/coated functionalities

- Battery (primary, secondary)
- Battery Charger
- Photovoltaic
- Display, Light source – OLED, EL, electroluminescent, thermochromic, etc.
- Sensor – chemical, bio, climatic, pressure
- Memory
- RFID
- diodes
- Transistors
- ISS – Smart Objects, Smart Sensor, Smart Textiles

Passive components

- Electronic circuits
- Antennas – RFID
- Capacitors, resistors, coils, transformers

Functional layers

- Healthcare applications
- Drugs
- Termochromic, photochromic
- Catalytic layer
- Textile finishing layers
- Explosives

Differences to conventional coating/printing process?

- Safety - printing materials, fabrication process
- Printing/coating materials, printing substrates
- Printing forms
- Interaction of materials
- Strict observance of technology
- Printing/coating process quality/stability
- Post treatment condition
- Storing of the products
- Long term stability
- Never-ending and limitless opportunities to use or characterize anything

Substrates for printed functionalities/electronics

Flexible

- PET, PEN, PI (Kapton, Neopulim), PC, PVC
- Polyolefine - PE, PP
- Synthetic papers – Printex (PES/PAL), Synaps (PES), Tyvek (HDPE), Telin (polyolefin)
- Paper – uncoated paper, primer
- Nanocellulose
- Glass – 25 to 100 μm
- Metals

Rigid

- Paper – heavy paper weight
- Cardboard
- Thick polymeric substrate (PET, PEN, PI, PC, PE, P0, etc.)
- Glass – float, quartz, etc.
- Ceramic – Al₂O₃, (Rubidum, Alum), AI₃, etc.
- Metals
Materials for printed/coated structures

- Conductive
  - Metal composite – based on (Ag, Cu, Au, Ni, Pt, etc.)
  - Different shape and sizes of particles (globules, flakes, rods, wires)
  - Ag based most used
    - Up to 30% conductivity of bulk Ag
  - Cu – usually based on precursors CuO
  - Photonic sintering, reduction agents
  - Other metal for specific purposes
  - High temperature firing – Ag, Au, Pt, etc.
  - Precursors of metals
- Carbon composite (graphite, carbon black, etc.)
- Carbon based (graphene, GF, CNT, SWCNT, MWNT)

Materials for printed/coated structures - semiconductive

- Inorganic semiconductors
  - ZnO, ZnS, As$_2$S$_3$, TiO$_2$, WO$_3$, MoO$_3$, etc.
  - Si dispersions
  - TCO
- Sn doped oxide s ITO, FTO, ATO
- Zinc doped oxide AZO, GZO
- Mainly as a transparent conductors
- Prepared by sol-gel, nanoparticles ink, CVD

Materials for printed/coated structures - (Semi)conductive

- Polymers
  - PEDOT:PSS – (in-situ 3000 S/cm, disp. 1000 S/cm)
  - Polyaniline
  - Polyacetylene
  - Polypyrrole
  - Polythiophene
  - PPy, PPV
  - PK, etc.
- Small molecules
  - TIPS - Pentacene
  - Rubrene
  - Phthalocyanines
  - Diketopyrrolopyrrole
  - Naphthalene
  - Ag$_2$, NPG, TIPS, Ru, CDP
  - Some others
  - Fullerenes

Materials for printed/coated structures - dielectrics

- Polymer based
  - From solution/dispersion of various polymers
    - PVC (ε ~ 3)
    - PC (ε ~ 2.8 – 3.4)
    - PVDF (ε ~ 6)
    - PMMA (ε ~ 3)
  - Radiation induced polymerization (UV, EB)
    (Acrylate based (ε ~ 3))
  - Thermally induced polymerization (Pyr, acrylates with proper initiators)
- Composites
  - Based on particles of inorganic materials with high dielectric constant
    - BaTiO$_3$ (ε ~ 1000)
    - SiO$_2$ (ε ~ 300)
    - TiO$_2$ (ε ~ 100)
    - Al$_2$O$_3$, MgO (ε ~ 9)
    - HfO$_2$ (ε ~ 20)
**Printing techniques - InkJet**

- Absence physical printing form
- Relatively high resolution and high precise registration
- Relatively high range of thickness of printed layers

<table>
<thead>
<tr>
<th>Media Format</th>
<th>Sheets, R2R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ink Waste</td>
<td>Low</td>
</tr>
<tr>
<td>Printing Speed</td>
<td>Up to 280 m.min⁻¹</td>
</tr>
<tr>
<td>Ink Viscosity</td>
<td>1-50 mPa.s</td>
</tr>
<tr>
<td>Wet Thickness</td>
<td>1-500 µm</td>
</tr>
<tr>
<td>Dry Thickness</td>
<td>0.01-100 µm</td>
</tr>
<tr>
<td>Resolution</td>
<td>10 µm</td>
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</tbody>
</table>

- Problems with clothing of nozzles
- Quality strongly influenced by printing speed
- Long time run stability
- Large amount of interfaces

**Printing techniques - Gravure**

- Very stable printing process
- Highest printing quality
- High printing speed
- Printing form resistant to solvents
- Reverse gravure for precise coating

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<tr>
<td>Printing Speed</td>
<td>Up to 500 m.min⁻¹</td>
</tr>
<tr>
<td>Ink Viscosity</td>
<td>10-20 000 mPa.s</td>
</tr>
<tr>
<td>Wet Thickness</td>
<td>5-80 µm</td>
</tr>
<tr>
<td>Dry Thickness</td>
<td>0.02-80 µm</td>
</tr>
<tr>
<td>Resolution</td>
<td>3 µm</td>
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</tbody>
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- Expensive printing form/ cylinder
- Mainly gravure is suited to flexible substrates

**Printing techniques - Screen printing**

- Most used production technique
- Variety of thickness of layers
- Relatively easy preparation of stencil

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<td>Low</td>
</tr>
<tr>
<td>Printing Speed</td>
<td>Up to 50 m.min⁻¹</td>
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<tr>
<td>Ink Viscosity</td>
<td>100-20 000 mPa.s</td>
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<tr>
<td>Wet Thickness</td>
<td>3-1000 µm</td>
</tr>
<tr>
<td>Dry Thickness</td>
<td>0.02-1000 µm</td>
</tr>
<tr>
<td>Resolution</td>
<td>6 µm</td>
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- Printing speed, high viscosity

**Printing techniques - Flexography**

- Stable printing process
- High printing speed
- Rigid and flexible substrates
- Relatively inexpensive printing form

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<tr>
<td>Printing Speed</td>
<td>Up to 1000 m.min⁻¹</td>
</tr>
<tr>
<td>Ink Viscosity</td>
<td>10 -1 000 mPa.s</td>
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<tr>
<td>Wet Thickness</td>
<td>5 - 30 µm</td>
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<tr>
<td>Dry Thickness</td>
<td>0.03 - 10 µm</td>
</tr>
<tr>
<td>Resolution</td>
<td>30 µm</td>
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- Limited thickness of layers
- Uniformity of topology of fine lines
- NIP pressure is crucial
Printing techniques – Pad printing, offset gravure

- Rigid and flexible substrates
- Printability of 3D surface
- Printing quality
- Printing speed

**Media Format**
- Sheets, R2R

**Ink Waste**
- Low

**Printing Speed**
- Up to 120,000 parts/hr

**Ink Viscosity**
- 10 - 1000 mPa.s

**Wet Thickness**
- 5 - 80 μm

**Dry Thickness**
- 0.05 - 20 μm

**Resolution**
- 25 μm

Others „printing“ techniques for μ-Patterning

- Nanoimprinting lithography NIL
- Soft Lithography
  - Microcontact Printing μCP
  - Micromolding in Capillaries MIMIC
  - Nanotransfer printing nTP
  - Replica molding REM
  - Microtransfer molding μTM
  - Solvent-assisted micromolding SAMIM

Printing techniques – Offset printing

- Printing speed
- High resolution
- Inexpensive printing plates fabrication
- Frequently used printing technique

**Media Format**
- Sheets, R2R

**Ink Waste**
- Low

**Printing Speed**
- Up to 1000 m/min

**Ink Viscosity**
- 10 - 100 Pa.s

**Wet Thickness**
- 10 μm

**Dry Thickness**
- 3 μm

**Resolution**
- 25 μm

Simple functional layers

- Antistatic
- Antimicrobial
- Barrier
- UV protective
- Luminescent
- Thermochromic
- Photochromic
- Electromagnetic shielding
- Antifogging
- Oxygen, moisture scavengers, etc.
Case study 1 - Antimicrobial layers
- Special functional material
- Creation of small amount of reactive form of oxygen – bacteriostatic effect with 99.99% efficiency
- Activated by visible light
- Nice blue tint for medical, some other colour under development
- Ink formulation developer for Flexography – passed production trials at 320 m/minute with several km produced

320 m/min

Case study 2 - Smart Nappies
- Developed Smart Nappies
- Moisture sensor with capability to measure state of fulfillment
- Flexography >200 m/minute
- For elderly people or babies
- Wireless management of monitoring with implementation to MIS
- Bluetooth communication for homecare/households optional
- Low price of sensor is crucial
- Implementation by producer of nappies

200 m/min

Case study 3 - Thermistors
- Medical
  - Monitoring of human body temperature map
  - Monitoring of local temperature or mapping of temperature within wound dress
- Wearables for free times activities
  - Human body temperature
  - Environmental temperature

SmartLife® Technology

Case study 3 - Thermistors
- Protection of human health of professionals
  - Army
    - Tactic vest/coat
    - Tactic helmet
  - Firefighters
    - Smart Gloves
    - Smart Suit/uniform

Flow sensing
- Gas
- Liquid
- Speedometer
- Accelerometer

Sensing in industrial application
Case study 3 – Thermistors, HR, LR NTC ink formulation

- DC Measurements
- T range ~ 25 – 75 °C
- 4-point method
- L50, L70, L90, L110, L130 was measured
- All IDE passed except 50/50 H μm
- Difference of resistance in dependence to real N° of SQ
- Finer IDE ~ lower resistance

Conclusion

Carefully inspect real market needs
The best is to start with the most simple functional layers/solution with relatively small technological requirements
The R&D of selected products needs strong interest, effort and financial support of industrial partner
The printing ink formulation, technology process have to be very good established/tailored, than the processes have to be strictly observed during the production.
The simple tools for estimating the functionality of products have to be present within printing house together with well understanding by personal.

COST Action FP1405
Active and intelligent fibre-based packaging – innovation and market introduction (ActinPak)

ActinPak is a pan European (COST) network of the leading experts in active and intelligent packaging of over 100 institutes, universities and companies from 37 countries. Main goal of action is to develop a knowledge-based network on sustainable, active and intelligent fibre-based packaging in order to facilitate its introduction on the market.

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