UV/EB curing technologies for textile innovative applications

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30th April 2012

Summary

- **Few words about CeNTI**
- **Objectives**
- **Introduction**
- **UV/EB radiation curing technology for textile innovative applications (work in progress at CeNTI):**
  - Hydrophobic and oleophobic surface treatment based on UV curable polymeric materials
  - UV Curing finishing lacquers able to improve the printing quality of flexible substrates
  - Photovoltaic (PV) textiles
  - UV-curable electrolytes for electrochromic devices

What role does CeNTI play?

1. **R&D and innovation**
   i. Materials & devices
   ii. Methods & processes
2. **Small scale prototyping/production**
   i. Multilayer coated/printed
   ii. Multicomponent fibres
   iii. Interactive devices
3. **Integration**
   i. Systems integration
   ii. Embedded electronics

Programs & Figures

- **1st phase investment (2007-2008): 5 M€**
- **2nd phase investment (2011): 2 M€**

- Fibres & Polymers
- Polymers & Functional Materials
- Functional Materials
- Organic Electronics
- Embedded Systems & Electronics
- Numerical Simulation & Testing

- **2010**
- *35 R&D FTE staff*
- *1.7 M€ turnover*
- *+ 40 industrial driven projects*
- *(typically from 1 to 24 months)*

Outputs

- **Ultra high barrier films**
- Gas barrier
- Organic LEDs
- Organic Sensors
- Conductive fibres and films
- **Super-hydrophobic and super-oleophobic**
- Biocolouring
- Abrasion resistant & anti-scratch
- Anti-Slip & Grip-Enhanced Surfaces
- High insulation
- Selfcleaning
- Chemical agents release
- Flame retardant

Outputs

- **Electrochromic materials**
- Heating bands
- Embedded Biometric sensors: temperature, heart-rate, motion and touchpads/keypads
- Integrated gas sensors
- Wireless data communication to mobile platforms
- Drug release materials
- Supercapacitors
- Low weight thermoplastic materials
- High performance adhesives
- **Organic solar cells**

- **1st Prize Clean Tech Bes Inovação 2010**

Radiation Curable Coatings Technologies

Industrial Applications

- Graphic Arts
- Inks
- Commercial and industrial printing sectors
- Lamination technologies
- Packaging
- Electronic Industries
- Others...

- Textiles Industry?

Radiation Curable Coatings Technologies

Current surface treatments

Thermally initiated polymerization reactions, using water-based formulations

Significant amounts of chemicals, energy and water

E beam and/or UV-curing techniques

- **Energy conservation and cost saving**
- **Fast polymerization rates**
- **Innovative surface functionalities**

Textile innovative applications

Hydrophobic and oleophobic surface treatment based on UV curable polymeric materials

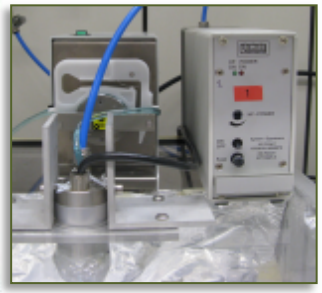
Objective:

Development of a surface treatment based on UV-curable polymeric materials to provide hydrophobic and oleophobic properties to different textile substrates (cotton fabric and polyester knitted fabric).

UV curable lacquer:

Component/Formulation (% W/W)	(%)
Glycol diacrylate	79
Polyisocyanate	5
Photoinitiator	5
1-propanol	10
Perfluorocarbon dimethacrylate	1

Hydrophobic and oleophobic surface treatment based on UV curable polymeric materials



Coating	Ultrasonic spraying deposition
	flow rate: 5 mL/min; power: 50%; compressed air: 0.3 bar; deposition time: 70 s
Drying	Laboratory stove
	100ºC; 2 min
UV curing	Laboratory UV curing unit
	Nitrogen feed; irradiance level: 25 W/cm^2; 6-12 min

Hydrophobic and oleophobic surface treatment based on UV curable polymeric materials

Hydrophobicity

Water Repellence Rating (WRR)

Test Liquid	Percent Composition of Test Liquid		Surface Tension Dynes/cm at 20°C
W	100	Water	72.8
1	90/10	Water/Isopropyl Alcohol	39.0
2	80/20	Water/Isopropyl Alcohol	32.0
3	70/30	Water/Isopropyl Alcohol	28.3
4	60/40	Water/Isopropyl Alcohol	26.6
5	50/50	Water/Isopropyl Alcohol	25.0
6	40/60	Water/Isopropyl Alcohol	24.3
7	30/70	Water/Isopropyl Alcohol	23.7
8	20/80	Water/Isopropyl Alcohol	23.3
9	10/90	Water/Isopropyl Alcohol	22.4
10	100	Isopropyl Alcohol	21.7

Oleophobicity

Oil Repellence Rating (ORR)

Oil Repellency Rating Number	Composition	Surface Tension Dynes/cm at 25°C
1	Kaydol® white mineral oil	31.5
2	65/35 Kaydol® white mineral oil/ n-hexadecane by volume at 21°C (70°F)	29.6
3	n-hexadecane	27.3
4	n-tetradecane	26.4
5	n-dodecane	24.7
6	n-decane	23.5
7	n-octane	21.4
8	n-heptane	19.8

3 small drops of the test liquid in two or three different areas on the test sample

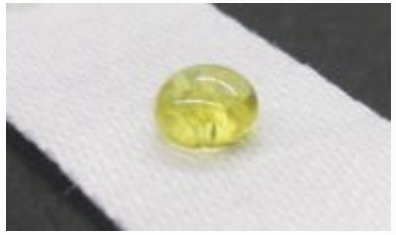
If after **10 seconds**, two of the three drops are still visible as spherical to hemispherical, the substrate passes the test

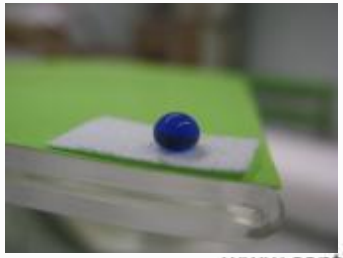
If after **30 seconds**, two of the three drops are still visible as spherical to hemispherical, the substrate passes the test

Hydrophobic and oleophobic surface treatment based on UV curable polymeric materials

General Conditions	flow rate: 5 mL/min; power: 50%; compressed air: 0.3 bar

Sample	Test conditions			Repellence level	
	Deposition time (sec)	Drying temp. (ºC)	UV curing time (min)	WRR	ORR
Cotton fabric	70	100	6	**5**	**6**
Polyester knitted fabric	70	100	12	**5**	**5**

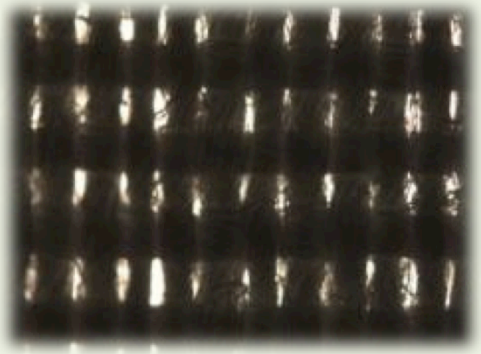




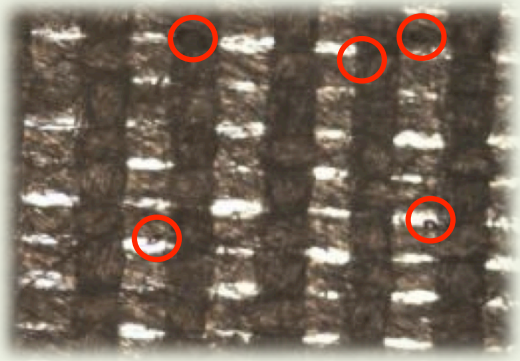
Hydrophobic and oleophobic surface treatment based on UV curable polymeric materials

Cotton fabric

Control sample



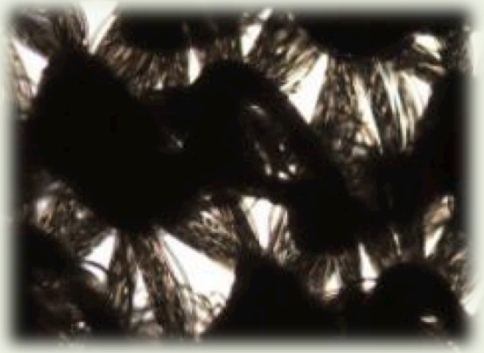
Treated sample



Polyester knitted fabric

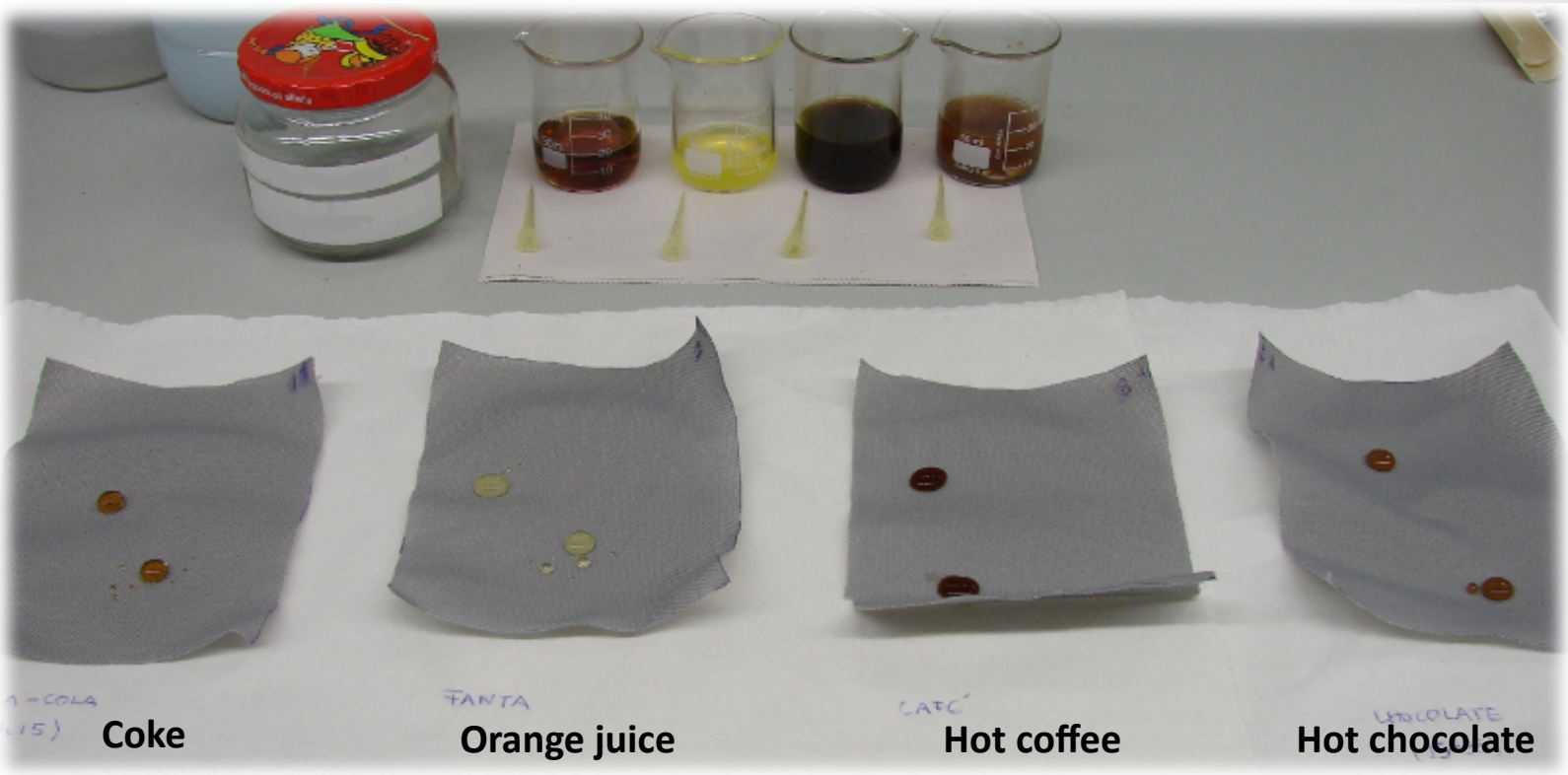
Control sample

Treated sample



Hydrophobic and oleophobic surface treatment based on UV curable polymeric materials

Resistance to staining and cleanability of woven or knitted textile materials



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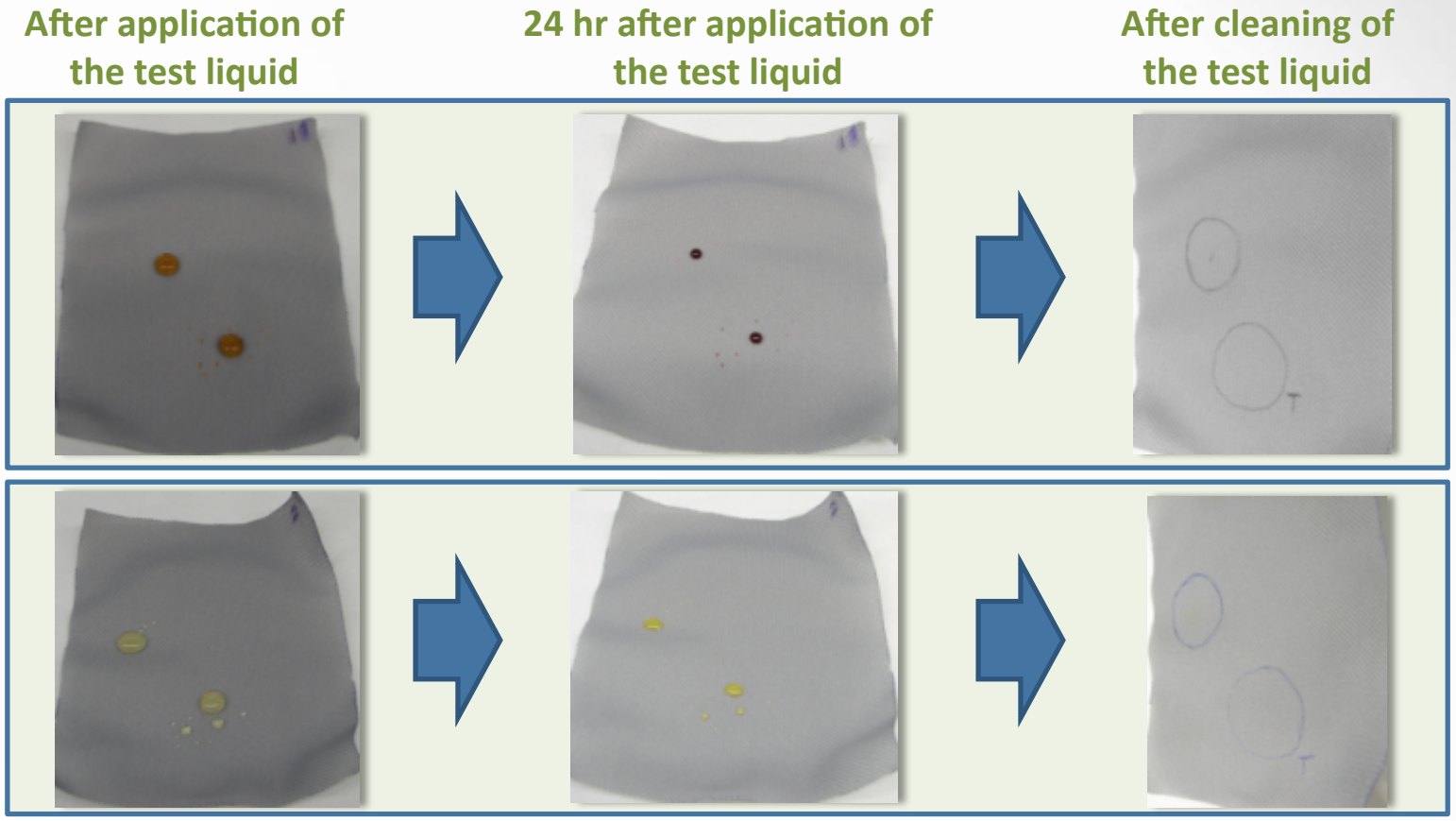
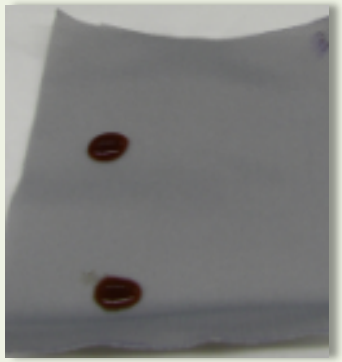
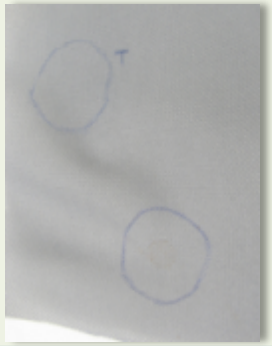
Resistance to staining and cleanability of woven or knitted textile materials



Hydrophobic and oleophobic surface treatment based on UV curable polymeric materials

Resistance to staining and cleanability of woven or knitted textile materials

	After application of the test liquid	24 hr after application of the test liquid	After cleaning of the test liquid
Hot coffee			
Hot chocolate			

UV curable lacquer for Digital Printing

Objectives/Benefits:

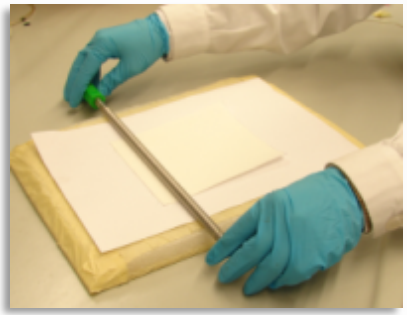
Improvement of printing quality of textile substrates

UV curable lacquer:

Typical composition:

- 58.9% Modified chlorinated polypropylene/isobornyl acrylate
- 20.0% Urethane acrylate dispersion
- 4.0% Photoinitiator
- 17.1% Solvent

UV curable lacquer for Digital Printing



Coating	Metering rod (Meyer bar) coating
	Wet thickness film: 24 µm **Weight:** 20-25 g/m^2
Drying	Laboratory stove
	100ºC; 15 min
UV curing	500mm pilot line equipment
	300 or 600 W 8-11 m/min

UV curable lacquer for Digital Printing

Pilot line equipment:

Equipment features:

- Roll-to-roll system
- 500 mm width
- Continuous/Semi-continuous process

Lamp specifications:

Length	50 cm
Type	Medium pressure mercury arc lamp
Power	200-600 W

UV curable lacquer for Digital Printing

UV curing

Test conditions:

- WITHOUT drying step
  - 300 W
  - 600 W
- WITH drying step
  - 300 W
  - 600 W

Single-, double- and triple-pass

Samples treated with UV curable lacquer:

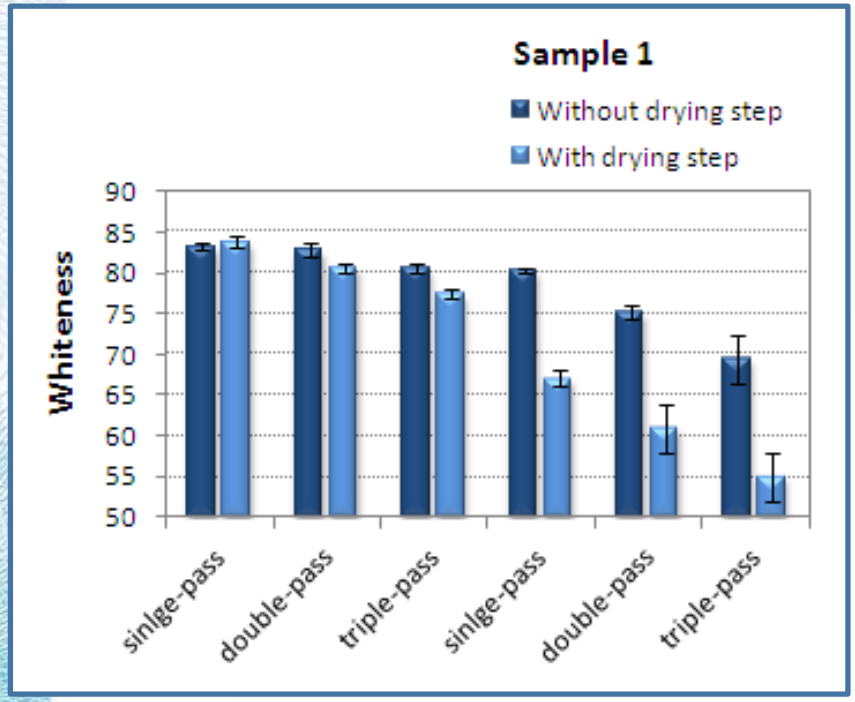
Sample 1	Textile substrate 1 + UV curable lacquer
Sample 2	Textile substrate 2 + UV curable lacquer

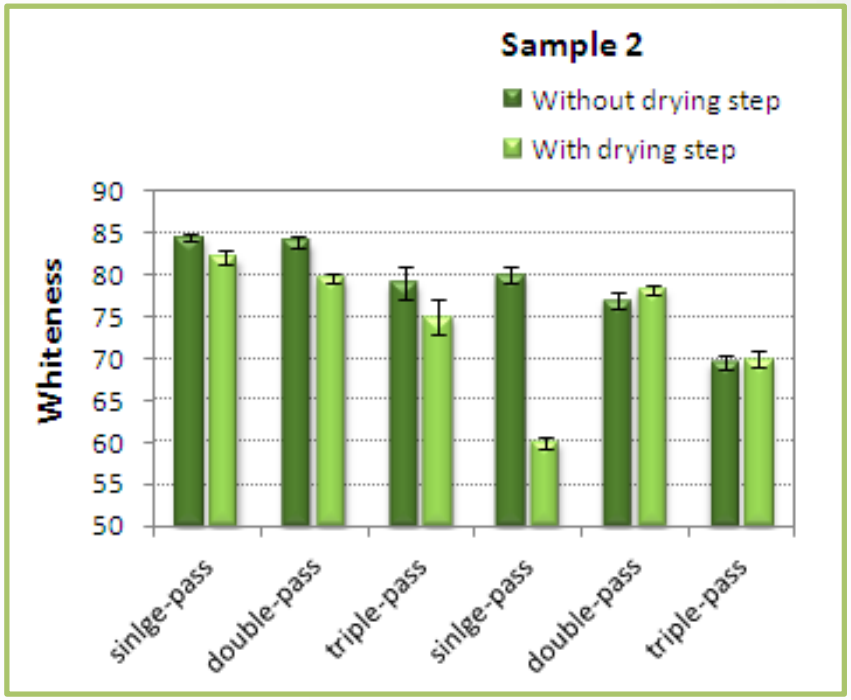
UV curable lacquer for Digital Printing

Whiteness

Spectrophotometer:

Spectraflash SF450 (DataColor International)





UV curable lacquer for Digital Printing

Print quality evaluation

Evaluation parameters:

- **Drying**
- **Color intensity**
- **Ink adhesion**

The treatment with UV curable lacquer results in the attainment of printability with good quality

High Barrier Films for Organic PV

Objectives:

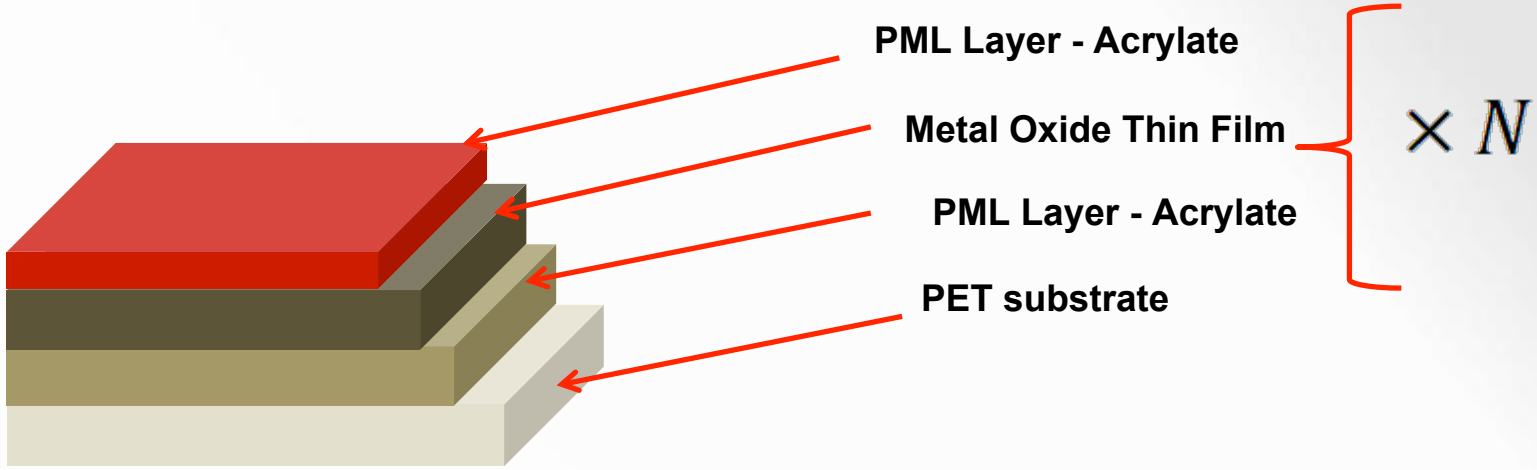
Developing flexible high barrier films for the encapsulation of flexible organic solar cells and other flexible organic electronic devices;

Special emphasis has been given to the development of textile based solar cells (using the textile structure as a substrate for the subsequent organic films);

Applications:

- Encapsulation of organic electronic devices such as OLEDs, OPVS, Organic TFTs and low-cost organic sensors;
- Replace glass/flexible glass as the encapsulant material;
- High transparency, flexibility and high barrier properties;

Photovoltaic (PV) textiles



- **Vacuum Multilayer processing:**

•Plasma Treatment of PET substrate
•Polymer Multilayer Technology;
•Reactive Sputtering Technology;
•Static and Roll2Roll Processing;
• In-Line processes;

Polymer Multilayer Process- PML

Polymer nanolayers:

1.Atomization ;

2. Flash Evaporation;

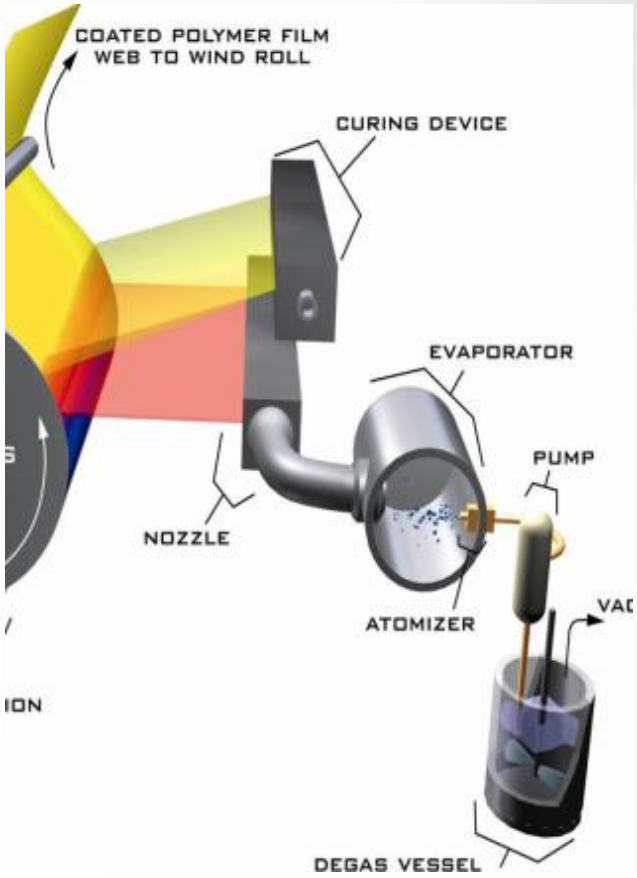
3.Deposition;

4.Condensation;

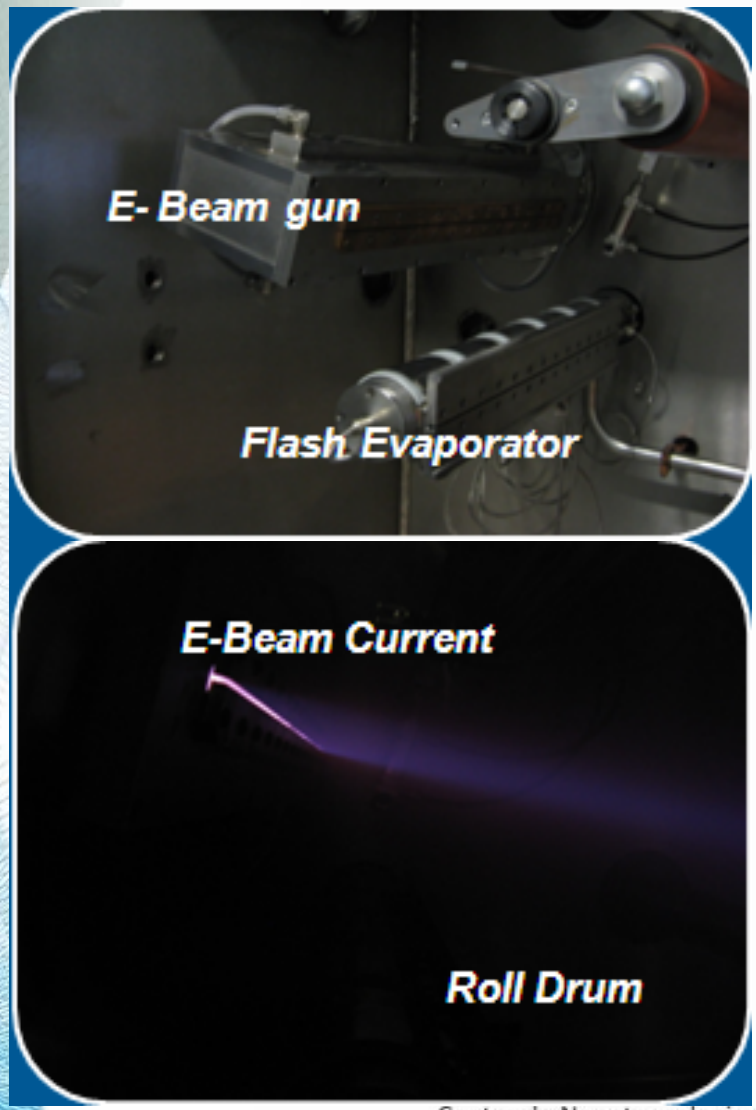
5. E-Beam Curing

Key Issues:

- Cross-linking (depth, efficiency)
- Molecular Weight (> 200MW)
- Speed (process, Flow rate)
- Condensation efficiency



Polymer Multilayer Process



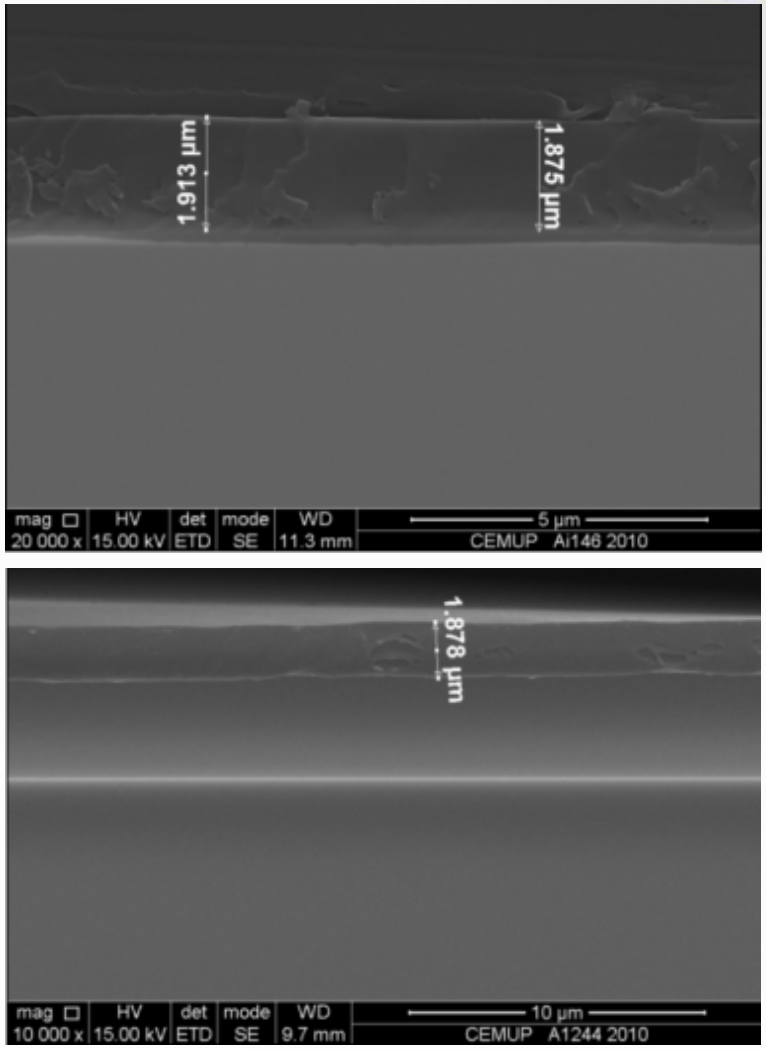
Polymer Layer Deposition w/ E-Beam

- In line monomer/oligomer deposition;
- E-Beam polymerization (up tp 5kW),
- High control of film thickness (from 10nm to 1000nm);
- Static and roll-2-roll depositions up to 100m/min;
- Monomer/oligomer depostion up to flash temperatures of 400ºC;
- 0.5m wide web roll highly uniform deposition;

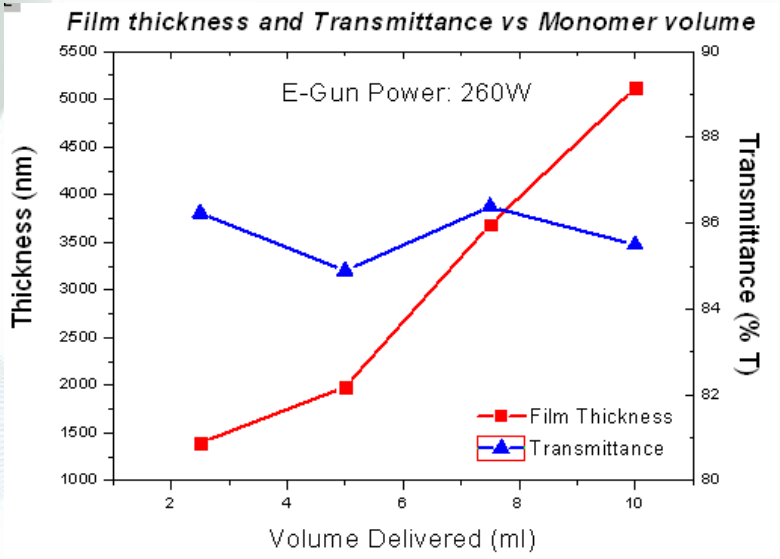
PML Layer

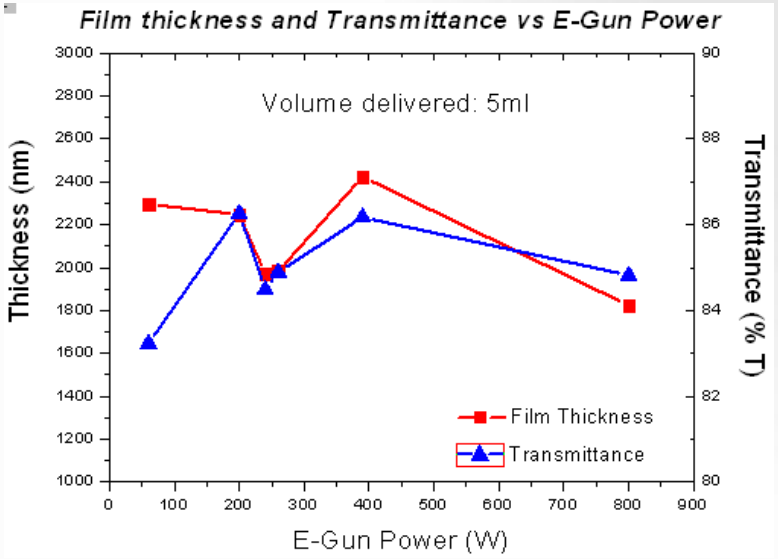
- Films present high uniformity for thicknesses below 5µm (SEM analysis)

- Films present good adhesion to the substrates: 5B ASTM D3359-7



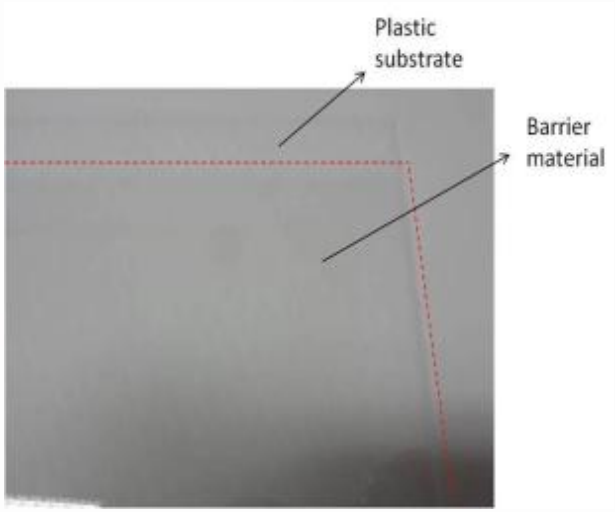
PML Layer

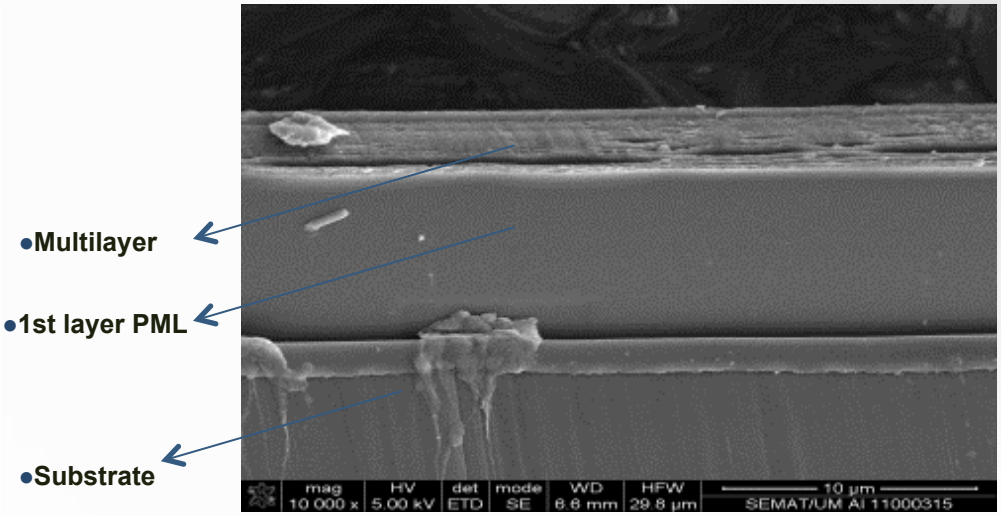




- The processed polymer films present high transparency values (average transparency in the 400-700nm region);
- The transparency of the films does not present significant variations with he increase of film thickness and E-gun/curing power (cross-linking of polymer);

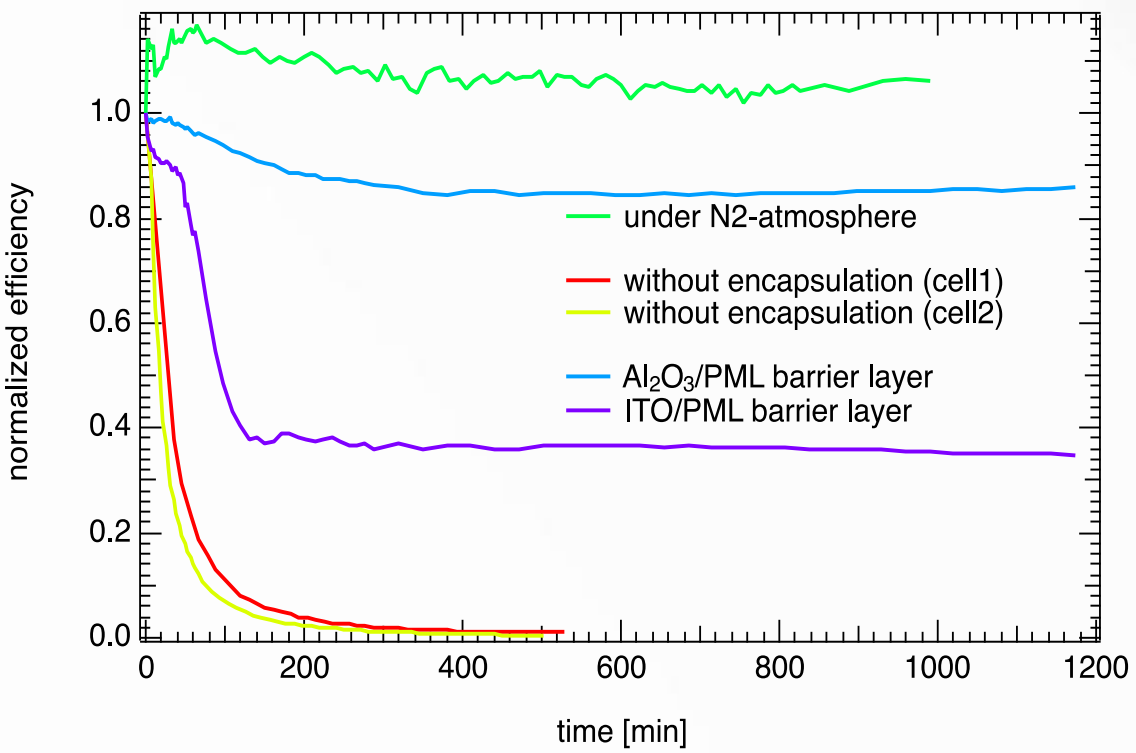
Multilayer Structure





- The metal-oxide intermediate layer are typically 10-20nm thick sputter coated thin films;
- Metal-oxides: Al2O3, ITO, TiO2, SiO2;
- High yield Dual Magnetron R2R sputtering system is assembled in-line with the PML system;

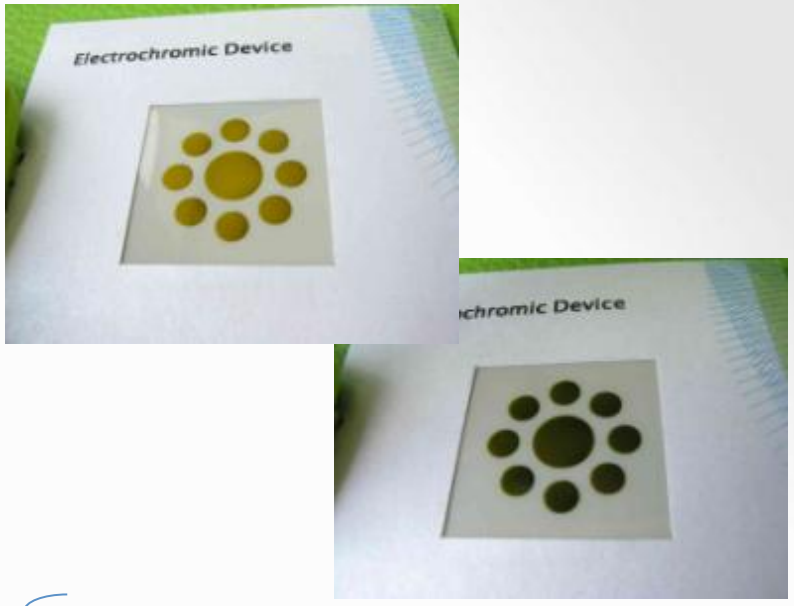
High barrier films



- Degradation of OPV cells under different conditions
- OTR: 0.01 $cm^3\ m^{-2}\ day^{-1}$;
- WVTR: 0.001 $g\ m^{-2}\ day^{-1}$

UV-curable electrolytes for electrochromic devices

ELECTROCHROMIC SYSTEMS



Applications

- Small displays
- Smart windows
- Auto-dimming rearview mirrors
- Smart labels
- …

V

- Electrical conductor
- **Electrochromic layer**
- **Polymeric electrolyte**
- **Ion-storage layer**
- Electrical conductor

Typical electrolyte composition

Ionic salt

Polymeric network

Plasticizer

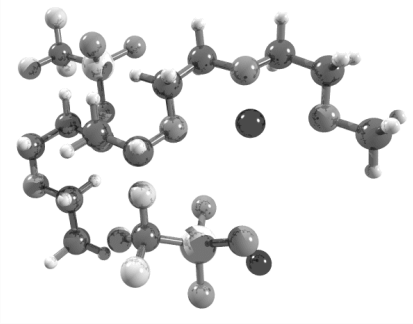
UV-curable electrolytes for electrochromic devices

Old methodology:

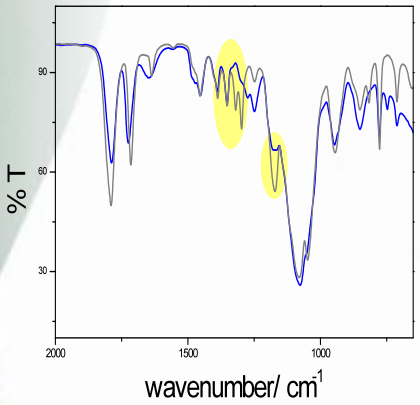
- Solvent evaporation
- Very slow: > 30 min.
- Release of large quantities of organic solvents to the environment.

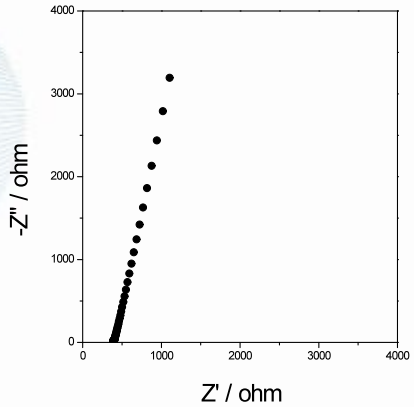
UV-CURABLE ELECTROLYTES

- Oligomeric chains containing photo-reactive groups
- Photoinitiators
- Ionic salts
- Plasticizers



UV-curable electrolytes for electrochromic devices





ONGOING WORK

Development flexible transparent/opaque UV curable electrolytes which could be processed by screen-printing.

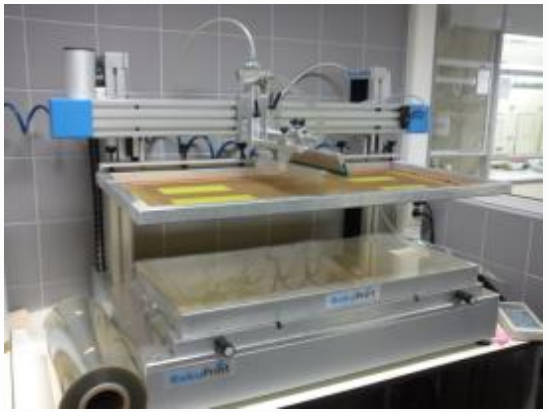
•*RESULTS*

•Self-supporting and good adhesive properties

•Relative high ionic conductivities (measured by EIS – electrochemical impedance spectroscopy)

•High transparency / high opacity

•Curing times: 5-15 min (depending on film thickness)



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