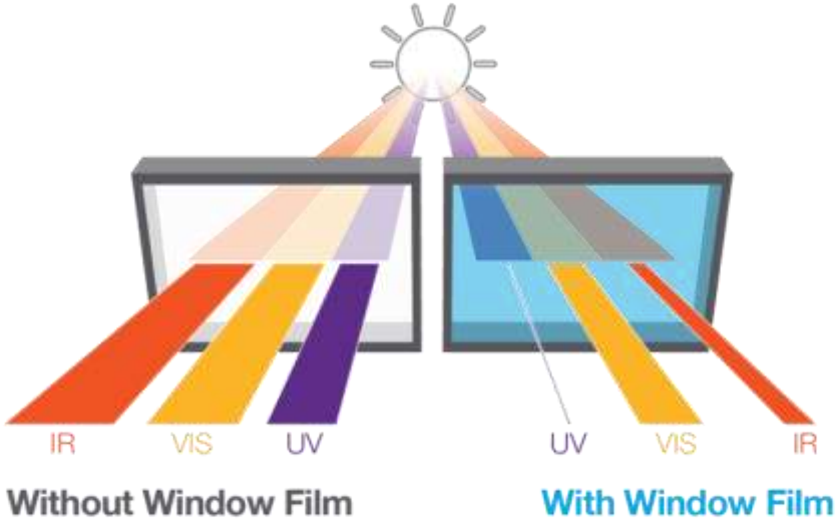
Fraunhofer Institute for Process Engineering and Packaging IVV

New nano-functional coatings for shrink films

Stefan Schiessl, 31st May 2022

4th Joint Symposium on Nanotechnology

Agenda



(https://www.crodasmartmaterials.com/en-gb/product-finder/product/1482-Atmer_1_1006

UV-Blocking - Motivation

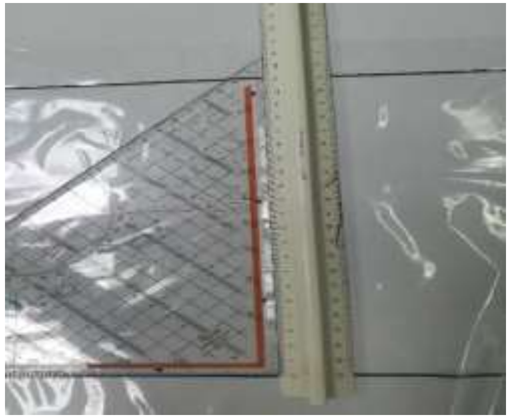
- **There is an increasing interest/demand for UV blocking shrink film for both fresh red meats and printed items**
  - UV light plays a critical role in brown discoloration of meat, since it encourages metmyoglobin formation.[1]
  - Indoor and outdoor UV light rays contribute to severe color loss, paper embrittlement and deterioration.
- **The UV blocking additive effective threshold in a thin film causes the film to be opaque.**

not UV protected UV protected

[1] Hood, D. E. (1980) Factors affecting the rate of metmyoglobin accumulation in pre-packaged beef. Meat Science, 4: 247-265

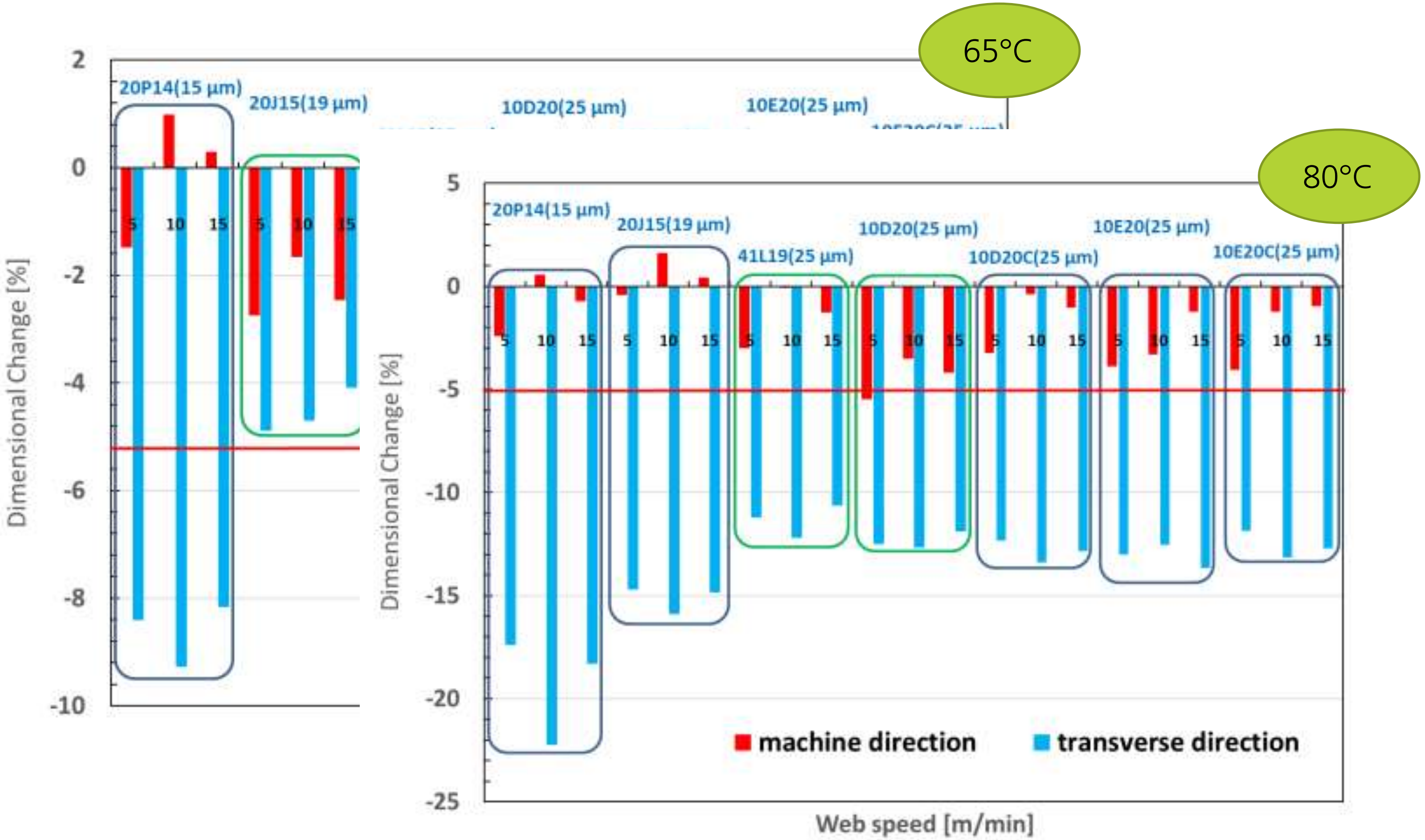
UV-Blocking - Materials & Methods

Web Dimensional Change % of PE shrink films



Dimensional change % in transverse-direction

Dimensional change % in machine-direction



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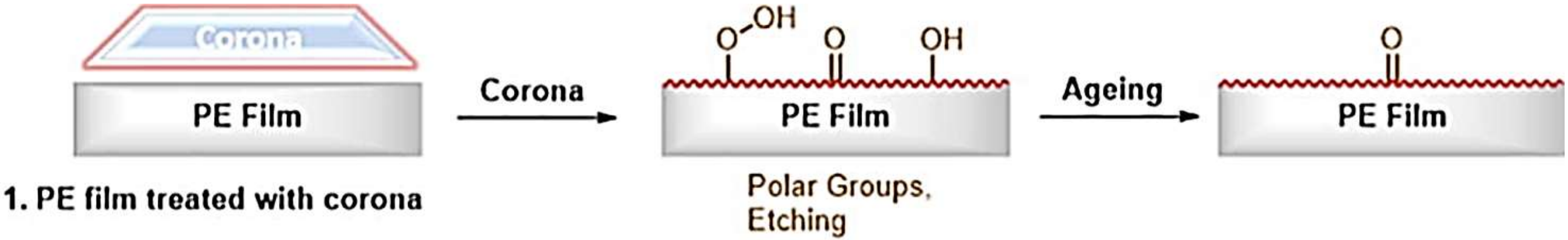
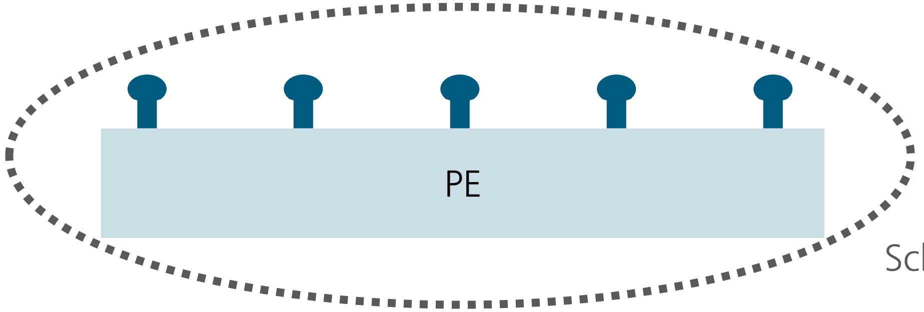
UV-Blocking - Materials & Methods

Physical pre-treatment of PE shrink film with Corona Discharge





Schematic representation

[2] Dai, L., & Xu, D. (2019). *Polyethylene surface enhancement by corona and chemical co-treatment. Tetrahedron Letters, 60(14), 1005–1010.* doi:10.1016/j.tetlet.2019.03.0

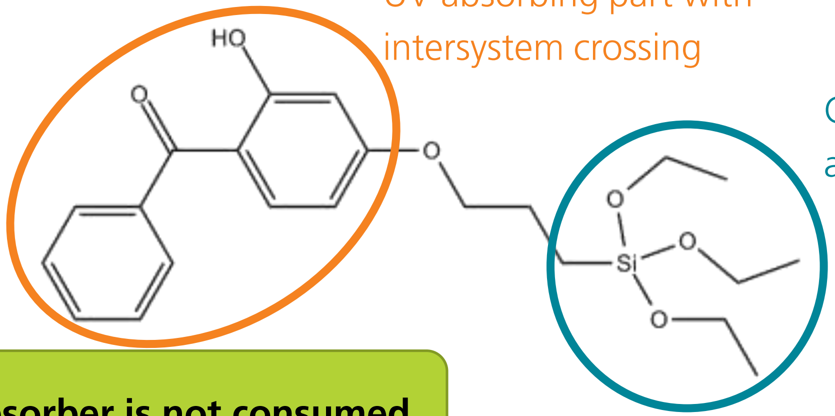
UV-Blocking - Materials & Methods

Composition of SiUV lacquer – diphenyl ketone based formulation

2-Hydroxy-4-(3-Triethoxysilylpropoxy)diphenylketone (SiUV)

UV absorbing part with intersystem crossing

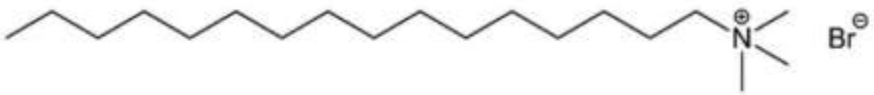
Covalent bonding to corona activated PE surface



Absorber is not consumed

Schematic representation

Cetyltrimethylammonium Bromide (CTAB)



0.1 M sodium hydroxide (NaOH)

Double distilled water

Ethanol (99.9 %)

EtOH/Water based formulation → fast and safe curing

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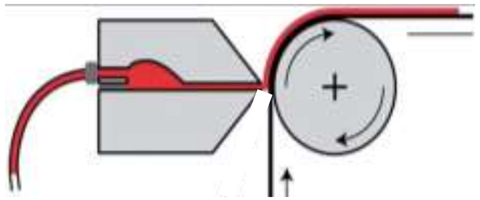
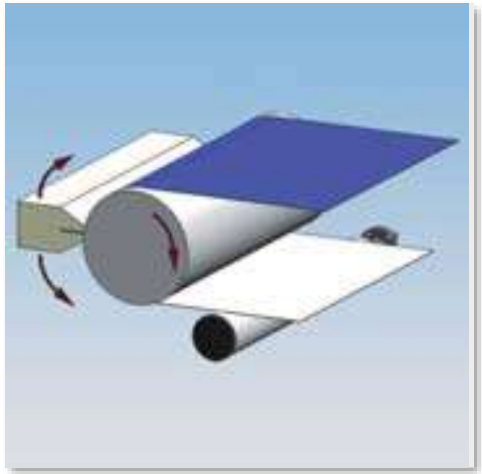
UV-Blocking - Materials & Methods

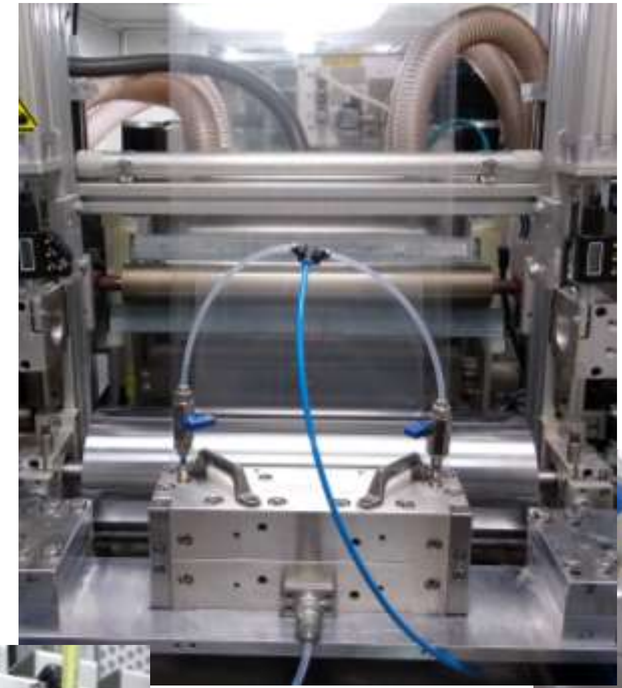
From semi-automated lab coating to R2R coating machine

UV-Blocking - Materials & Methods

Slot-die Coating technique

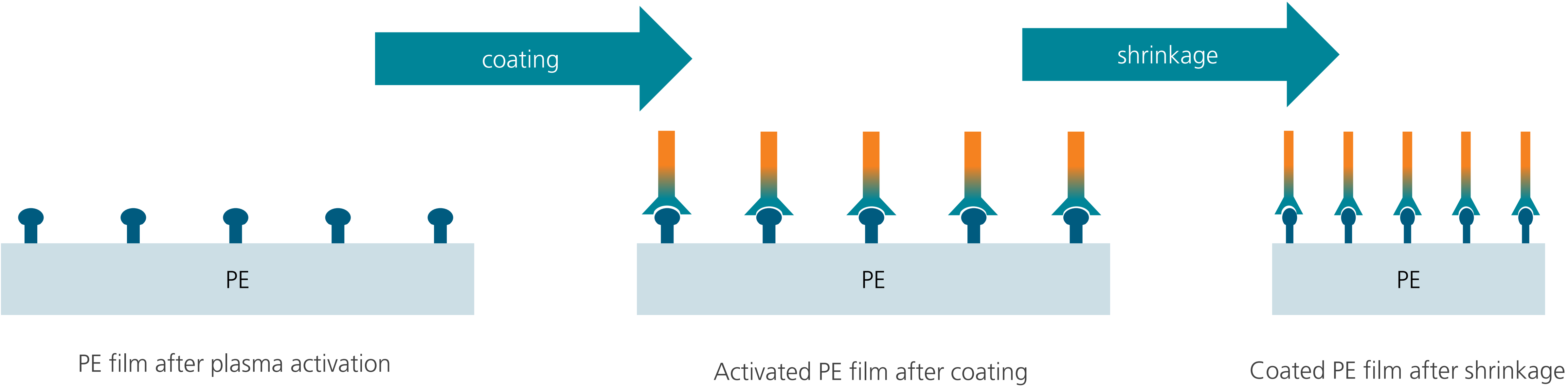






UV-Blocking - Results

Schematic representation of shrinkable polymeric films

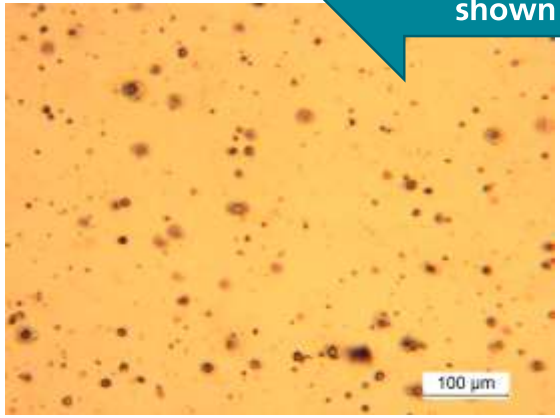


No cross-linking in-between UV blocking groups, therefore no delamination or cracking during shrinkage

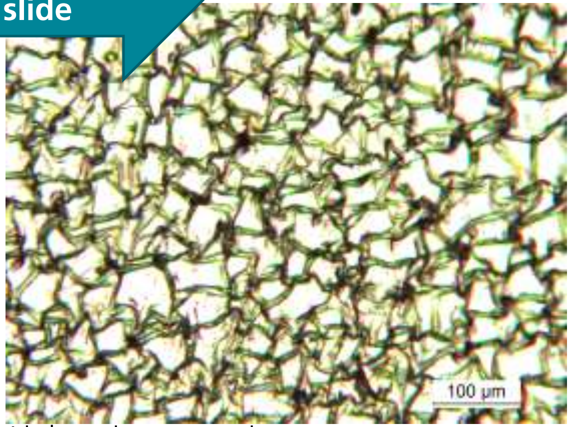
UV-Blocking - Results

Typical behavior of coated films after shrinkage


Difference in transmission shown next slide



Light microscope image



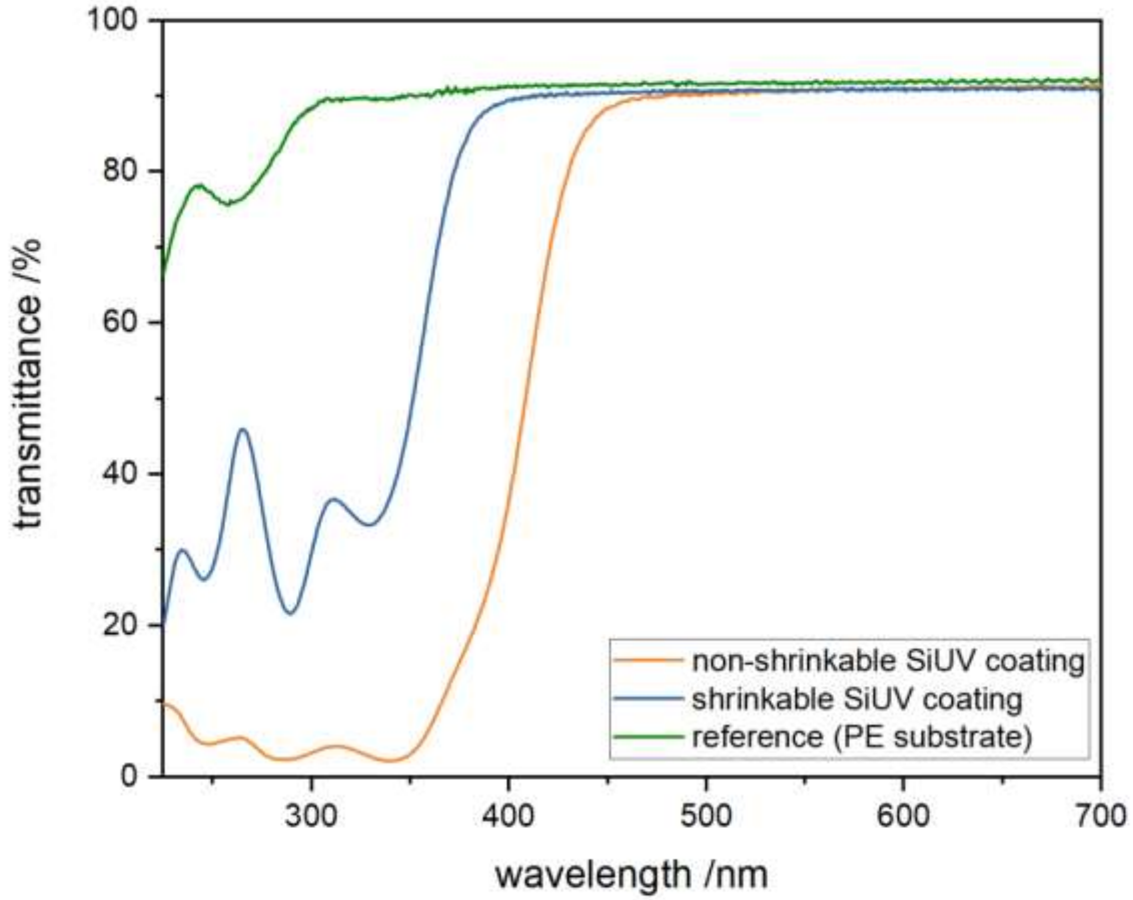
Light microscope image

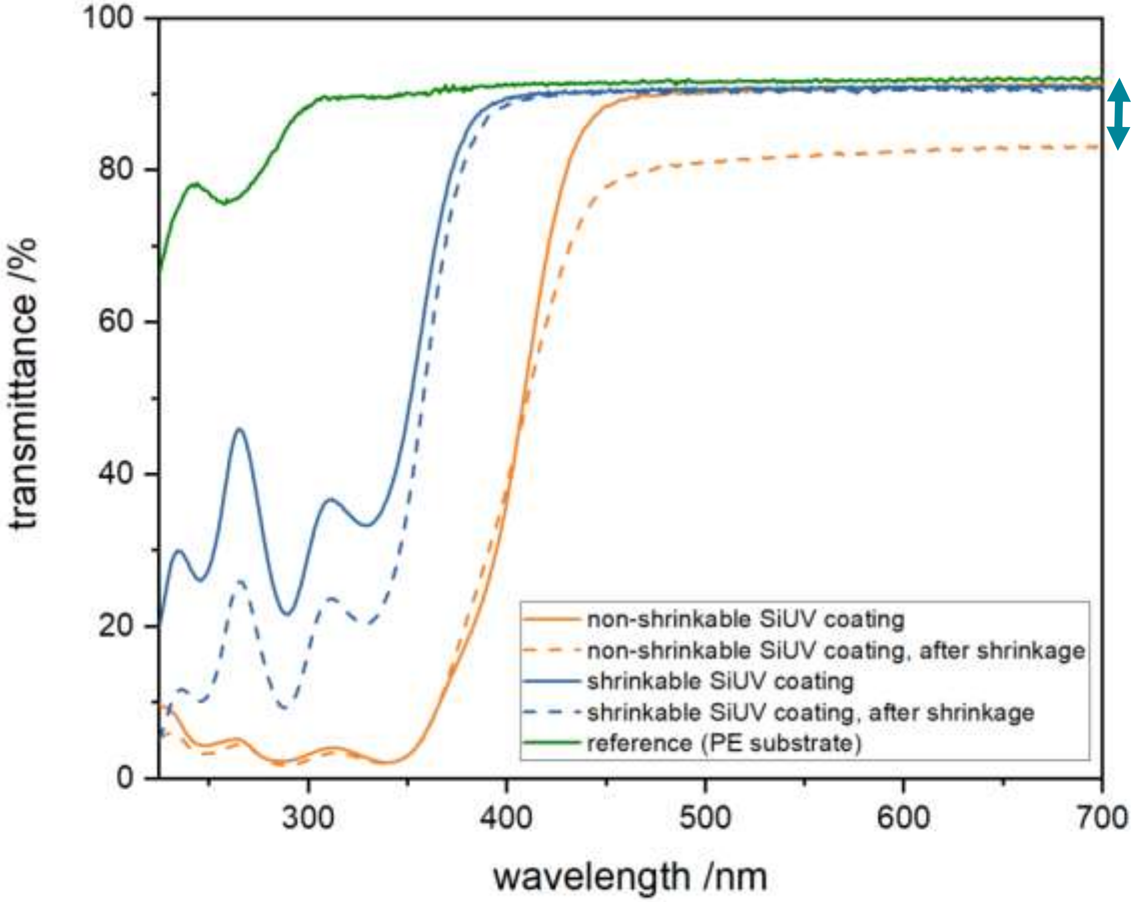
Coating is acting via adhesion and cohesion forces, meaning bonding between substrate and lacquer (adhesion) and cross-linking in-between the lacquer (cohesion).

The cross-linking leads to a certain level of rigidness, and during shrinkage the coating is cracking or delaminating

UV-Blocking - Results & Discussion

Transmission measurements

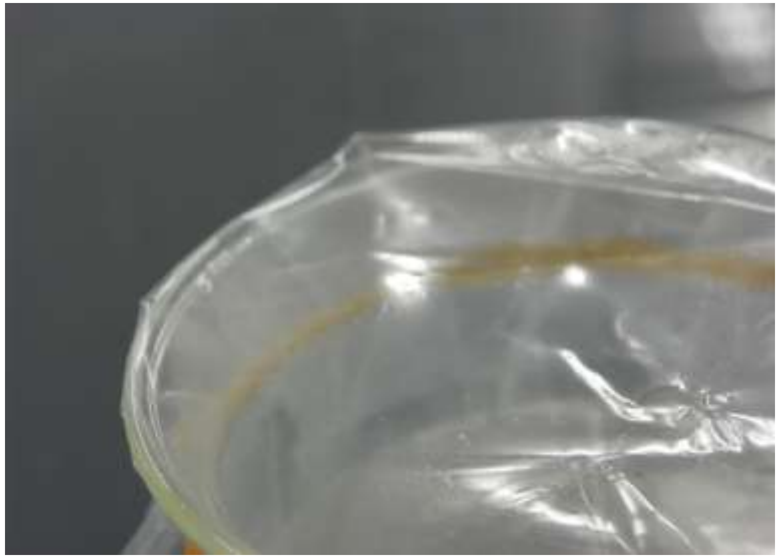




Anti fogging (AF) - Motivation

- AF films currently lack antifogging initiation time and long term functionality
- It is required to reach the onset of full antifogging properties, immediately
- No migration into the film bulk (when polar polymers are present, i.e. EVOH, EVA)

after one hour of cold fog test

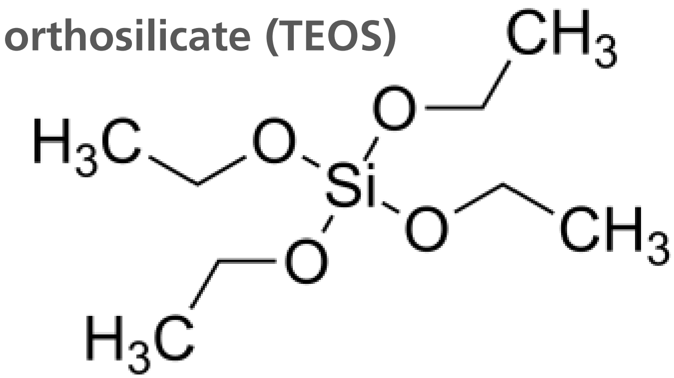


after five hours of cold fog test

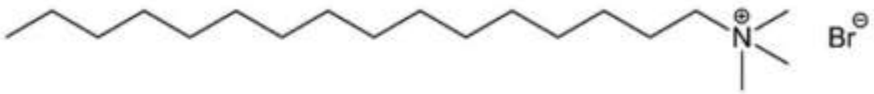
Anti fogging - Materials & Methods

Composition of AF lacquer – SiO_2 based formulation

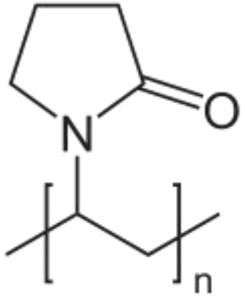
Tetraethyl orthosilicate (TEOS)



Cetyltrimethylammonium Bromide (CTAB)



Polyvinylpyrrolidone (PVP)



0.1 M sodium hydroxide (NaOH)

Double distilled water

Ethanol (99.9 %)

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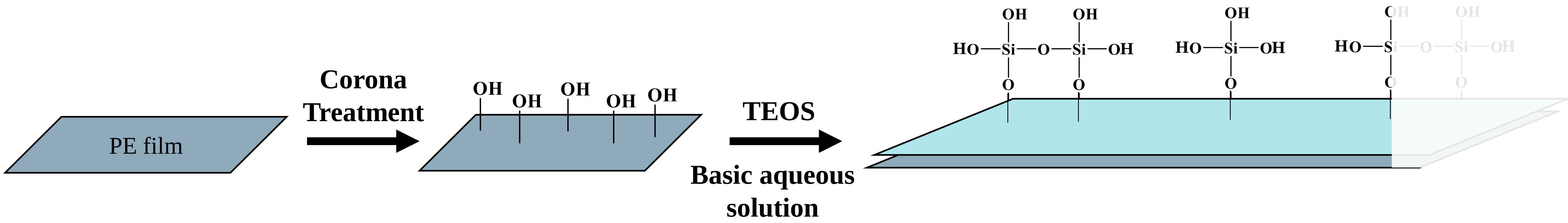
Anti fogging - Materials & Methods

Composition of AF lacquer – SiO_2 based formulation



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Anti fogging - Materials & Methods

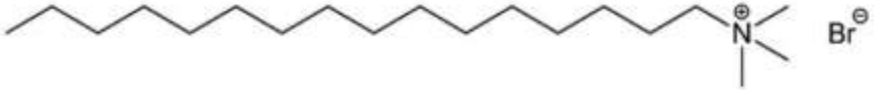
Composition of AF lacquer – SiO_2 based formulation

→ shrinkable, sealable AF film

Previously tried proteinoid coatings

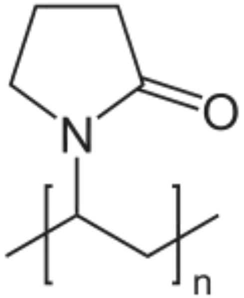
- *Have not been sealable*
- *Appeared sticky → problem on rolls*
- *Showed worse AF properties*

Cetyltrimethylammonium Bromide (CTAB)



→ Uniformity/stability of the coating between coating and curing

Polyvinylpyrrolidone (PVP)



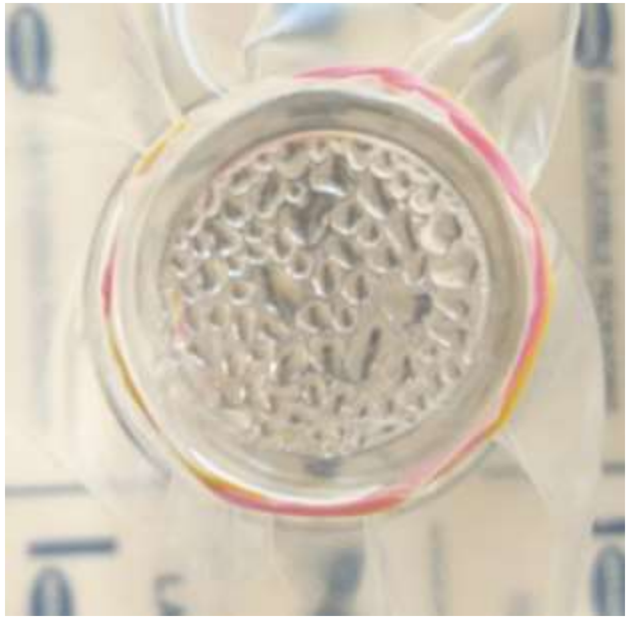
→ Sealing of the film

Anti fogging - Results

Film type	After 10 min	After 1 hour	After 24 hours
Reference (no AF property)	A	A	B
SiO_2 (on PE shrink film)	B+	C	C
AF5 (commercial non-shrink AF film)	D	E	D

Rating:

E	**Completely transparent**	**Excellent**
D	**Transparent, small isolated droplets**	**Acceptable**
C	**Coverage of large droplets**	**Poor**
B	**Foggy with small and large droplets**	**Poor**
A	**Fog. Coverage of small round droplets**	**Very poor**



Conclusions

- **Shrink films are more sensitive to functional coatings regarding the curing temperature and web tension → web tension of 10 N and curing temperature not higher than 60°C**
- **Successful coating of UV-blocking and AF formulations with slot-die technique**
- **The advantage of the new development is the covalent bonding of the UV protective nanocomposite on the shrink film, so that it does not release from the film during shrinkage. The film stays transparent.**
- **Due to the low amount of cross-linking within the coating layer, coating layer shrinks together with film without cracking and/or delaminating**
- **Thin silane-based coatings on polymeric films enabled UV-blocking and anti-fog functionalities, which are durable (permanent)**

Patent applications

- S. Margel, M. Kolitz Domb and E. Sason. "Anti-fogging proteinoids and composition comprising same". US patent application 2017/0042627 A1, PCT patent application PCT/IL2018/051269

- S. Margel and N. Kanovsky. "Engineering of durable thin mesoporous silica micro/nano-particle coatings onto polymeric films for industrial applications: anti-fogging protection and hydrophobic/superhydrophobic coatings". US provisional application 63/067,903 (Aug. 2020).

- S. Margel and Taly Iline-Vull. "Thin silane-based UV-blocking coatings on polymeric films". US Provisional Patent Application 63/069,735 (August 25 2020).

Acknowledgements

Funding

BMBF – Bundesministerium für Bildung und Forschung
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INNOVATIVE NANOPARTICLE-BASED FUNCTIONAL COATINGS BY OPTIMIZED COATING PROCESSES AND NOVEL ENERGY EFFICIENT DRYING PROCESSES - "NEEDS" (2018-2022)

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