Aluminum oxide barrier coatings on polymeric substrates

Carolin Struller

PhD research student

Manchester Metropolitan University, Bobst Manchester Ltd.

Nick Copeland

Bobst Manchester Ltd.

Peter Kelly, Chris Liauw

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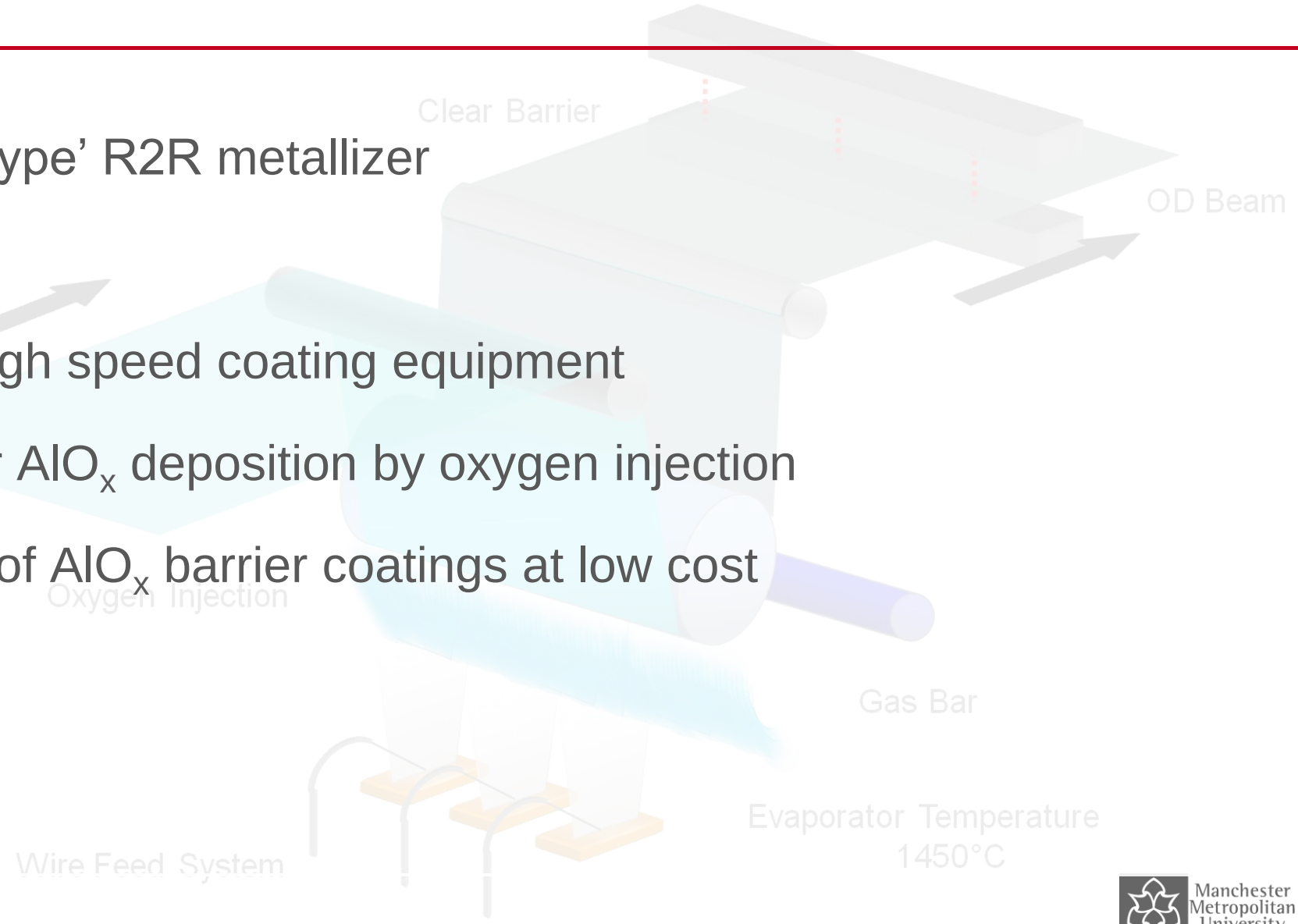
Outline

- Introduction
- Objective
- Results
  - > Barrier performance
  - > Surface topography (DIC, SEM, AFM)
  - > Coating thickness (TEM)
  - > Coating to substrate adhesion
  - > Surface energy of AlO_x coating
- Summary and conclusions

AlO_x coating process – Reactive thermal evaporation

Industrial ‘boat type’ R2R metallizer



- ➔ Standard high speed coating equipment
- ➔ Modified for AlO_x deposition by oxygen injection
- ➔ Production of AlO_x barrier coatings at low cost

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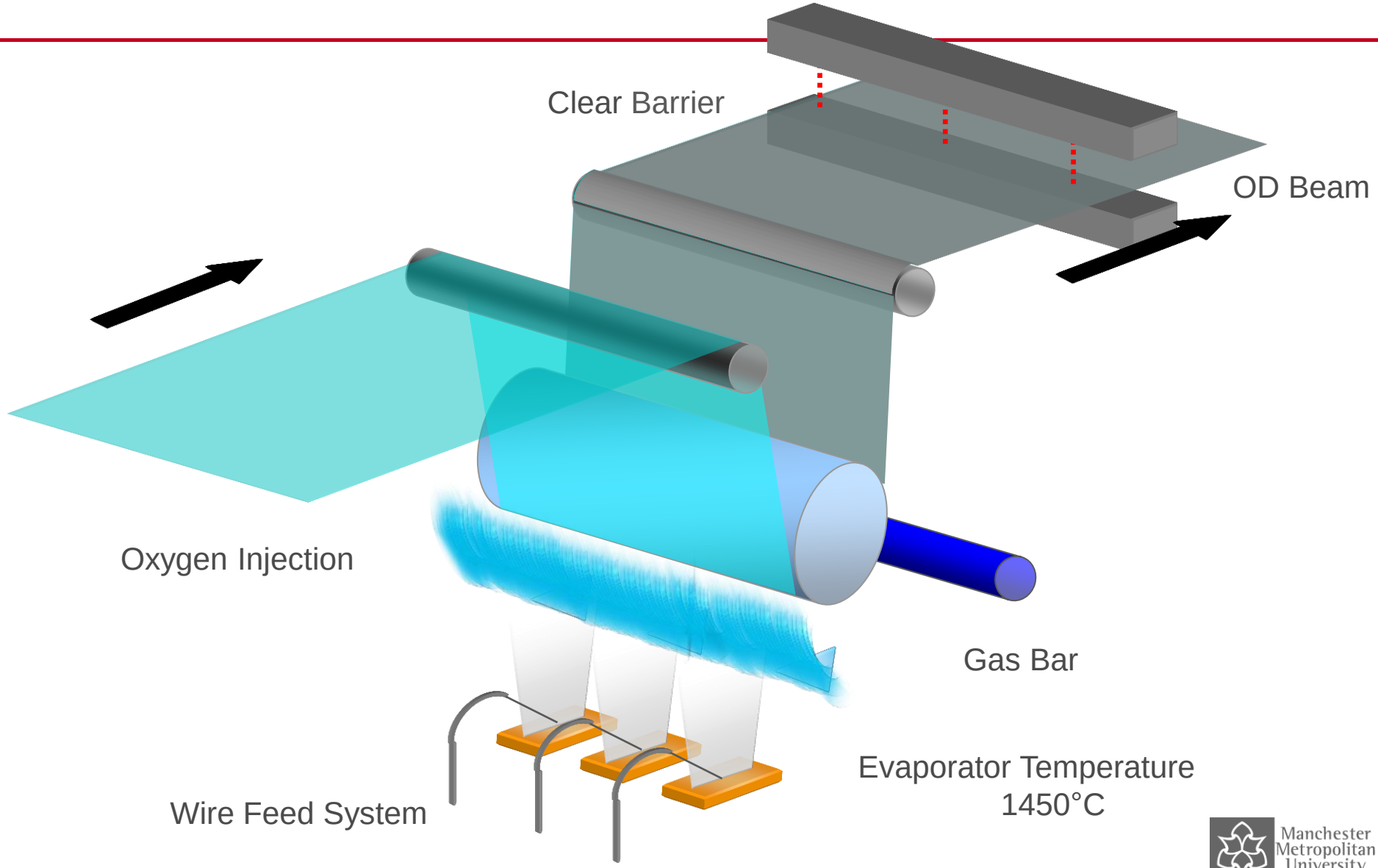
AlO_x coating process



Why ceramic clear barrier coatings?

Advantages over polymer based transparent barrier films (PVdC, EVOH)

- No barrier loss at high RH (e.g. for EVOH)
- Thickness in nm-range (PVdC/EVOH µm-range)
- Economical benefits (raw material consumption & cost)
- Recyclable as single layer material

Advantages over metallized polymer films

- Product visibility
- Microwaveability, Retortability
- Suitable for metal detectors

Objective

➔ Food packaging application of AlO_x coated polymer films

➔ Aims:

- Barrier performance of AlO_x coated films comparable to metallized films
- Replacement of traditional clear barrier films (polymer based with PVdC & EVOH)

Film, description		OTR* $cm^3/(m^2\ d)$	WVTR** $g/(m^2\ d)$
BOPP, 20 µm	Plain	2000 – 2500	4 – 7
	EVOH coextruded barrier film[1] (29 µm)	1 – 1.5	4.5
	PVdC coated[1] (26 µm)	20	4.2
	Metallized 2.2 OD	≤ 100	≤ 1
PET, 12 µm	Plain	100 – 150	40 – 50
	Metallized 2.2 OD	≤ 2	≤ 1

*OTR 23 °C, 50 % RH
**WVTR 37.8 °C, 90 % RH

[1] 'Development of new BOPP Barrier Films by Coextrusion and Simultaneous Biaxial Orientation' Brueckner Maschinenbau GmbH, Siegsdorf, Germany, Dr. M. Wolf, Dr. J. Breil, Dipl.-Ing. R. Lund

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Barrier performance of AlO_x coated films

- AlO_x on PET ➔ Reliable barrier properties: OTR < 1 cm³/(m² d)
  WVTR < 1 g/(m² d)
- AlO_x on BOPP ➔ Variation of barrier properties depending on substrate

BOPP film	Plain		AlO_x coated	
	OTR* cm³/(m² d)	WVTR** g/(m² d)	OTR* cm³/(m² d)	WVTR** g/(m² d)
BOPP A, 30 µm	≈ 1600	≈ 4.0	150 – 200	≤ 4
BOPP B, 15 µm	≈ 2700	≈ 7.0	≤ 100	≤ 6
BOPP C, 20 µm	≈ 2400	≈ 6.0	≤ 50	≤ 6
BOPP D*, 18 µm	≈ 500	≈ 4.5	≤ 1	≤ 1

*OTR 23 °C, 50 % RH
**WVTR 37.8 °C, 90 % RH

*Film supplied by Brückner Maschinenbau GmbH & Co.KG, Siegsdorf, Germany

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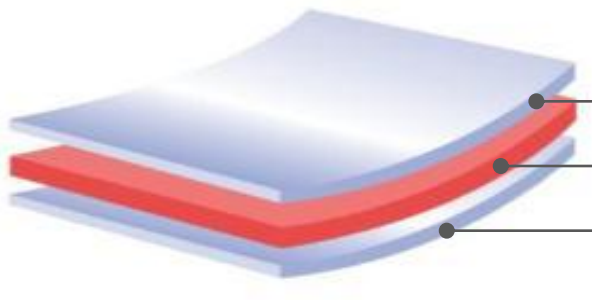
Barrier performance – Effect of plasma treatment (BOPP C)



- Standard packaging grade BOPP film
- Corona treated
- 20 µm thickness
- 3 layer structure

Trial	Plasma treatment	OTR*		WVTR**	
		cm³/(m² d)	BIF	g/(m² d)	BIF
Plain film	-	≈ 2400	-	≈ 6	-
1	**No**	47.00 ± 5.35	**51**	5.89 ± 0.23	**1**
2	**PRE**	35.33 ± 3.05	**68**	6.08 ± 0.17	**1**
3	**PRE + POST**	25.35 ± 1.38	**95**	4.73 ± 0.07	**1.3**

*OTR 23 °C, 50 % RH **WVTR 37.8 °C, 90 % RH

➔ Clear improvement of OTR with pre- and post-treatment

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Barrier performance – Effect of plasma treatment (BOPP D)

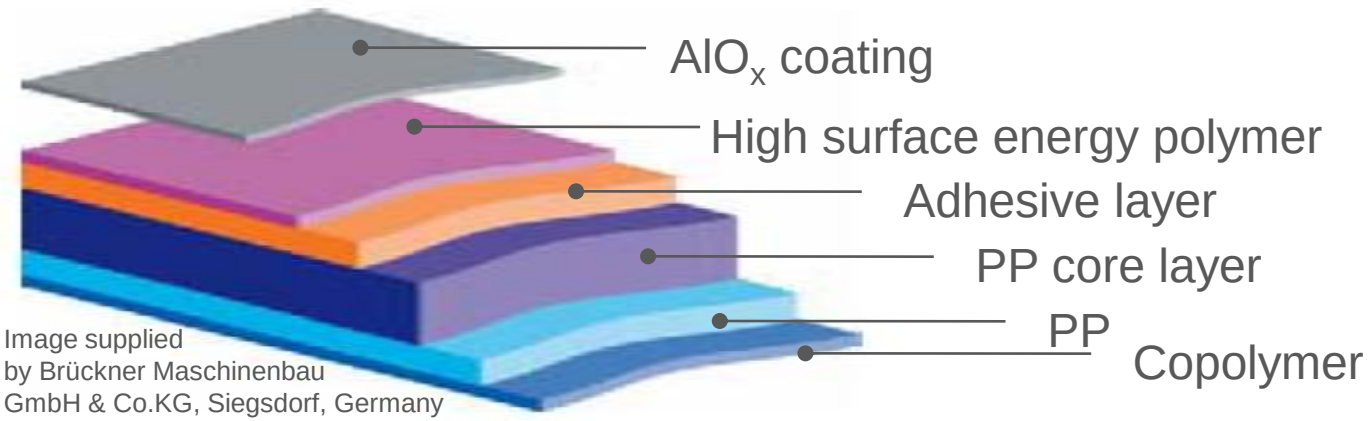

Image supplied by Brückner Maschinenbau GmbH & Co.KG, Siegsdorf, Germany

- Special skin layer
- 18 µm thickness
- 5 layer structure

Film supplied by Brückner Maschinenbau GmbH & Co.KG, Siegsdorf, Germany

Trial	Plasma treatment	OTR*		WVTR**	
		$cm^3/(m^2\ d)$	BIF	$g/(m^2\ d)$	BIF
Plain film	-	≈ 500	-	≈ 4.5	-
1	**No**	0.89 ± 0.01	**562**	2.18 ± 0.07	**2**
2	**PRE**	0.83 ± 0.30	**602**	0.62 ± 0.07	**7**
3	**PRE + POST**	0.60 ± 0.14	**833**	0.55 ± 0.25	**8**

*OTR 23 °C, 50 % RH **WVTR 37.8 °C, 90 % RH

➔ Clear improvement of WVTR with pre-treatment

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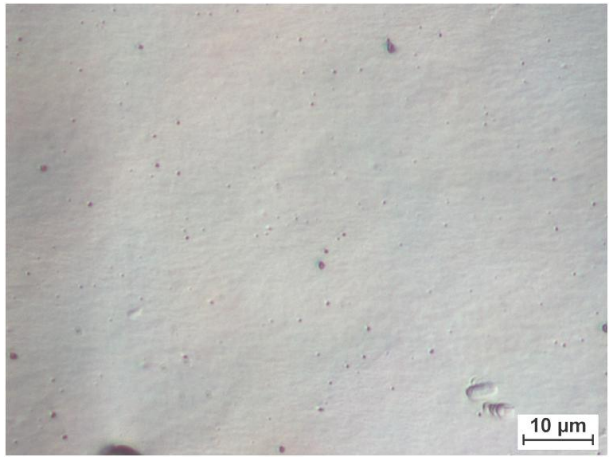
DIC analysis of plain BOPP films

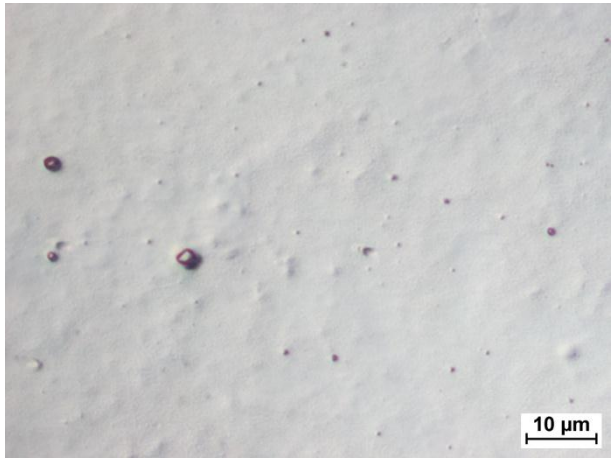
- Differential interference contrast light microscopy
- 3D presentation of surface topography
- Antiblock (AB) particle size and distribution density in film surface

BOPP A



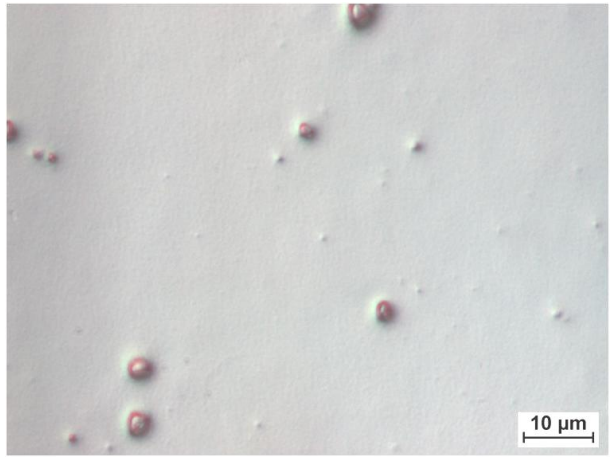
➔ Many small ABs, fewer large ABs

BOPP B



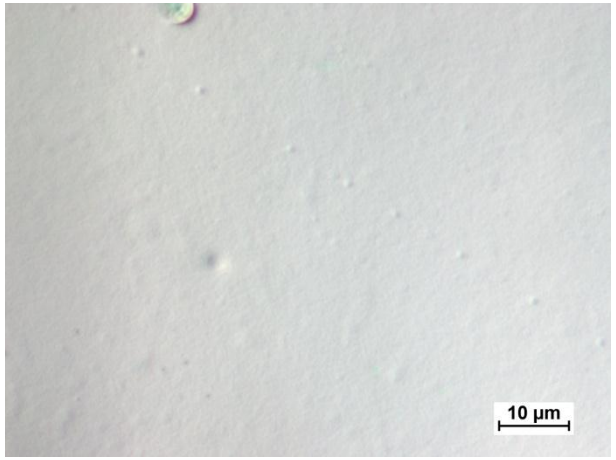
➔ Many small ABs, fewer large ABs

BOPP C



➔ Substantially larger ABs

BOPP D*



➔ No ABs

*Film supplied by Brückner Maschinenbau GmbH & Co.KG, Siegsdorf, Germany

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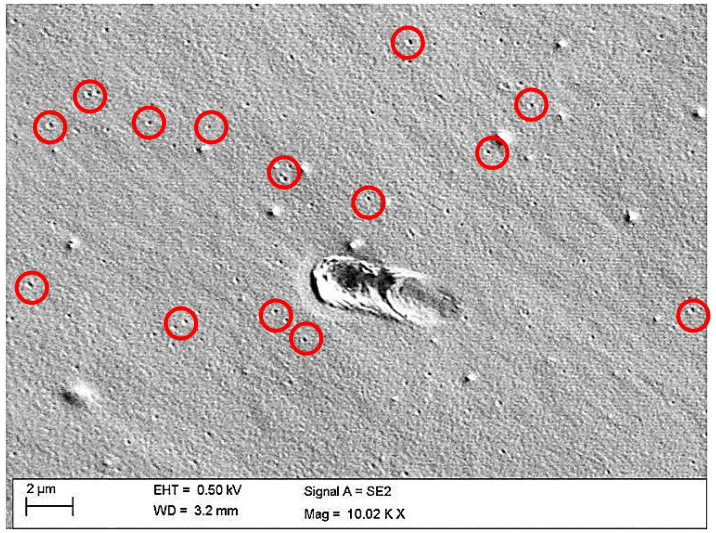
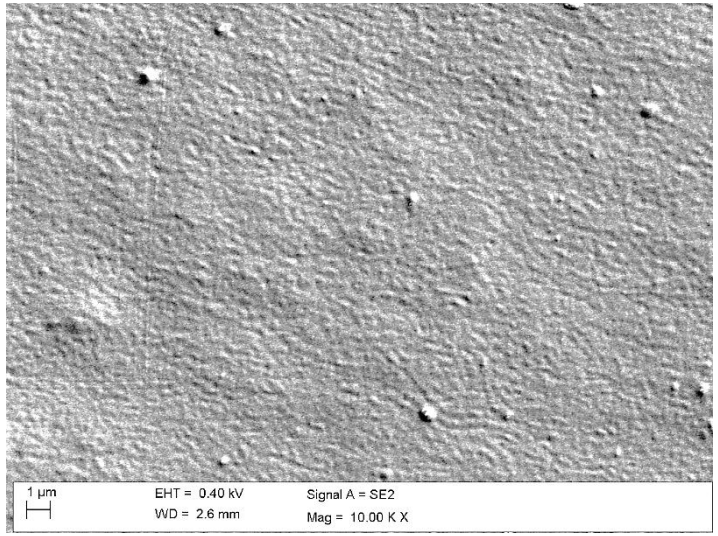
SEM analysis of BOPP films

- Scanning electron microscopy
- No conductive layer applied to avoid masking of surface details
- Low acceleration voltage of 0.4/0.5 kV
- ‘Grainy’ surface structure for BOPP (‘orange-peel’)

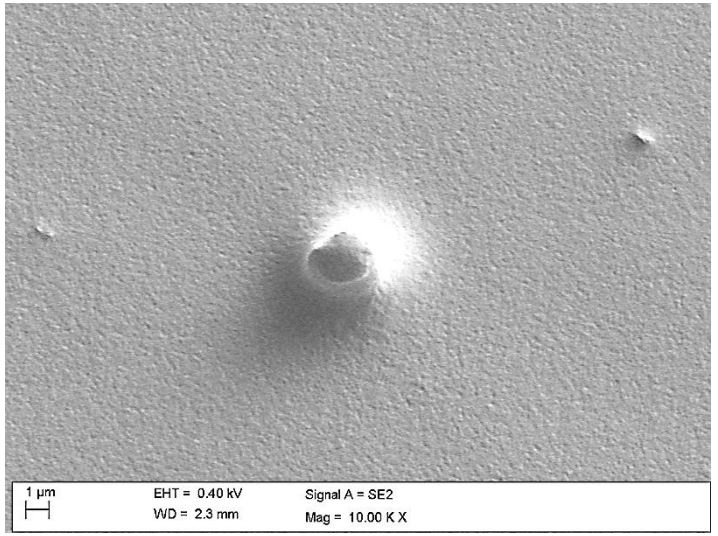
BOPP A



BOPP B



BOPP C



➔ Surface defects ‘dimples’ on BOPP A

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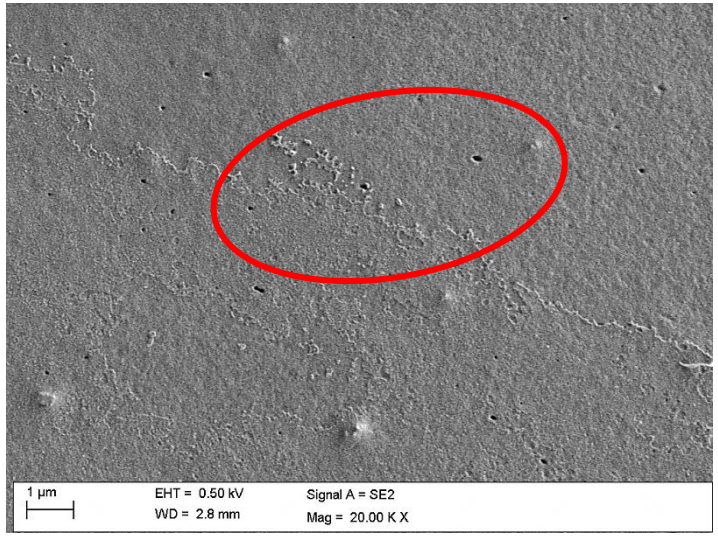
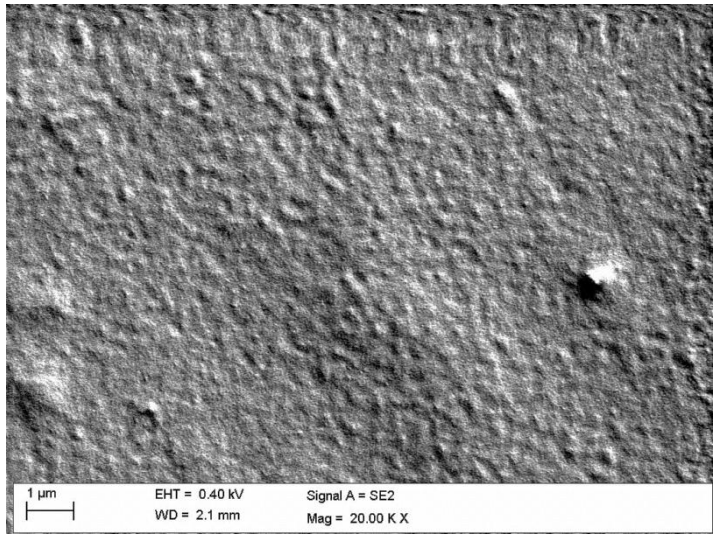
SEM analysis of AlO_x coated BOPP films

- AlO_x coating reproduces plain film surface topography

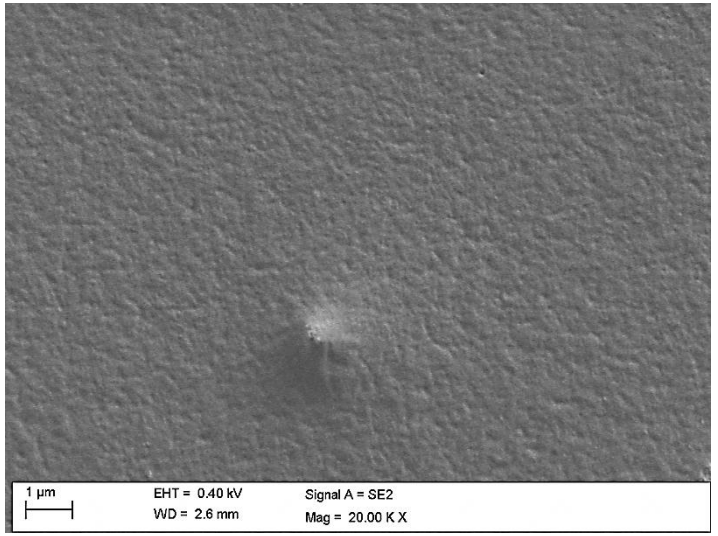
BOPP A



BOPP B



BOPP C



➔ AlO_x coating on BOPP A shows pores and growth/thickness irregularities
➔ Assumption: Pores in AlO_x on BOPP A cause high OTR

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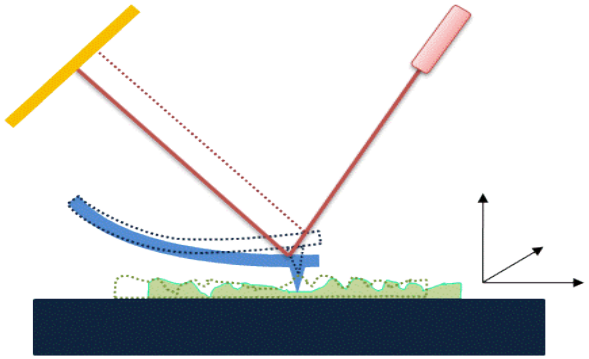
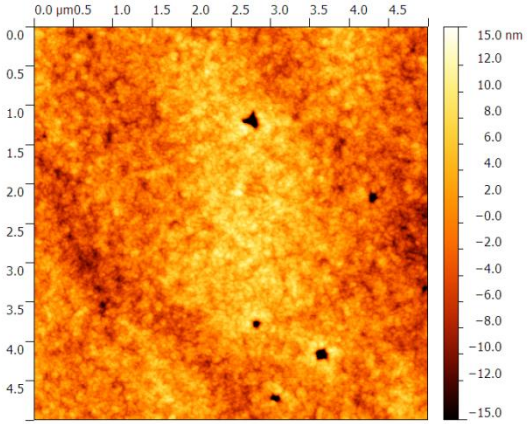
AFM anlysis of plain and AlO_x coated films

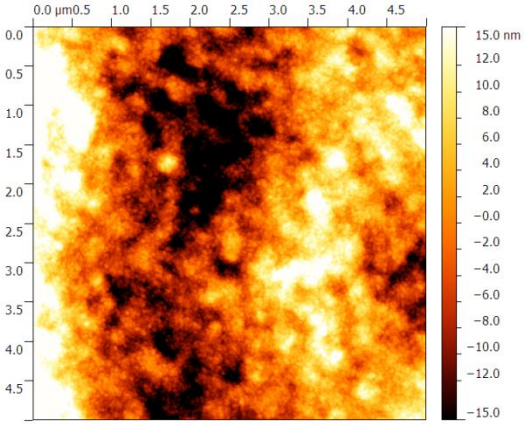
- Atomic force microscopy
- Confirms SEM results
- AlO_x coating reproduces plain film surface topography
- 5 x 5 µm² scans for plain BOPP films



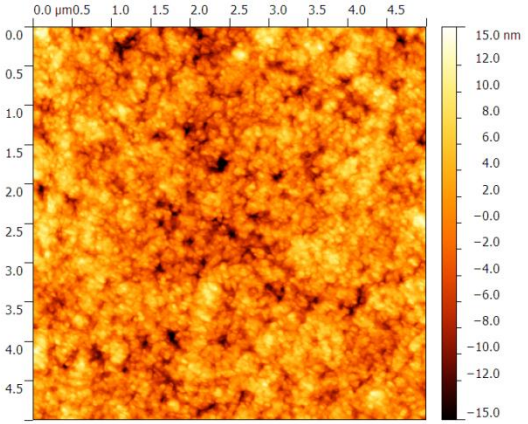
BOPP A
RMS 4.1



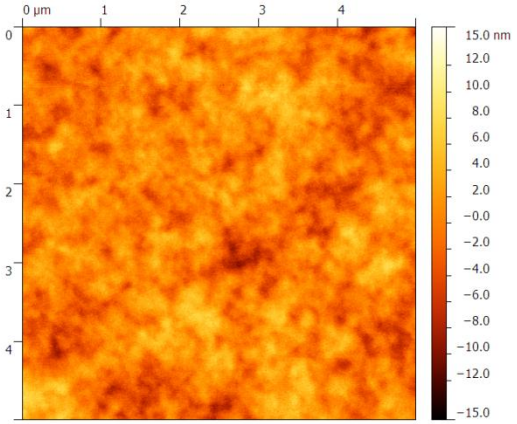
BOPP B
RMS 5.7



BOPP C
RMS 4.1



BOPP D*
RMS 2.8



➔ Surface defects on BOPP A

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AFM analysis – Roughness data

Film	Plasma treatment	Root mean square nm	Roughness average nm
BOPP A	Plain film	4.1 ± 0.7	3.3 ± 0.5
OTR 150 - 200	**PRE**	3.8 ± 0.5	3.0 ± 0.4
BOPP B	Plain film	5.7 ± 1.8	4.5 ± 1.5
OTR ≤ 100	**PRE**	5.8 ± 0.9	4.6 ± 0.7
	PRE + POST	6.0 ± 0.7	4.8 ± 0.6
BOPP C	Plain film	4.1 ± 0.3	3.2 ± 0.2
OTR ≤ 50	**PRE**	4.6 ± 0.2	3.6 ± 0.2
	PRE + POST	4.3 ± 0.3	3.4 ± 0.2
BOPP D*	Plain film	2.8 ± 0.2	2.2 ± 0.1
	PRE	2.9 ± 0.2	2.3 ± 0.2
	PRE + POST	3.0 ± 0.2	2.4 ± 0.1
PET	Plain film	1.6 ± 0.2	1.2 ± 0.2
	PRE + POST	1.8 ± 0.3	1.4 ± 0.3

- Tapping mode and pulsed force mode AFM
- Calculated from 5 x 5 µm² scans

➔ Plain and AlO_x coated films show similar surface roughness

*Film supplied by Brückner Maschinenbau GmbH & Co.KG, Siegsdorf, Germany

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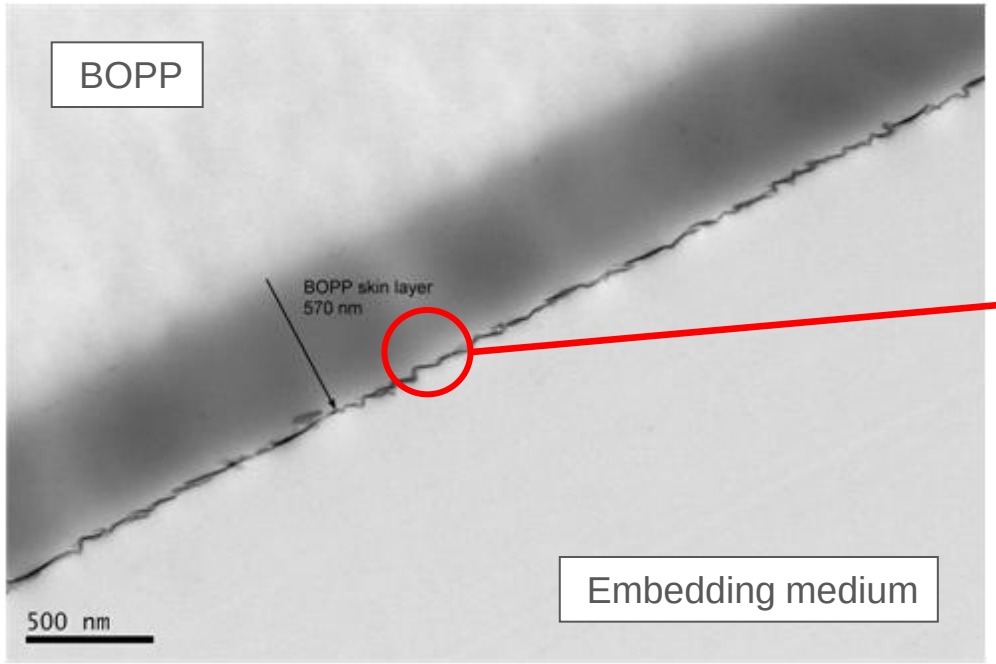
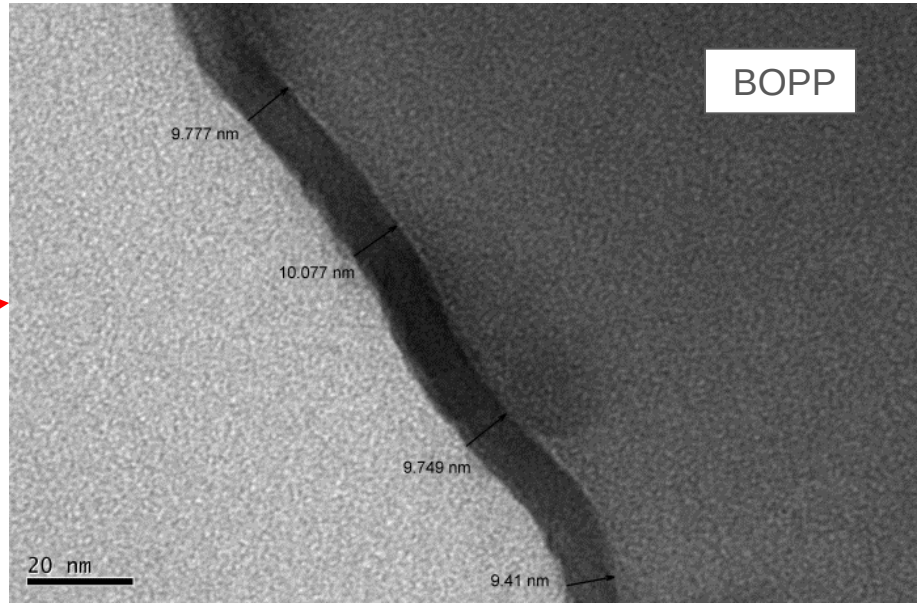
TEM analysis – AlO_x coating thickness

- Transmission electron microscopy
- Analysis of various AlO_x coated film samples
- TEM clearly reveals the common three layer structure of BOPP film
- AlO_x thickness in the range of 9 to 11 nm





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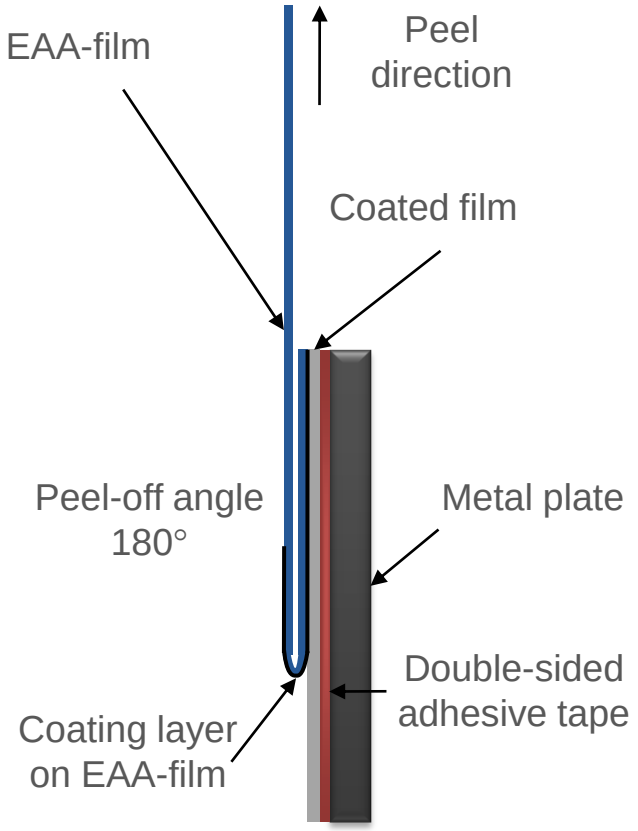
AlO_x adhesion – Peel test

- ‘EAA peel test for metal adhesion’ on AlO_x coated BOPP
- Peel tests possible as coating removal visible

Film	Plasma treatment	Peel force	
		N/(15 mm)	g/inch
BOPP A OTR 150 – 200	**PRE A**	3.88 ± 0.09	669 ± 15
	PRE B	3.68 ± 0.14	635 ± 24
BOPP B OTR ≤ 100	**No**	3.46 ± 0.08	597 ± 14
	PRE	3.51 ± 0.10	606 ± 18
	PRE + POST	3.50 ± 0.16	604 ± 27
BOPP C OTR ≤ 50	**No**	5.05 ± 0.17	871 ± 29
	PRE	5.07 ± 0.12	875 ± 22
	PRE + POST	5.04 ± 0.14	869 ± 23
	Metallized, PRE	1.09 ± 0.11	189 ± 19



EMA (European Metallizers Association) test procedure for metal adhesion (seal test)

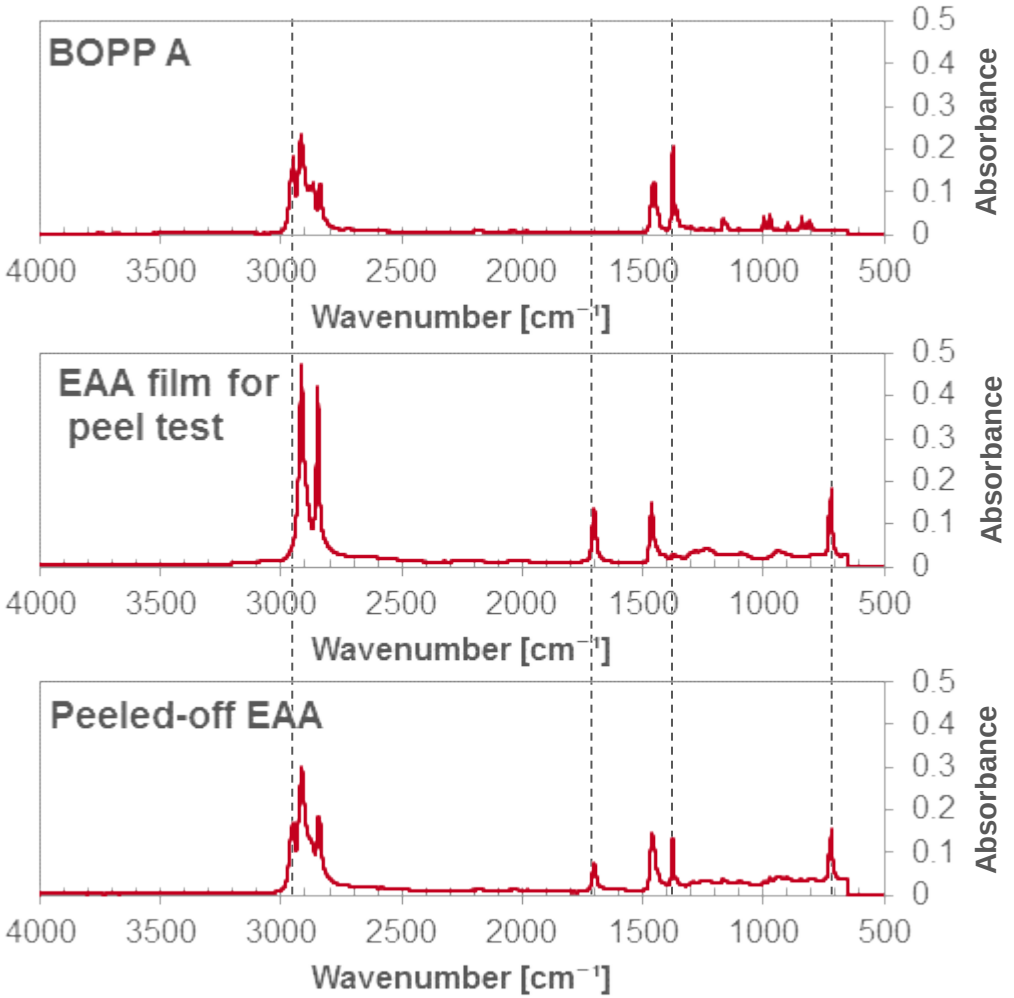
AlO_x adhesion – Peel test

- Very high peel forces obtained (a lot higher than for metallized BOPP)
- Peel force independent of pre-treatment
- Material peeled outside sealed area

➔ Analysis of peeled EAA via infra red spectroscopy (ATR FTIR) to identify polymer

➔ IR spectrum shows EAA and PP peaks

➔ Parts of BOPP film (skin layer) peeled off



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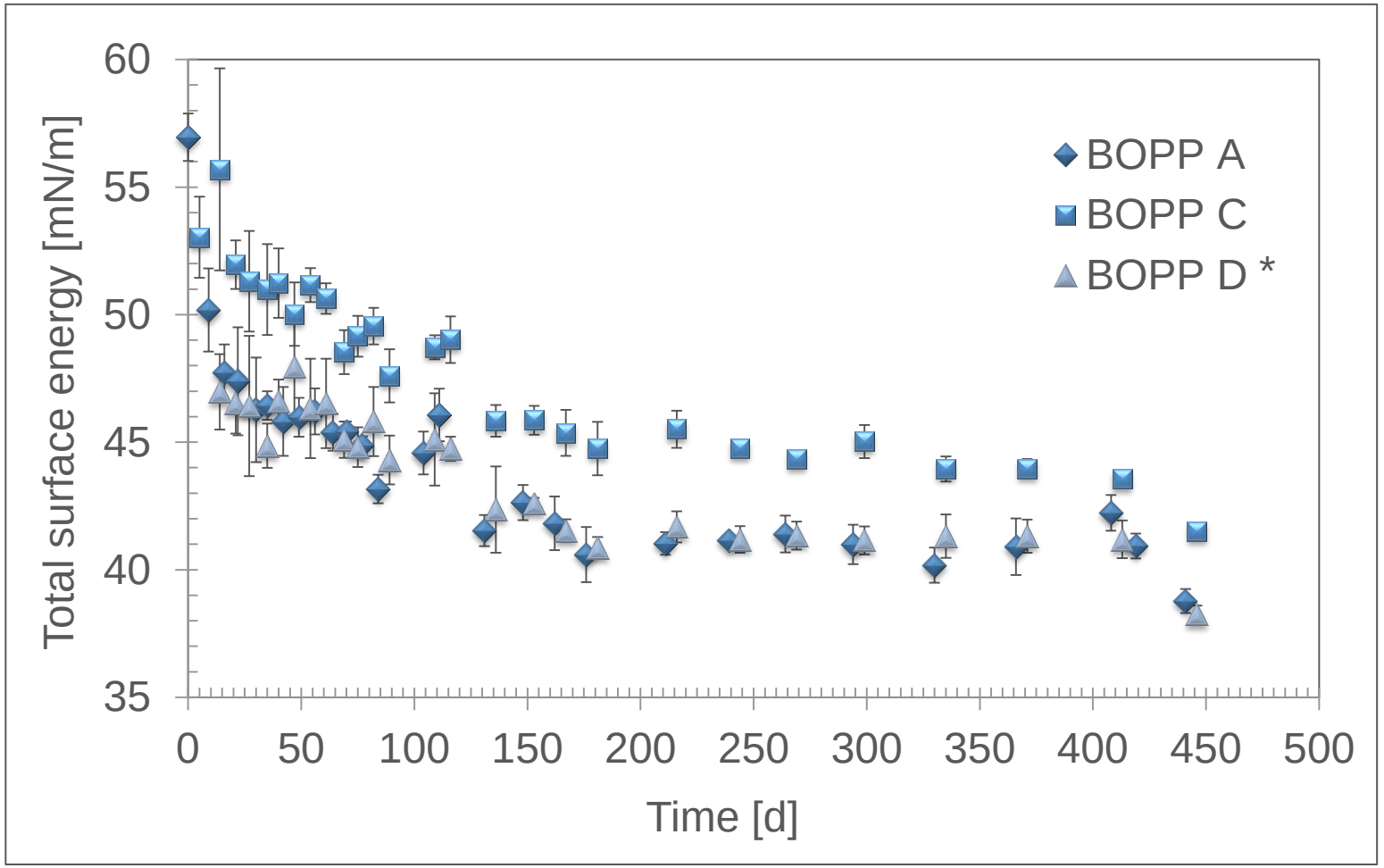
AlO_x surface energy – Change with storage time



- Drop of surface energy with storage time
- Drop of polar part of surface energy
- Drop due to contact of AlO_x with low surface energy BOPP (reverse side of film)
- Transfer of polymeric material

*Film supplied by Brückner Maschinenbau GmbH & Co.KG, Siegsdorf, Germany

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Barrier performance - Acrylate top coat

- Flash evaporation of monomer liquid
- Condensing liquid film conceals surface features of substrate
- Crosslinking via curing (electron beam radiation) → solid film
- Approx. 1 µm acrylate thickness
- Off-line top coat

Film	Description	OTR*		WVTR**	
		$cm^3/(m^2\ d)$	BIF	$g/(m^2\ d)$	BIF
BOPP B 15 µm	plain	≈ 2700	-	≈ 7	**-**
	AlO_x	85.56 ± 16.80	32	5.89 ± 0.18	**1.2**
	AlO_x + acrylate	2.05 ± 0.44	1317	3.88 ± 0.16	**1.8**
BOPP C 20 µm	plain	≈ 2400	-	≈ 6	**-**
	AlO_x	25.35 ± 1.38	95	4.73 ± 0.07	**1.3**
	AlO_x + acrylate	1.89 ± 0.31	1270	0.40 ± 0.01	**15**

*OTR 23 °C, 50 % RH
**WVTR 37.8 °C, 90% RH

Acrylate coating conducted by Sigma Technologies Int'l, LLC, Tuscon AZ, USA

Summary and conclusions

- Approx. 10 nm thin AlO_x barrier coating deposited onto film substrates
- While film surface defects affect barrier, roughness appears to have less impact
- AlO_x adhesion to the BOPP film is stronger than the intrinsic strength of the BOPP film
- AlO_x coated BOPP like metallized BOPP has a high dyne level which diminishes over time
- Special polymer skin layers and acrylate top coats significantly improve barrier properties of AlO_x coated BOPP films

Acknowledgements

- Brückner Maschinenbau GmbH & Co.KG, Siegsdorf, Germany (film supply)

- Innovia Films, Wigton, United Kingdom (access to analytical equipment)
- Fraunhofer Institute for Process Engineering and Packaging IVV, Freising, Germany (access to AFM)
- Sigma Technologies Int'l, LLC, Tuscon AZ, USA (acrylate coating)

- Dr. Charles A. Bishop, CAB Consulting Ltd.

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Thank You

Any questions?

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