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Vacuum coating of polymer films for packaging and technical applications

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2 Summary

2.1 Introduction

Per year about 15.000.000.000 m² of polymer films are vacuum web coated world wide, with a continuous, long-term growth of annually 8 to 12 % over the last decades. In this area, packaging films today represent about 2/3 of the overall volume. The rest is covered by decorative and technical applications like capacitors.

A lot of challenges and a strong need for technical innovations arise for this sector, mainly driven by the increasing functional demands that are caused by the trend to substitute heavy, but virtually impermeable packaging systems by lightweight and flexible ones:

- To achieve better barrier properties of flexible vacuum coated packagings against the permeation of gases and water vapour
- and to allow the use of abundant, less expensive and better recoverable substrate materials like polyolefines, thereby maintaining superior barrier properties.

For those subjects, the basic technical processes have already been tested on separate steps by different companies, but to achieve the necessary combination of these on industrial level, problems in technology transfer are immense. At present, there is a high uncertainty for obtaining a good final result of the process chain and large variations in properties may be observed on most products even in cases where the starting materials are exactly the same. The same is valid for the emerging areas - outside capacitor applications - where vacuum coated layers are used in technical applications. The project period was from December 1, 1998 to November 30, 2001.

2.2 Project Consortium

In order to study all production steps for producing high barrier films and laminates containing an inorganic barrier on industrial scale, a research institute formed a project consortium with 28 companies and one consultant, as to be seen in Figure 1.

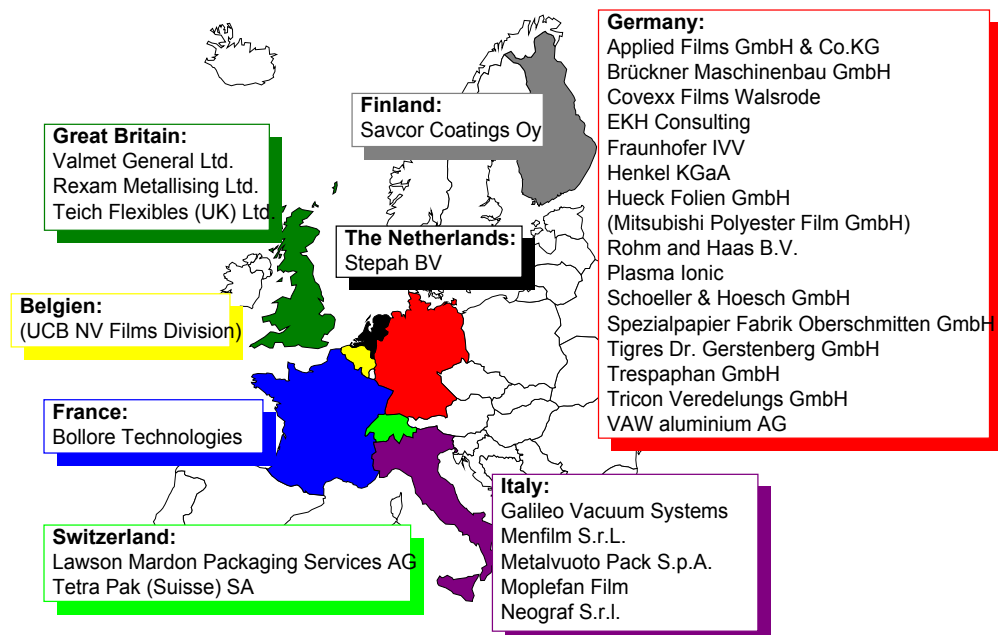


Figure 1: Project consortium (names in brackets are associated partners)

Before starting the Thematic Network in December 1998, 14 of the 30 project partners had already performed pre-competitive research in the field of vacuum web coating of BOPP films on industrial scale between 1996 and 1998 in a project that was funded by the Bavarian government. From collaborating with 29 partner in the field of vacuum web coating of polymer films for packaging and technical applications on lab and industrial scale, the project partners benefited from studying the whole production chain and not only their own process. Especially the integration of the own process in previous and following process steps including hand-shakes between the different production steps was investigated and benchmarked.

There, even competitors performed research work together. For ensuring an open discussion of

- the critical points along the production chain,
- the objectives of the research activities and
- project results,

the project work was performed on pre-competitive level. The project partners were exploiting the project results mainly in the area of food and pharmaceutical packaging. Some of the participating companies used the developed project know-how also for technical applications, as security labels, isolating panels, electromagnetic shielding and high protection against visible or UV light. The project activities and results helped the research institute to initiate new research projects with relevance to the European packaging, photovoltaic, display and insulating industry.

2.3 Objectives

By researching on a pre-competitive level, the main goals of the project were

- to link industrial R&D activities ongoing in different companies,
- to achieve a better hand shake between industrial partners active along the process line,
- to jointly achieve improvements in the quality of products by simultaneous evaluation of process innovations in the production chain,
- to improve and to harmonize the techniques of measurement and testing, as layer thickness and adhesion, and
- to understand the relevant mechanism of permeation through films containing an inorganic barrier layer.

In detail, the impact of the following parameters along the process chain of high barrier laminates were analysed within the scope of the project on industrial and lab scale:

- film resin (polypropylene and polyethylene terephthalate),
- stretching technique (linear or bubble sequential, simultaneous)
- pre-treatment of substrate films (Corona, flame, plasma),
- vacuum deposited inorganic barrier layers (Al, SiO_x and AlO_x),
- vacuum web coating parameters (source, web speed, wire feed rate, layer thickness) and

- 8th: thickness of Al layers, for coating on BOPP films (repetition of 6th sequence)
- 9th: pre-treatment, wire feed rate, web speed and Al layers thickness, for coating on BOPP films

3 Test sequences

3.1 1st test sequence

3.1.1 Target

The target of the 1st test sequence was to investigate the impact of the properties of BOPP substrate films on adhesion, gas and water vapour permeability of following intermediate and finally laminated film products.

3.1.2 Set-up

Samples of 8 different BOPP films, as to be seen in Figure 2, were produced by 5 different companies and Al vacuum coated in one process run in a production coater. In the next step, the different samples were adhesive laminated with two different solvent free two component polyurethane adhesives against a 20 µm thick BOPP film by using only one lab lamination machine. During the whole test sequence, all different substrate films were coated and laminated at the exact same conditions by using for each step the same machine. Hence differences in the properties of the coated and laminated films could be directly traced to the different substrate films. Additionally, one Al coated terpolymer (terpo) and one Al coated copolymer (copo) film were laminated by using a second polyurethane adhesive for studying the influence of the lamination step on the final product properties.

<u>Film production step</u>		-->	<u>Al Coating Step</u>	-->	<u>Lamination step</u>
Substrate BOPP film type and orientation method label in production line			Results of optical density measurment after coating		Adhesive lamination against 20 µm BOPP
terpo A	simultaneous stretching	put together on 1 roll for being Al coated in one single coating run at the same conditions	2.0		films broke at lamination
terpo B	bubble expansion		2.3		adhesive A
terpo C	subsequent stretching		2.2		adhesive A
					adhesive B
copo D	subsequent stretching		2.0		adhesive A
					adhesive B
copo E	subsequent stretching		2.0		adhesive A
copo F	subsequent stretching		2.0		adhesive A
copo G	subsequent stretching	1.9		adhesive A	
copo H	subsequent stretching	2.0		adhesive A	

Figure 2: Set-up of the 1st industrial test sequence: influence of type of substrate film on the properties of the vacuum web coating and lamination step

3.1.3 Results

The **surface structure** of the BOPP films strongly depends on the film production and pre-treatment processes, as to be seen in Table 1. The Al coated BOPP film, produced by blown film extrusion plus bubble stretching, has the highest optical density, as to be seen in Figure 3. Because all different films were coated in the vacuum web coater at one single run, all Al layers contain the same amount of Al atoms. Due to oxidation of the Al layers, their top and bottom sides consist of aluminium oxide. Smoother films possess a lower effective surface, a lower area for oxidation of the Al layer and, therefore, a higher optical density. As measured, the smoother the film surfaces are the higher is the optical density of the deposited Al layers.

The **peel strength** (adhesion) of the aluminium layers on the BOPP films was between 0.24 (terpo C) and 2.7 (copo G) N/15mm. The adhesion of the Al layers on the different BOPP films strongly depends on the film type. The adhesion of Al layers on copolymer films is by one order of magnitude higher than on terpolymer films. By using flame instead of Corona pre-treatment, the adhesion can be also increased. A further investigation of the pre-treatment step was performed in the 2nd test sequence.

The **OTR** ranges from 43 to 100 cm³/m² d bar and the **WVTR** from 0.08 to 0.3 g/m² d for the Al coated films. In contrast to the general expectation, films with the lowest adhesion values show the highest permeation barriers. Therefore, high adhesion values are not a requirement for good barriers. But the adhesion must be high enough to ensure, that the coated layer is not removed during the following process steps. As a consequence, both parameters must be optimised separately.

Lamination of the aluminium coated films against 20 µm thick BOPP films by applying a two component polyurethane adhesive reduces for all films the oxygen permeability, as to be seen in Figure 3. The lowest OTR is 8.7 cm³/m² d bar and WVTR 0.14 g/m² d, but depending on the used adhesive and substrate film, the water vapour barrier is reduced in most cases. Only the water vapour barrier of the copolymer films could be improved by the lamination step. By using adhesive A, the WVTR is increased for all samples with the exception of copo E. Adhesive B results always lower OTR and WVTR values for the terpo C and copo D BOPP films.

The bond strength of almost all samples (not copo D adhesive B) is higher than 0.8 N/15 mm and there is almost no correlation between the peel strength of the coated films and the laminates thereof.

Table 1: AFM measurements at the 1st industrial test sequence: influence of type of substrate film on surface roughness of the Al coated films

BOPP + Al	mean value of 5 samples of 5x5 µm		
	Ra [nm]	Rq [nm]	Ra / Rq
terpo A Corona	4,8	6,0	0,80
terpo A flame	4,8	6,1	0,78
terpo B Corona	4,6	5,8	0,79
copo E Corona	5,3	6,6	0,80
copo G Corona	7,1	8,9	0,80

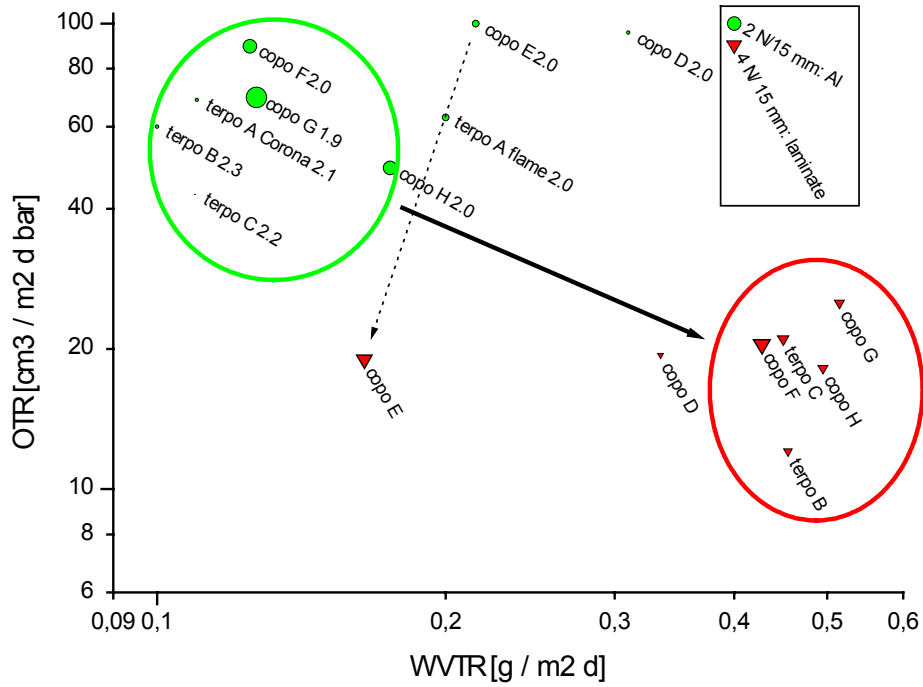


Figure 3: Results of the 1st industrial test sequence: influence of substrate film on the properties of the vacuum web coating and lamination step. The size of the dots indicates relative adhesion values of coated layers and bond strengths of the laminates

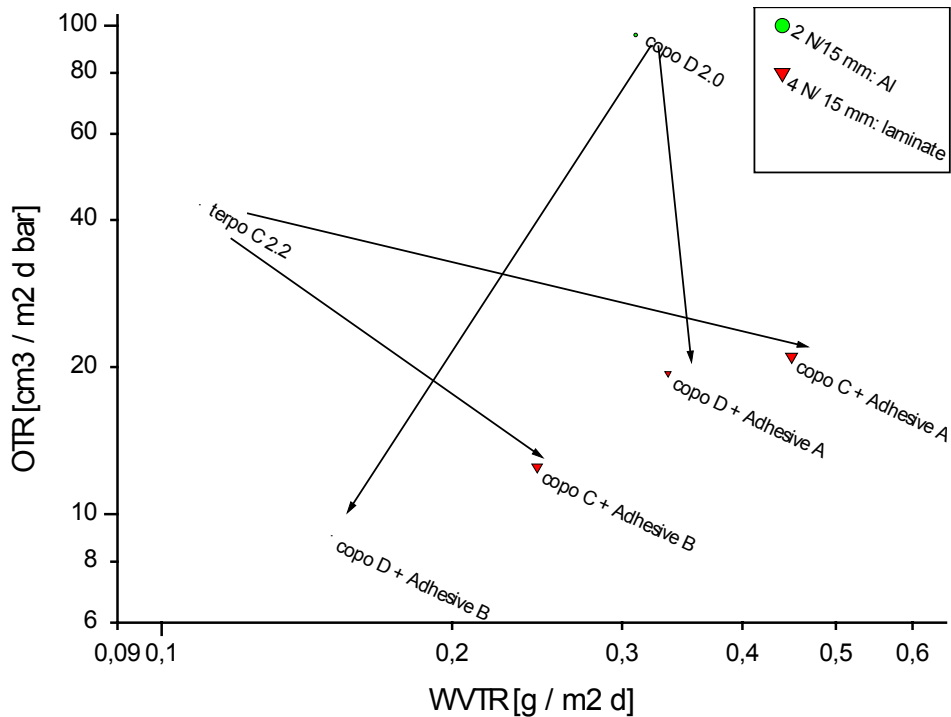


Figure 4: Results of the 1st industrial test sequence: influence of lamination step on the properties final laminate for two different BOPP substrate films. The size of the dots indicates relative adhesion values of coated layers and bond strengths of the laminates

The achievements of this test sequence are the revealed correlations between the pure BOPP films and their functionality after the 2 process steps Al coating and lamination.

The best obtained values overall were:

	BOPP/Al		BOPP/Al/adhesive/BOPP	
adhesion [N/15 mm]	copo G	2.7	copo F	4.8
OTR [cm ³ /m ² d bar]	terpo C	43	copo D*	8.7
WVTR [g/m ² d]	terpo B	0.08	copo D*	0.14

The results of the lamination step demonstrate again, that for developing high barrier films the whole process chain must be optimised and tuned to the final product.

In spite of the higher effort in preparing substrate film, the results are not as good as the best available technology today. This demonstrates the hand-shake problems arising from the multi-partner structure in the Thematic Network and the fact that there is still a large area for improvement.

3.2 2nd test sequence

3.2.1 Target

As already know from pre-projects and literature studies, the pre-treatment type and level of BOPP films before vacuum web coating have a major impact on adhesion and permeation values after coating. The target of the 2nd test sequence were to investigate the impact of pre-treatment methods for BOPP films on their functionality after Al coating.

3.2.2 Set-up

The BOPP films were produced on a pilot plant. The different applied pre-treatment techniques were Corona and flame pre-treatment at the film production site as well as inline plasma pre-treatment inside the production vacuum web Al coater. After applying no, single and double treatment 6 different BOPP copolymer films were Al coated.

The oxygen and water vapour transmission rates through all 6 coated BOPP films were measured as well as the adhesion of the coated layers on the BOPP films.

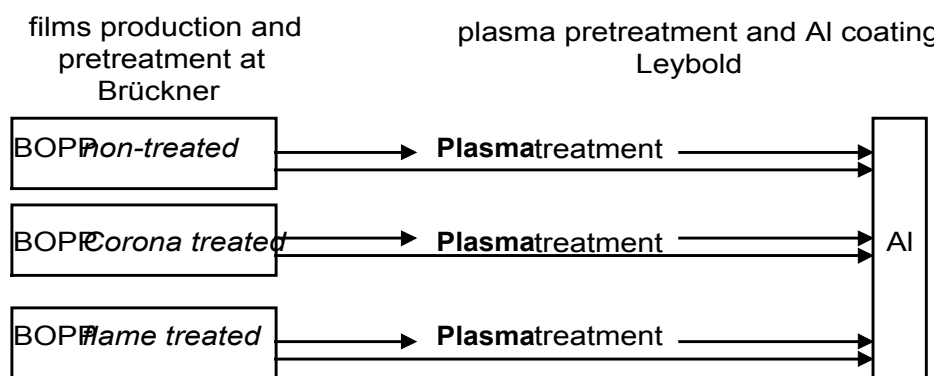


Figure 5: Set-up of the 2nd industrial test sequence: influence of type of pre-treatment on the properties of aluminium vacuum web coated BOPP copolymer films

3.2.3 Results

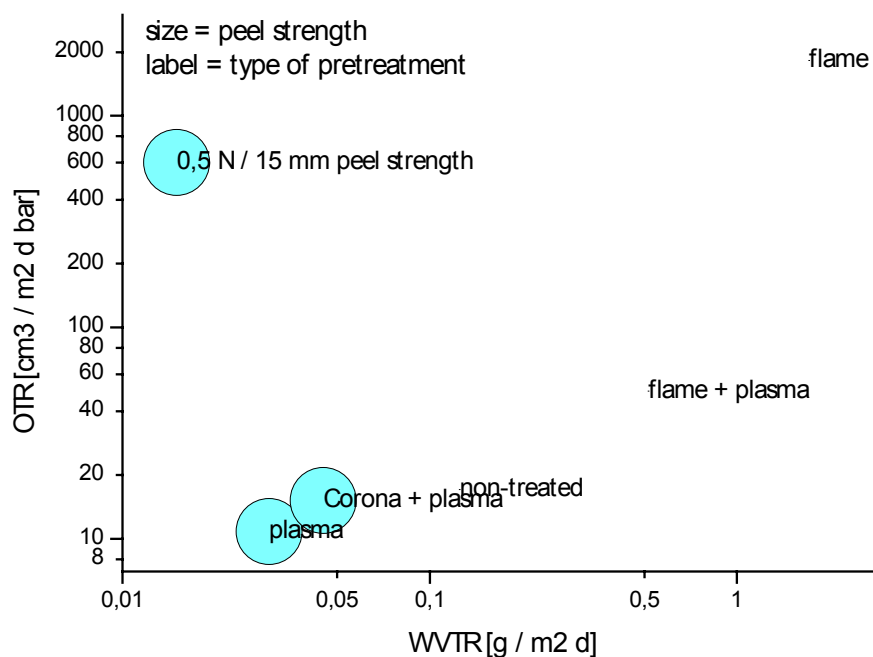
The **peel strength** (adhesion) of the aluminium layers on the different pre-treated BOPP films was between 0.06 (non-treated) and 0.55 (plasma and Corona + plasma) N/15mm, as to be seen in Figure 6. The adhesion strongly depends on the pre-treatment. In contrast to the terpolymer films of the 1st

test sequence, Al adheres better on homopolymer films subjected to Corona pre-treatment than on flame treated ones.

The **OTR** ranges from 10 to 50 cm³/m² d bar and the **WVTR** from 0.03 to 1.7 g/m² d for the Al coated films.

The best pre-treatment for this BOPP homopolymer film is the single plasma pre-treatment for getting lowest OTR and WVTR values as well as high adhesion.

The best barrier films are produced by the single inline plasma pre-treatment of the BOPP films and the pre-treatment at the film production site reduces the adhesion and barrier properties.



Pretreatment	WVTR	OTR	adhesion
	[g/m ² d]	cm ³ /m ² d bar]	[N/15mm]
plasma	0,03	10,83	0,55
Corona + plasma	0,045	15,15	0,55
non-treated	0,125	17,05	0,06
flame + plasma	0,515	49,95	0,35
flame	1,72	1827	0,1

Figure 6: Results of the 2nd industrial test sequence: influence of type of pre-treatment on the properties of aluminium vacuum web coated BOPP homopolymer films. The size of the dots indicates relative adhesion values of coated layers

The best obtained values overall were:

	pre-treatment	BOPP/Al
--	----------------------	----------------

adhesion [N/15 mm]	plasma	0.55
OTR [cm ³ /m ² d bar]	plasma	10.8
WVTR [g/m ² d]	plasma	0.03

3.3 3rd test sequence

3.3.1 Target

The targets of the 3rd test sequence was to investigate the impact of different lamination techniques, as adhesion and extrusion lamination, on the final properties of Al coated or oxide coated BOPP laminates.

3.3.2 Set-up

The adhesive lamination step can improve the oxygen barrier due to the synergetic effect between the inorganic barrier layer and the polar adhesive. A very widely used lamination technique, especially in the United States, is the extrusion lamination of Al coated BOPP film against a BOPP film by using special grades of extruded PE as adhesives. As to be seen in Figure 7, a 16 μm thick Corona pre-treated BOPP film was Al, AlO_x or SiO_x coated and laminated against a 20 μm thick BOPP film by adhesive or extrusion lamination. Film production and coating was done at industrial scale but the lamination on lab scale. Additionally an Al coated 17 μm thick BOPP flame pre-treated film was used for both lamination techniques. The barrier properties of the adhesive laminated samples are still in the measuring pipeline.

The oxygen and water vapour transmission rates through all 4 coated and 9 laminated films were measured as well as the adhesion of the coated layers on the BOPP films and the peel strength of the laminates.

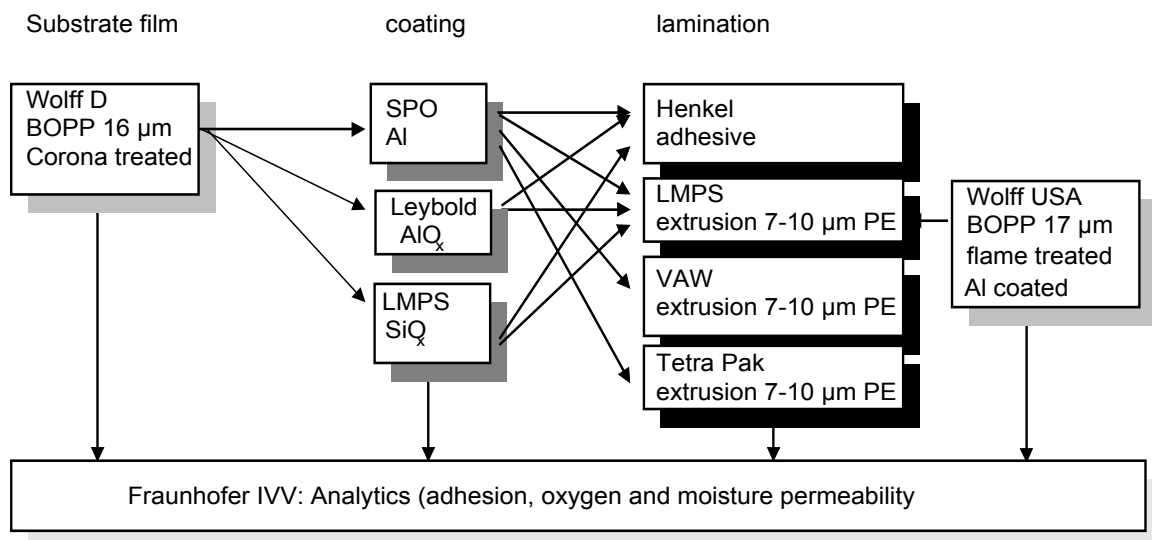


Figure 7: Set-up of the 3rd test sequence: Adhesive versus extrusion lamination

3.3.3 Results

All extrusion laminated films have a very low **bond strength (adhesion)**, because the extrusion lamination process of BOPP films is much more difficult to control than the adhesive lamination. There a high extrusion temperature increases the adhesion of the PE to the inorganic barrier layer but melt the co-extruded layer of the BOPP substrate film. Therefore, the extrusion lamination step requires a special designed BOPP substrate film, for example BOPP homopolymer flame or plasma pre-treated.

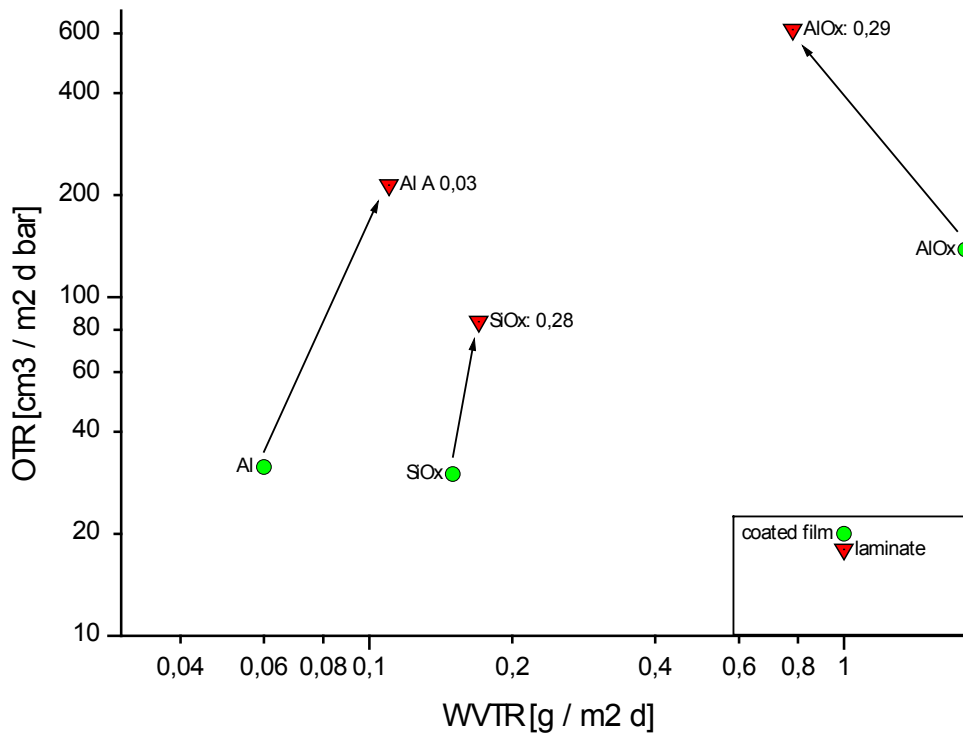


Figure 8: Results of the 3rd test sequence: Extrusion lamination of BOPP film coated with different inorganic barrier layers. The numbers indicate the bond strength N/15 mm.

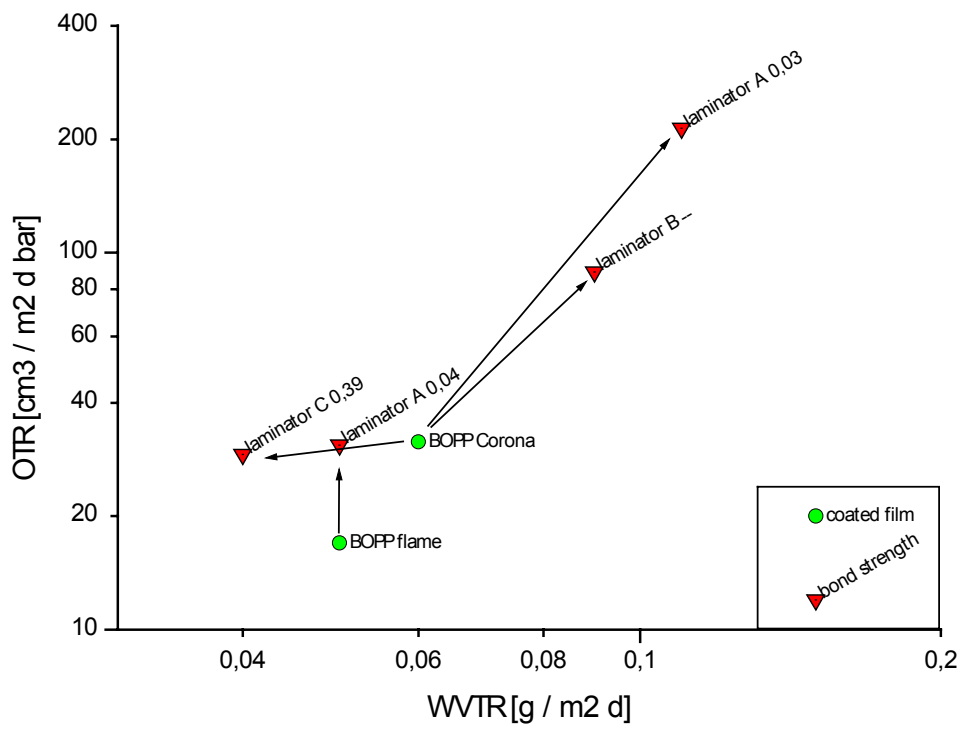


Figure 9: Results of the 3rd test sequence: Extrusion lamination of different Al coated BOPP film at three different pilot plants. The numbers indicate the bond strength N/15 mm

The **OTR** ranges from 17 to 180 cm³/m² d bar and the **WVTR** from 0.05 to 1.7 g/m² d for the Al, AlO_x or SiO_x coated films, as to be seen in Figure 8 and Figure 9. The oxygen barrier of the Al coated

films is slightly lower than the oxygen barrier of the SiO_x coated films, even after adhesive or extrusion lamination. The Al coated films have here the better water vapour barrier. Barrier properties of AlO_x coated films are inferior by one order of magnitude compared to Al or SiO_x coated films and laminates.

Here, the extrusion lamination does not improve the oxygen barrier, but it can improve the water vapour barrier. This may result from a synergetic effect between the inorganic barrier layer and the non-polar extruded PE layer next to it.

As measured in the 1st test sequence, the adhesive lamination step improves the oxygen barrier by one order of magnitude, the water vapour barrier - depending on the substrate film - only slightly. In contrast, the extrusion lamination does not improve the oxygen barrier but can improve the water vapour barrier depending on the type of substrate film and the extrusion lamination process. Therefore, adhesive lamination shall be applied if polymer films are requested for high oxygen barrier and extrusion lamination for high water vapour barrier. The extrusion lamination process, however, is more difficult to handle.

Laminating the films by extrusion lamination demonstrates, that the thermal impact reduces the oxygen and water vapour barrier for both films in the same order of magnitude.

The best obtained values overall were:

	BOPP/coated layer		BOPP/coated layer/adhesive/BOPP	
adhesion [N/15 mm]	copo/SiO _x	2.7	copo/SiO _x /adhesive lamination	4.9
OTR [cm ³ /m ² d bar]	copo/SiO _x	29	copo/SiO _x /adhesive lamination	4.7
WVTR [g/m ² d]	homo/Al	0.06	homo/Al/extrusion lamination	0.04

3.4 4th test sequence

3.4.1 Target

To achieve a common basis for the technical options to prepare packaging films with outstanding properties, i.e. very high barrier properties or mechanical properties on the basis of substrates other than BOPP, especially PET, vacuum coated with barrier layers. For polymer films, the major industrial vacuum web coating techniques are the cheap boat and the flexible electron beam (e-gun) evaporation systems. Both coating techniques can be used for the Al coating process. In order to compare the two techniques according to coated film and laminate properties, the 4th industrial test sequence was set-up.

The target of the 4th test sequence was to compare the performance of different coating machinery and coating techniques of the project partners.

3.4.2 Set-up

As to be seen in Figure 10. There, a standard PET film was Al coated by three different Al boat and one e-gun evaporator. The Al boat coaters are optimised for Al production coatings and the e-gun coater is normally used for oxide coatings, as SiO_x or AlO_x. The thickness of the coated layers was adjusted to the industrial relevant optical density of OD 2.0 (Al layer thickness of 40 – 50 nm). The different coated films were laminated against a 70 µm PE film by applying the same adhesive systems and laminator used in the 1st and 3rd test sequences.

The microstructure of the coated Al layers was investigated by AFM and TEM. For TEM analysis, the PET substrate film must be dissolved and the Al layer fished out of the solvent with a sample holder. Then, the grain size distribution of the Al layers can be measured by TEM.

The oxygen and water vapour transmissions rate through all 6 coated and 7 laminated films was measured as well as the adhesion of the coated layer on the BOPP films and the peel strength of the laminates.

Film production step		Al coating step		lamination step	
Substrate film	Al coating	Optical Density of Al layer on PET film	PUR Adhesive lamination against 70 µm PE		
PET	boat evapoartor A	--> 1.8	-->	adhesive A	
	boat evapoartor B	--> 1.8	-->	adhesive A	
	boat evapoartor B	--> 2.0	-->	adhesive A	
	boat evapoartor B	--> 2.6	-->	adhesive A	
	boat evapoartor E	--> 2.1	-->	adhesive A	
	e-gun evapoartor	--> 1.9	-->	adhesive A	
				adhesive B	

Figure 10: Set-up of the 4th test sequence: boat versus e-gun evaporation

3.4.3 Results:

The e-gun evaporation results in a higher Al layer **adhesion** of 0.6 N/15mm than the boat evaporation (0.3 to 0.4 N/15 mm) as to be seen in Figure 11.

The **OTR** and **WVTR** depends on the evaporation techniques as well as the used coater. Depending on layer thickness and coating equipment, it ranges from 0.8 to 1.7 cm³/m² d bar and the WVTR from 0.2 to 0.4 g/m² d. The highest oxygen barrier values are measured at the thick boat evaporated sample and the highest moisture barrier values at medium thick boat evaporated sample.

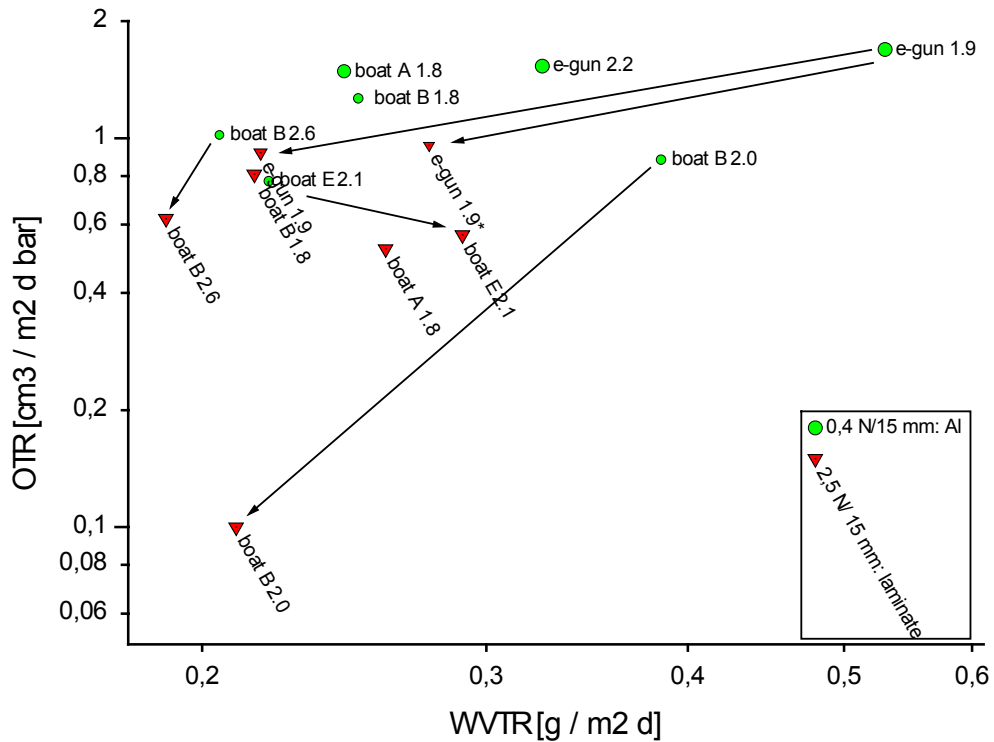
Lamination of the aluminium coated films against 70 µm thick PE films by applying a two component polyurethane adhesive (A) reduces for all films the oxygen permeability, as to be seen in Figure 11. The bond strength of almost all laminates is higher than 2.1 N/15 mm.

The lamination step can improve the oxygen and moisture barrier, but there is no clear correlation between the permeation values before and after lamination.

After lamination, no significant difference in WVTR between e-gun and boat evaporation can be identified. The boat evaporation results in lower OTR. The lowest OTR is below 0.1 cm³/m² d bar and WVTR 0.19 g/m² d. The barrier of the final laminate can be increased by replacing adhesive A against adhesive B.

Differences between the electron beam and boat evaporation can be detected after the Al coating of the PET films in terms of adhesion, OTR and WVTR. The boat evaporation result in Al coated films with the better water vapour barrier. But after lamination, the peel strength are equal and also the WVTR values. Depending on the boat evaporator, there may be a slight advantage for this coating type in OTR. More important than the coating technique is the thickness of the Al layers, because especially for WVTR, thicker layers result in higher barriers.

For AFM analysis of an Al coated film, the whole film is placed on the sample holder of the AFM and the topography and phase image are obtained. In Figure 12, the **particle sizes** of the AFM phase image of Al layers coated on PET films by different coaters and coating techniques are compared to the grain sizes measured by TEM.



Al coating type	OD	PET/Al			PET/Al//PE		
		WVTR	OTR	adhesion	WVTR	OTR	bond strength
		[g/m ² d]	[cm ³ /m ² d bar]	[N/15mm]	[g/m ² d]	[cm ³ /m ² d bar]	[N/15mm]
boat A	1.8	0,245	1,485	38	0,26	0,5195	2,5
boat B	1.8	0,25	1,265	28	0,2155	0,8085	2,55
boat B	2.0	0,385	0,88	27	0,21	0,1	2,6
boat B	2.6	0,205	1,02	25	0,19	0,6215	2,6
boat E	2.1	0,22	0,775	27	0,29	0,5645	2,52
e-gun*	1.9	0,53	1,69	40	0,2175	0,917	2,29
e-gun	1.9	0,53	1,69	40	0,2765	0,958	2,12
e-gun	2.2	0,325	1,53	40			

Figure 11: Results of the 4th test sequence: The properties of Al coated PET films and laminates for boat and e-gun evaporation. The size of the dots indicates relative adhesion values of coated layers

Because the same grain size distribution is measured by AFM and TEM, the particles in the AFM phase images are grains of the Al layers. Hence the faster and easier AFM analysis can be used for measuring the grain size distribution of vacuum deposited Al layers.

The different grain sizes are due to different condensation conditions of the Al layer that mainly depend on evaporation technique (boat – e-beam), web speed, evaporation rate and chill roll temperature.

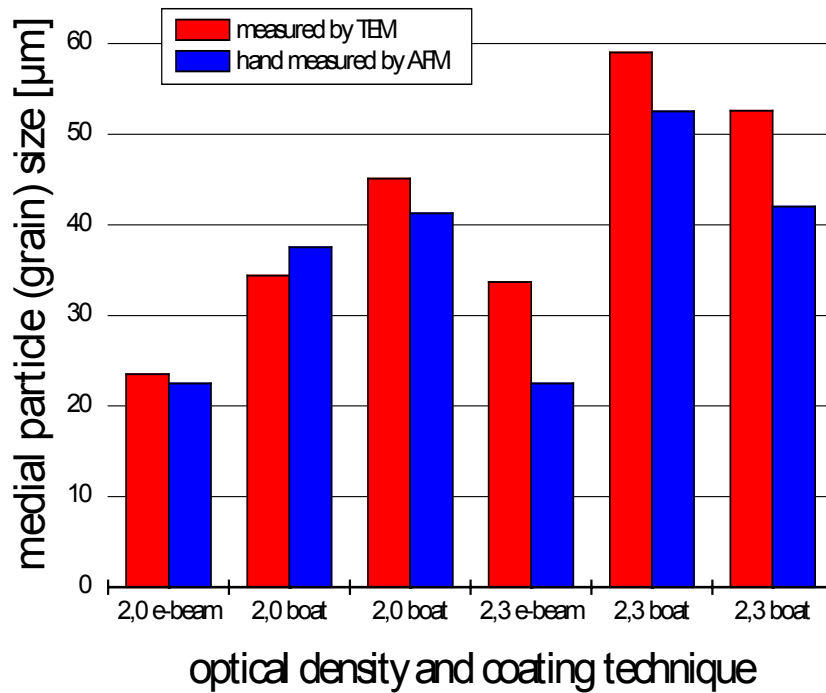


Figure 12: Particle (grain) size distribution of Al layers coated on PET films by different coaters and coating techniques

The achievements of this test sequence are the comparison between electron beam and boat evaporated Al layers on PET films and laminations thereof.

The best obtained values overall were:

	PET/Al		PET/Al/adhesive/PE	
adhesion [N/15 mm]	e-gun (OD: 2.2)	0.4	boat B (OD: 2.6)	2.6
OTR [$\text{cm}^3/\text{m}^2 \text{ d bar}$]	boat E (OD: 2.1)	0.78	boat E (OD: 2.1)	0.56
WVTR [$\text{g}/\text{m}^2 \text{ d}$]	boat B (OD: 2.6)	0.2	boat B (OD: 2.6)	0.19

3.5 5th Test Sequence

3.5.1 Target

The target of the 5th test sequence was to correlate the thickness of Al layers vacuum web deposited on PET films to their functionality after coating and adhesive lamination.

3.5.2 Set-up

One selected type of PET film was vacuum web coated with 6 different thick Al layers by 1 project partner using a pilot plant equipped with a boat evaporator. The thickness of the Al layers were varied by the web speed. The coated films were adhesive laminated against PE films.

The oxygen and water vapour transmission rates through all 6 coated and 6 laminated films were measured as well as the adhesion of the coated layers on the PET films and the peel strength of the laminates.

For the standardization of the adhesion measurement, the peel strength of the coated and laminated films were measured by applying different test set-ups.

An aluminium layer coated on a polymer film oxidizes on its surfaces to aluminium oxide. Due to the higher light transmittance of the aluminium oxide compared to the pure Al, the total light transmittance of the coated layers increases and the measured optical density decreases. The optical density is the simplest experimental set-up and therefore the most used thickness measurement system by the aluminium coating industry. Other industrial methods are X-ray fluorescence (XRF) and surface conductivity, whereby XRF is detecting also the oxidized aluminium atoms.

In order to evaluate the comparability of different testing systems for measuring the thickness of Al coated layers, the thickness of each layer was measured by optical density, XRF, SEM and surface resistance.

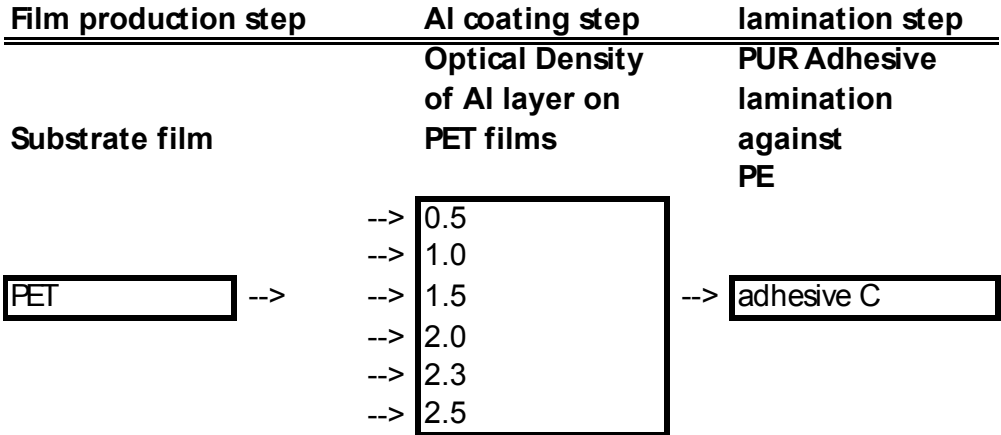


Figure 13: Set-up of the 5th test sequence: PET films coated with different thick Al layers by boat evaporation

3.5.3 Results

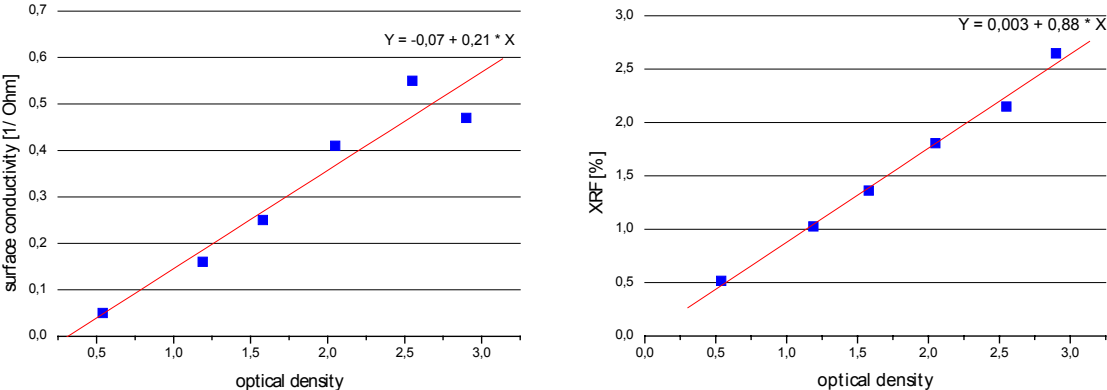


Figure 14: Thickness measurement of vacuum web coated Al layers on PET films by surface resistance (left side) and XRF (right side) versus optical density

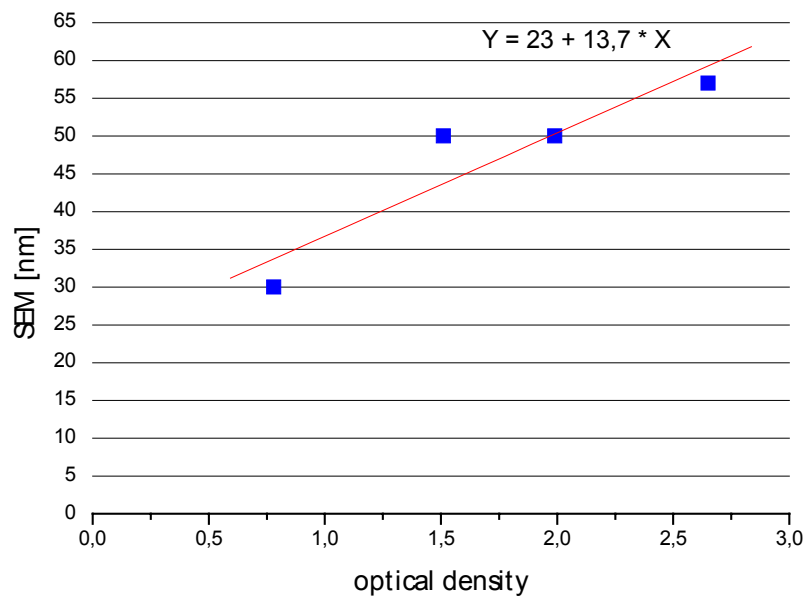


Figure 15: Thickness measurement of vacuum web coated Al layers on PET films by SEM versus optical density

As to be seen in Figure 14 and Figure 15, the **thickness** of the 6 different thick Al layers vacuum web coated on the PET films were measured by SEM, XRF, optical density (OD) and surface conductivity.

The surface conductivity, the XRF signal and the thickness of the SEM measurements show a linear increase with the optical density. The surface conductivity has no offset at OD 0, because both methods detect only the pure fraction of the aluminium layer. An offset at OD 0 is obtained by SEM and in a smaller amount by XRF, because both methods detect in addition to pure aluminium layers also oxide layers.

These results demonstrate, that thickness measurement of Al layers vacuum coated on polymer films can be correlated between the different techniques (OD, SEM, XRF, surface conductivity).

As to be seen in Figure 16, **OTR** and **WVTR** of the coated films and laminates decreases with the Al layer thickness. As expected from the previous results, the lamination process has a higher impact on the OTR than on WVTR. According to the previous experience of the project partners and literature, it was not expected, that Al layers thicker than OD 2.5 have better oxygen and water vapour barriers.

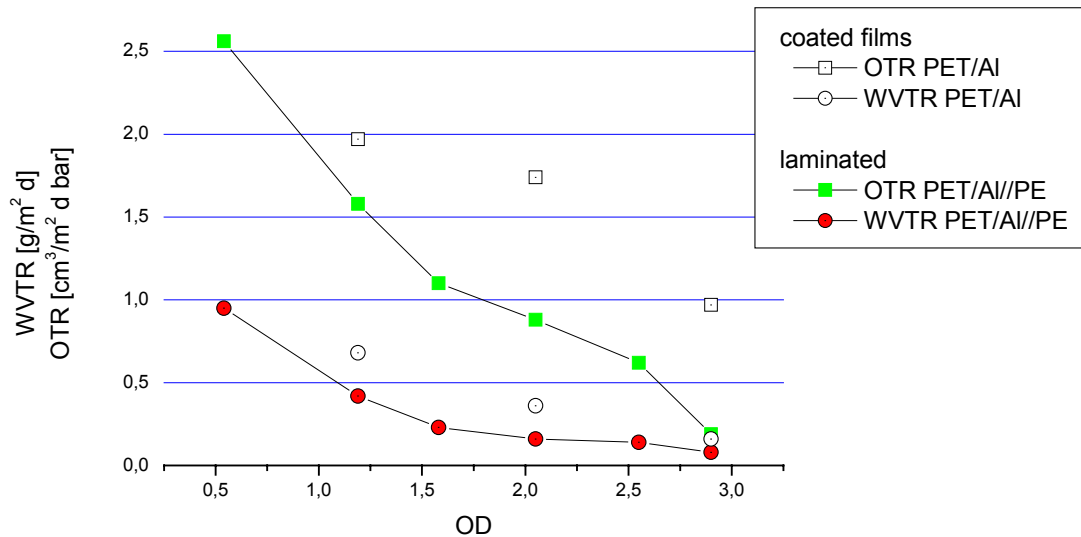


Figure 16: OTR and WVTR of PET/Al films and PET/Al/PE laminates containing different thick Al layers

The **adhesion** of the aluminium layers increases with layer thickness for the coated and non-laminated films, as to be seen in Figure 17. But for the laminated films, not all aluminium could be removed from the PET substrate film by the peel strength measurements. The amount of removed aluminium grows with the layer thickness and there is a large discrepancy between peeling-off at 90 or 180°. Therefore peel strength measurements of different laminates can only be compared, if all measurement conditions are exactly identical.

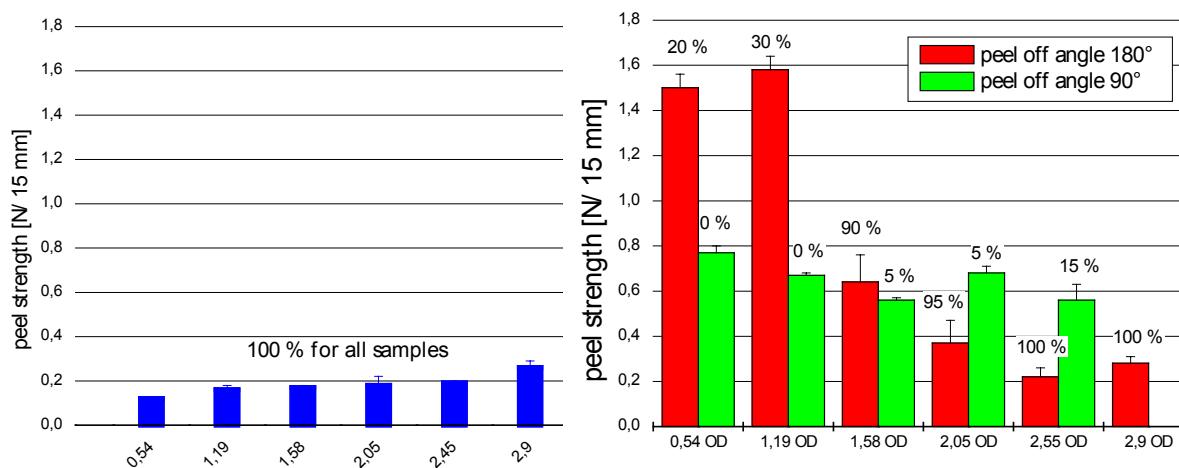


Figure 17: Peel strength (adhesion) measurements of PET/Al films (left hand side) and PET/Al/PE laminates (right hand side), percentages indicate the amount of Al removed from the PET substrate film

The adhesion and peel strength were also measured by sealing different polymer films on the Al coated PET films for adhesion measurements. The measured peel forces and the point of failure depend strongly on the peel-off angle. Also the type of used peel-off films impacts the adhesion value, as to be seen in Figure 18.

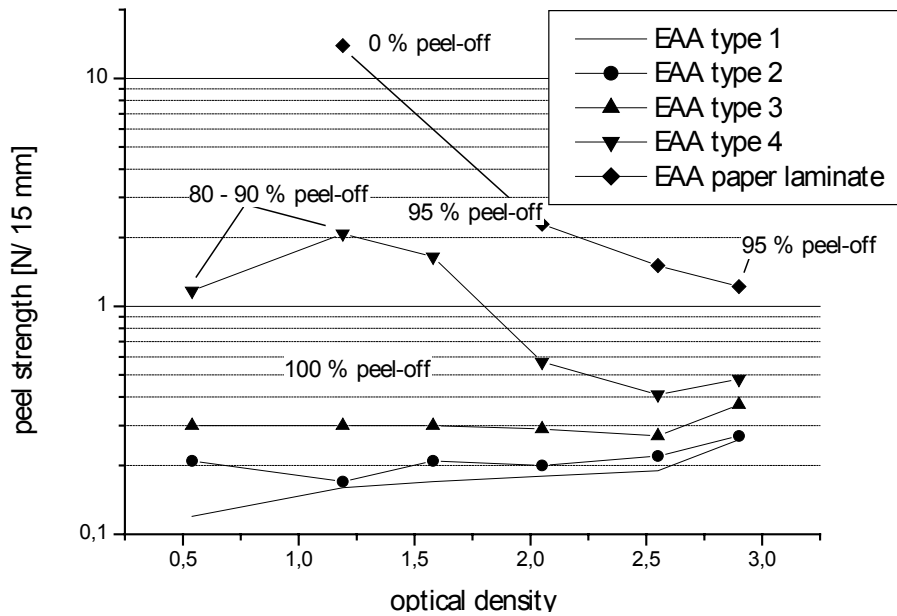


Figure 18: EAA-peel-test on PET/Al with different types of EAA peel stripes

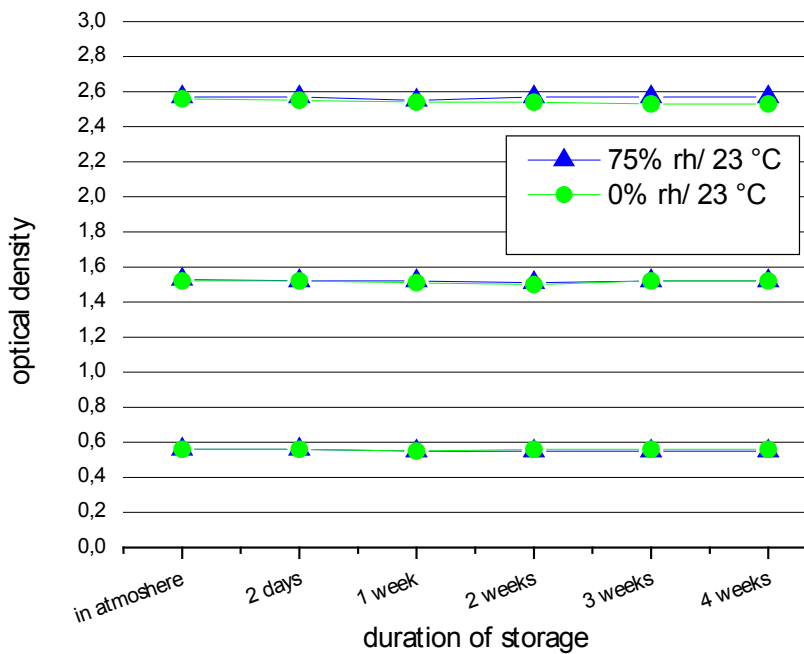


Figure 19: Storage of Al coated PET films at different relative humidity

As to be seen in Figure 19, the storage of Al coated films at different relative humidity (0 and 75 %) does not change the OD. Therefore, no further post-oxidation of the Al layers apparently occurs even by storing the films at higher relative humidity of 75 %. Al coated films can be stored at higher relative humidity without changing the OD.

Best obtained values overall were:

	PET/Al		PET/Al/adhesive/PE	
adhesion [N/15 mm]	OD: 2.5	0.26	OD: 2.1	1.6
OTR [cm ³ /m ² d bar]	OD: 2.5	0.97	OD: 2.5	0.19
WVTR [g/m ² d]	OD: 2.5	0.16	OD: 2.5	0.08

3.6 6th Test Sequence

3.6.1 Target

The target of the 6th test sequence was to correlate the thickness of Al layers vacuum web coated on BOPP films to their functionality after coating and adhesive lamination.

3.6.2 Set-up

The set-up of the 6th test sequence is equivalent to the 5th test sequence. Here, the substrate and lamination films consist of BOPP films instead of PET or PE films.

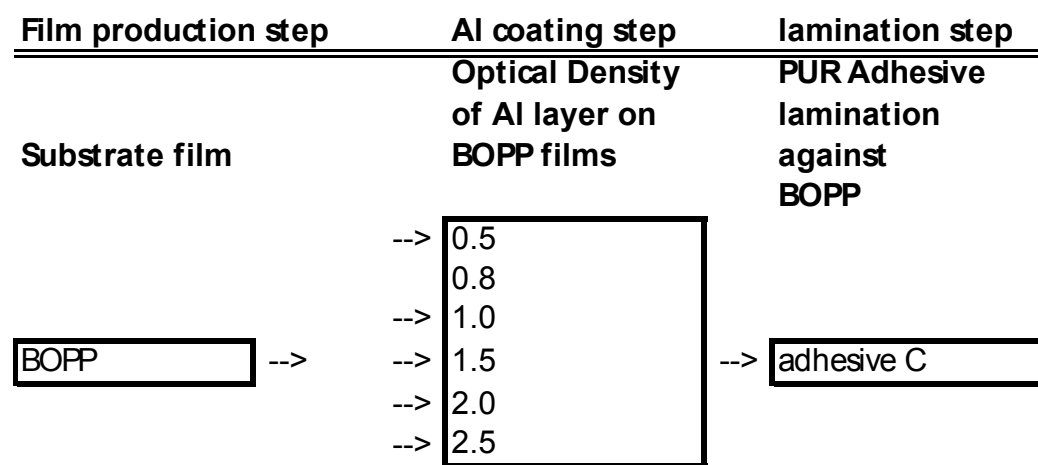


Figure 20: Set-up of the 6th test sequence: BOPP films coated with different thick Al layers by boat evaporation and adhesive laminated

3.6.3 Results

Similar to the results of the **peel strength** measurements of the 5th test sequence, the change in peel-off angle strongly impact the amount of peeled-off aluminium, as to be seen in Figure 22.

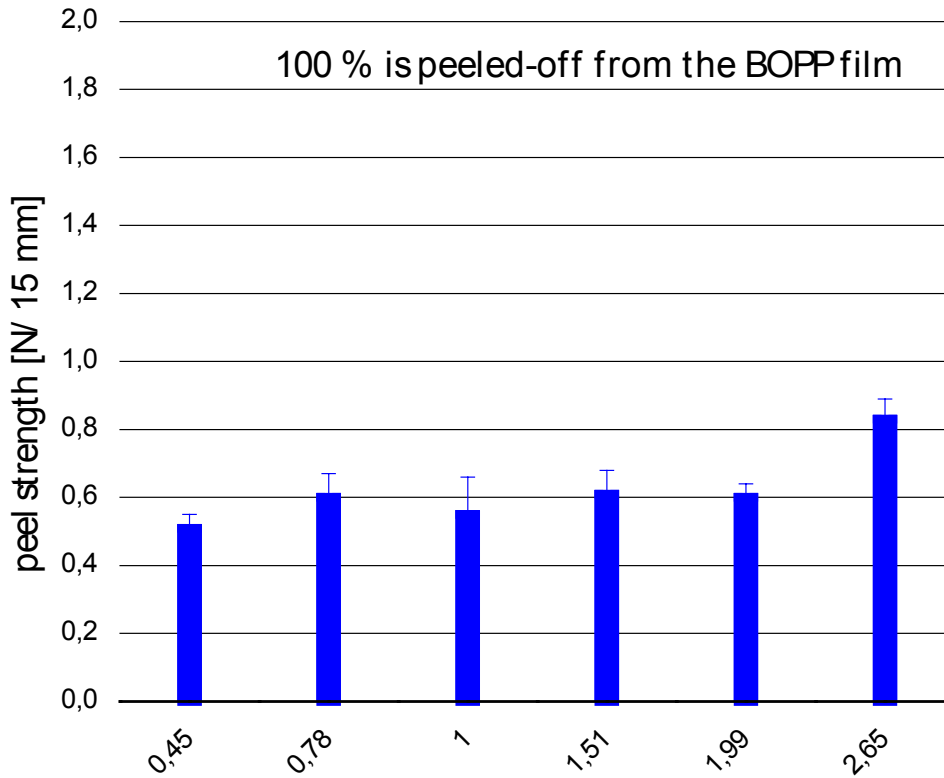


Figure 21: Peel strength (adhesion) measurements of BOPP/Al films, percentages indicate the amount of Al removed from the BOPP substrate film

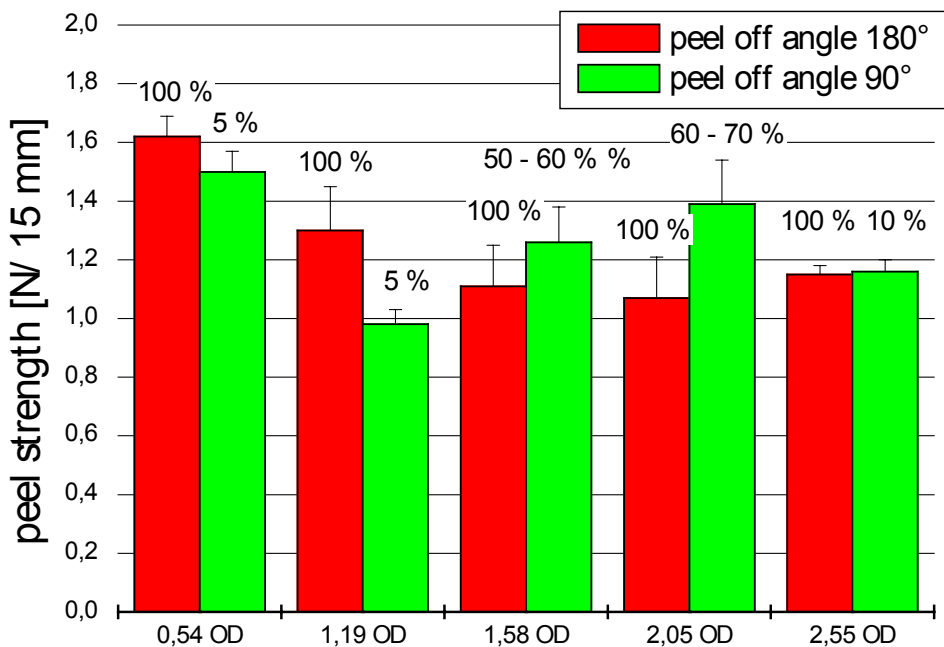


Figure 22: Peel strength (adhesion) measurements of BOPP/Al//BOPP laminates, percentages indicate the amount of Al removed from the BOPP substrate film

Due to the too high **OTR** and **WVTR** (plotted in Figure 23) by one to two orders of magnitude compared to the values of the 1st test sequence (BOPP/Al with OTR of 43 cm³/m² d bar and WVTR of 0.08 g/m² d), this test sequence had to be repeated as 8th test sequence.

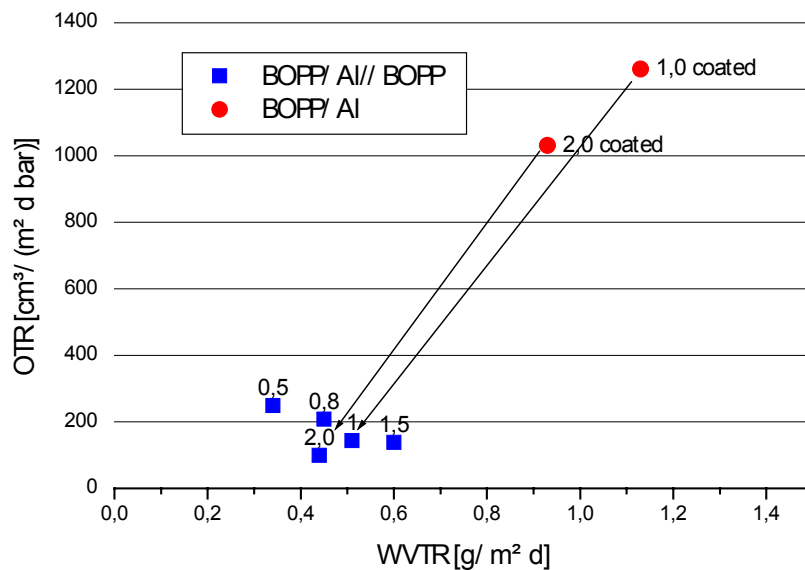


Figure 23: OTR and WVTR measurements of BOPP/Al and BOPP/Al//BOPP coated with different thick Al layers (The given numbers indicate the optical density.)

In spite of using an industrial set-up of the test sequence, the obtained barrier values are much worse than expected.

The best obtained values overall were:

	BOPP/Al		BOPP/Al/adhesive/BOPP	
adhesion [N/15 mm]	OD: 2.5	0.82	OD: 0.5	1.62
OTR [cm ³ /m ² d bar]	OD: 2.5	971	OD: 2.0	99
WVTR [g/m ² d]	OD: 2.5	0.69	OD: 2.0	0.44

3.7 7th Test Sequence

3.7.1 Target

The target of the 7th test sequence was to verify the obtained trend of the 5th test sequence. Additional to work in the 5th test sequence, the impact of other production parameters, as plasma pre-treatment and lamination technique, were investigated for different thick aluminium layers.

3.7.2 Set-up

Similar to the 5th test sequence, PET films with 3 different optical densities were Al coated by varying the web speed on pilot plant equipped with a boat evaporator. As additional parameters,

- aluminium was coated on non-treated and plasma pre-treated PET-films,
- the aluminium coated films were adhesive and extrusion laminated.

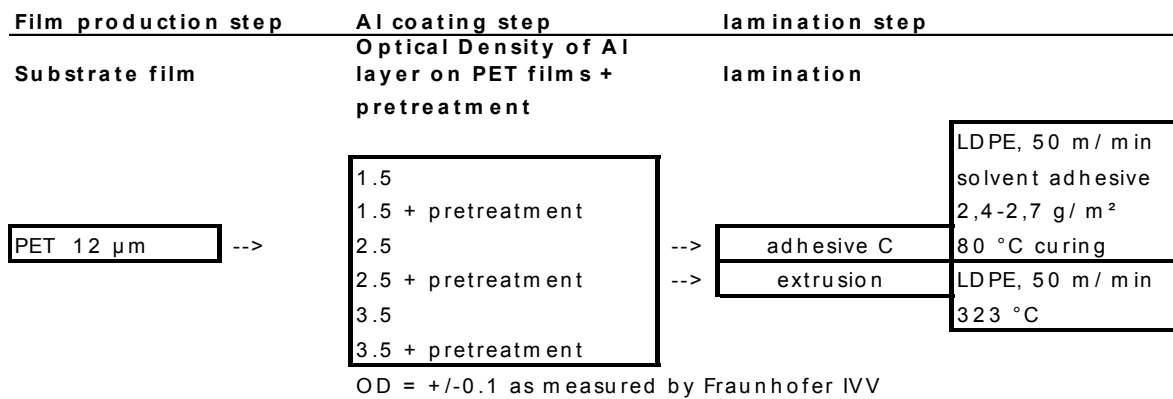


Figure 24: Set-up of the 7th test sequence: PET films pre-treated, coated with different thick Al layers by boat evaporator and extrusion or adhesive laminated

3.7.3 Results

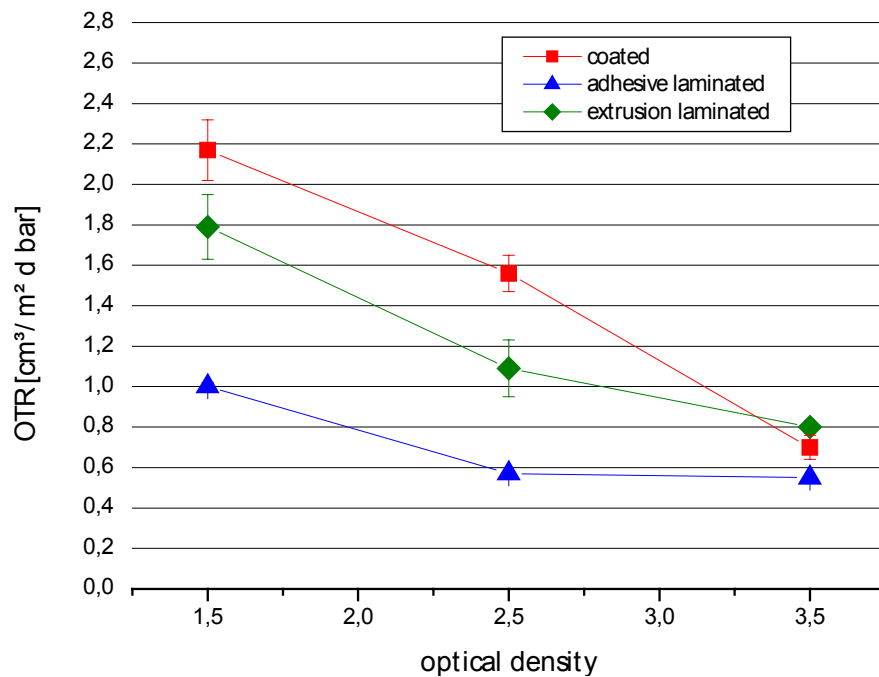


Figure 25: OTR of PET/Al films and PET/Al/PE laminates (**no plasma pre-treatment**) coated with different thick aluminium layers and lamination techniques

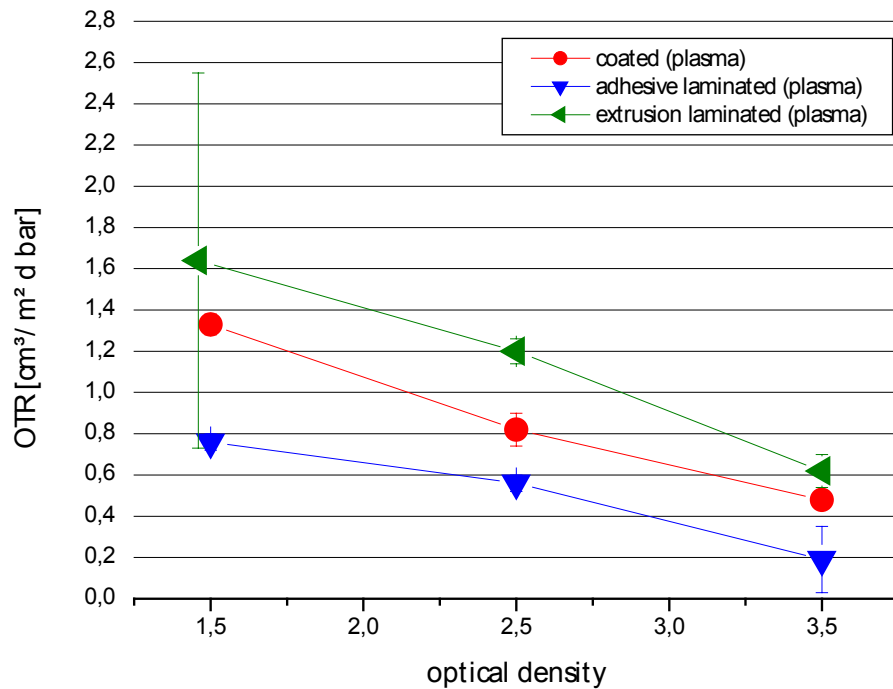


Figure 26: OTR of PET/Al films and PET/Al/PE laminates (**plasma pre-treatment**) coated with different thick aluminium layers and lamination techniques

The measured **OTR** and **WVTR** are plotted in Figure 25 and Figure 26. The OTR measurements show a nearly linear decrease with increasing optical density for almost all films and laminates. Only the untreated extrusion laminated film showed no further reduction in OTR at OD=3.5.

WVTR are plotted in Figure 27 and Figure 28. Similar to the OTR, best barrier properties against the permeation of water vapour can be reached by applying plasma pre-treatment on the PET films before coating and to increase the thickness of the Al layer. Figure 29 and Figure 30 summarize the OTR and WVTR values of coated and laminated films. Barrier properties are improved by the thickness of the Al layer. The lamination step increases the water vapour barrier for both lamination techniques. But, depending on the Al layer thickness, the extrusion lamination step can reduce the oxygen barrier. Similar to the results of the previous test sequences, the adhesive lamination results in better oxygen barrier laminates.

Compared to extrusion lamination, the higher oxygen barrier of the adhesive laminated films is based on

- the lower thermo-mechanical stress on the Al layers during the lamination step and
- the higher oxygen barrier of the adhesive in combination with the synergetic effect between the adhesive and Al layers.

The polyethylene applied as thermo-formable adhesive during the extrusion lamination step has a higher water vapour barrier than the polyurethane adhesive. Therefore the final water vapour barriers of the extrusion laminates are higher than of the adhesive laminates. Here the damage of the water vapour barrier by the extrusion process is compensated by the higher barrier properties of the applied adhesive.

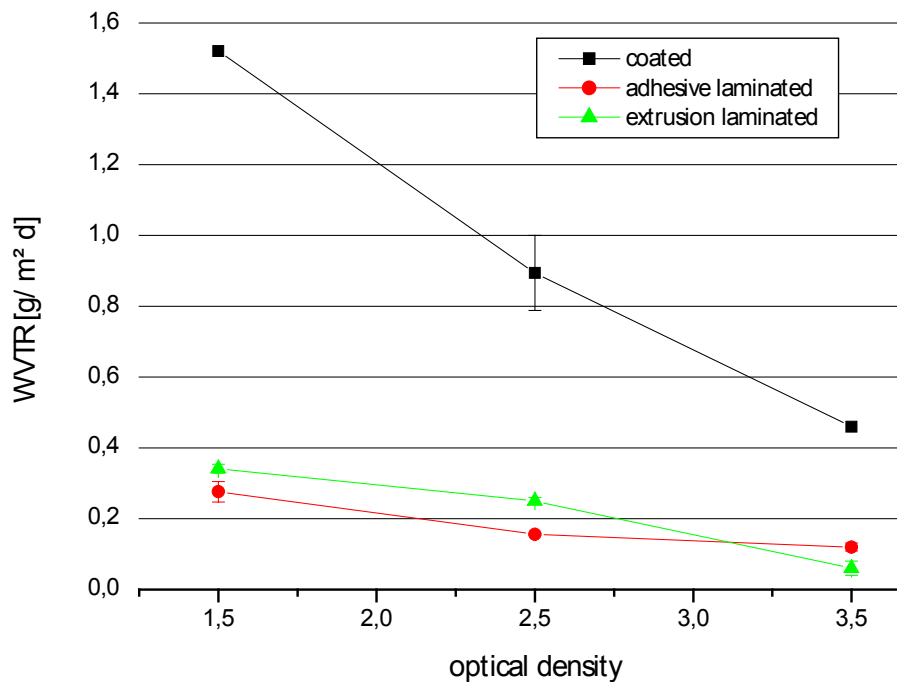


Figure 27: WVTR of PET/Al films and PET/Al//PE laminates (**no plasma pre-treatment**) coated with different thick aluminium layers and lamination techniques

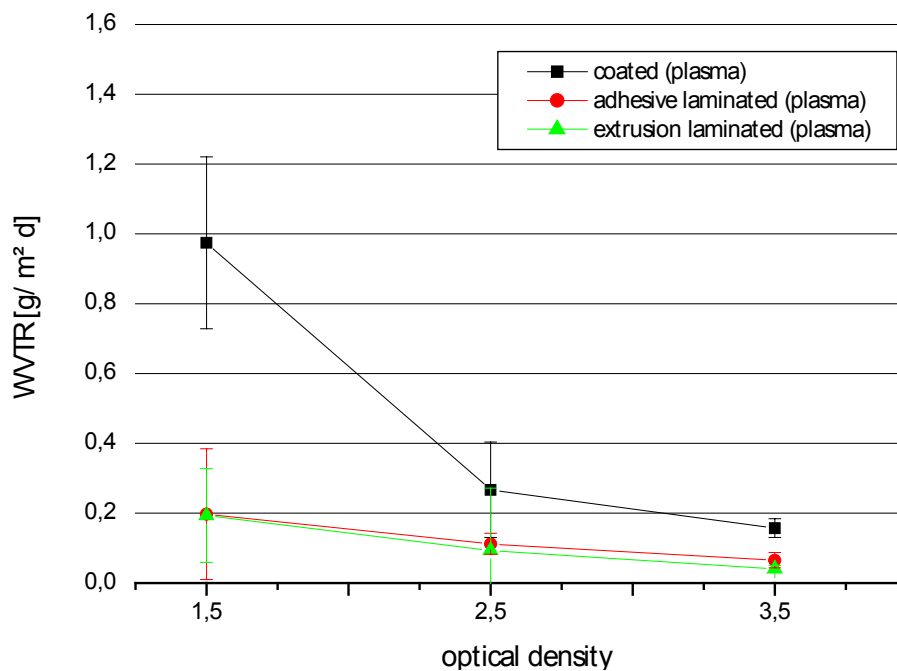


Figure 28: WVTR of PET/Al films and PET/Al//PE laminates (**plasma pre-treatment**) coated with different thick aluminium layers and lamination techniques

The AFM pictures of non-treated and plasma pre-treated PET films coated with aluminium showed no significant difference in **roughness** and **topography**.

The measured reduction in OTR must therefore have a different origin. **Light microscopy** revealed that the total area of „light holes“, which must not be automatically pin holes can be reduced by the use of plasma pre-treatment. This would explain the lower OTR of plasma pre-treated films. Interestingly the total number of defects is nearly identical in both cases, as to be seen in Table 2.

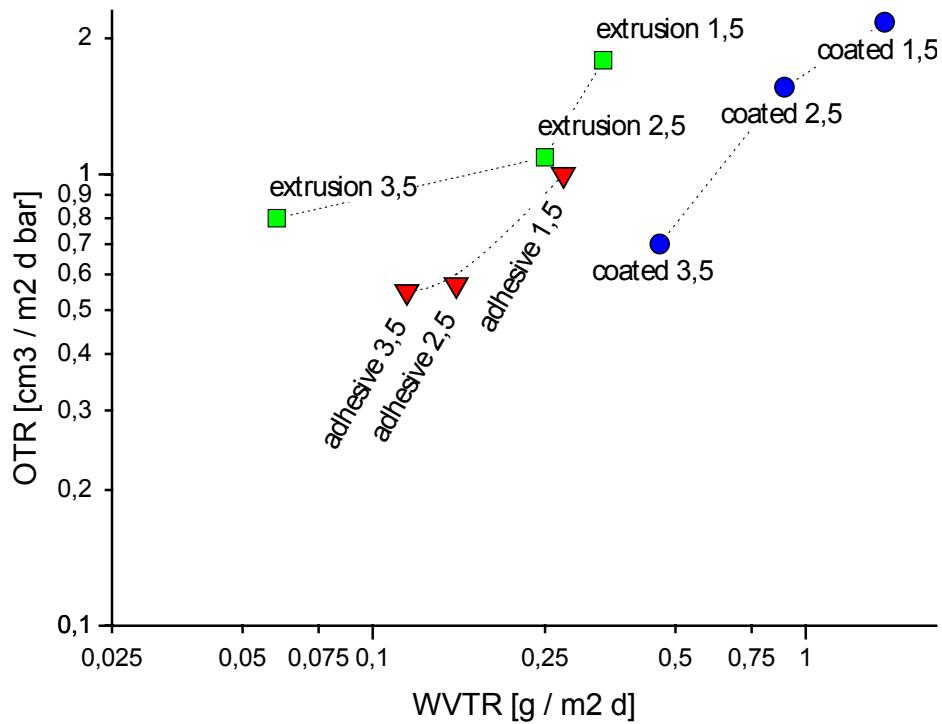


Figure 29: WVTR and OTR of PET/Al (coated) PET/Al/PE laminates (adhesion or extrusion) coated on **non-treated** PET films; the numbers indicate the optical density of the Al layers

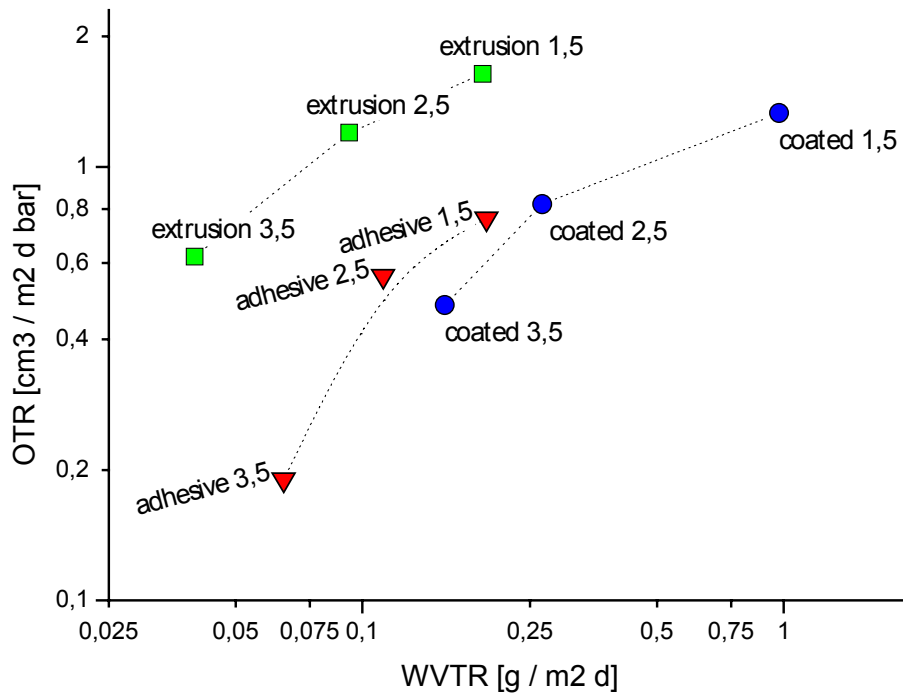


Figure 30: WVTR and OTR of PET/Al (coated) PET/Al/PE laminates (adhesion or extrusion) coated on **plasma pre-treated** PET films; the numbers indicate the optical density of the Al layers

Table 2: Histograms of light holes in different thick Al layers coated on non-treated and plasma pre-treated PET films

	non-treated	plasma pre-treated
OD 1.5	<p>total number of defects: 666 total area of defects: 2659 μm^2</p>	<p>total number of defects: 384 total area of defects: 1502 μm^2</p>
OD 2.5	<p>total number of defects: 297 total area of defects: 972 μm^2</p>	<p>total number of defects: 283 total area of defects: 989 μm^2</p>
OD 3.5	<p>total number of defects: 126 total area of defects: 719 μm^2</p>	<p>total number of defects: 129 total area of defects: 442 μm^2</p>

The impact of the thickness of the aluminium layer on defect density, defect area, adhesion, OTR and WVTR on the non-treated and plasma pre-treated samples is summarized in Table 3 and Table 4.

Table 3: Summary: Impact of different OD on defined parameters

		Increasing OD					
		Adhesion of Al layer	Lamination strength	Oxygen barrier	Moisture barrier	Number of defects	Area of defects
non-plasma	Al coating	↑		↑	↑	↓	↓
	Adhesive lamination		→	↑	↑		
	Extrusion lamination		↓ ?	↑	↑		
Plasma treated	Al coating	→		↑	↑	↓	↓
	Adhesive lamination		→	↑	↑		
	Extrusion lamination		→	↑	↑		

Table 4: Summary: Impact of plasma treatment on defined parameters

	Non-plasma → plasma treated					
	Adhesion of Al layer	Lamination strength	Oxygen barrier	Moisture barrier	Number of defects	Area of defects
Al coating						
Adhesive lamination						
Extrusion lamination						

It can be conclude from this test sequence, that

- plasma pre-treatment of PET films improves the oxygen and water vapour barrier after coating and lamination,
- aluminium coatings thicker than OD 2.5 results in higher barrier films and laminates,
- adhesive lamination results in better oxygen barrier films and
- extrusion lamination results in better water vapour barrier films, but can reduce the oxygen barrier.

Best obtained values overall were:

	PET/Al		PET/Al/PE	
adhesion [N/15 mm]	OD: 3.5	0.5	(adhesive) OD: 3.5	2.7
OTR [$\text{cm}^3/\text{m}^2 \text{ d bar}$]	OD: 3.5	0.48	(adhesive) OD: 3.5	0.19
WVTR [$\text{g}/\text{m}^2 \text{ d}$]	OD: 3.5	0.16	(extrusion) OD: 3.5	0.04

3.8 8th Test Sequence (Repetition of the 6th test sequence)

3.8.1 Target

The target of the 8th test sequence was to correlate the thickness of Al layers vacuum web coated on BOPP films to their functionality after coating and adhesive lamination.

3.8.2 Set-up

Similar to the 6th test sequence, BOPP films with 6 different optical densities were produced by varying the web speed of the pilot plant. The films were adhesive laminated against a LDPE film, as to be seen in Figure 31.

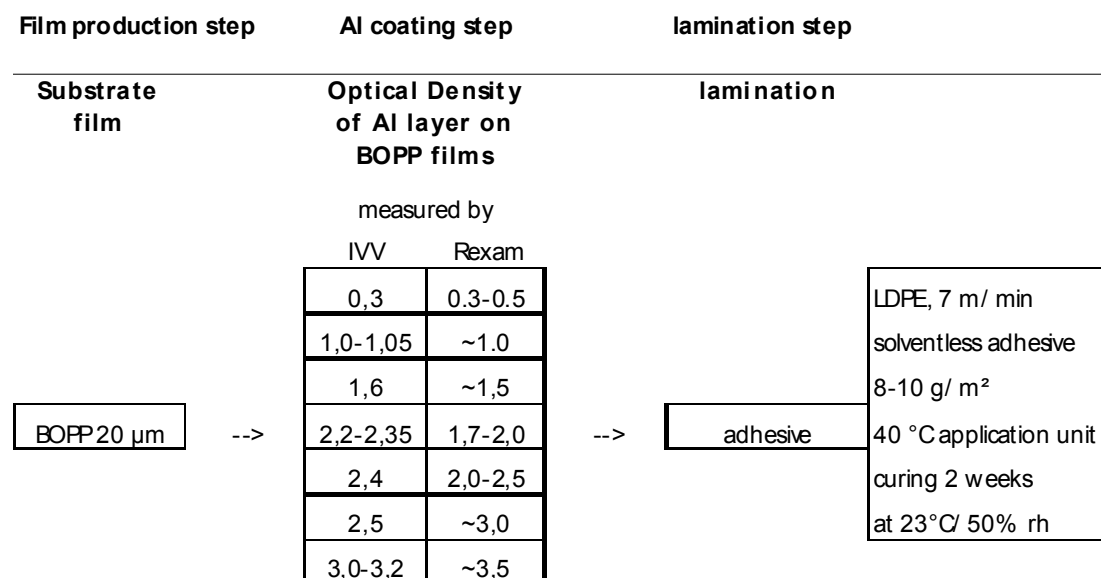


Figure 31: Set-up of the 8th test sequence: BOPP films coated with different thick Al layers by boat evaporator and adhesive laminated

3.8.3 Results

The **peel strength** of the Al coated BOPP films and the OTR of the coated and laminated films were measured. As to be seen in Figure 32, the adhesion of the Al layers is twice of the peel strength of Al layers on PET films and decreases with higher Al layer thickness by 10 %.

The **OTR** through the different coated and laminated films are plotted in Figure 33. The OTR of the coated films are by two orders of magnitude higher than the best values obtained within the project. However, the lamination step reduces the OTR drastically down to 10 cm³/m² d bar. This is only twice as much as the lowest OTR through a BOPP laminate.

The high improvement of the oxygen barrier by the lamination step can be caused by spitting during Al deposition. The spitting creates pores in the substrate film and a defect in the coated layer. Hence, at the defect there is a pore through the substrate film and the barrier layer resulting in high transmission rates. After the lamination step, the pore is covered with the polyurethane layer and the

transmission rate drastically reduced by the synergetic effect between the Al and the polyurethane layer.

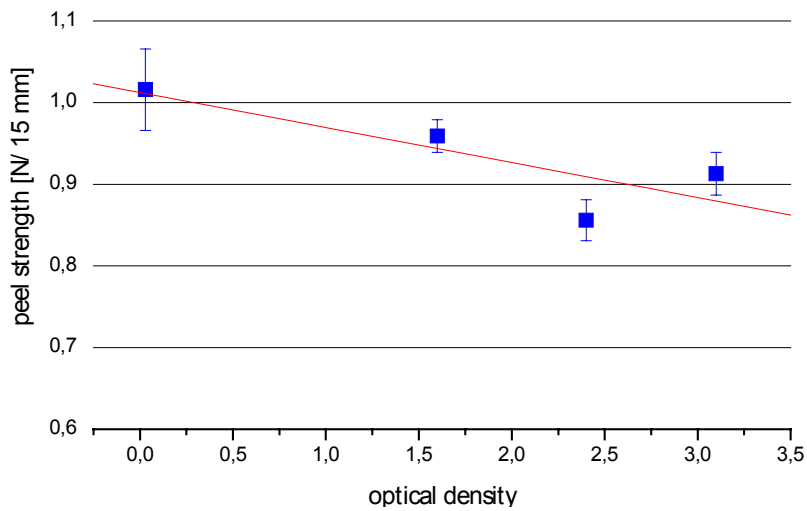


Figure 32: Peel strength (adhesion) of different thick Al layers coated on BOPP films

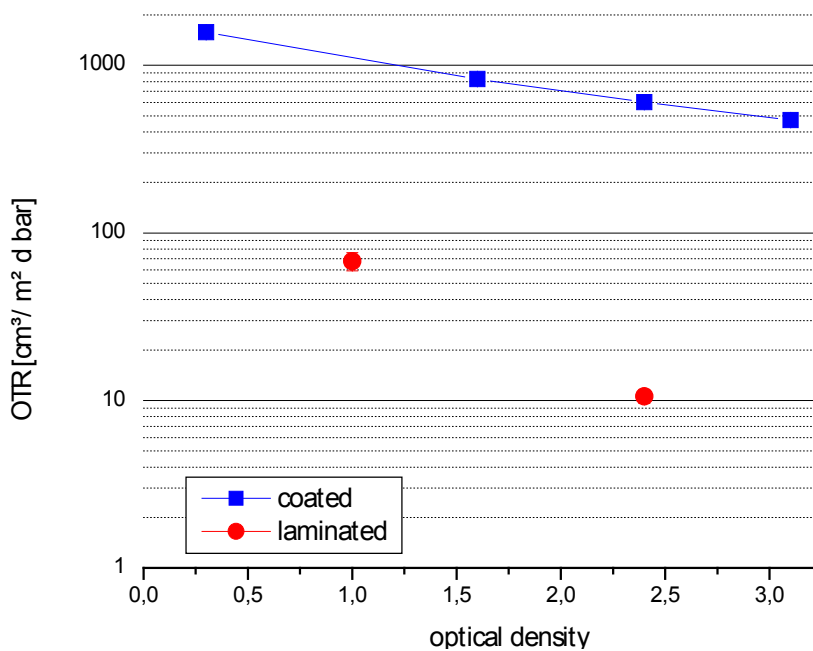


Figure 33: OTR through different thick Al layers coated on BOPP films and laminates

Best obtained values overall were:

	PET/Al		PET/Al/adhesive/PE
adhesion [N/15 mm]	OD: 3.5	1.0	not measured
OTR [cm³/m² d bar]	OD: 3.5	472	OD: 2.5 11
WVTR [g/m² d]	not measured		not measured

3.9 9th Test Sequence

3.9.1 Target

The target of the 9th test sequence was to study the impact of different Al coating parameters on the properties and functionality of Al coated BOPP films and extrusion laminated films. In this test sequence the influence of plasma pre-treatment, web speed and wire feed rate on grain size, light pores, barrier properties and adhesion was investigated.

3.9.2 Set-up

BOPP films were coated with 4 different optical densities using a pilot plant. The Al layer thickness was varied by changing web speed and wire feed rate so, that similar ODs could be produced at different feed rates and web speeds, as to be seen in Figure 35. Both parameters – web speed and wire feed rate – were varied by a factor of 1.5 and change the optical density between OD 2 and 3. Additionally two types of the samples were produced, non-pre-treated and plasma pre-treated in the metallizer. The pre-treatment was kept at constant power for all web speeds, hence an increase of web speed reduces the effective pre-treatment power per film unit. The BOPP film was already pre-treated at the film production site. After the coating process the reel was slit in two parts.

One part of the coated reel was directly analysed. The other part was extrusion laminated against LDPE/PET and then analysed, as to be seen in Figure 34.

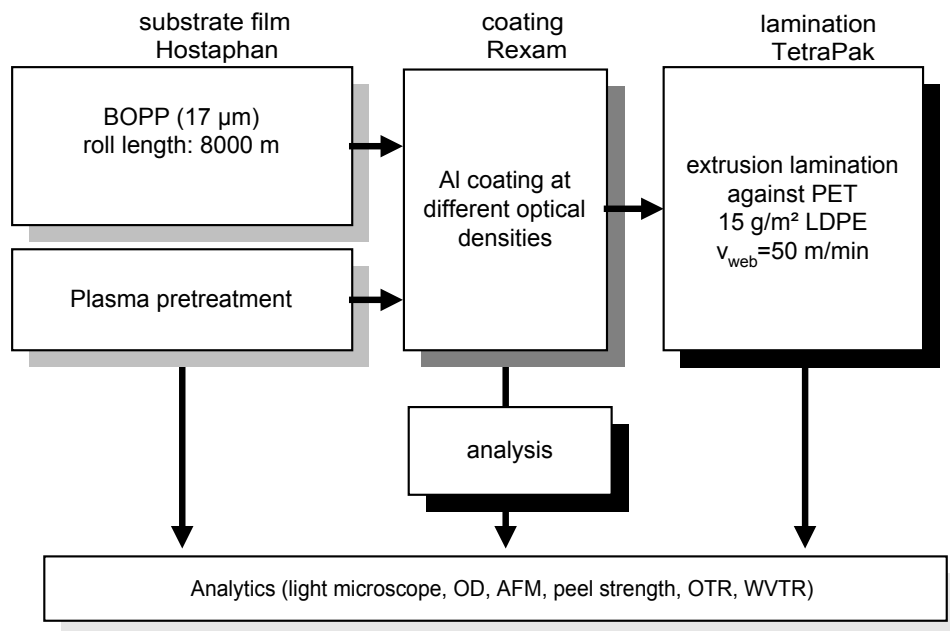


Figure 34: Set-up of the 9th test sequence: BOPP films coated with different thick Al layers by boat evaporator and extrusion laminated

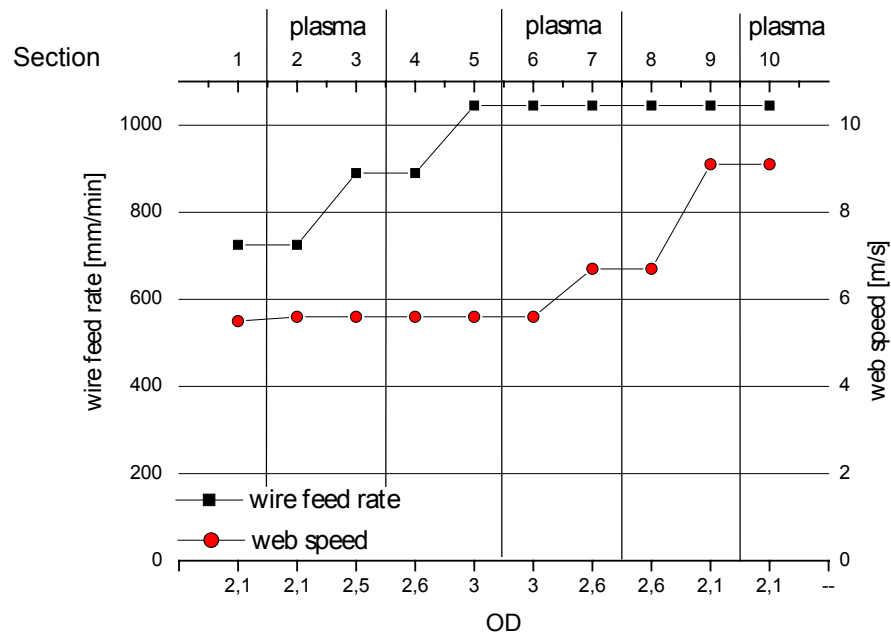


Figure 35: Set-up of the 9th test sequence: BOPP films coated with different thick Al layers by boat evaporator: (The different section number are listed on top and the optical densities on the bottom.)

3.9.3 Results

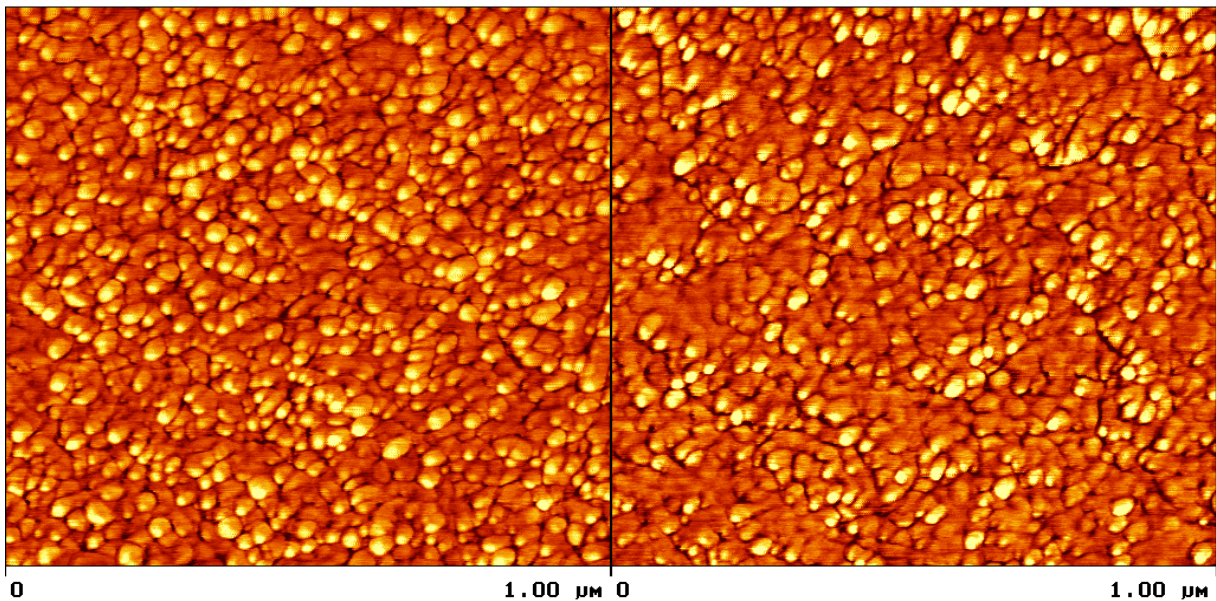


Figure 36: Analysis of grain structure of vacuum coated Al layers by AFM phase image, (identification of samples, see Figure 35)
 left hand side: non-plasma pre-treated (section 1)
 right hand side: plasma pre-treated (section

2)

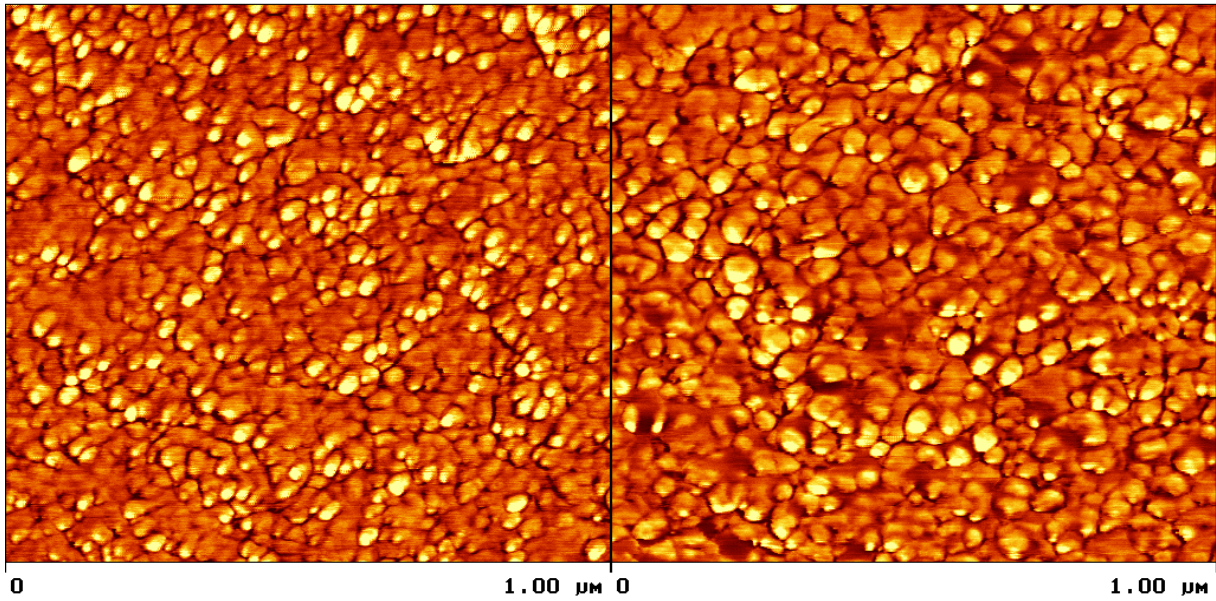


Figure 37: Analysis of grain structure of vacuum coated Al layers by AFM phase image, (identification of samples, see Figure 35)
left hand side: wire feed rate 725 mm/min (section 2)
right hand side: wire feed rate 1045 mm/min (section 6)

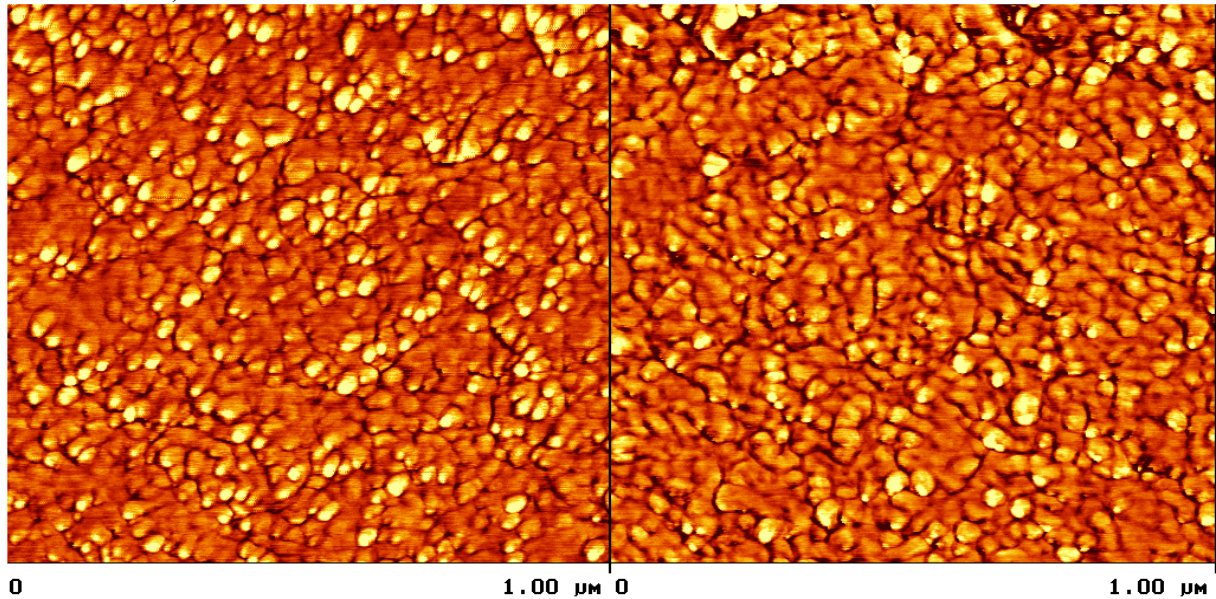


Figure 38: Analysis of grain structure of vacuum coated Al layers by AFM phase image, (identification of samples, see Figure 35)
left hand side: speed 5.5 m/s (section 2)
right hand side: speed 9.1 m/s (section 10)

The **grain sizes** of the deposited Al layers can be analysed by AFM phase images. Comparing Al layers deposited on Corona pre-treated BOPP films to on Corona/plasma pre-treated BOPP films reveals no significant different in the layer structure, as to be seen in Figure 36. Increasing the layer thickness also enlarges the grain sizes, as to be seen in Figure 37.

Al layers of OD 2.1 deposited at higher web speeds and wire feed rates have larger grains and the layer structure is more faded.

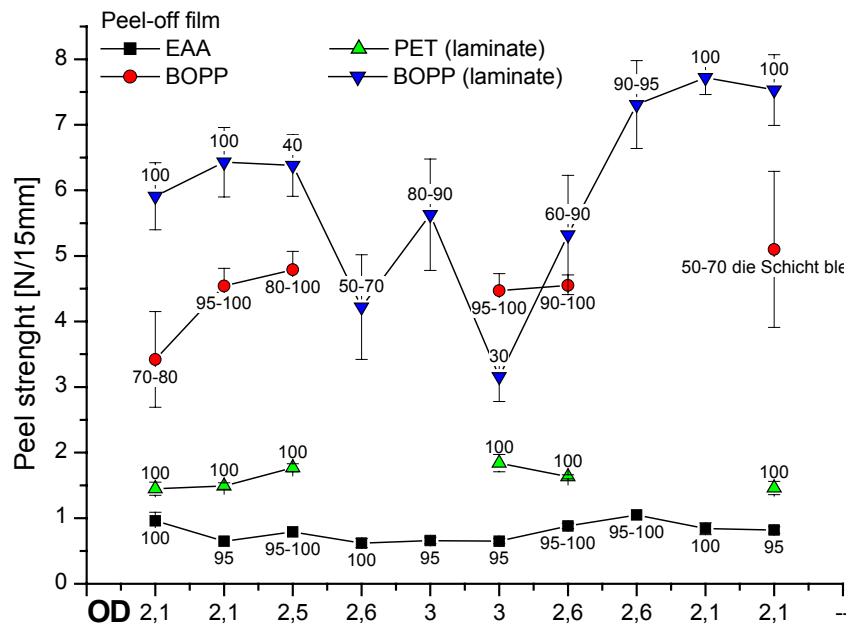


Figure 39: Adhesion (peel strength) measurement of Al coated BOPP films and laminates of the 9th test sequence, where the peeled off film was either the substrate film (BOPP) or the laminate film (EAA,PET) (identification of samples, see Figure 35)

The **adhesion measurements** were done at various conditions:

Coated films (for measurement sealed against EAA film)

- 1) Heat sealed EAA film peeled off
- 2) BOPP side peeled off

Laminated films

- 3) PET film peeled off the laminate PET/LDPE/metallized BOPP
- 4) BOPP side peeled off the laminate PET/LDPE/metallized BOPP

- 1) No clear impact on adhesion (EAA-peel off test) of wire feed rate and web speed could be found, as in almost every case at least 95% of the aluminium was peeled off from the BOPP film. Therefore the point of failure should be between the aluminium coating and the BOPP substrate. Typical adhesion values were all around 0.7-1 N/15mm.
- 2) In contrast to this, the peel strengths by peeling off the BOPP film were much higher and showed a tendency to increase with optical density (changing wire feed rate). Whereas the influence of different web speeds was not significant. The point of failure for the measurement condition seems to be the metal itself or the interface BOPP/Al.
- 3) Here again no clear impact of web speed and wire feed rate on adhesion could be seen. In every case all Al was removed from the BOPP films. Again the point of failure is located at the interface metal – BOPP. Adhesion values were around 1.5–1.8 N/15mm.
- 4) Peeling of the BOPP side of the PET/LDPE/metallized BOPP laminate point in the same direction as the cases stated above, as in most cases the amount of peeled off Al from the BOPP film was around 100%. Peel strength for these samples were remarkable high with values of 6-8 N/15mm.

As to be seen in Figure 40, the plasma pre-treatment of the non-plasma pre-treated BOPP films reduce the **OTR** for samples produced at different wire feed rate. At faster web speed, the impact of plasma pre-treatment on the OTR is no more significant. This can be led back to the reduction of effective pre-treatment power at higher web speeds.

Comparing the samples with the same OD produced at different web speeds and wire feed rates shows, that the lower OTR values are obtained at high web speeds and wire feed rates. Here, the higher evaporation rate repress the impact of the background pressure inside the vacuum web coater.

For **WVTR** no clear trend could be found, as the measurements varied strongly, as to be seen in Figure 41. Increasing web speed (wire feed rate unchanged) results in thinner Al-layers (lower OD) and worse WVTR.

As described above, the Al-coated BOPP films were extrusion laminated against LDPE/PET-films. For these laminates plasma pre-treatment lead to a reduction in OTR, as to be seen in Figure 42. Also the increase in wire feed rate tended to result in lower OTR. On the other hand higher web speeds produce lower optical densities (thinner films) and higher OTR.

Also for the laminates the influence of the different coating conditions on WVTR showed no obvious correlation, as to be seen in Figure 43.

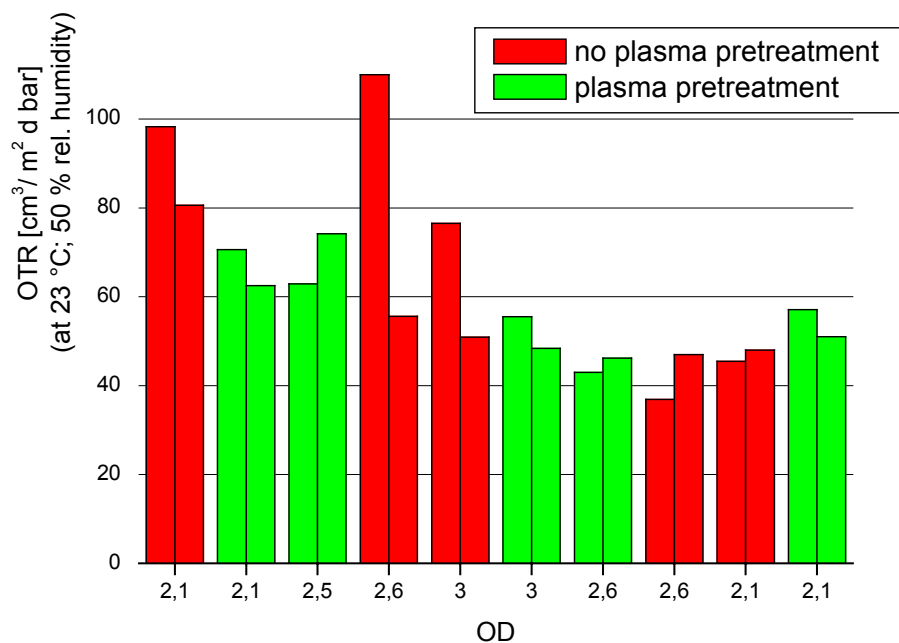


Figure 40: OTR through the different Al coated BOPP films of the 9th test sequence (identification of samples, see Figure 35)

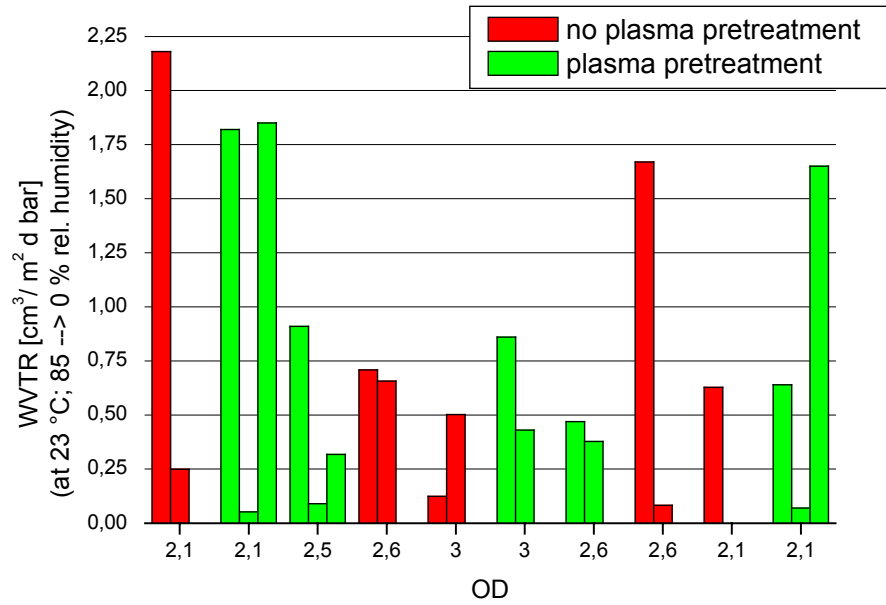


Figure 41: WVTR through the different Al coated BOPP films of the 9th test sequence (identification of samples, see Figure 35)

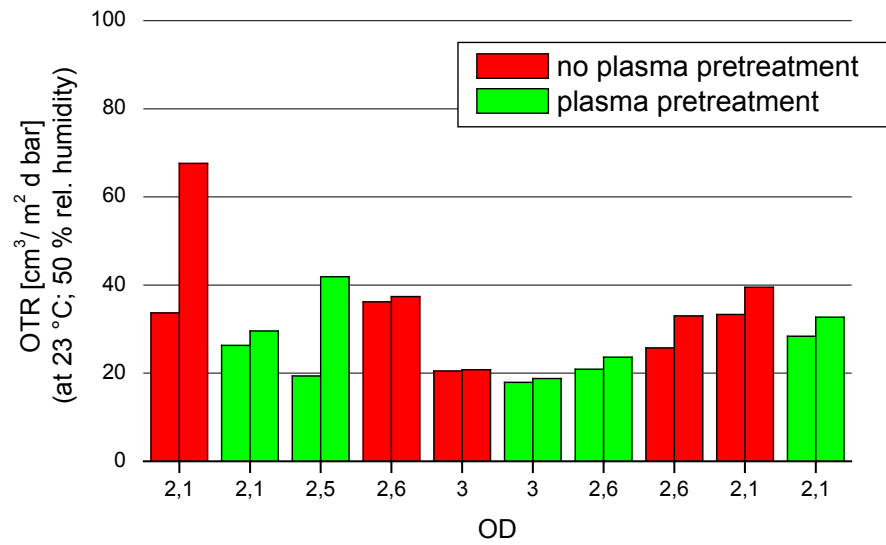


Figure 42: OTR through the different Al coated BOPP films extrusion laminated against PET films of the 9th test sequence (identification of samples, see Figure 35)

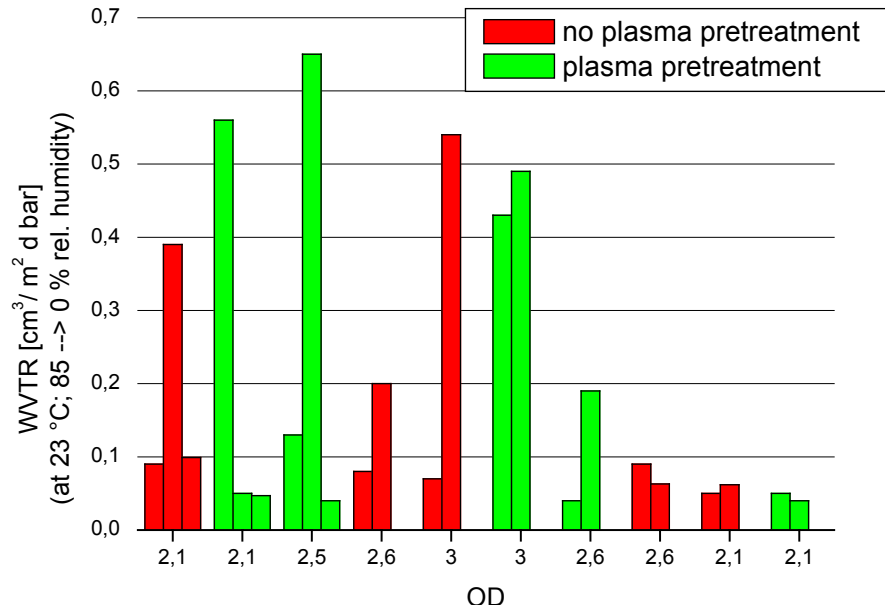


Figure 43: WVTR through the different Al coated BOPP films extrusion laminated against PET films of the 9th test sequence (identification of samples, see Figure 35)

Table 5: The following table summarizes the whole 9th test sequence:

	BOPP-AI			BOPP-AI/PE/PET (laminates)		
	Plasma pre-treatment	wire feed rate increase	web speed increase	Plasma pre-treatment	wire feed rate increase	web speed increase
Grain size	small or no increase	relative large increase	small or no increase			
Defects	large reduction	large reduction	relative large increase			
Adhesion	no trend	small increase	no change	small increase	small reduction	small increase
OTR	small or no reduction	relative large reduction	no change	relative large reduction	relative large reduction	relative large increase
WVTR	No clear trend; differences between several measurements exceed differences between samples					

Best obtained values overall were:

	BOPP/AI		BOPP/AI/PE/PET	
adhesion [N/15 mm]	OD: 2.1	5.1	OD: 2.1	7.7
OTR [cm ³ /m ² d bar]	OD: 2.6	37	OD: 2.5	18
WVTR [g/m ² d]	OD: 2.1	0.05	OD: 2.5	0.04

4 Permeation mechanism

Light holes in a Al layer can be pores for the permeation of molecules or consist of AlO_x. Then, they are still a permeation barrier. The light hole distribution of Al coated BOPP films were measured at a magnification of 200 by light microscopy. The final distribution is the average of 10 different samples with a measurement area of 98,800 μm².

The results for the different films are plotted in Figure 36 to Figure 45 and Table 1. The light holes can be reduced by plasma pre-treatment, increasing the web speed and the thickness of the coated layers. This correlates very well to the reduction of OTR by changing this coating parameters and demonstrates again, that the OTR is correlated to the light holes.

The OTR through the coated and laminated films containing an inorganic layer can be calculated in a **first order approach** by assuming:

- circle shaped defects,
- organic layers have no pores
- transmission rate Q through a vacuum coated film is given by

$$Q = Q_0 n \pi r_0^2 (1 + 1.18 d / r_0),$$

where r_0 : mean pore radius,
 d : thickness of the substrate film,
 n : density of pores per areas,
 Q_0 : transmission rate through substrate film without inorganic layer

- transmission rate Q through a vacuum coated and laminated film is given by

$$Q^{-1} \approx Q_1^{-1} + Q_2^{-1} + Q_3^{-1} =$$

$$= (Q_{01} n \pi r_{01}^2 (1 + 1.18 d_1/r_{01}))^{-1} + (Q_{02} n \pi r_{02}^2 (1 + 1.18 d_2/r_{02}))^{-1} + Q_{03}^{-1}$$

where r_0 : mean pore radius,
 d_1 : thickness of the substrate film,
 d_2 : thickness of the adhesive layer,
 n : density of pores per areas,
 Q_{01} : transmission rate through single substrate film
 Q_{02} : transmission rate through single adhesive layer
 Q_{03} : transmission rate through single lamination film

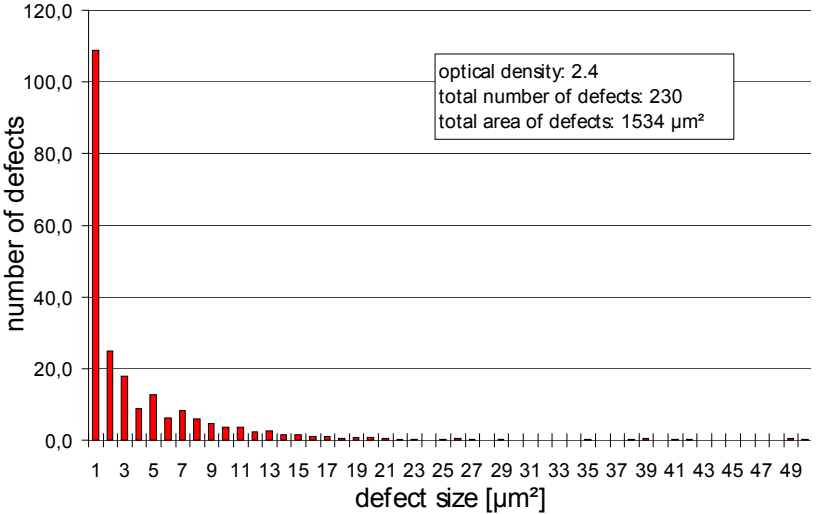
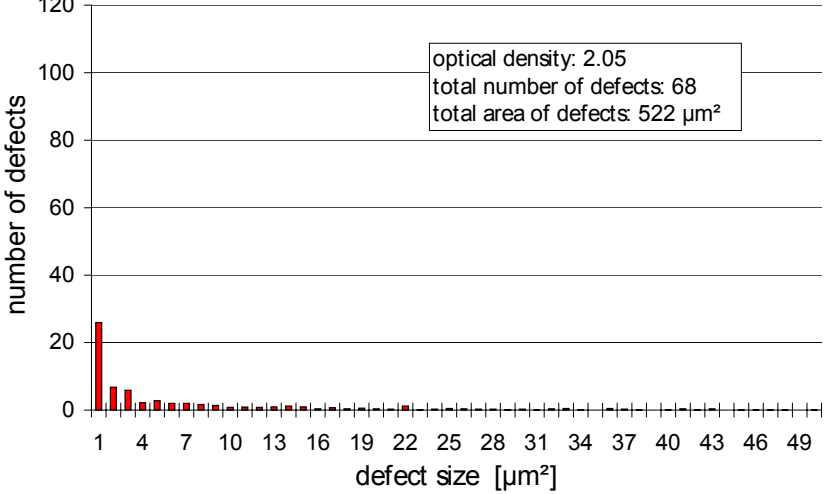
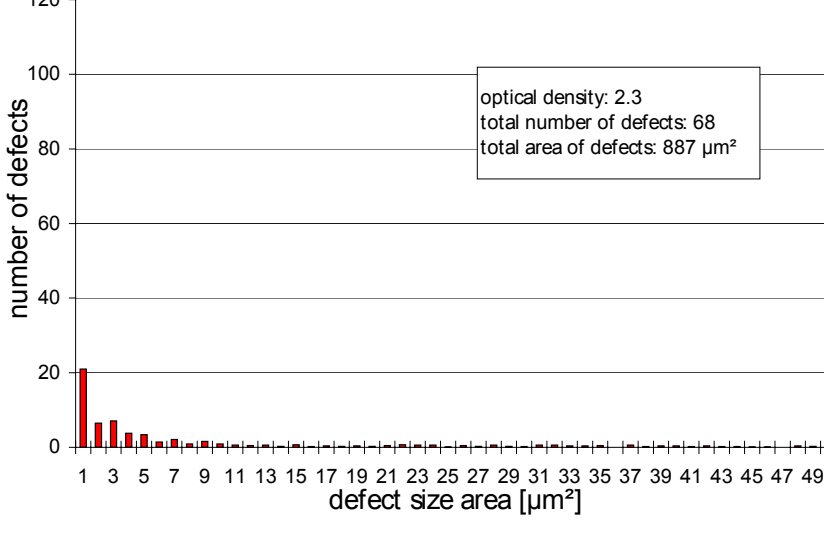
The calculated OTR for the coated and laminated films are listed in Table 7. The calculated value of coated film from the 8th sequence is about the measured value. For the lower OTR of the 1st sequence, there is difference of order 2 between the measured and calculated value. For the laminate, the calculation overestimated the OTR by a factor of 5. For the 9th test sequence, the calculated values are overestimating the OTR by a factor of up to 1.8.

These results indicate, that the light pores within an Al coater layer can be correlated to its OTR for high transmission rates. But the method must be refined.

The calculation overestimates the oxygen transmission rate for lower transmission rates. There, the small pores contribute proportionally more to the total transmission rates. The small pores with a surface area of 1 μm² have a radius of 0.56 μm, in the range of the wave length of the light. The light is diffracted at the small pores. The diffractions images are larger than the real pores and the pore sizes as well as the calculated transmission rates are overestimated.

But in spite of these limitations, the results indicate, that the light pores within an Al coater layer can be correlated to its OTR. But for a more precise prediction of the OTR, numeric simulation simulations must be applied.

Table 6: Analysis of light pores in Al coated films and laminated by light microscopy.

Data	Defect distribution
<p>BOPP-Al (8th test sequence)</p> <p>area of samples: 98800 μm^2 number of samples: 10 magnification: 200 measured OTR: 550 $\text{cm}^3/\text{m}^2 \text{ d bar}$</p>	 <p>optical density: 2.4 total number of defects: 230 total area of defects: 1534 μm^2</p>
<p>BOPP-Al (1st test sequence)</p> <p>area of samples: 98800 μm^2 number of samples: 10 magnification: 200</p> <p>measured OTR: 94 $\text{cm}^3/\text{m}^2 \text{ d bar}$</p>	 <p>optical density: 2.05 total number of defects: 68 total area of defects: 522 μm^2</p>
<p>BOPP-Al//PE (8th test sequence)</p> <p>area of samples: 98800 μm^2 number of samples: 10 magnification: 200</p> <p>measured OTR: 10,6 $\text{cm}^3/\text{m}^2 \text{ d bar}$</p>	 <p>optical density: 2.3 total number of defects: 68 total area of defects: 887 μm^2</p>

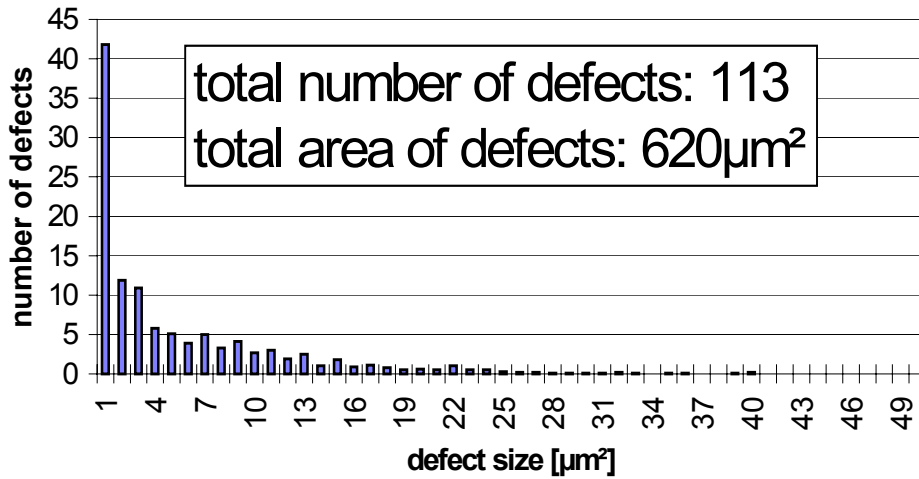


Figure 44: Analysis of light holes in Al coated on non-plasma pre-treated BOPP (Section 1) (identification of samples, see Figure 35)

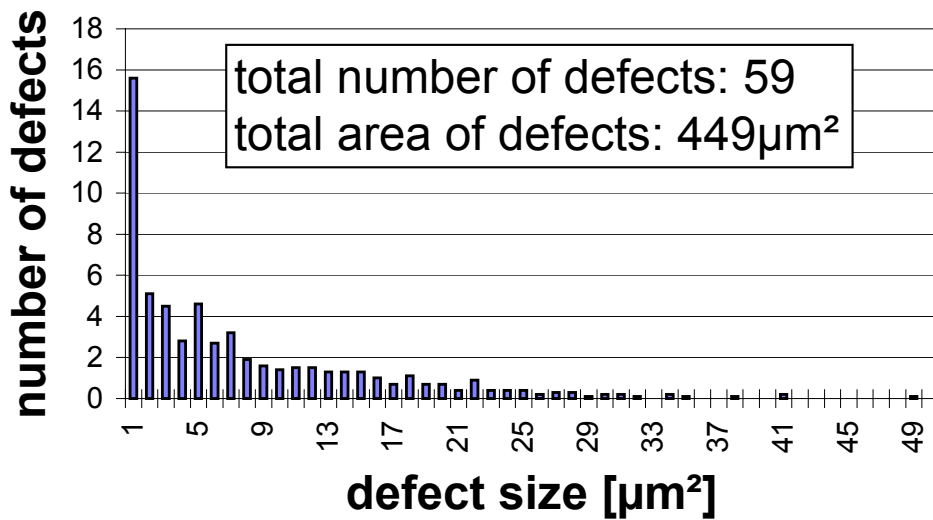


Figure 45: Analysis of light holes in Al coated on plasma pre-treated BOPP (Section 2) (identification of samples, see Figure 35)

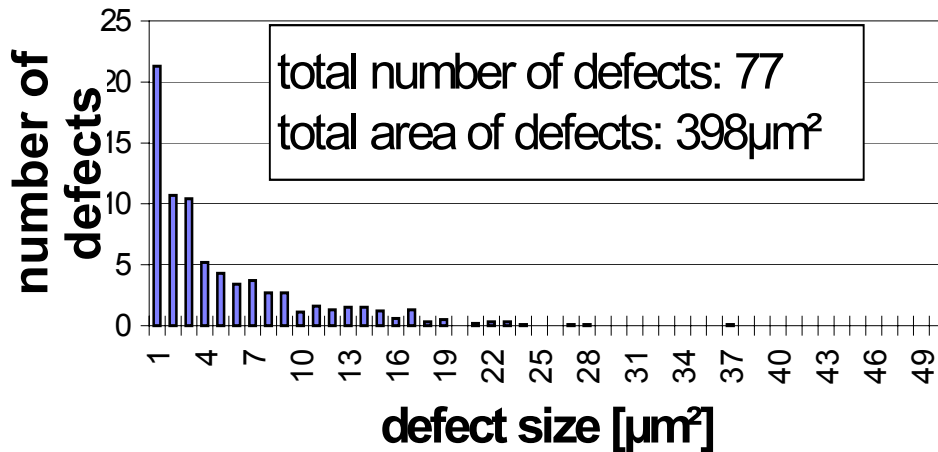


Figure 46: Analysis of light holes in Al coated on non-plasma pre-treated BOPP (Section 10) (identification of samples, see Figure 35)

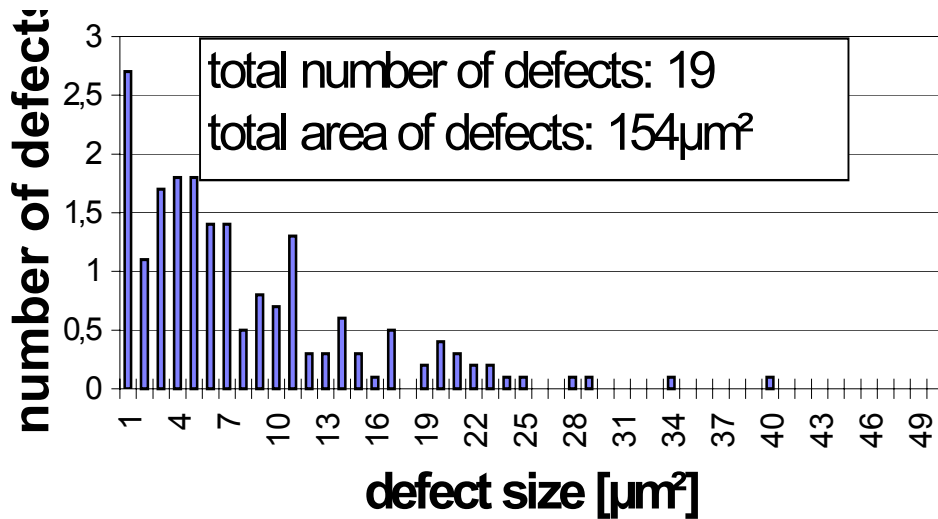


Figure 47: Analysis of light holes in Al coated on non-plasma pre-treated BOPP (Section 6) (identification of samples, see Figure 35)

Table 7: Comparison of measured and calculated OTR values

cm ³ /m ² d bar	calculated OTR	measured OTR
1st sequence (OD: 2.05)	183	94
8th sequence (OD: 2.4)	522	550
8th sequence (OD: 2.3; laminated film)	50	11
9th test sequence, sample 1	152	81 / 98
9th test sequence, sample 10	79	51 / 57
9th test sequence, sample 2	76	63 / 71
9th test sequence, sample 6	72	48 / 56

In order to correlate light pores, shape of the light pores more systematically to the OTR, the OTR were numerically simulated. The assumption for setting up the **numerical simulations** were:

- Because of the low solubility of oxygen in the BOPP films and no chemical reactions between the oxygen and the polymer, the permeation can be described by the 1st and 2nd Fick law.
- The diffusion coefficient is concentration independent.
- The defect distribution is homogenous. Hence periodic boundary conditions can be applied.
- There is no interaction between the different defects.

The concentration profile of an Al coated PET film (12 μm thickness) is shown for a 4 μm^2 large hole in the Al layer in Figure 48. At the Al coated side, the concentration decreases with the distance from the defect. Hence, most of the permeating molecules must pass the PET material at the defect. For industrial application, it can be concluded, that a thin layer of high barrier polymer material must increase the barrier of the total system drastically.

Close to the non-coated side, the concentration is almost homogenous, as expected for a polymer. For industrial application, it can be concluded, that as long as the total transmission rate is controlled by the defect, thickening the polymer films does not increase the barrier of the coated film.

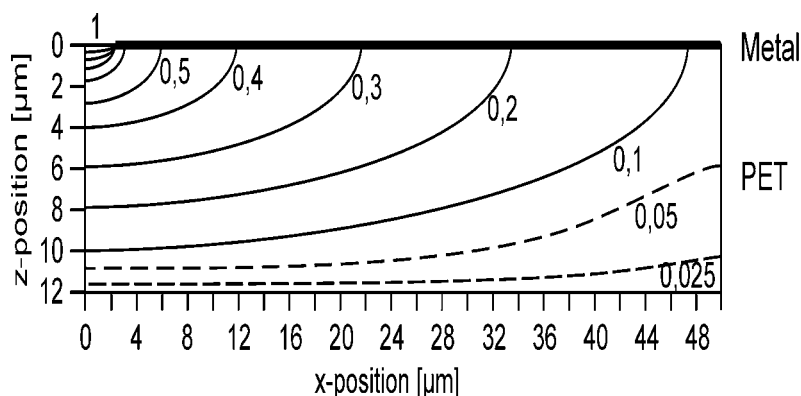


Figure 48: Concentration profile of an Al coated PET film (12 μm thickness) for a 4 μm^2 large hole in the Al layer

Numerical simulations were performed for the system above, where the film thickness, the defect sizes and distribution were varied. The results are plotted in Figure 49 and compared to the models of

- Prins/Hermans [PRINS, W.; HERMANS, J. J. Theory of permeation through metal coated polymer films. *J. Phys. Chem.* 63 (1959), S. 716-719], and
- Rossi/Nulman [ROSSI, G.; NULMAN, M. Effect of local flaws in polymeric permeation reducing barriers. *J. Appl. Phys.* 74 9 (1993), S. 5471-5475].

As expected, the OTR increases with the defect size, plotted as coefficient of defect area to total film surface. The simulated values differ from values of the two models by less than 15 %. Both models assume no interaction between the defects. Because of the good correlation between the here simulated and the literature values, it can be assumed, that there is no interaction between the different defects.

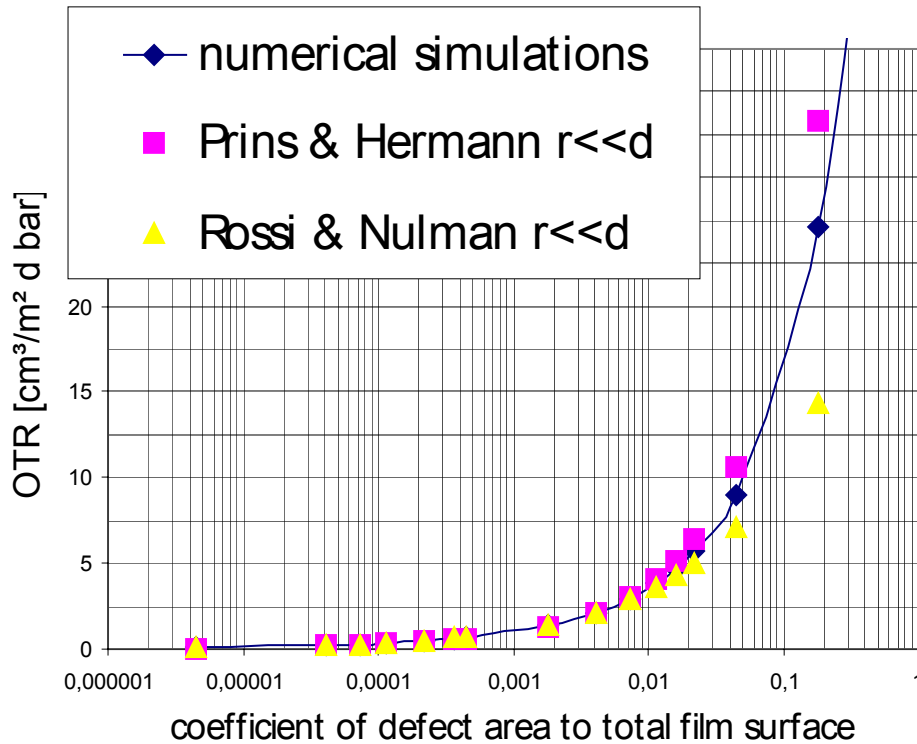


Figure 49: Calculation of OTR through an Al coated PET film (12 μm thickness)

The defect distribution of an Al coated BOPP film from the 1st test sequence analysed by light microscopy, as to be seen in Table 6, was used for numerical simulating the OTR. The calculated value is $100 \text{ cm}^3/\text{m}^2 \text{ d bar}$ and very close to the measured OTR of $94 \text{ cm}^3/\text{m}^2 \text{ d bar}$. The OTR calculated by numerical simulation is much closer to the measured value than the value calculated by the first order approach (Table 7).

This result demonstrates, that the numeric simulations can be a useful tool for the quantification of OTR and for the identification of the water vapour permeation mechanism.

One major task of the network consists in identifying and quantifying the permeation mechanism of oxygen and water vapour through polymer films containing an inorganic barrier layer. All the results of the different test sequences and the input of the project partners are the base for the following model:

The oxygen permeation through vacuum web coated barrier layers, like Al, AlO_x and SiO_x , predominantly occurs at macroscopic defects in the range of $0,5 \mu\text{m}$. There is practically no permeation through the bulk material of the layers.

There is another mechanism for the permeation of water vapour through the barrier layers due to non-linear effects, mainly generated by high solubility/condensation of substances that can be really condensed in capillaries. Capillaries can form at microscopic defects and grain boundaries. In contrast to oxygen permeation dominated by the macroscopic defects in the barrier layer, the permeation of water vapour and aroma substances depends also on the microstructure of the layer.

For **oxygen**, the macroscopic defects in the vacuum coated barrier layers are the bottleneck for permeating molecules. Due to the sideways diffusion to and from the bottlenecks in the polymer layers (substrate film or adhesive) next to the barrier layer, the polymer close to the defects influences the total permeability much stronger than at the outsides of the laminate. Hence, many small holes in a

barrier layer are much more efficient in compromising the system's barrier properties than a few large holes with the same total area.

Due to capillary effects in the barrier layer, **water vapour** can also permeate at microscopic defects and maybe grain boundaries. A higher density of these diffusion channels reduces the impact of the sideways diffusion in the polymer layers next to the barrier layer. There is a lower synergy in permeation barrier between the barrier layer and the attached polymer for water vapour than for oxygen. There are different permeation mechanism for the different permeating substances. Different weights are observed for the synergetic effect between the barrier layer and the polymer layers next to it.

Comparing the improvement factors from the vacuum web coating step and the final lamination process, it follows, that

- for **oxygen**, the vacuum web coating and the lamination step show highest improvement effects in the same order of magnitude, and
- for **water vapour**, the barrier is extremely dependent on the structure of the vacuum web coated layers in combination with the lamination step.

In terms of a quantitative prediction, the mechanism of the oxygen permeation is well understood, but not for water vapour and especially for the aroma permeability, where we still need a lot of systematic investigations.

5 Discussion of project work

Before starting the Thematic Network, 14 of the 29 project partners had performed pre-competitive research in the field of vacuum web coating of BOPP films on industrial scale between 1996 and 1998, in a project was funded by the Bavarian government. Because of the good experience in collaborating with the different companies involved in the process chain of vacuum web coated barrier films, these companies joined the proposal for the Thematic network submitted to the European commission.

The target of the partners for continuing their collaboration and doubling the number of partners was to create a wider platform that covers the whole production chain. Based on the platform, the different companies intended to realize their role in the production chain and how developments within the own company can lead to better quality of the final products and cost reduction. They wanted also to identify new fields of application for their products, especially outside the packaging market.

The project proposal of the Thematic network was based on the results obtained in the pre-project by the 14 project partners. There, the best barrier films and laminates were produced by using polymer films produced on lab scale. For the Thematic Network, these values were taken as a basis to define quantitative milestones. Values for oxygen and water vapor transmittance and for adhesion (peel strength) were extrapolated from the previous research and set as milestones for the industrial research that is accompanying the network activities.

In this procedure, however, the problems for achieving those figures in industrial environment were underestimated. Also for some test sequences only pilot plants could be used, that were not best optimised to the whole production chain. The new partners in the Thematic Network started from different technical background and the total number of partners involved was larger. Therefore, the previous figures could still not be achieved. This clearly demonstrates the need for the network partners to proceed in the development activities and to increased the functionality of their products and the capacity of their processes.

For reaching the ambitious target values of the project proposal, the hand-shakes between the different companies in the production chain must still be improved. This work can either be performed by

companies having integrated all production steps (like Mobil Plastics, USA, or Toray Films, Japan and USA), or by a network of companies. Only if all production steps are adapted to each other, the proposed target values can be obtained. However the adhesion, peel strength, OTR and WVTR values of the industrial coated and laminated films easily fulfil the present specifications of the industry, as proposed by the European Metallizer's Association, as to be seen in Table 8 and Table 10.

Conclusively, the planned objectives for performing industrial pre-competitive research together with competitive companies are reached in terms of

- creating a research platform,
- performing and evaluating 9 industrial test sequences,
- increasing the knowledge of the participants, especially in the field of permeation mechanism and adhesion measurement,
- standardizing of measurement technique,
- producing intermediate and final products that exceed industrial the requirements of the European Metallizer's Association, and
- identifying critical points as starting points of new research activities.

The totally achieving of the proposed values would have rounded off the performed project work.

Table 8: Comparison of **adhesion and peel strength** [N/15mm] of the achieved values to the specification of the European Metallizer's Association, the best results of the pre-project and to the target figures for the Thematic Network

Adhesion [N/15mm]	EMA	Best results in pre-project	Proposed target figures for the Thematic Network	Reached by the Project Group	Method
BOPP/Al EAA peel strength	resistant to tape test	1.4	0.8	2.7	Copo, Corona, boat OD 2.7, 1 st sequence
PET/Al EAA peel strength	resistant to tape test	not investigated	0.8	0.6	plasma, e-beam OD 2.3, 4 th sequence
BOPP/Al//BOPP laminare strength	no specification	2	0.8	4.8	Copo, Corona, boat OD 2.0, 1 st sequence
PET/Al//PE laminare strength	no specification	not investigated	0.8	1.6	plasma, boat OD 1.5, extrusion, 7 th sequence

Table 9: Comparison of **OTR values** [cm³/m² d bar] of the achieved values to the specification of the European Metallizer's Association, the best results of the pre-project and to the target figures for the Thematic Network

OTR [cm³/m² d bar]	EMA	Best results in pre-project	Proposed target figures for the Thematic Network	Reached by the Project Group	Method
BOPP/Al	< 200	15	20	9.8	homo, plasma, boat OD 2.5, 2 nd sequence
PET/Al	< 1	not investigated	0.2	0.71	Corona, boat OD 2.0, 4 th sequence
BOPP/Al//BOPP	no specification	4	10	4.7	copo Corona, SiO _x adhesive, 3 rd sequence
PET/Al//PE	no specification	not investigated	0.1	0.1	plasma, boat OD 3.5, 7 th sequence

Table 10: Comparison of **WVTR values** [g/m² d] of the achieved values to the specification of the European Metallizer's Association, the best results of the pre-project and to the target figures for the Thematic Network

WVTR [g/m² d]	EMA	Best results in pre-project	Proposed target figures for the Thematic Network	Reached by the Project Group	Method
BOPP/Al	< 0.4	0.03	0.03	0.03	homo, plasma, boat OD 2.5, 2 nd sequence
PET/Al	< 1	not investigated	0.4	0.16	plasma, boat OD 3.5, 7 th sequence
BOPP/Al//BOPP	no specification	0.08	0.01	0.04	copo Corona, SiO _x adhesive, 3 rd sequence
PET/Al//PE	no specification	not investigated	0.1	0.08	plasma, boat OD 3.5, extrusion, 7 th sequence

6 Conclusions

Despite the fact, that world wide are 15.000.000.000 m² of films metallized per year, there are still a lot of not well-known parameters for obtaining continuously high barrier films

6.1 Adhesion measurement

Peel strength measurements performed at different conditions can only be compared, if there is the same point of failure (impact of peel-off angle and EAA film). This is the starting point of the first correlation between the EAA peel strength of Al layers on films and laminate strength.

6.2 Layer analysis

The grain size distribution of deposited Al layers can be measured simply by AFM.

E-beam evaporation produces here smaller crystals than boat evaporation.

The defect distribution of the vacuum coated layers can be correlated to the barrier properties in a first order approximation. More systematic correlation between light pores, shape of the light pores and barrier properties of deposited layers must be revealed by the numeric simulation of the transmission rates and a better resolution in defect size measurements

6.3 Permeation through laminates containing vacuum web deposited barrier layers

The theoretical models of the oxygen permeation mechanism can be applied in a way, that

- the defect distribution of the vacuum coated layers can be correlated to the barrier properties for high transmission rates by a first order calculation, and
- more systematic correlation between light pores, shape of the light pores and barrier properties of coated layers could be revealed by the numeric simulation of the OTR.

The barrier results mainly form a synergetic effect between

- barrier layers (Al, SiO_x, AlO_x) and
- polymer layers next to it (substrate, adhesive).

The permeation mechanism of **oxygen** is determined by

- the density and type of macroscopic defects (bottlenecks) in the barrier layer and
- the polymer material at the defects.

Work hypothesis for the non-linear permeation mechanism of **water vapor**

- microscopic defects (defects in layer, grain boundaries)
- capillary effects

The barrier of Al layers is produced by oxidation of the boundary layers

The following production parameter are important for achieving high oxygen barriers:

- plasma pretreatment
- thick Al layers
- high evaporation rates and web speeds
- barrier adhesive lamination

The following production parameter are important for achieving high water vapour barriers:

- plasma pretreatment, thick Al layers

- extrusion lamination (in optimal conditions)
- high barrier adhesive lamination

Here, some processes seems to be better than other. But important for the final customers are the desired product properties more important than differences in the processes. Best barrier values can be obtained, if every point in the production chain is optimised in regard to the total chain.

The pre-competitive research activities in this project performed on industrial pilot and production equipment focus on revealing correlations between process parameters and product properties. Therefore, the process conditions used in the experiments had to be different to the proprietary conditions which would normally be used in commercial production. In consequence, the product properties achieved are not necessarily representative of the best achievable after process optimisation. But the project partners uses the revealed correlations for the optimisation of their products. The best process combination can only reach best results after process optimisation, depending on the know-how and skills of the different companies.

6.4 Project structure

The project structure is useful to study the complex influence of all processing steps on the final product properties, under industrial conditions. The identification of critical points leads to new R&D projects. In vacuum web coating, there are many basic technical problems that can be evaluated on industrial scale, on a pre-competitive basis

Research together with competitors can be successful, if performed on pre-competitive level in the fields of

- standardization,
- identification and quantification of basic mechanisms

7 Glossary

AFM	atomic force microscopy
BOPP	biaxially oriented polypropylene
copo	copolymer
e-gun	Electron beam gun
homo	homopolymer
OD	optical density
OTR	oxygen transmission rate through films or laminates
PE	polyethylene
PET	polyethylene terephthalate
PUR	polyurethane adhesive
SEM	scanning electron microscopy
TEM	transmission electron microscopy
terpo	terpolymer
WVTR	water vapour transmission rate through films or laminates
XRF	X-ray fluorescence

8 Acknowledgments

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