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Process Transfer of PECVD Gas Barrier Coatings Between PE-HD and PP Hollow Bodies

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Process Transfer of PECVD Gas Barrier Coatings Between PE-HD and PP Hollow Bodies

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Abstract: This study investigates the plasma enhanced chemical vapor deposition (PECVD) coating process transfer between PE and PP substrates. An inverse relationship is observed between the barrier improvement factor (BIF) and applied energy density (E), with PE showing a stronger response. The same process gas ratio optimizes both materials, suggesting geometry influences the barrier effect more than material. However, the barrier on PP is limited, indicating poorer compatibility to functionalization. The development of the intermediate layer did not improve the barrier performance. FESEM analyses and scratch tests suggest material damage during coating application. Further research is needed to optimize the coating process.

Keywords: PECVD, Barrier Coating, Substrate Influence, FESEM, OTR, Energy Density

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Introduction

In the realm of surface technology, Plasma Enhanced Chemical Vapor Deposition (PECVD) coatings have emerged as a promising solution for creating completely recyclable and highly functional barrier packaging [1,2]. The flexibility of the PECVD process with regard to the coating chemistry is one of its most significant advantages. However, to harness this potential, it is imperative to understand the coating-substrate interface, especially when different substrate materials are involved. This understanding is crucial as it directly influences the coatability of the substrate material.

In light of this, coating systems are often designed with at least two layers: a functional barrier layer and an interface layer. The interface layer serves as a bridge between the functional coating and the substrate, with its chemistry tuned to form covalent bonds with both the substrate and the barrier. This paper presents a study that investigates the influence of both layers on the coatability of two polyolefinic materials, namely polypropylene (PP) and polyethylene (PE). The substrates were bottles with a volume of 125 ml. Geometry was identical for both materials. A definitive screening design (DSD) was implemented for both layers, incorporating six parameters: power, pulse on time, pulse off time, precursor and oxygen gas flow, and process pressure.

The findings from this study provide valuable insights into the PECVD process and its application in the development of recyclable and functional barrier packaging. They also contribute to a broader understanding of the interaction between coating systems and substrate materials, paving the way for further advancements in this field.

Methods and Materials

Reactor for the Inner Coating of Hollow Bodies

The concept of internal coating of hollow bodies by means of microwave ignited PECVD was first presented by IKV [3]. In the case of this study, four magnetrons (Muegge GmbH, Reichelsheim) generate microwaves with a peak power of 1000 W, each of which is fed into the reactor via concentrically arranged and slotted waveguides. Process gases are fed into the hollow body through a gas lance made of polytetrafluoroethylene (PTFE) and also dosed by means of a mass flow controller (MKS Instruments Deutschland GmbH, Munich).

Energy Density Parameter

Different descriptions have been proposed [4,5] to assess the energy introduced into the coating process. An equation (equation 1) that specifically describes pulsed microwave processes has been formulated by Hegemann [6].

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$$\varepsilon = \frac{P \cdot \frac{t_{on}}{t_{on} + t_{off}}}{F_P + r_{gas} F_A}$$

Power (P) is multiplied by the duty cycle, which describes the ratio of the pulse on time (t_{on}) to a whole pulse duration ($t_{on} + t_{off}$). The averaged power is divided by the corrected gas flow, which consists of the precursor flow (F_P) and the auxiliary gas flow (F_A) multiplied by the gas correction factor (r_{gas}). The gas correction factor has been empirically derived by Hegemann and accounts for the partial fragmentation and integration of the auxiliary gas (here oxygen) into the coating [7].

Oxygen Transmission Rate (OTR)

An O_2-permeability tester (M8700, Systech Instruments Ltd., Thame, UK) was used to measure the OTR. All measurements were carried out at a constant temperature and relative humidity (23.0 ± 0.1°C), in accordance with DIN 53380-3 and ASTM D3985. At least two samples were tested for each test point.

FESEM

A Sigma HD VP type Field Emission Scanning Electron Microscope (FESEM) from Carl Zeiss Microscopy GmbH, Jena, Germany, was used to observe the surface topography. The electron beam was generated by a Schottky field emission cathode and has a diameter of a few nanometers, thus achieving high focusing.

Coating Development and Process Parameters

Two separate coating developments were conducted iteratively for the development of the dual layer (barrier/intermediate layer) coating. First, the barrier layer was subjected to parameter variation while the intermediate layer was held constant. The statistical analysis of the parameter-barrier relationship was assessed and parameters for improved barrier performance derived. Next, the barrier layer was held constant while the intermediate layer was developed in order to achieve improved barrier-substrate bonding. The coating developments were conducted using a definitive screening design (DSD). Process parameters are varied on three levels, which are given in Tables 1 and 2. Further information about the utilization of DSD for the development of PECVD coatings can be obtained elsewhere [8].

The hypothesis for the role of the intermediate layer in enhancing the coating-barrier interface is twofold. Firstly, the chemical bond of the highly polar SiO_x-coating to unpolar plastic substrates is bridged by a silicon organic SiOCH-coating that has organic and inorganic functional groups. Secondly, oxygen ion bombardment during application of the SiO_x layer can cause degradation of the

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substrate due to the surplus energy from the process. A thin SiOCH layer can be utilised to absorb the surplus energy by the oxidization process during oxygen ion bombardment [9].

Table 1. Process parameter space for the barrier layer development.

Level	Power [W]	Pulse on time [ms]	Pulse off time [ms]	Oxygen flow [sccm]	HMDSO flow [sccm]	Pressure [Pa]
1	800	6	80	100	3	10
2	900	8	100	200	4	15
3	1000	10	120	300	5	20
Optimized	800	10	80	237	3.5	10

Table 2. Process parameter space for the intermediate layer development.

Level	Power [W]	Pulse on time [ms]	Pulse off time [ms]	Oxygen flow [sccm]	HMDSO flow [sccm]	Pressure [Pa]
1	750	2	80	-	5	30
2	850	3	100	-	10	33
3	950	4	120	-	15	36

Results and Discussion

The results of the coating development are assessed by analyzing the barrier performance and evaluated by FESEM analysis in the following section.

Influence of the Energy Density on Barrier Performance

The first iteration of the coating development focuses on the barrier layer. The barrier improvement factor (BIF, $OTR_{uncoated}/OTR_{coated}$) is plotted over the applied energy density (E) in J/cm³ in Figure 1. Uncoated OTR values are 0.2036 $\frac{cm^3\,(std)}{bottle\,\times\,day}$ for PE and 0.1172 $\frac{cm^3\,(std)}{bottle\,\times\,day}$ for PP. During development of the barrier layer the intermediate layer has been constantly kept at parameters displayed for level 2 in Table 2. It is striking that an inverse relationship can be observed between the two variables, indicating that BIF decreases as energy density increases. Regarding the influence of the substrate material, a more pronounced response by PE is observed compared to PP. The higher structural integrity under thermal load or ion bombardment of PE can be posited as a hypothesis for this behavior. A similar increase of the BIF for PP at lower energy densities is conceivable. It should be mentioned, however, that energy density levels cannot be decreased indefinitely in order to sustain high cross linking levels for the SiO_x coating.

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It should be emphasized that the statistical analysis of the test plans for both materials shows that the parameters HMDSO and oxygen flow are significant. In addition, the same process gas ratio (3.5 sccm HMDSO and 237 sccm oxygen) is identified as the local optimum for both materials. This is an interesting observation, as the barrier effect seems to be determined more by the geometry than by the material. The BIF values are of course significantly higher for PE due to the higher OTR values in the uncoated state. The trend in connection with energy densities is less pronounced for PP. In conclusion, the barrier layer appears to reach an optimum under the same conditions, but the absolute functionality of PP is clearly limited in direct comparison. Consequently, the PP shows poorer coatability under the same process conditions. The intermediate layer was therefore subsequently subjected to a development.

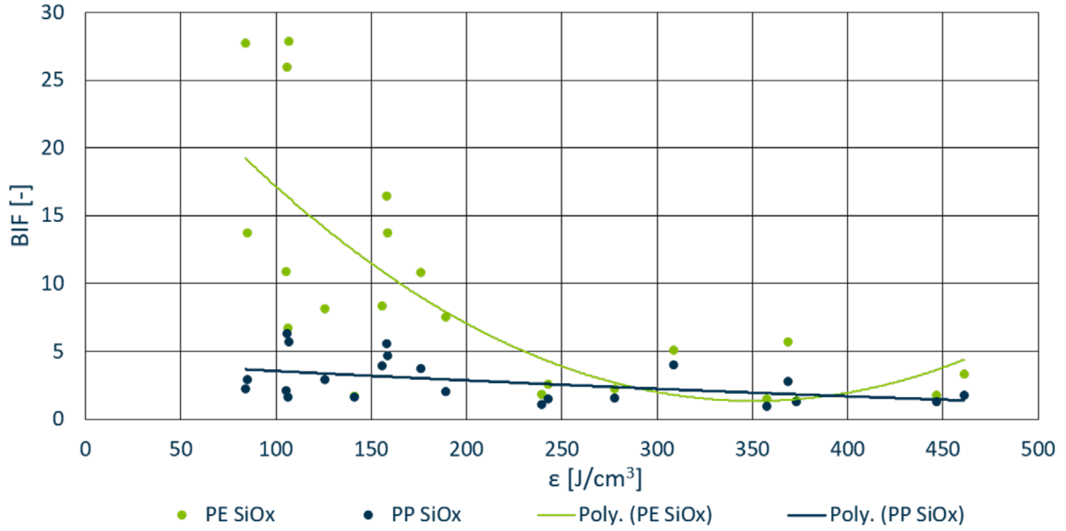

Figure 1. Barrier improvement factor over energy density (Barrier layer).

For the development of the intermediate layer the barrier layer has been kept constantly kept at the derived parameters from the first iteration displayed in the last line of Table 1. In direct comparison to the development of the barrier layer, the development of the intermediate layer shows no further improvement to the previously best barrier performance (Figure 2).

Therefore, the initial hypothesis of the protective function of the intermediate layer during the application of the barrier layer could not be confirmed. The discussed process window might not have been sufficient, since a protective layer should be applied that combines a thin and homogeneous cover of the whole sample surface. Further research should be conducted to clarify the cause for this observation.

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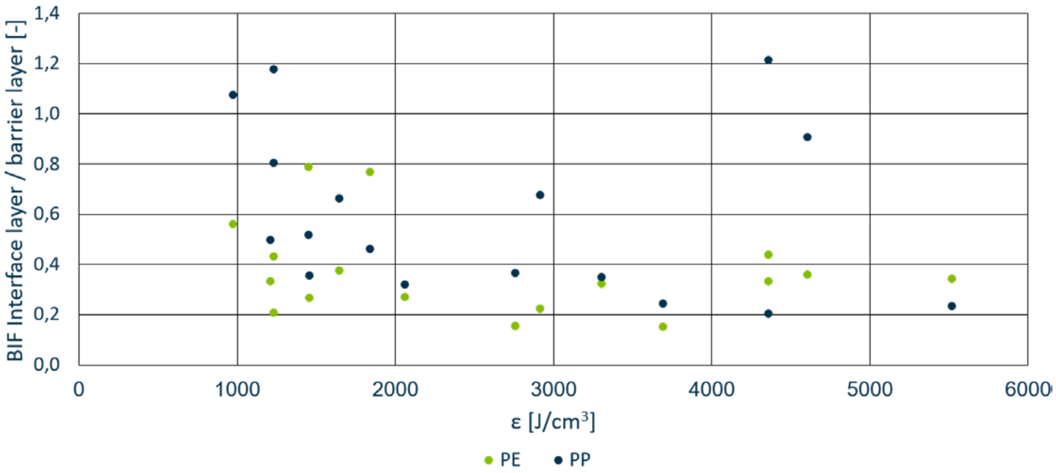

Figure 2. Barrier improvement factor over energy density (Intermediate layer).

Field Emission Scanning Electron Microscopy

FESEM analyses have been carried out to understand how the significantly lower barrier function of coated PP in comparison to PE came about. Representative images are presented in Figure 3. Before coating, both surfaces appeared very smooth. PE had some deformations that indicate cold deformations during production. The surface structure of coated PE appears very smooth while a noticeable deformation of the surface structure is observed for PP. This deformation appears to be a combination of wrinkles in the plastic and a droplet-like pattern. The droplets could be a sign of local delamination. A similar error pattern can be observed in etching experiments [10]. Delamination can be a sign for degradation of the substrate material. The direct comparison illustrates a strong indication of material damage as the cause of the inhibited coatability of PP.

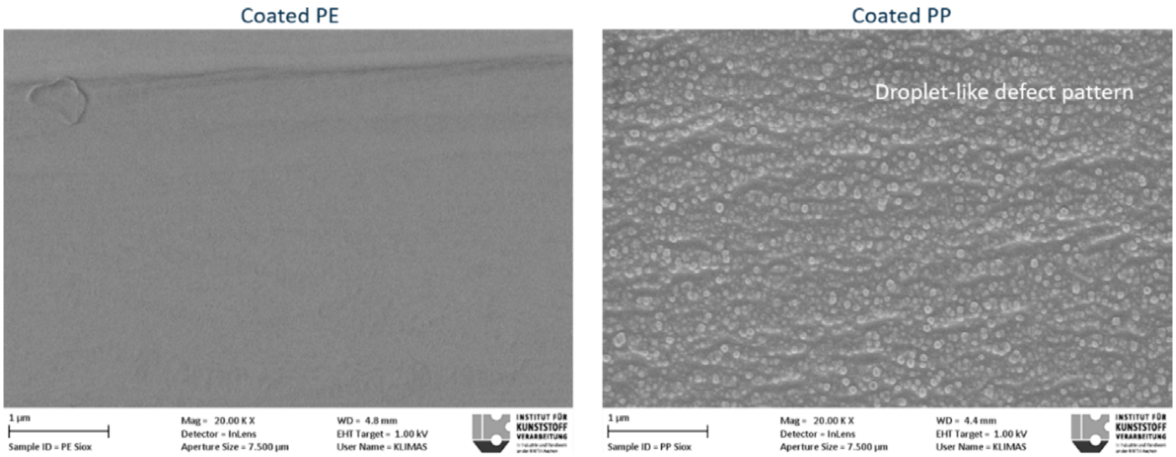

Figure 3. Comparison of coated PE and PP (SiOCH/SiOx).

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In order to further clarify the cause for the damage pattern, scratch tests have been conducted. The images can be observed in Figure 4. Coated samples have been scratched with a scalpel in order to visualise a mechanical damaging of the coatings on both materials. For PE, a very sharp edge can be observed that represents the scalpel incision very well. The surrounding coating surface is interspersed with fine, close-meshed cracks, which indicate a high degree of brittleness and strong adhesive bonding to the substrate. For PP, the coating seems much more loosely bonded to the substrate and delamination occurs far beyond the edge of the incision. The chemical bond seems to be inhibited by the degraded material. In conclusion, the inhibited coatability of PP seems to be closely linked to the damage of the substrate surface as a result of temperature load and ion bombardment.

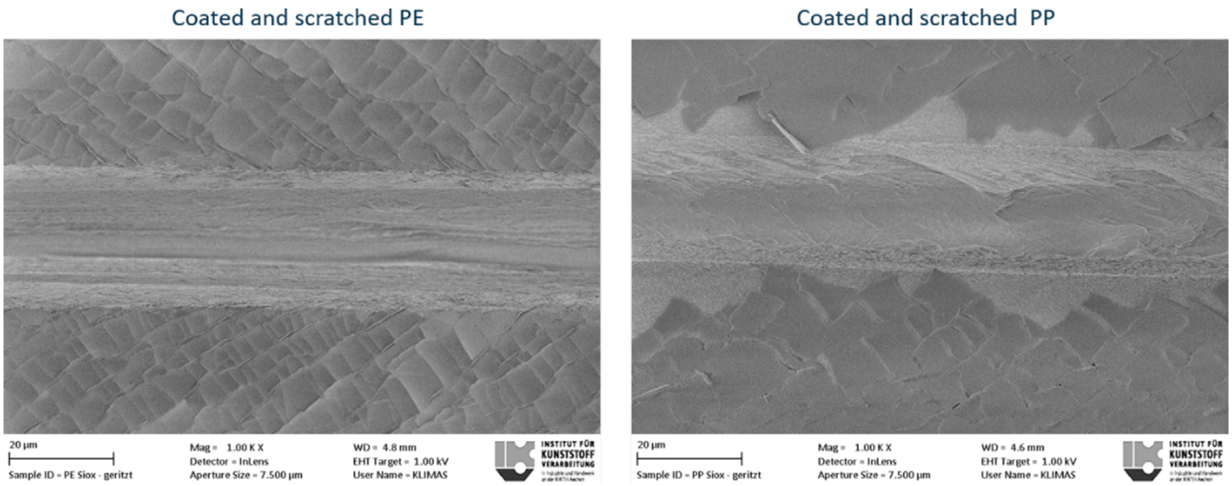

Figure 4. Investigation of scratched coatings on PE and PP.

Conclusion

The process transfer of PECVD coatings between different substrate materials, specifically PE and PP, reveals significant differences in their response to the coating process. The BIF shows an inverse relationship with the applied energy density, with PE demonstrating a more pronounced response compared to PP. This could be attributed to PE's higher structural integrity under thermal load or ion bombardment. Interestingly, the same process gas ratio is identified as the local optimum for both materials, suggesting that the barrier effect is influenced more by the geometry than by the material itself. However, the absolute functionality of PP is limited in comparison to PE, indicating poorer coatability under the same process conditions.

The development of the intermediate layer did not result in further improvement to the barrier performance, contradicting the initial hypothesis of its protective function during the application of the barrier layer. This calls for further research of the hypothesis. FESEM analyses and scratch tests provide strong indications of material damage during coating application as a cause for the inhibited coatability of PP. The surface structure of coated PP shows noticeable deformation, which could be a sign of substrate material degradation.

In conclusion, the inhibited coatability of PP seems to be tightly linked to the damage of the substrate surface as a result of temperature load and ion bombardment. Further research is needed to fully understand these observations and to optimize the coating process for different substrate materials.

References

1. H. Yasuda and Y. Matsuzawa, “Economical Advantages of Low-Pressure Plasma Polymerization Coating,” *Plasma Processes and Polymers*, vol. 2, no. 6, pp. 507–512, 2005.
2. L. Kleines, T. Blasius, and R. Dahlmann, “PECVD barrier coating systems on post-consumer recyclates for food contact applications,” *Surface Engineering*, vol. 38, 10-12, pp. 968–976, 2022, https://doi.org/10.1080/02670844.2023.2181258
3. P. Plein, “Method of coating hollow bodies” DE 3632748 C2.
4. R. Hippler, Ed. *Low temperature plasma physics: Fundamental aspects and applications,* 1st ed. Berlin, Weinheim: Wiley-VCH, 2001.
5. H. Yasuda, “Plasma polymerization for protective coatings and composite membranes,” *Journal of Membrane Science*, vol. 18, pp. 273–284, 1984, https://doi.org/10.1016/S0376-7388(00)85039-5
6. D. Hegemann, “Plasma Polymer Deposition and Coatings on Polymers,” in *Comprehensive Materials Processing*: Elsevier, 2014, pp. 201–228.
7. D. Hegemann and M.-M. Hossain, “Influence of Non-Polymerizable Gases Added During Plasma Polymerization,” *Plasma Processes and Polymers*, vol. 2, no. 7, pp. 554–562, 2005, https://doi.org/10.1002/ppap.200500041
8. P. Alizadeh, S. Wilski, and R. Dahlmann, “Definitive screening design for the development of alkali resistant PECVD coatings for returnable PET bottles,” *Progress in Organic Coatings*, vol. 172, p. 107064, 2022, https://doi.org/10.1016/j.porgcoat.2022.107064
9. T. d. l. Arcos et al., “PECVD and PEALD on polymer substrates (Part II): Understanding and tuning of barrier and membrane properties of thin films,” 2023.
10. S. Wilski et al., “Mechanisms of oxygen permeation through plastic films and barrier coatings,” *Journal of Physics D: Applied Physics*, vol. 50, no. 42, p. 425301, 2017, https://doi.org/10.1088/1361-6463/aa8525

DOI: https://doi.org/10.51573/Andes.PPS39.GS.NN.2