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Investigation and Comparison of Alternative Oxygen Barrier Coatings for Flexible PP Films as Food Packaging Material

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Abstract: One of the EU's ambitious goals is to ensure all plastic packaging is reusable or recyclable by 2030. However, achieving higher recycling rates, particularly in flexible multilayer food packaging, is challenging due to the combination of diverse materials. This highlights the importance of designing for recyclability and exploring alternative barrier solutions. In this study, several types of coatings, such as ORMOCER® (Fraunhofer-ISC, Würzburg, Germany) Michem® Flex B3513 (Michelman International Belgium SRL, Aubange, Belgium), and PVOH (Kuraray Europe GmbH, Frankfurt am Main, Germany), are applied on different polypropylene substrates, including cast PP (CPP70), SiOx, and AlOx-coated PP films. The effect of double coating and optimized curing conditions of ORMOCER® on the oxygen permeability of CPP70 was also investigated. The results showed significant improvements in the barrier properties of PP/SiOx and OPP/AlOx films, and OTR values less than 0.1 $cm^3/m^2 \cdot d \cdot bar$ were achieved. It was also found that ORMOCER® and Michem® Flex B3513 could enhance the oxygen barrier property of CPP70 and the OTR value reduced by a factor of 88 and 551, respectively.

Keywords: barrier coatings; ORMOCER®; inorganic–organic hybrid polymers; SiOx; AlOx; BOPP coating; PVOH; flexible packaging; OTR

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1. Introduction

Plastic is one of the most attractive materials for packaging applications due to its durability, lightweight nature, and flexibility. However, the current linear model of the plastic economy and the associated excessive amounts of plastic waste are not sustainable. Currently, the transition from a linear economy towards a circular economy is necessary, and research and innovation are the pivotal drivers to reach this goal. To address these issues, the EU has set ambitious targets to increase the reuse and recycling rates of plastics. In accordance with EU regulations regarding packaging and packaging waste [1], all plastic packaging on the EU market must be reusable or recyclable in a cost-effective manner by 2030. Furthermore, the mandatory recycling rate for plastic packaging should increase to 50% by 2025 and reach 55% by 2030. Nevertheless, increasing the recycling rate can present a challenge, particularly when multiple materials are combined [2,3] or contaminants are present [4]. Consequently, the design for recycling is highly important, with several different guidelines offering advice on this matter [5,6].

Flexible multilayer food packaging is considered a candidate for redesign to improve its recyclability. Flexible multilayer materials utilize resources in an efficient way and provide a very wide range of properties, such as reducing the overall size and weight of the packaging, minimizing food loss and waste, and lowering the environmental impact of packaging. According to Flexible Packaging Europe [7], approximately 50% of the total number of packaging units used in the food industry are flexible packaging materials. Depending on the material's structure, flexible packaging can be either monolayer or multilayer [8]. By combining different layers of materials through the extrusion process (coextrusion) for polymers or through the lamination process for combining polymers with non-polymers such as paper or aluminum, various functionalities, such as different mechanical and barrier properties, can be incorporated into the multilayer structure. As a result, multilayer packaging offers a wide range of protective properties that improve the shelf life of the packaged food [2,3].

Coextrusion is the most economical method for producing multilayer products [9–11]. Polyethylene (PE) and polypropylene (PP) are commonly used in flexible packaging [12]. However, since they are non-polar and highly permeable to oxygen [13], polar polymers such as ethylene vinyl alcohol (EVOH), polyamide (PA), polyvinylidene chloride (PVDC), and polyethylene terephthalate (PET) are added to the packaging structure to enhance oxygen barrier properties and extend the food's shelf life [14,15]. EVOH and PA6 are the most common oxygen barrier polymers used in coextruded film structures due to their very good oxygen barrier properties [12,16,17]. EVOH provides excellent barrier properties against oxygen. However, its barrier performance is highly influenced by relative humidity. Moreover, it is rigid, easily cracked under bending stress, and difficult to thermoform due to its highly crystalline nature. To overcome these challenges, EVOH is often sandwiched between two layers of PA6 to improve the thermoformability of the structure [12,14,17]. PA6 also offers moderate oxygen barrier properties, temperature and tear resistance, durability, and clarity, and it is most commonly used where high mechanical strength is required [17,18].

However, due to the incompatibility of the polymers used in multilayer materials and the diverse processing properties involved in recycling, these materials cannot be recycled with the current mechanical recycling infrastructure [3,8]. In the case of EVOH and PA in PE-based multilayer packaging, the RecyClass Guidelines state that concentrations of EVOH above 5% negatively affect the recyclability of PE films [19]. Additionally, PE and PA polymers are incompatible, which leads to limitations in the recycling process [16].

As a potential solution to enhance the insufficient oxygen barrier properties of mono-polyolefins and replace the functions of multilayer composite materials, using mono-polyolefins as a base material with alternative oxygen barrier coatings could be considered. If the coating material is not recyclable or is difficult to recycle, it reduces the overall recyclability of the base material. This suggests that it is necessary to remove coating layers to improve the recyclability, which requires a considerable amount of cost and energy [20]. However, according to the CEFLEX Designing for a Circular Economy Guidelines, if the polyolefin content exceeds 90% of the total weight of the packaging structure, the material is classified as a mono-material and is fully compatible with the polyolefin mechanical recycling process. Accordingly, up to 10% of other materials can be incorporated into the packaging structure without affecting its recyclability [21].

Specifically, for mono-polyolefin-based flexible packaging coated with barrier layers such as PVOH, EVOH, acrylic, SiOx, and AlOx, the CEFLEX Guidelines state that the coated polyolefin flexible packaging remains compatible with polyolefin mechanical recycling if the amount of each coating layer does not exceed 5% of the total weight of the packaging structure [21].

Currently, various barrier coatings, such as organic, inorganic, and biopolymer coatings, can be applied to packaging materials with different techniques [22]. For this purpose, coating technology is widely used to add desired properties to the substrate through a coating layer [9]. Each type of coating provides different properties and specific benefits and limitations. It is also important to use coating materials that are safe for both people and the environment. Therefore, it is essential to select the appropriate coating for each application to comply with safety and sustainability regulations.

A method to improve the barrier performance of monolayer films is to apply inorganic–organic hybrid polymers as a coating agent [23]. ORMOCER®, a hybrid material, a trademark of the Fraunhofer-Gesellschaft, is synthesized through a sol–gel process, which combines the flexibility of organic polymers with the durability and barrier properties of inorganic materials [24,25]. This synthesis method results in coatings that can significantly improve the barrier performance of substrates. The presence of organic functionalities enables ORMOCER® to undergo a crosslinking process via thermal or photochemical treatment. This process results in the modification of the structure and an increase in the density of both the inorganic and organic networks, which impacts barrier properties [26,27]. Hybrid polymers can be applied as thin, transparent coatings on a variety of substrates, such as polymers, metals, and ceramics, and provide different properties that can be attributed to either glass, ceramic, organic polymer, or silicone [24,28]. For instance, a very thin coating layer of ORMOCER®, with a thickness of less than 5 µm on packaging substrate, can provide highly effective barrier properties against water vapor, oxygen, and aroma. Despite their advantages, this hybrid polymer is currently considered an expensive coating compared to other coating materials [22].

Polyvinyl alcohol (PVOH) is a further barrier coating agent that is also widely used in packaging material. It is biodegradable, semi-crystalline, and exhibits excellent film-forming properties. Furthermore, it is water soluble and very suitable for water-based barrier coatings. Regarding food safety, based on the United States Food and Drug Administration (FDA), the German Federal Institute for Risk Assessment (BfR), and the European Medicines Agency (EMA), it is considered a safe material and suitable for use in food contact applications [29–31]. The crystalline structure and the hydrogen bonds between polymer chains contribute to its high barrier properties against oxygen [32]. A variety of studies have reported that the application of a PVOH coating on a range of polymer films can result in a reduction of the oxygen transmission rate [31–34].

The other functional and sustainable water-based coating agent is Michem® Flex, developed by Michelman International. This innovative coating offers environmentally friendly solutions in the packaging industry for flexible packaging as well as paper substrates [35]. It enhances the barrier properties and extends the shelf life of packaged food through the application of a low coating weight layer. According to Cooper [36], Michem® Flex could reduce the oxygen permeability of biaxially oriented polypropylene (BOPP) film by a factor of 320.

In the past few decades, the vacuum vapor deposition of an extremely thin layer of aluminum coating on polymer substrates, known as metallization, has been widely used in the packaging industry to provide excellent oxygen and water vapor barrier properties [37,38]. However, these metallized plastic films are still considered to be one of the most challenging materials to recycle [39]. Factors such as structural complexity, contamination by food residues, interactions with sorting infrastructures, and the resulting gray color of recyclates all contribute to the reduced recyclability of metallized films [3,39–41].

In recent years, high-barrier transparent vapor-deposited films, based on silica or aluminum oxide, have also become a common component of food packaging materials. Compared to EVOH, whose oxygen barrier properties are reduced after the sterilization process, these vapor-coated films offer sterilizable, retortable, and microwaveable packaging materials [42–44]. The gas barrier protection provided by SiOx vapor deposition has the potential to reduce permeation by approximately 100 times [45]. Furthermore, vapor deposition of SiOx and AlOx coatings on polyolefin films offers the potential to reduce the oxygen transmission rate (OTR) by approximately 90% [46,47]. BOPP-AlOx films typically exhibit a visible transparency that ranges from 91% to 93% in comparison to BOPP films [42]. A variety of articles and reports have suggested that the application of SiOx or AlOx to single polymer films could serve as an alternative approach to the replacement of multilayer packaging materials and to the improvement of their recyclability [3,4,15,48–50]. Since SiOx and AlOx vapor deposited coatings are typically extremely thin, often in the nanometer range and representing less than 5% of the total weight of the substrate, they do not interfere with the recycling process. Consequently, the coated films can be considered a mono-material [6,50].

However, it should be noted that PP-AlOx or PP-SiOx films may not always provide sufficient oxygen barrier properties [27,47]. The gas barrier properties of transparent films based on silica or aluminum oxide coatings are highly dependent on factors such as substrate surface properties, coating chemistry, deposition method, coating adhesion, coating thickness, and the presence of defects [44,51–53]. Both vapor-deposited coating films are very delicate, have limited flex and crack resistance, and are extremely sensitive to scratching and folding [45,47,54]. Even with thicker coating layers, there is still a possibility of microscopic and nanoscopic defects in the oxide coating films [24,55–57]. These defects have an adverse effect on the barrier performance and mechanical resistance of the coated films [44]. For instance, BOPP-AlOx film begins to lose its oxygen barrier properties after approximately 1.5% elongation [42]. Tension during the printing or laminating process [58] or even during web handling [59] can lead to cracks forming in the coated film, which subsequently affects the barrier properties of the AlOx coating. Similarly, according to Leterrier [44], some cracks develop in PP-SiOx films after a 1.6% elongation, which significantly affect the film's mechanical resistance and barrier performance. Additionally, exposure of PP-SiOx film to higher temperatures for longer periods of time (from 120 °C to 140 °C for 30 min) resulted in the formation of cracks in the coating due to thermal expansion of the PP film, leading to severe loss of barrier performance of single SiOx coating layers [60]. These defects can be overcome by applying an additional layer of coating to improve the barrier performance of AlOx or SiOx coatings on polymer films.

The objective of this study was to investigate various alternative barrier solutions on different PP substrates, including cast PP, as well as PP substrates coated with silicon oxides (SiOx) and aluminum oxides (AlOx), to enhance the barrier properties of polyolefin films. The goal was to utilize mono-polyolefin films to improve oxygen barrier properties by substituting the functions of multilayer composite materials with a focus on investigating the effect of curing conditions on OTR and DSC analysis.

2. Materials and Methods

2.1. Materials

2.1.1. Substrate Films

Three different substrate films were employed in this study: corona-treated cast PP film (CPP70), vapor deposition PP film coated with silicon oxide (PP/SiOx), and biaxially stretched PP film vapor deposition coated with aluminum oxide (OPP/AlOx). The substrate thicknesses were measured using a digital micrometer (KÄFER Präzisions Messtisch P7K) at ten individual spots of the substrates, and an average of the ten measurements was determined. Details concerning the substrate films are presented in Table 1.

Table 1. Substrate description and thicknesses.

Substrate Film	Description	Substrate Thickness (μm)
CPP70	Cast PP with corona discharge	70
PP/SiOx	PP films vapor deposition coated with silicon oxide	22
OPP/AlOx	Biaxially stretched PP film vapor deposition coated with aluminum oxide	20

2.1.2. Coating Agents

The inorganic–organic hybrid polymer ORMOCER® with a solids content of 30%, further denoted as CBS004 (a three-component system), was purchased from Fraunhofer-ISC, Würzburg, Germany. PVOH, with the trade name Exceval AQ-4104, an ethylene-modified polyvinyl alcohol with a degree of hydrolysis of 98–99 mol%, was provided by Kuraray Europe GmbH (Frankfurt am Main, Germany). Michem® Flex B3513, further denoted as MCHB3513, a ready-to-use transparent high-oxygen barrier water-based coating with a solids content of 10%, was provided by Michelman International Belgium SRL, Aubange, Belgium.

2.2. Methods

2.2.1. Preparation of CBS004

The CBS004 three-component system was employed for the coating of films at laboratory scale. One advantage of this system is that all three components remain stable at room temperature and can be mixed as needed. Component one comprises a mixture of silanes, while component two consists of a Zr complex dissolved in alcohol, and component three is an Al salt in dilute acid. For the synthesis of CBS004, 45.7% of component one, 22.8% of component two, and 31.5% of component three were used, respectively. Component two was added to component one under vigorous stirring and mixed for 10 min. Subsequently, an ice bath was employed to cool the solution. Component three was slowly added to the mixture of components one and two over a period of 20–30 min. The addition of component three induces an exothermic reaction, resulting in a slight increase in the temperature of the solution. Throughout the addition of component three, the ice bath was maintained to ensure that the temperature remained below 20 °C. Thereafter, the mixed batch gradually began to warm up until room temperature was reached. The solution was stirred for at least 16 h and then filtered through a 0.8 µm cellulose acetate syringe filter to eliminate any impurities.

2.2.2. Preparation of PVOH

A 10% *w*/*v* aqueous PVOH solution was used as the coating agent, and the solution was prepared by dissolving the PVOH in hot deionized water (95 °C) with continuous stirring at 1200 rpm. After 60 min, the PVOH was completely dissolved, and then the solution was cooled from 95 °C to room temperature.

2.2.3. Coating Method and Conditions

A motorized automatic coater (Coatmaster 510 Basic-V, Erichsen, Hemer, Germany) was used to apply the coatings on films at laboratory scale. All PP/SiOx, OPP/AlOx, and CPP70 films were coated individually with CBS004, MCHB3513, and PVOH, with a wet film thickness of 40 µm. For the SiOx and AlOx PP films, the coating was applied on the vapor-deposited coated side, while the corona-treated side was used for the CPP70. After applying the coating, thermal treatment was applied to the coated films with CBS004, MCHB3513, and PVOH at different times and temperatures as shown in Table 2.

Table 2. Substrates, coating, and thermal treatment conditions used in single coating.

Substrate	Coating Agent (40 µm wet)	Thermal Treatment
PP/SiOx, OPP/AlOx, CPP70	CBS004	100 °C (20 min)
	MCHB3513	70 °C (30 min)
	PVOH	50 °C (10 min)

Since cast PP film is widely used in the packaging industry, the impact of single and double coating on its barrier properties was also investigated. In the double coating process, CBS004 and MCHB3513 were used as primers, each applied with a thickness of 15 µm (wet). The samples were then cured at 100 °C for 20 min and at 70 °C for 30 min, respectively. After curing, a second layer of CBS004, MCHB3513, and PVOH was applied with a wet film thickness of 40 µm. The coated films were then thermally treated under different conditions, as detailed in Table 3.

Table 3. Coatings and thermal treatment conditions used in CPP70 double coating.

Substrate	**Coating Agent**		**Thermal Treatment**
	First Coating (15 µm wet)	**Second Coating (40 µm wet)**	**First Coating/Second Coating**
CPP70	CBS004	CBS004	100 °C (20 min)/100 °C (20 min)
		MCHB3513	100 °C (20 min)/70 °C (30 min)
		PVOH	100 °C (20 min)/50 °C (10 min)
	MCHB3513	CBS004	70 °C (30 min)/100 °C (20 min)
		MCHB3513	70 °C (30 min)/70 °C (30 min)
		PVOH	70 °C (30 min)/50 °C (10 min)

The CPP70 film was additionally coated with CBS004 on a semi-industrial scale at the Fraunhofer ISC to compare the results obtained on a laboratory scale. Since thermal treatment alters the ORMOCER® structure through a crosslinking process, the correlation between the degree of crosslinking and oxygen barrier properties was examined by coating CPP70 with CBS004 at a thickness of 15 µm (wet), and the coated films were subjected to various curing conditions, as detailed in Table 4. These findings were subsequently compared with a sample coated on a semi-industrial scale at the Fraunhofer ISC.

Table 4. Curing time and temperatures used for CPP70 coated with CBS004 at laboratory and semi-industrial scale.

Coating Scale	**Laboratory**		**Semi-Industrial**	
Coating speed	10 mm/s		83 mm/s (5 m/min)	
	Temperature (°C)	Time (min)	Temperature (°C)	Time (s)
Curing conditions	60	20	100	20
	80	5 and 20		
	100	5 and 20		
	130	5 and 20		

2.3. Characterization

2.3.1. Determination of Oxygen Transmission Rate

Oxygen transmission rate was measured using an OTR instrument (Labthink C230M, Jinan, China) equipped with a coulometric oxygen sensor according to ASTM D3985-05. All measurements were carried out at 23 °C and 50% relative humidity. Measurements were performed in triplicate for each sample.

2.3.2. Determination of Degree of Crosslinking

Differential scanning calorimetry (DSC 4000, Perkin Elmer, Waltham, MA, USA) was used to measure the degree of crosslinking of ORMOCER® under different curing conditions. For this purpose, CBS004 solution was poured into DSC crucibles and cured in a laboratory oven under the same conditions used for curing CPP70 coated with CBS004 at a laboratory scale, as illustrated in Table 4. Afterwards, the crucibles were sealed and placed into the DSC device. The samples were heated up to 200 °C at a rate of 5 °C per minute under nitrogen gas at a rate of 20 mL/min.

3. Results and Discussion

3.1. Oxygen Barrier Properties

3.1.1. Single Coating

A high oxygen barrier property is essential to keep packaged food products fresh and to protect them from oxidation. The OTR results for uncoated CPP70, PP/SiOx, and OPP/AlOx, single-coated at laboratory and semi-industrial scale are shown in Table 5.

Table 5. OTR results of uncoated CPP70, PP/SiOx, OPP/AlOx as well as single coated with CBS004, MCHB3513, and PVOH, at laboratory and semi-industrial scale.

Substrate	Coating Scale	Wet Coating Thickness (µm)	Coating Agent	OTR ($cm^3/m^2 \cdot d \cdot Bar$)
PP/SiOx	Laboratory	40	Uncoated CBS004 MCHB3513 PVOH	0.536 ± 0.259 0.061 ± 0.061 0.005 ± 0.002 0.006 ± 0.001
OPP/AlOx	Laboratory	40	Uncoated CBS004 MCHB3513 PVOH	6.134 ± 1.802 0.076 ± 0.054 0.035 ± 0.050 0.279 ± 0.470
CPP70	Laboratory	40	Uncoated CBS004 MCHB3513 PVOH	1516.64 ± 39.17 17.41 ± 1.17 2.75 ± 1.49 259.99 ± 69.01 *
	Semi-industrial	No information provided	CBS004	35.59 ± 7.66

* There was insufficient adhesion between PVOH and CPP70.

- PP/SiOx, OPP/AlOx

The results showed that vapor deposition of AlOx and SiOx on a thin PP film could provide a high oxygen barrier property. The OTR value for the uncoated PP/SiOx film was approximately 0.536 $cm^3/m^2 \cdot d \cdot bar$, while the OTR value for the uncoated OPP/AlOx film was approximately 6.134 $cm^3/m^2 \cdot d \cdot bar$. As shown in Table 5, the barrier performance of PP/SiOx and OPP/AlOx films was significantly improved by the addition of further layers of CBS004, MCHB3513, and PVOH. This resulted in a reduction in OTR to a higher barrier film range of less than 0.1 $cm^3/m^2 \cdot d \cdot bar$. The reduction in OTR by the application of CBS004 to inorganic barrier layers such as AlOx and SiOx may be attributed to synergistic effects that influence the density of the inorganic network. As highlighted by Amberg-Schwab et al. [61], the oxygen barrier properties of ORMOCER® are greatly influenced by the density of both the organic and inorganic networks.

By combining a hybrid polymer with a vapor-deposited metal oxide (MeOx) coating, such as silicon or aluminum oxide, additional Me-O-Me covalent bonds can be formed. These covalent bonds increase the density of the inorganic network, resulting in additional barrier effects and excellent barrier properties [27,55,62]. The other likely reason could be attributed to the interaction between ORMOCER® and the residual Si-OH groups on the surface of the SiOx film. This interaction increases the bonding to the SiOx surface while simultaneously reducing the level of microporosity within the SiOx layer [27]. Furthermore, in metal oxide-coated films there is always the possibility of the presence of microscopic and macroscopic defects, and applying ORMOCER® could potentially modify these defects and improve the barrier performance [24]. This could be the reason exceptionally low OTR values were obtained for both SiOx and AlOx PP films coated with CBS004.

Although the composition of the commercial MCHB3513 coating remained undisclosed, it could provide exceptionally low OTR values when combined with SiOx and AlOx films. The use of PVOH resulted in improved oxygen barrier properties for both SiOx and AlOx PP films. Similar behavior was also reported in the patents of Sawada et al. [63], owned by Mitsubishi Kasei Corp., Jacques et al. [58], assigned to Michelman Inc., Cincinnati, OH, USA, and Ettridge et al. [64]. In their patents, they stated that the combination of PVOH with SiOx, also AlOx vapor deposition-coated films could provide high gas barrier packaging film. The improvement in oxygen barrier properties could be attributed to hydrogen bonding interactions between PVOH and the silica or aluminum oxide substrates. Rashad et al. [65] stated that a very strong hydrogen bond could be formed between the aluminum oxide and hydroxyl groups in PVOH. According to Kim [66], strong hydrogen bonding could be formed between the silicate network and the PVOH, which could improve the oxygen barrier properties of BOPP by a factor of 50.

- CPP70

In the case of CPP70, because of the absence of functional and polar groups in polyolefin molecule structure, PP film is highly permeable to oxygen molecules [67]. As shown in Table 5, uncoated CPP70 exhibits a poor barrier property against oxygen with an OTR value of 1516 $cm^3/m^2 \cdot d \cdot bar$. According to Amberg-Schwab [24], applying a single layer of hybrid polymers on polymeric substrates, particularly polyolefins, would be sufficient to improve the barrier properties and reduce the oxygen transmission rate. According to the results presented in Table 5, applying a single layer of CBS004 could improve the oxygen barrier property and reduce the oxygen permeability by a factor of 88, reaching 17.41 $cm^3/m^2 \cdot d \cdot bar$. The OTR value of the semi-industrial coating scale (35.59 $cm^3/m^2 \cdot d \cdot bar$) was also consistent with the results at laboratory scale, an indication of a good correlation between the two coating processes.

The MCHB3513 coating resulted in a significant reduction in oxygen permeability and improved the oxygen barrier property of CPP70 by 551 times, with the OTR value changing from 1516 $cm^3/m^2 \cdot d \cdot bar$ to 2.75 $cm^3/m^2 \cdot d \cdot bar$. This finding was consistent with the results reported by Cooper [36].

PVOH generally provides good oxygen barrier properties due to its crystallinity and the presence of a strong intermolecular force, which is derived from the hydroxyl groups in its structure [68,69]. However, despite these advantages and its good film formation ability, it could not be applied to the CPP70 film. It should be mentioned that, even though the CPP film was corona treated, there was poor adhesion and insufficient interfacial wetting, resulting in difficulties in achieving a continuous and uniform distribution of coating on the CPP film surface. As a result, part of the PVOH layer separated from the film surface immediately after coating. Since PP does not contain any polar or active groups in its structure, it exhibits very low surface energy, resulting in poor wettability [67]. One possible solution to increase wettability and adhesion is through secondary treatments such as corona treatment. However, it has been noted that the effectiveness of the corona treatment on the film decreases and becomes less reliable over time during storage or due to environmental conditions. It was recommended that the corona treatment be carried out immediately prior to the coating process [70]. In addition, based on information provided by the supplier and other research studies, the use of a primer layer such as polyurethane or a polyethylene imine could improve the adhesion between PVOH and polyolefin film [64]. However, in this study, CBS004 and MCHB3513 were used as primers, and the results were investigated in the double coating section.

3.1.2. Double Coating

The OTR results of the double coating of CPP70 are shown in Table 6. The results showed that the use of CBS004 and MCHB3513 as primers in the double coating process significantly reduced the oxygen permeability, resulting in very low OTR values ranging from 0.1 to 1 $cm^3/m^2 \cdot d \cdot bar$. Additionally, the adhesion of the PVOH was significantly improved, resulting in a continuous and uniform distribution of the PVOH film over the primer. It is important to note that the combinations of CBS004/PVOH and MCHB3513/PVOH extremely improved the oxygen barrier properties of CPP70 by factors of 20,000 and 38,000, respectively, with OTR values changing from 1516 $cm^3/m^2 \cdot d \cdot bar$ to 0.075 and 0.040 $cm^3/m^2 \cdot d \cdot bar$.

Table 6. OTR results of CPP70 double coated with CBS004, MCHB3513, and PVOH at laboratory scale.

Substrate	Coating Agent		OTR
	First Coating (15 µm wet)	**Second Coating (40 µm wet)**	**(cm^3/m^2·d·bar)**
CPP70	CBS004	CBS004	9.314 ± 1.79
		MCHB3513	0.129 ± 0.04
		PVOH	0.075 ± 0.10
	MCHB3513	CBS004	0.211 ± 0.33
		MCHB3513	0.101 ± 0.10
		PVOH	0.040 ± 0.06

3.1.3. Effect of ORMOCER® Curing Conditions on Oxygen Barrier Properties

Thermal treatment after applying the inorganic–organic hybrid polymers can modify the structure via the crosslinking process and increase the density of both the inorganic and organic networks which in turn improves the barrier properties. The OTR results of CPP70 coated with CBS004 (15 µm wet) cured at different times and temperatures compared to the semi-industrial coating, are illustrated in Figure 1. The results showed that single-layer coating significantly reduced the oxygen permeability of CPP70. The OTR value decreased from 1516 cm^3/m^2·d·bar to below 100 cm^3/m^2·d·bar at all different curing conditions.

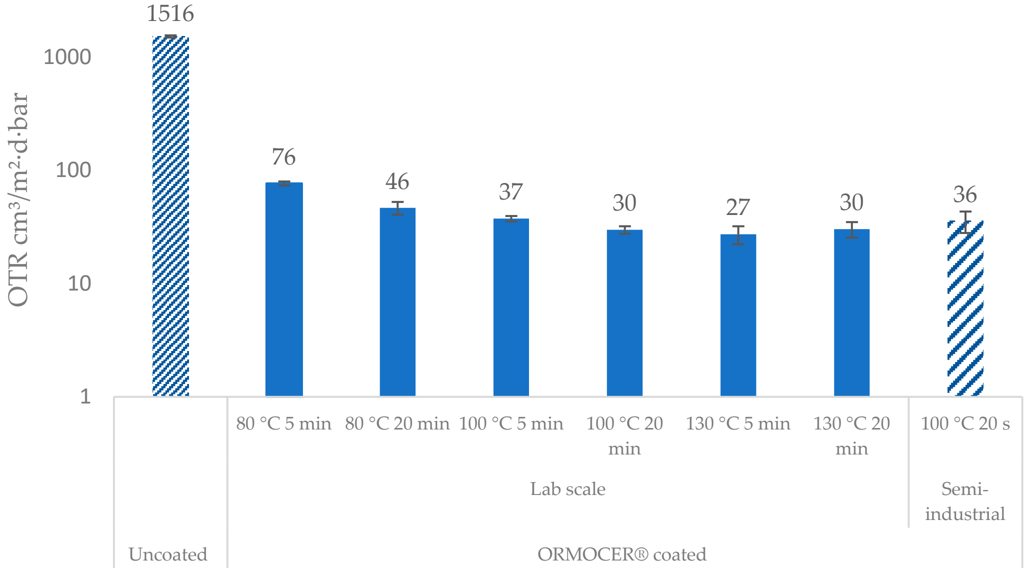

Figure 1. OTR results of CPP70 single coated with ORMOCER® CBS004 (15 µm wet) cured at various times and temperatures at lab scale compared to semi-industrial coating.

The results showed that curing conditions play a crucial role in determining the oxygen barrier properties. However, it is essential to select the appropriate conditions to obtain low and appropriate OTR values. Inadequate temperature and time can lead to insufficient crosslinking, resulting in higher OTR values compared to fully crosslinked conditions. To find suitable curing conditions, various conditions were assessed by several researchers.

Amberg-Schwab et al. [61] coated PP film with ORMOCER® at a laboratory and simulated industrial scale and cured the coated films at 100 °C for 120 min and 120 °C for 10 s, respectively. In other studies, Karl-Heinz Haas et al. [27] and Amberg-Schwab et al. [55] cured PP film coated with ORMOCER® at 130 °C for 60 min. The Fraunhofer-ISC [26] also stated that thermal curing occurs at temperatures below 150 °C.

As shown in Figure 1, the crosslinking process was initiated under the curing condition of 80 °C (5 min), resulting in a significant reduction in the OTR from 1516 to 76 cm^3/m^2·d·bar. However, as can be seen, increasing time and temperature from 80 °C

(5 min) to 100 °C (20 min) reduced the oxygen permeability from 76 to 30 $cm^3/m^2 \cdot d \cdot bar$. This reduction could be due to insufficient crosslinking density at 80 °C, which was improved by increasing the temperature and curing time. It is important to note that the lowest OTR value was obtained at 130 °C (5 min) and that increasing the curing time from 5 to 20 min did not result in any further reduction in OTR. An explanation for this phenomenon could be that at 130 °C (5 min), the ORMOCER®s were fully crosslinked, and no further crosslinking occurred when the curing time was extended.

As presented in Table 7, a single layer of CBS004 with a wet thickness of 15 µm cured at 80 °C for 5 min could improve the oxygen barrier property of uncoated CPP70 by approximately 95%, and by increasing the temperature and curing time at lab scale, the OTR could be improved by approximately 98%.

Table 7. OTR percentage improvement in CPP70 single coated with CBS004 (15 µm wet) cured at various times and temperatures at lab and semi-industrial scale compared to uncoated CPP70.

Substrate	Coating Scale	Curing Conditions		OTR Improvement
		Temperature (°C)	Time	Percentage (%)
CPP70	Laboratory	80	5 (min) 20 (min)	95.0 96.9
		100	5 (min) 20 (min)	97.5 98.0
		130	5 (min) 20 (min)	98.2 98.0
	Semi-industrial	100	20 (s)	97.7

The OTR results obtained in semi-industrial conditions, with the value of 36 $cm^3/m^2 \cdot d \cdot bar$, were correlated with the laboratory results, indicating that curing conditions in semi-industrial coating could achieve the optimum level of crosslinking, resulting in a low OTR value with an approximate 97.7% improvement in the oxygen barrier property, which is comparable to the laboratory scale. However, applying higher temperatures or extending the curing time in an industrial coating process can be a challenge and result in insufficient crosslinking, which can have an impact on the oxygen barrier property. In such cases, Amberg-Schwab et al. [61] suggested that post-curing at room temperature after the industrial coating process might increase the network density and, consequently, improve the oxygen barrier property over time.

The results in Table 5 and Figure 1 also showed that increasing the thickness of the CBS004 from 15 µm to 40 µm (wet cured at 100 °C for 20 min) could increase the oxygen barrier property, and the OTR value changed from 30 to 17.41 $cm^3/m^2 \cdot d \cdot bar$.

3.1.4. DSC Analysis for Degree of Crosslinking

Finding the appropriate curing condition to achieve the optimal level of crosslinking is very essential for improving the oxygen barrier properties of ORMOCER®. Since crosslinking reactions release heat due to their exothermic nature, analyzing different curing conditions using DSC could provide insight into the development of crosslinking reactions. The DSC analysis of cured CBS004 under different curing conditions is shown in Figure 2.

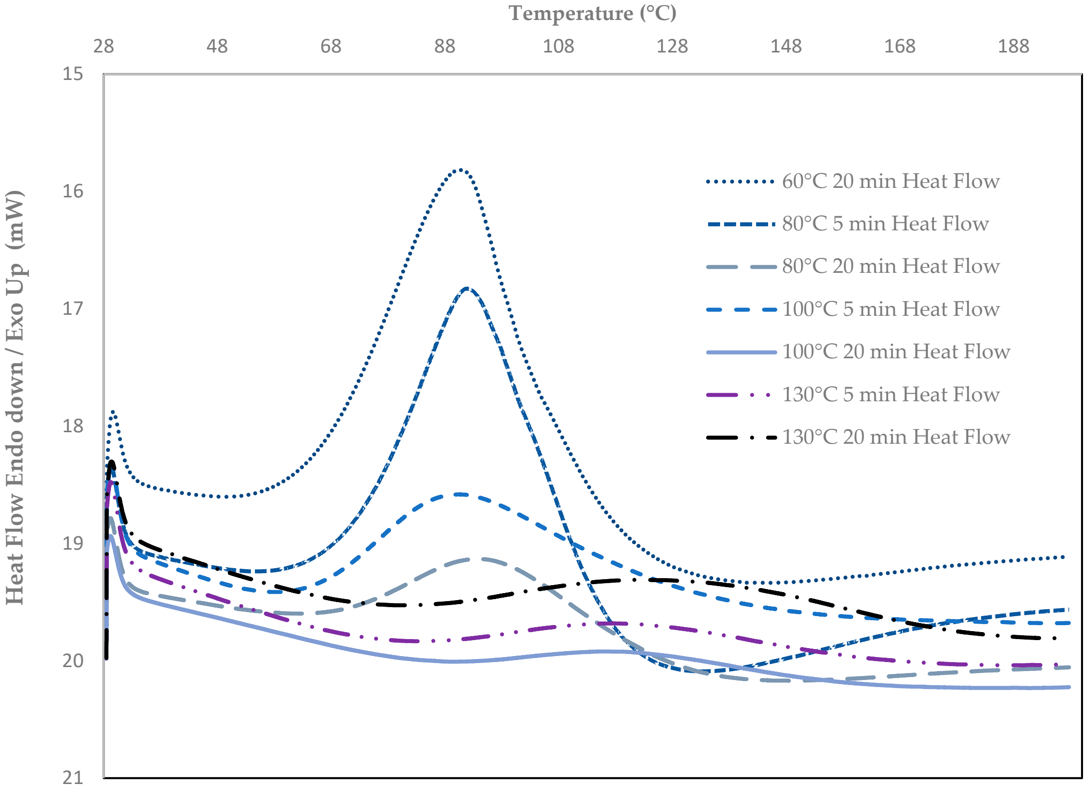

Figure 2. DSC analysis of cured CBS004 under various curing conditions.

The results showed that under certain curing conditions, such as 60–80 °C (20 min) and 80–100 °C (5 min), an exothermic peak could be observed around 90 °C on the DSC curve, mostly related to crosslinking reactions. The observed peak indicates that after the first heat treatment in the oven, some sites in the CBS004 remained unreacted, and by applying higher temperature and extending the curing time, these unreacted sites underwent crosslinking. During the second heat treatment, which has been done under the DSC, these unreacted sites underwent crosslinking at around 90 °C, generating heat and resulting in the observation of an exothermic peak. On the contrary, for other curing conditions such as 100–130 °C (20 min) and 130 °C (5 min), no exothermic reaction was observed at around 90 °C. This indicates that under these curing conditions, complete crosslinking may have occurred, and since no unreacted sites remained in the structure, no exothermic peak was observed during the second heat treatment under DSC. It should be noted that the lowest OTR values were obtained at 100–130 °C (20 min) and 130 °C (5 min), which was also in line with the DSC results.

4. Conclusions

The aim of this study was to investigate various alternative barrier solutions, such as ORMOCER®, Michem® Flex B3513, and PVOH, as well as different PP substrates, including cast PP and SiOx- and AlOx-coated PP films. The purpose was to improve the barrier properties of mono-polyolefin films with the aim of redesigning multilayer food packaging materials to enhance their recyclability. The main conclusions are as follows:

- Combining SiOx and AlOx with ORMOCER®, Michem® Flex, and PVOH resulted in high oxygen barrier properties for PP/SiOx and OPP/AlOx films.
- Deposition of a single layer of ORMOCER® improved the oxygen barrier property of uncoated CPP70 by approximately 95%. Under different curing conditions, OTR values in the range of 10–100 $cm^3/m^2 \cdot d \cdot bar$ were achieved. Optimization of the curing conditions further improved the barrier performance by approximately 98% and reduced the OTR within this range.

- Increasing the wet thickness of the ORMOCER® coating from 15 µm to 40 µm improved the oxygen barrier performance of CPP70 by a factor of 1.72, with the OTR value changing from 30 $cm^3/m^2 \cdot d \cdot bar$ to 17.41 $cm^3/m^2 \cdot d \cdot bar$.
- The OTR value at the semi-industrial coating scale correlated well with the laboratory scale, showed consistency between the two processes, and indicated that ORMOCER® could achieve an optimal level of crosslinking under semi-industrial curing conditions.
- Michem® Flex coating resulted in a significant reduction in oxygen permeability and could reduce the OTR value of CPP70 by a factor of 551, from 1516 $cm^3/m^2 \cdot d \cdot bar$ to 2.75 $cm^3/m^2 \cdot d \cdot bar$.
- The use of ORMOCER® and Michem® Flex as primer coatings in a double coating process improved the adhesion of PVOH and notably improved the oxygen barrier property of CPP70, achieving exceptionally low OTR values (OTR < 0.1 $cm^3/m^2 \cdot d \cdot bar$).

Overall, the application of barrier coatings such as ORMOCER®, Michem® Flex, and PVOH on several types of PP films, particularly CPP70, resulted in an improvement in the oxygen barrier property of PP films and showed very promising results for enhancing the barrier performance of monolayer polyolefin films as packaging materials.

Based on the findings of this study, very low OTR values (OTR < 1) were obtained for both single coated PP/SiOx and OPP/AlOx films, as well as double-coated CPP70 films. However, more extensive research is needed to enable a comprehensive comparison between single coatings (based on silica or aluminum oxide) and double coatings (with CPP70). Other key parameters, including the barrier performance of the coated films under different conditions (such as varying temperatures or mechanical loads), film flexibility, crack resistance, life cycle assessment, and cost efficiency, should also be considered. Additionally, the suitability of these barrier agents and coated films for the recycling process, as well as their recyclability in comparison to other high-barrier films that are currently available on the market, should be investigated.

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