R3PACK - REDUCE, REUSE, RETHINK PACKAGING TOWARDS NOVEL FIBRE-BASED PACKAGING AND REUSE SCHEMES

Grant Agreement No. 101060806

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LIST OF ABBREVIATIONS

CNC – Cellulose nano crystals
MFC – Microfibrillated cellulose
OTR – Oxygen transmission rate
PHA – Polyhydroxyalcanoate
PVD – Polymer vapor deposition
RH – Relative humidity
SEM – Scanning electron microscopy
SiOx – Silicon oxide
WVTR – Water vapor transmission rate

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EXECUTIVE SUMMARY

This document includes material selection and testing within R3PACK project in the substitution work package. The material selection was based on three main criteria such as advantageous technical characteristics for performance, sustainability/availability, and potential for large scale applications. Untreated paper and pre-treated paper with MFC and 3D molded trays are used as substrates. The coating solutions are being investigated under separate pilots. PHA, chitosan, natural waxes, starch, MFC and SiOx as coating systems were investigated under separate pilots and tested for their water and oil repellence, OTR and WVTR for their evaluation. This document is also intended to present overall characteristics of a packaging material via an overview of different pilots. In technical matters and material supply, the expertise and capacity of the consortium members was brought into service.

INTRODUCTION

In an era marked by growing environmental awareness and sustainability imperatives, the quest to reduce plastic usage in the food industry has taken center stage. Plastic packaging, once ubiquitous in the realm of food preservation and distribution, now faces increased scrutiny because of its harmful impact on the environment.
Recognizing this imperative for change, R3PACK mission is clear: to construct a comprehensive guideline for food manufacturers. This guideline will empower them to navigate the complex journey of substituting plastic packaging materials effectively.
R3PACK's ultimate goal is a substantial reduction in plastic usage within the food industry.
To accomplish this, systematic work for initiating a process that involves gaining a comprehensive understanding of the products, identifying their distinct barrier needs, and carefully selecting appropriate alternative materials was performed. Furthermore, we explore the complexities involved in integrating these materials into current production lines, guaranteeing a smooth and uninterrupted transition towards sustainable packaging solutions.
In this work package, partners of the R3PACK project explore the multifaceted challenges and opportunities that come with this transition, providing insights, recommendations, and best practices. By facilitating this transition, we aspire to foster a more sustainable future for the food industry, one where responsible packaging practices reduce environmental impact while ensuring the integrity and safety of products.

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1. CONTEXT

1.1 WP4 - PROJECT DESCRIPTION

R3PACK is a research and innovation project funded by the European Commission under the Grant Agreement 101060806, which aim is to reduce, reuse and rethink single-use plastic packaging. Within the given timeframe of the project the global objectives are:

- to develop sustainable fibred-based packaging solutions to substitute the existing solutions made with plastic and
- implement economically and environmentally viable reuse schemes to reduce plastic waste as well as extend packaging lifecycle.

R3PACK's consortium gathers 24 organizations from 7 different countries, bringing together key actors of the food value chain, from the packaging manufacturer to the retailer, combined with experts in the food sector, from companies providing innovative solutions to universities. With their combined expertise R3PACK will move from R&D to commercial real-life demonstration to secure fast and extensive uptake of industrially relevant, cross-sectorial, cost-effective technologies and reuse models allowing immediate substitution of complex multi-layer plastic packaging.
Cellulosic materials inherently lack the barrier properties necessary to effectively package demanding food products. Presently, commercially available solutions involving cellulosic substrates rely on fossil-based coatings and/or lamination to achieve various levels of barrier functionality. However, within the R3PACK project and especially **the substitution work package WP4**, alternative solutions have been identified. These include the application of Micro-fibrillated cellulose (MFC) onto paper substrates, the processing of Polyhydroxyalkanoates (PHA), the use of starch-based formulation, the deposition of silicon oxide (SiOx), as well as aerosol-based and airless coating techniques. These innovations hold the potential to significantly enhance the technical performance of cellulose-based packaging materials, eliminating the dependence on plastic while maintaining effective barrier properties.
The project approach towards substitution is designed to address and solve the three main challenges the involved actors of the value chain face today:

- Improvement of the barrier properties of the final solutions.
- Securing the machinability and the effective identification, adaptation, and use of existing assets.
- Securing the cost-effectiveness, competitiveness, and environmental impact of the developed solutions.

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WP4 INVOLVED PARTNERS	LOGO	PARTNER CONTRIBUTION
BIM KEMI		Surface analysis, preparation, formulation, formulation, deposition, evaluation
BIOEXTRAX		PHA provider, PHA preparation
FIBERLEAN		MFC provider, surface preparation
FRAUNHOFER		Deposition, machinability evaluation, shelf-life analysis
GASCOGNE		Paper provider, Deposition, cost optimisation
GUILLIN/THIOLAT		Molded fiber and cardboard provider, deposition, cost optimization
INNOVHUB		Recyclability and compostability evaluation
POLIMI		Financial modeling, cost optimisation
RISE		Surface analysis and preparation, formulation, deposition, evaluation
(RE)SET		Work Package management

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1.2 FOOD PRODUCTS AND BARRIER PROPERTIES

Our project encompasses a vast array of food products, each bearing its unique set of characteristics and requirements when it comes to packaging. From perishable goods like fresh produce and dairy to pantry staples such as dry cereals and canned goods, the diversity within the food industry is nothing short of astonishing.

This diversity extends to the varying shelf lives of products, with some needing protection for mere days and others requiring preservation over extended periods. Moreover, the specific barrier properties, whether it be resistance to moisture, oxygen, or other environmental factors, must align precisely with the distinct needs of each item.

Beyond preservation, the mode of packaging also varies widely. While some products thrive in flexible pouches, others demand rigid containers or specialized forms.

In essence, there is no one-size-fits-all solution. Instead, R3PACK project recognizes the need for adaptable and tailored packaging solutions. The key lies in the proper selection and customization of materials for each product category. This ensures not only the preservation of freshness and quality but also minimizes waste and environmental impact.

As we venture into this project, this work package mission is clear: to provide a comprehensive guideline that equips food manufacturers with the knowledge and tools to make informed decisions. By understanding the unique demands of their products, they can select or develop the right packaging materials and adapt them to their production lines. In doing so, we pave the way for a future where sustainable packaging practices are as diverse and dynamic as the foods they protect.

Packaging with effective barrier properties plays a crucial role in preserving and maintaining the quality of food products. These barrier properties are

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responsible for shielding food items from detrimental elements such as moisture, oxygen, bacteria, ultraviolet (UV) light, and even unwanted odors. The objective is to establish an efficient barrier between the external environment and the packaged food, thereby preventing premature deterioration and contamination.
The shelf life of food products is directly linked to the quality of their packaging and its barrier properties. Inadequate packaging can lead to rapid product degradation, reducing freshness and food safety. For instance, improper food packaging for perishable items like fruits and vegetables can result in wilting, loss of texture and flavor, as well as a decrease in nutritional value. On the other hand, an excellent oxygen barrier is crucial for items susceptible to oxidation, such as oils and fats, to prevent rancidity.
The preservation requirements vary significantly from one type of food to another. Dairy products, meat-based items, bakery products, fruits, vegetables, dry goods, and ready-to-eat meals all have specific demands in terms of packaging and barrier properties, such as oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) barriers (Figure 1).
Ultimately, food packaging with effective barrier properties is indispensable for maximizing the shelf life of products, reducing food waste, and ensuring consumer safety. They cater to the diverse packaging and preservation needs of food items, thereby contributing to maintaining product quality and safety throughout their lifecycle, from production to consumption.

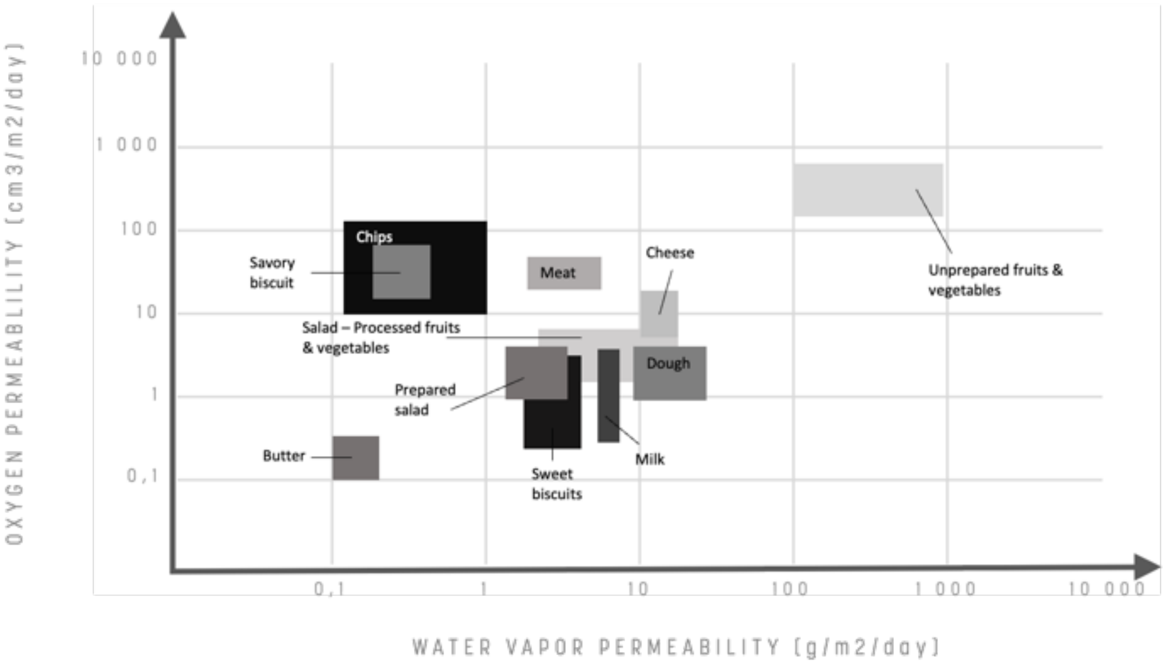

Figure 1. *Overview of R3PACK's food products barrier property's needs (OTR and WVTR) to preserve and maintain their shelf-life.*

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1.3 SUBSTITUTION OF PLASTICS BY CELLULOSIC-BASED SUBSTRATES

1.3.1 ADVANTAGES AND LIMITS OF PLASTIC PACKAGING

Plastics have long held a central role in the food packaging industry, and not without reason. These synthetic polymers possess a unique combination of characteristics that naturally make them attractive for this critical application (Geyer et al, 2017). Their exceptional malleability allows for the creation of a wide range of shapes, sizes, and designs, tailored to the diversity of food products. Moreover, plastics are distinguished by their excellent barrier properties, providing effective protection against external elements such as moisture, oxygen, fats, and UV radiation. This ability to preserve the freshness of food while extending its shelf life makes them an indispensable choice for many packaging applications.

However, the desire to work with sustainable alternatives to plastics in the field of food packaging has become a paramount concern. While these materials boast numerous undeniable qualities, they also contribute to significant environmental issues, including plastic pollution and the persistence of plastic waste in ecosystems for centuries (Gontard et al. 2022).

This raises the crucial question of the need to find more environmentally friendly materials.

Yet, finding a more environmentally friendly material able to compete with plastics in the realm of food packaging is not a straightforward task. No single material can simultaneously offer all the essential properties of plastics, from malleability to barrier properties to ease of large-scale and fast production. This means that researchers and innovators face a complex challenge: how to rethink the packaging to tend to plastics performance while minimizing their environmental impact, going from the feedstock to the end-of-life.

This ongoing quest for more sustainable alternatives remains at the forefront of the food packaging industry's concerns, thereby stimulating innovation and creativity in the search for solutions that are more respectful for the planet.

1.3.2 CELLULOSIC SUBSTRATE: THE IDEAL CANDIDATE, WITH INTRINSIC DRAWBACKS

Cellulose is the most abundant biobased polymer on the Earth, typically sourced from wood pulp or agricultural residues, sustainable, widely available, biodegradable, and compostable in the environment, which makes a good candidate to face the complex challenge for replacing plastics in food packaging. Cellulosic substrates can be processed by different ways, in order to obtain 2D (paper, cardboard), 3D (dry-, wet-molded fibre, etc.) or even more complex formats. Moreover, paper-based packaging is well recycled: According to Eurostat report, fiber-based packaging has the highest recycling rate in volume (81,6%) against 38% for plastics in 2020 (Statista, 2023).

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However, the primary challenge is linked to the intrinsic properties of cellulosic fiber-based materials, i.e. a porous structure with a rough surface and a strong affinity to water and oil products, providing low protection against liquids, moisture, oxygen, and other environmental factors.

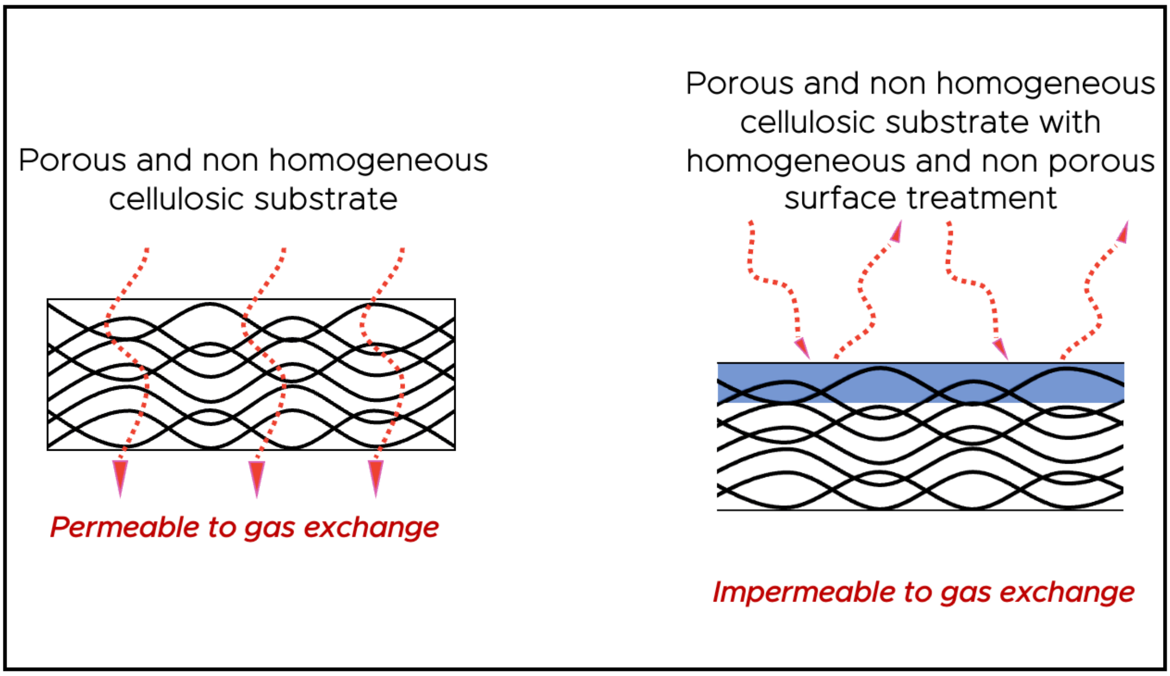

Figure 2. *Diagram illustrating the porous structure of cellulose substrates and gas exchange with and without surface treatment.*

Researchers are actively working on functionalization, incorporating coatings or additives to strengthen their barrier capabilities while preserving their ecological attributes.
Furthermore, transitioning from plastic-based to cellulosic substrate packaging often requires adaptations in production processes and equipment due to the materials' lower flexibility and increased fragility compared to plastics. This demands technical investments and innovation to ensure efficient and economically viable production.
Lastly, it's crucial to educate consumers about the benefits and limitations of cellulosic packaging, ensuring it meets expectations regarding product protection, convenience, and shelf life. Consumer perception and acceptance play a vital role in the successful transition to more environmentally friendly packaging. Despite these challenges, research and innovation continue diligently to leverage the advantages of cellulosic substrates while mitigating their limitations, making them a promising choice for eco-conscious food packaging solutions.

1.4 SELECTION OF RELEVANT MATERIALS

A cellulosic substrate alone, while environmentally friendly and versatile, will not provide the protection required for food products. Its inherent properties are limited in terms of barrier capabilities against moisture, oxygen, and other external factors that can compromise food quality and safety. Therefore, it is

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essential to functionalize the cellulosic substrate, enhancing its performance by adding specialized coatings, treatments, or additional materials. This functionalization process ensures that the substrate meets the specific requirements of food packaging, extending shelf life, preserving freshness, and safeguarding the integrity of the products it contains. In essence, the combination of a cellulosic substrate with tailored functionalization is the key to achieving effective and sustainable food packaging solutions.
In the context of this project, we have undertaken an in-depth exploration to identify materials of interest capable of enhancing the properties of cellulosic substrates while optimizing fiber usage.
Our approach seeks to offer a range of synergistic materials that, when combined with cellulosic substrates, significantly enhance their performance while preserving their biodegradable and renewable nature. This intelligent combination of materials paves the way for packaging solutions that are both robust and environmentally conscious, thus meeting the evolving needs of the food industry in terms of sustainability and product protection.

Polyhydroxyalkanoates (PHA)
PHAs represent a valuable material in the field of food packaging (Koller et al, 2014). Their appeal lies in their bio-sourced nature, as they can be produced from agricultural by-products or organic waste, contributing to a reduction in reliance on petrochemical raw materials. Additionally, PHAs exhibit properties like traditional plastics in terms of flexibility, mechanical strength, and ease of processing, making them easy to integrate into existing production chains. One of their most significant advantages is their excellent barrier properties, which enable them to preserve the freshness of food by protecting it from moisture, oxygen, and other undesirable elements. By combining these characteristics with their renewable origin, PHAs emerge as a promising option to meet the growing demand for sustainable and environmentally friendly food packaging solutions.

Microfibrillated Cellulose (MFC)
MFCs are fine nanofibrils of cellulose, obtained through mechanical fragmentation of native cellulose. Their nanometric structure grants them a high specific surface area and an exceptional ability to reinforce the substrates' matrix. Additionally, MFC's high specific surface area can be leveraged to enhance the adhesion of coatings or protective additives (Raynaud S., PhD manuscript, 2017).
MFC can reinforce the structure of the cellulosic substrate, thereby improving its mechanical strength and stability. This enhanced robustness is particularly valuable for packaging that needs to withstand physical stresses, such as bulk product packaging.
MFC plays a crucial role in preparing the surface of cellulosic substrates by reducing their porosity. Due to their micro/nanoscale nature, MFC can penetrate deep into the substrate's structure, filling void spaces and thereby reducing porosity. This pore-filling action creates a more uniform and less porous surface, significantly enhancing resistance to the penetration of moisture, oxygen, and other undesirable agents. Consequently, MFC contributes to strengthening the barrier properties of the cellulosic substrate, making it a more effective option for food packaging.

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Chitosan
Chitosan is a cationic polysaccharide derived from chitin, the primary component of crustacean shells, but it can also be extracted from alternative sources such as larvae and fungi.
The use of fungal-derived chitosan in packaging applications offers significant advantages compared to chitosan sourced from crustaceans or larvae. Firstly, fungal chitosan provides a non-allergenic alternative, thereby alleviating concerns related to food allergies. Additionally, unlike the seasonal, fishing-dependent harvest for crustacean chitosan, fungal chitosan can be produced more steadily and consistently, ensuring continuous availability. Furthermore, the utilization of fungal chitosan aligns with ethical concerns regarding animal welfare, as it does not require the use of crustaceans or larvae, making it a more environmentally and ethically sustainable choice for packaging materials (Iber et al, 2021).
Chitosan can be applied as a coating onto the cellulosic substrate (Mujtaba et al, 2022). Its natural antimicrobial capability helps prevent food spoilage by inhibiting the growth of microorganisms. This is especially beneficial for perishable products like meat and dairy. Chitosan can also contribute to enhancing the gas barrier of the cellulosic substrate, thereby improving shelf life.

Natural Waxes
Waxes, especially natural waxes like carnauba wax, are lipids that form protective coatings for food items. These waxes create a hydrophobic barrier that prevents moisture from penetrating, thereby preserving the freshness of food products. They are commonly used to coat packaging materials, such as waxed paper, for wrapping foods like cheese or fruits. Natural waxes, like carnauba wax derived from palm leaves, are of particular interest due to their biodegradability and sustainability, making them a preferred choice for eco-friendly food packaging solutions (Pashova et al, 2023).

Starch
Starch is a polysaccharide composed of long chains of glucose. When transformed into films or coatings, starch offers compelling barrier properties against moisture and oxygen, making it ideal for preserving the quality of food products. It can also enhance the mechanical strength of packaging materials. Importantly, starch sourcing from non-food crops ensures that it does not compete with food production, aligning with sustainable and eco-friendly practices in food packaging solutions (Li et al, 2019).

SiOx
The use of silicon oxide (SiOx) to enhance the barrier properties of cellulosic substrates in food packaging offers a promising solution (Bratovcic et al, 2015). It is important to note that SiOx alone does not provide barrier properties but rather enhances pre-existing ones. SiOx can be deposited as a thin layer onto cellulosic substrates to further improve their already existing barrier properties. This approach strengthens resistance to environmental factors such as moisture, oxygen, and other undesirable elements, thus contributing to enhanced food preservation while preserving the environmental advantages of cellulosic substrates, which are renewable and biodegradable. Silicon oxide

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provides an eco-friendly solution to optimize and bolster existing barrier properties while reducing reliance on plastics in food packaging.
By intelligently combining these materials with a cellulosic substrate, it should be possible to create comprehensive food packaging that addresses the specific needs of each product. This approach offers a sustainable, environmentally friendly, and high-performing solution for food preservation while reducing reliance on plastics and meeting the growing sustainability requirements in the food industry.

MATERIAL / PROPERTIES	CELLULOSE	MFC	PHA	STARCH	WAX	SIOX DEPOSITION	CHITOSAN
MECHANICAL PROPERTIES	+	+	+	+			
SURFACE PREPARATION		+		+			+
WATER BARRIER			+		+		+
GREASE BARRIER		+	+	+	+		+
OXYGEN BARRIER (OTR)		+	+		+	+	+
WATER VAPOR BARRIER (WVTR)			+	+	+	+	+
BARRIER ENHANCEMENT						+	
RESSOURCE AVAILABILITY	HIGH	HIGH	HIGH	HIGH	LOW	HIGH	HIGH
MATURITY FOR PAPER-BASED PACKAGING APPLICATION	INDUSTRIAL	INDUSTRIAL	PILOT	INDUSTRIAL	R&D	PILOT	R&D

Table 1: *Summary of Table of Key Properties of the Various Materials Selected for WP4 Research*

Disclaimer: The term "resource availability" focuses on the abundance or scarcity of raw materials, exemplified by cellulose, the most prevalent natural polymer on Earth. However, cellulosic substrates, despite being produced in large quantities, have diverse applications, and the increasing demand across various sectors places them under strain, posing a potential challenge.

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2. R&D PILOTS: RESULTS AND DISCUSSIONS

The launch of R&D pilots has been decided within consortium based on the discussions on materials, type of substrates (paper or tray) as well as technical requirements. Materials display different properties as mentioned in Table 1, but also specific physicochemical behaviour, as well as different level of process efficiency.

A multilayer structure is a common strategy that is preferably applied when designing cellulosic-based packaging materials requiring almost all barrier properties. Each layer will provide or enhance one or several barrier properties with the possibility of synergies between layers and materials.

As mentioned in the material section, MFC is a nanoscale material generated from biomass and can provide grease and oxygen barrier properties to a cellulosic substrate. However, MFC is hydrophilic and sensitive to water which implies a combination with other materials to reach water barriers (water vapor and liquid). It is also necessary to make sure that the obtained oxygen barrier properties are preserved at higher relative humidity since MFC can swell with higher moisture content. If MFC swells it can affect the adhesion between the other barrier layers or to the substrate and hence the barrier properties can be impaired. It was therefore decided to use MFC as a surface preparation pre-coating with different deposition technique depending on the type of substrate (paper or tray).

2.1 R&D PILOTS WITH 2D SUBSTRATE

In R3PACK project, several attempts for coating were performed on 2D substrates to reach out the required technical specifications. Commercial standard papers from Gascogne and Fiberlean (bleached and unbleached quality) were chosen and tested from available papers. Substrates from Fiberlean were uncoated or MFC-coated with a patented deposition technology.

Since different food packaging may have specific needs, it is a challenging task to meet all packaging requirements with a single type of functionalization. However, there is continuous development in functionalization technologies and materials for addressing multiple requirements simultaneously. The ideal case is to develop functionalization that provide barriers against moisture, oxygen, and contaminants while also ensuring food safety and compliance with regulations.

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2.1.2 PHA-BASED SOLUTIONS

Depending on how and in which material form of PHA is applied, differences in barrier properties would be obtained. To identify easier deposition processes and a possible improvement in barrier properties, different strategies of PHA application were investigated. PHA was either laminated or coated as a dispersion on an uncoated or MFC pre-coated substrate (Figure 3).

Figure 3. *Schematic of PHA applied on paper substrate, with or without MFC pre-coating.*

Materials

PHA was supplied by Bioextrax AB and from external companies. PHA emulsion was supplied by external company.

Following papers were used as substrate:
Fiberlean uncoated and unbleached paper
Fiberlean uncoated and bleached paper
Fiberlean MFC precoated and unbleached paper
Fiberlean MFC precoated and bleached paper
Bleached Kraft paper 48 gsm from external company.

PHA application techniques and associated performance

Depending on substrates (paper with or without MFC), different application techniques of MFC were used.

Dispersion/emulsion coating application processes involve coating material and consist in a deposition of a thin and uniform layer or multilayers to a paper substrate. Various barrier coatings will provide specific properties such as humidity control, oxygen permeability, aroma barrier, grease-proofing, heat resistance, peel ability, sealing, airtightness, or light protection. In comparison with lamination, dispersion coating processes will provide a lighter package that will be easier to transport, as well as better recyclability with less rejected cellulosic fibres.

Thermal lamination on the other hand, is a process that uses heat to melt a barrier film layer (very often plastic materials) onto a paper or plastic substrate. Lamination remains the traditional method for preserving printed materials and has the benefit of creating a homogeneous, dense barrier layer without any pinholes.

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A) PHA laminated on uncoated paper

PHA polymers are thermoplastic and can easily be processed using conventional hot-pressing equipment. Thermoplastics are of general interest as they are commonly used in food packaging because they can be quickly and economically softened by heat to form the shape needed to fulfil the packaging function, by using extrusion-injection moulding, extrusion blowing or hot-pressing processes. A simple example from everyday life is common households' items such as ice-cubes that exemplify the thermoplastics principle. Ice will melt when heated but readily solidifies and crystallizes when cooled creating a practical example.

PHA films with reproducible thicknesses were hot-pressed using a laboratory pressing tool. The desired film thickness was related to the temperature, the pressure and time, also influenced by the intrinsic thermo-mechanical properties of PHAs. The sample consisted of a powder that was placed directly into the film hot-pressing tool without prior preparation (Figure 4). The evaluation of this method showed that homogeneous, pinhole-free, and thermally stable PHA films could be produced.

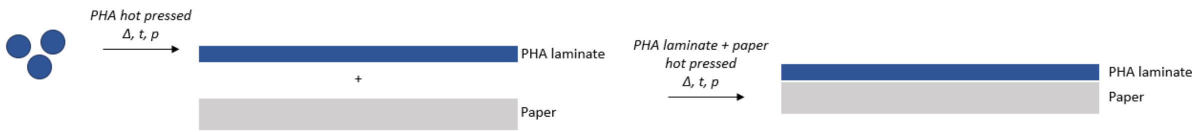

Figure 4. *Schematic of paper PHA lamination process.*

Before the lamination of the PHA film on the paper, the press parameters were again evaluated and optimized, to obtain good adhesion between PHA film and paper with a controlled impregnation and create a continuous top layer on the paper surface. This optimisation should induce a good substrate for barrier performance.

In fact, the PHA laminated substrate obtained by this process showed good adhesion, very promising water vapor barrier but no oxygen barrier. The SEM microscopy image of a cross-section of the PHA laminated paper (Figure 5) shows a homogeneous PHA layer on top of the paper surface.

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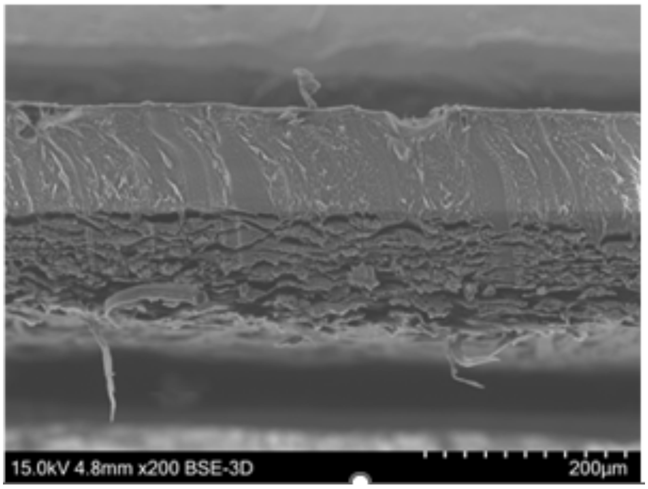

Figure 5. *SEM images of 200x magnitude of a cross-section of PHA laminated paper.*

B) PHA laminated on MFC-coated paper

To bring oxygen barrier, the same strategy was also evaluated on bleached paper coated with MFC (Figure 6). However, adhesion between MFC layer and PHA laminate was not good, and the multi-layer structure showed a very bad cohesion.

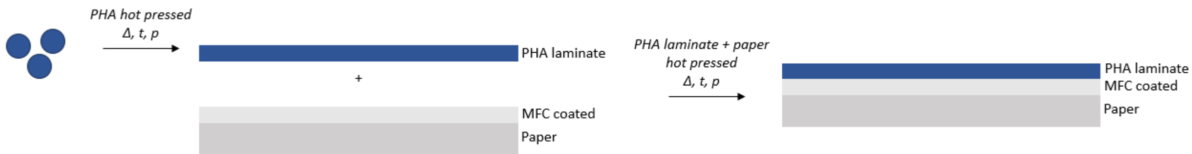

Figure 6. Schematic of *PHA laminate on MFC coated paper process.*

To overcome this problem, a PHA based dispersion coating was applied with a bar coater on the MFC-coated paper (Figure 7). Different numbers of layers of PHA coating were obtained to observe a possible increase of barriers.

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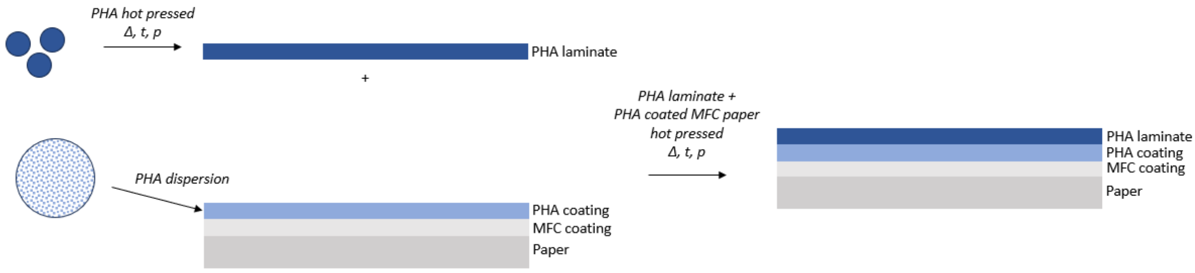

Figure 7. *Schematic of PHA laminate on MFC-coated paper, pre-coated with a PHA coating layer.*

Using optimized press conditions, the adhesion of the multilayers was improved from poor adhesion to very good adhesion, even with the presence of MFC on the surface of the paper. A good adhesion is crucial to provide strong sealing and avoid any leakages within the packaging structure during the shelf-life of food products. Successfully, the multilayer structure was not over-pressed, preventing the total impregnation oh PHA within cellulosic fibres to maintain the barriers. Indeed, very good water vapor and extremely good oxygen barriers were obtained, with OTR < 1 cc/m^2/day (23°C, 50%RH).

C) PHA dispersion coating on MFC-coated and uncoated paper

The barrier performance of PHA dispersion coating was evaluated on both MFC-coated and uncoated paper, prepared with a deposition of one or several layers (Figure 8, Figure 9).

The material has shown a good water vapor barrier of 7 - 10 g/m^2/day at 23°C, 50% RH. However, it seems that grease barrier is only present with the presence of MFC on the surface of paper. However, compared to the laminated MFC coated paper structure, none of the functionalized papers here showed an oxygen barrier. It seems that the dispersion coating layer of PHA is not sufficient to bring this barrier, maybe due to a layer that is not dense enough or the presence of pinholes.

Considering this issue, different strategies were investigated to improve oxygen barrier by tuning the structure of the substrate, i.e., calandering of MFC-coated paper as well as hot-pressing of PHA/MFC-coated paper. This resulted in no change of water vapor and grease barrier, but no increase of oxygen was observed.

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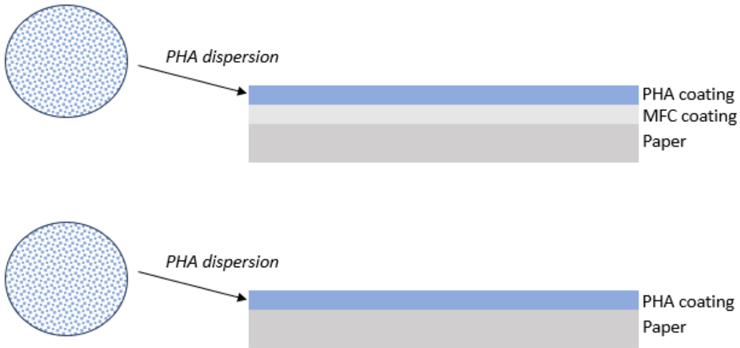

Figure 8. *Schematic of PHA dispersion coated paper with and without MFC.*

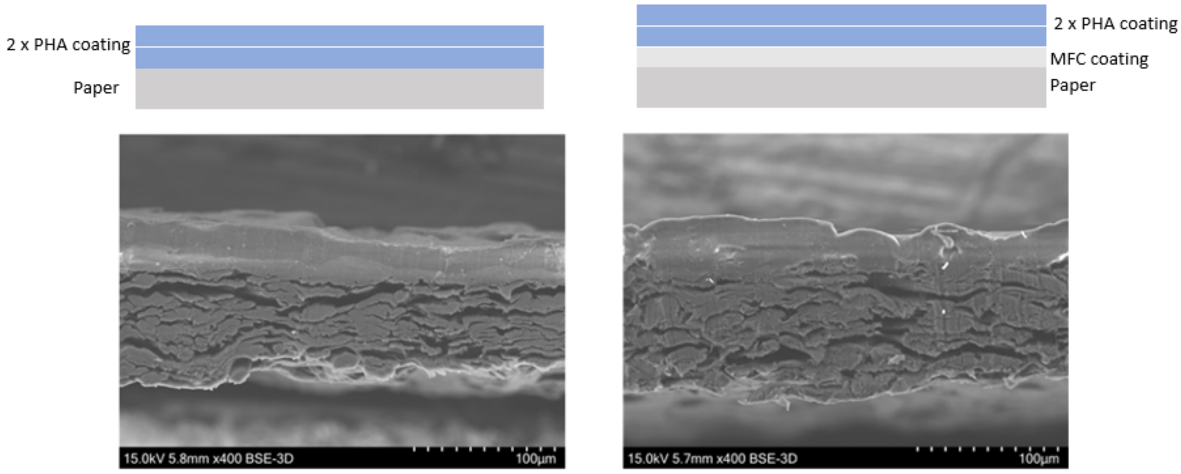

Figure 9. *SEM images at 300x magnitude of a cross-section of a) base paper coated with double layers of PHBV based dispersion and b) MFC paper coated with double layers of PHBV based dispersion.*

D) PHA commercial emulsion on MFC-coated and uncoated paper

PHA emulsion was prepared, and one or two layers were applied by bar-coating on the different substrates, i.e., MFC-coated and uncoated papers (Figure 10).

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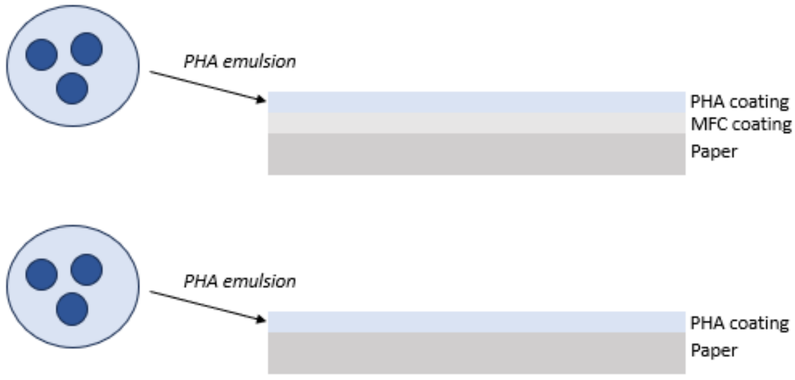

Figure 10. *Schematic of PHA emulsion coated paper with and without MFC.*

The PHA emulsion was deposited on different substrates at one or two layers of coating. Two layers of PHA emulsion showed better results of liquid water and fat resistance compared to one layer. WVTR values obtained with this strategy were between 36 and 52 g/m²/day at 23°C and 75% RH.

E) Summarize of all PHA application strategies

Water vapor and oxygen barriers.

The barrier properties, i.e., WVTR and OTR (23°C, 50%RH), obtained with the different PHA application strategies on several 2D paper substrates were summarized in Figure 11. OTR (23°C, 50%RH) values were in the range of 1-90 cc/m²/day and WVTR between 3 and 7 g/m²/day.

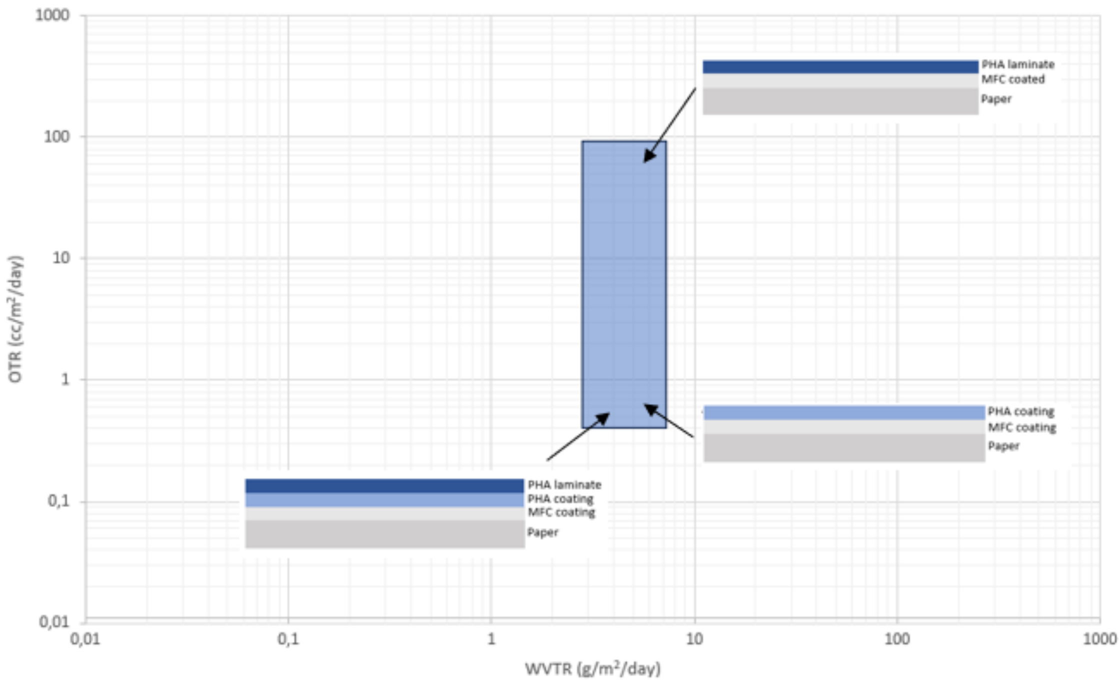

Figure 11. *OTR and WVTR measured for three different material combinations of PHA deposition on paper substrate, performed at 23°C and 50%RH.*

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The MFC paper showed poor grease barrier properties. This was also so when a PHA laminate was applied to a base paper. However, a combination of PHA laminate and MFC in a multilayer was investigated and verified with another grease resistance test and from this, results were obtained showing an existing grease barrier. Thus, it was confirmed that a PHA laminate needed an MFC paper to provide a grease barrier.

Other packaging properties to be considered: sealing, machinability, and shelf-life

A) Sealing properties

Tests of adhesion strength for laminated papers (uncoated and MFC-coated) were performed and resulted in a fiber tear, indicating that the PHA laminate/fiber adhesion strength was stronger than the paper strength. A typical adhesion strength is 1 - 10 MPa. Results showed z-strength of about 1.8 MPa (cohesion forces between fibres). Thus, the manual peel tests of the laminates adhered firmly to the substrates corresponded to an adhesion strength > 2 MPa.

B) Machinability

There are possibilities to tailor the molecular structure of PHA and thus be able to create a flexible PHA film laminate. This is also beneficial for scale-up trials such as coating extrusion, with physico-chemical and thermo-mechanical allowing better processability in melting processes. Higher tensile strength and flexibility allow to prevent the brittleness of PHA laminate and thus the cracks on the paper. PHA belongs to the bioplastics with a high melt flow index, which is desirable. The melt strength correlates with melt flow index and with the ability to tailor the PHA properties, melt strength can be fine-tuned.

Regarding lamination, PHA has been investigated on a lab scale with double sided compression thermoforming into films to be laminated on paper in a subsequent step. On an upscale pilot trial using extrusion coating, the molten film will be drawn down from the die into the nip between two rolls below the die - the water-cooled chill roll and a rubber-covered pressure roll – and further onto the paper web. Important factors to consider when upscaling PHA laminate: coating melting temperature, air gap, melt flow index, coating speed, coating thickness, preheating of substrate and nip pressure. On this point, temperature, melt flow index, coating thickness, preheating of substrate and nip pressure have been partially investigated on a lab scale. More tests need to be done to relate the lab tests to the processing conditions for scale-up trials with coating extrusion.

Regarding dispersion coating, the dispersion solution is applied to the surface of paper to form a solid, non-porous film after drying. On a lab scale, bench coaters are used for rod coating of one to several layers and with the choice of rod size, rotational speed, loading pressure. On a pilot scale, there are different application methods for dispersion coating rod/blade/curtain. Process

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parameters are drying method, drying temperature, chill roll temperature and line speed. The dispersion solution will have different requirements for scaled-up experiments with high speeds and thus increased shear rates. The viscosity of a coating is directly related to the concentration of the coating solids in the dispersion. Primarily the dispersion dry solid will need to be adjusted for the scaled-up trials.

C) Shelf life

Tailoring the molecular structure of PHA can bring more flexibility with improved impact resistance and toughness. Furthermore, flexible packaging based on PHA has the advantage of being more easily degradable, mainly linked to the degree of crystallinity of the PHA copolymer. Moreover, a recent study from Doineau et al (2022) shows the ability of PHBV-based packaging materials to be reused after 50 dishwashing cycles, resulting in an overall migration below 10 mg.dm^{-2} according to EU legal limits (European Commission Règlement, N°10/2011). This study showed a food contact ability and thus a maintained product safety with a low migration of PHA material within the food product, as well as a ability to be reused.

2.1.3 STARCH-BASED SOLUTIONS

Starch-based and partly fossil free coatings were applied on MFC-coated or uncoated paper substrates and the barrier properties and performance of multilayer structures were evaluated (Figure 12).

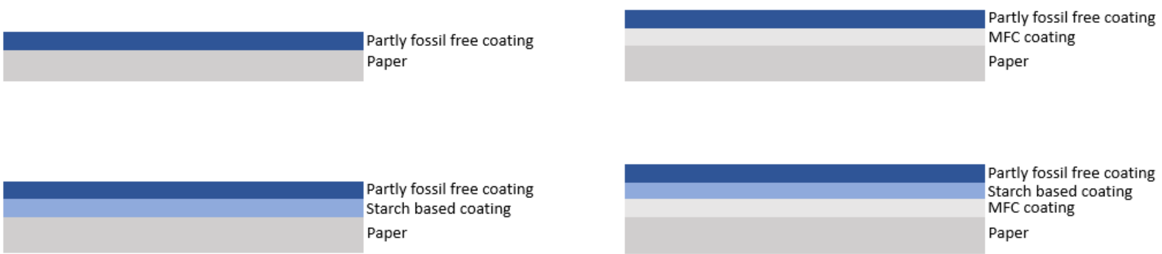

Figure 12. *Schematic of partly fossil free and starch-based coatings deposited on MFC-coated or uncoated paper.*

Materials:

A starch-based barrier formulation was used as barrier or as a primer layer. A partly fossil free barrier formulation was used as a top coating.

Following paper substrates were used as substrate:
Fiberlean uncoated and unbleached paper
Fiberlean uncoated and bleached paper
Fiberlean MFC precoated and unbleached paper
Fiberlean MFC precoated and bleached paper.

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Combinations of partly fossil free and starch-based coating products and associated performance

The starch-based barrier coating was used as a primer with the partly fossil free barrier as a top coating on the different Fiberlean substrates. One layer of the partly fossil free barrier was also coated on Fiberlean paper and evaluated.

The coated substrates were tested for liquid water, moisture, oxygen and grease resistance. Overall, the combination of the starch-based barrier and the partly fossil free barrier gave good results for all parameters tested for both uncoated and MFC pre-coated substrates (Figure 13). However, only one layer of the partly fossil free barrier without MFC pre-coating did not perform well against grease and oxygen but gave good water vapor and liquid barriers. Finally, one layer of the partly fossil free barrier on the MFC pre-coated substrates performed well for all parameters.

WVTR was measured on samples with partly fossil free barrier or in a combination with starch-based barrier. The extent of surface coverage on the paper substrates varied. The WVTR was less than 50 g/m²/day for all samples except for the sample from primer layer and top coating on uncoated unbleached paper.

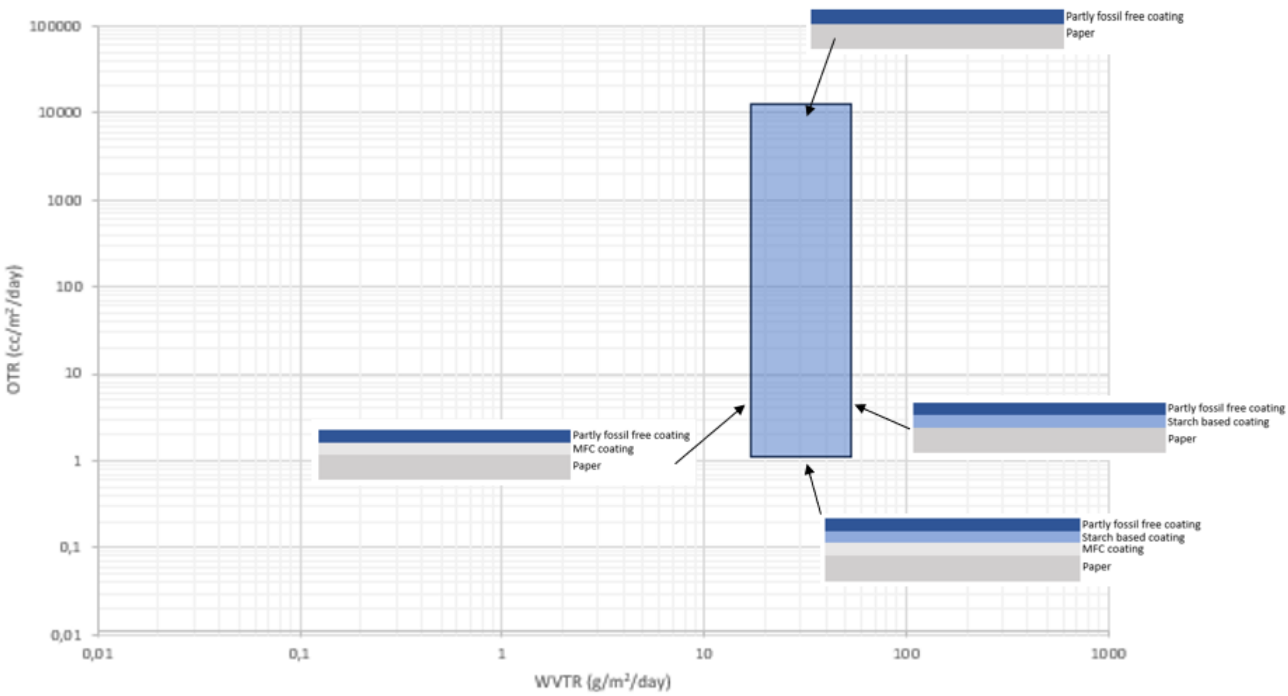

Figure 13. *OTR (23°C, 50%RH) and WVTR (23°C, 75%RH) for partly fossil free and starch-based coatings deposited on MFC-precoated or uncoated paper substrates.*

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Other packaging properties to be considered: upscaling and associated machinability

Pilot trials with the starch-based barrier and the partly fossil free barrier are planned. Risks and obstacles with upscaling could give potential problems to achieve an even coating thickness and effectiveness of the barriers due to machinability limitations and rheological properties of the barrier. The equipment used in pilot trials are very different compared to the test in the laboratory. Another risk is not being able to achieve proper drying of the barriers and if the barriers would possess blocking tendences. Delays of both the raw materials used in the barriers and the paper substates used in the trials are also a risk.

2.1.2 WAX-BASED SOLUTIONS

The possibility to use carnauba wax as a barrier was evaluated. The wax was added a dispersion coating on paper or in combination with other materials. Different barrier formulations using different combinations of carnauba wax together with other components of formulations such as chitosan and/or PHA emulsion (Figure 14).

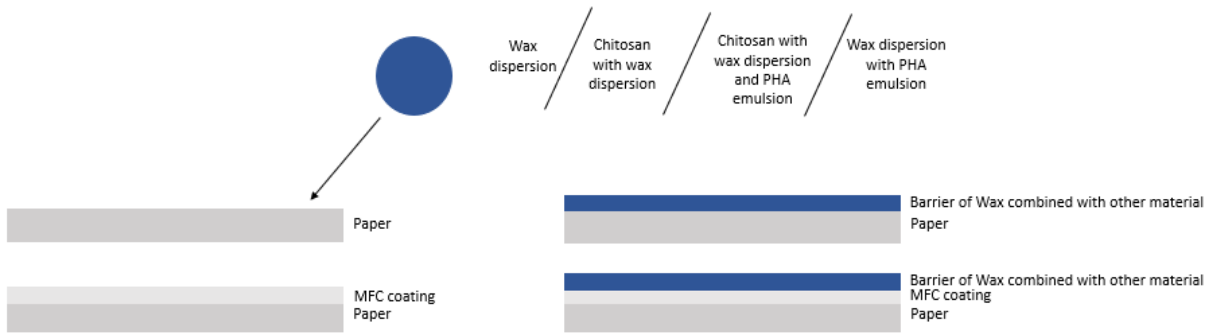

Figure 14. *Schematic of different combinations of wax-based barrier formulations coated on MFC-precoated or uncoated paper.*

Materials

Carnauba wax was supplied from external company.
Chitosan was supplied from Alpha Chitin.
PHA was supplied from Bioextrax AB.

Following paper substrates were used:
Fiberlean uncoated and unbleached paper
Fiberlean uncoated and bleached paper
Fiberlean MFC precoated and unbleached paper

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Fiberlean MFC precoated and bleached paper
Bleached Kraft paper 48 gsm.

Wax-based combination coating and associated performance

All barriers were applied by rod coating, one or two layers, and thereafter dried. Carnauba wax dispersion was coated on bleached kraft paper. The dispersion was added in one layer. The Cobb60 value was 47 g/m^2.

Chitosan with carnauba wax dispersion was coated on all substrates, one or two layers. Lower Cobb60 values were obtained on the paper substrates with MFC coating, both unbleached and bleached MFC coated paper. The KIT value for these samples were 12.

The dispersion of chitosan, carnauba wax, PHA emulsion and carnauba wax, PHA emulsion were coated on bleached kraft paper. The Cobb60 values were between 3-31 g/m^2.

The use of only carnauba wax dispersion as a coating did not show good results of water or grease resistance. The material needs to be formulated together with a film forming material to guarantee better surface coverage. Carnauba wax formulated together with chitosan, PHA emulsion or combined with both chitosan and PHA emulsion gave better results. Overall, the results showed a good potential of the materials as barriers. However, the results were not good enough compared to other tests in the project. The formulations would need more work and a lot of lore investigations. Due to lack of raw materials of chitosan and the low performance, no further tests were made with carnauba wax material.

2.1.3 SIOX INORGANIC TECHNOLOGY SOLUTION

Materials

SiOx was applied as an inorganic barrier layer. A commercially available SiOx target was used for the PVD.

Following papers were used as substrates:
Fiberlean uncoated and unbleached paper
Fiberlean uncoated and bleached paper
Fiberlean MFC precoated and unbleached paper
Fiberlean MFC precoated and bleached paper
Gascogne kraft paper with CNC coating on top.

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SiOx PVD deposition solution and associated performance

Physical vapor deposition (PVD) is a vacuum-based coating process, in which the evaporated material, such as aluminum, or in this case transparent Siliconoxide (SiOx), is physically heated with an electron beam before it condenses on the cooler substrate forming a layer that is only a few nanometers thick (Kienel et al, 1992). This is controlled by a quartz thickness monitor.

A SiOx layer was deposited on kraft paper from Gascogne with CNC coating and bleached as well as unbleached paper from Fiberlean coated with MFC. This was done to evaluate if the substrates are suitable for SiOx deposition (Figure 15). This is a very delicate process with paper as a substrate and therefore a suitable precoating is needed to minimize the surface roughness. If the surface roughness is too high, it might lead to preferential nucleation or shadowing effects of the inorganic coating, which will then result in defects. Another important factor is the hygro-expansion of the paper. Since PVD is performed in vacuum at dry conditions, the paper shrinks. If the paper is then exposed to moisture from the atmosphere, the fibres expand again and can lead to tension and cracks in the inflexible inorganic surface.

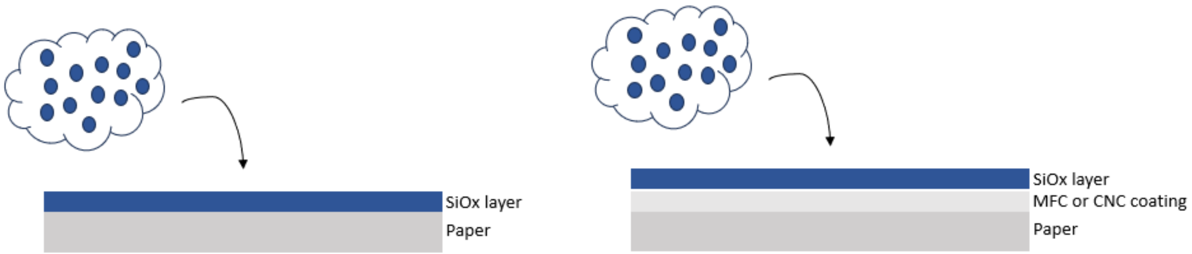

Figure 15. *Schematic of SiOx deposition on MFC-, CNC-coated or uncoated paper.*

WVTR was measured at 23°C and 85%RH, OTR at 23°C and 50%RH. The WVTR was not measured for substrates without SiOx since no barrier properties from MFC or CNC itself could be expected (Figure 16).

The kraft paper from Gascogne with CNC coating had a good oxygen without the SiOx layer, but the coating was quite inhomogeneous. The SiOx deposition did not enhance the barrier properties.

The barrier properties of two different papers from Fiberlean, bleached and unbleached, with a MFC coating could not be improved with SiOx coating.

These results lead to the conclusion that papers with their respective precoating are not yet suitable for SiOx deposition. Improvements can be made by choosing substrates with a smoother surface and low hygro-expansion, but also by selecting a precoating that forms a more plane underground and has some barrier properties itself which can be improved by the inorganic layer. Additionally, an upscaled process often less susceptible to variations in the coating procedure than coatings in single batches in lab scale.

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The barrier properties of a SiOx layer deposited on different paper sheets precoated either with MFC or CNC were evaluated and presented below. The SiOx was deposited via PVD.

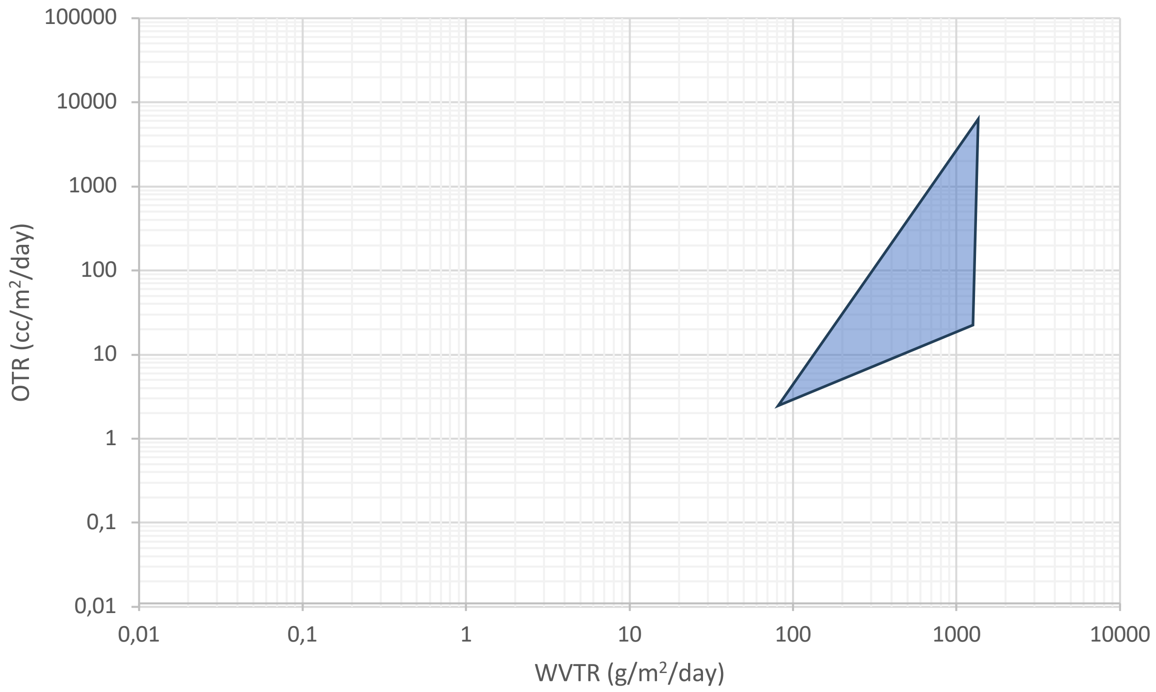

Figure 16. *OTR and WVTR for paper coated with SiOx deposition and performed at 23°C and 85%RH.*

Other packaging properties to be considered: sealing, machinability, availability, cost material and recyclability

A) Sealing properties

SiOx behaves glass-like and is not sealable. Therefore, a sealable topcoat is needed. This can also help with protecting the inorganic layer from abrasion.

B) Machinability

The inorganic layer is glass-like and therefore very rigid which means the material must be handled rather careful and cannot endure too much stress in form of folding and creasing. Barrier properties should be evaluated again after packaging formation to determine realistic barrier properties.

C) Availability and cost of material

The SiOx layers are optically transparent and applied with only a few nanometers thickness whilst providing barriers comparable to barriers obtained by metallization. Therefore, the SiOx layers do not rise any issues when it comes to recycling unlike metallization, which can lead to grey discoloration of the

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recycled fibers (4evergreen report, Circularity by design guideline for fibre-based packaging, version 2, 2023).

Nevertheless, PVD with SiOx is a cost intense process mainly related to the vacuum system use. In addition to that, the application on paper is not trivial and needs preparation. Therefore, the costs need to be seen in relation to the packaging goods.

D) Recyclability

Due to the layer being very thin and transparent, it should not be an issue for recyclability.

2.2 R&D PILOTS WITH 3D SUBSTRATE

Cellulosic trays from Guillin were used as substrate. Different combinations of barrier materials were spray coated on the trays (Figure 17). Trays used for food packaging today is often laminated with plastic film.

Figure 17: *Schematic of single or multilayer spray-coated cellulosic tray substrate*

Materials with barrier properties were spray coated on cellulosic tray. Different combinations of materials and different coating weights were evaluated. Materials used were MFC, chitosan and two different barrier products from Bim Kemi. This pilot used a 3D substrate compared with the other pilots using 2D substrate. That does the evaluation of performance of this material was carried with different perspective. The barriers were applied with spray coating technique which made it necessary to prepare the barriers with special physical properties.

Materials

MFC from Fiberlean were used.
The chitosan was supplied by Alpha Chitin.
Starch-based barrier formulation and partly fossil free barrier formulation from Bim Kemi were used.
Paper based trays from Guillin were used.

3D substrate's functionalization solutions and associated performance

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The paper tray was first coated with a biobased primer layer (Figure 18). This was either MFC or chitosan. The cellulosic nanomaterial in the primer layer will work as a transition between the paper tray and the top coating. The primer layer will give resistance to grease, and it is expected that the cellulose nanomaterial also can give gas barrier performance. Using MFC or chitosan will however not give protection for moisture. A commercially available barrier dispersion was spray coated on top of the primer layer and this material should compensate for the water sensitive primer layer.

Figure 18: *Schematic of single or multilayer spray-coated cellulosic tray substrate with biobased primer*

The gas permeability needs to be further improved. This can be done by either tailoring the primer layer (modification of material, size of material) or by improving the coating technique. Depending on the spray tool used, a better film of primer layer can be obtained which will help the gas barrier performance.

Suspension with suitable concentration was prepared of each material before spraying. Each layer of spray coated had a surface coating of 5-40 g/m^2. Both bottom and walls of the trays were analysed after spray coating. Homogeneous coating was obtained indicating that the 3D barrier application method was successfully managed.

Indication of barrier performance was evaluated by measuring Cobb60, Quick oil test, KIT and caprylic acid test.

Spray coating of MFC followed by chitosan and/or BIM products, the Cobb60 values was significantly lowered from 30-50 g/m^2 (for a reference material) to 0-10 g/m^2 depending on dosage order and coating weight. Depending on multilayer coating weight, the spray coated trays also showed grease resistance.

Other packaging properties to be considered: upscaling and machinability

Materials need to be sprayable, and it requires a consideration on rheology and dry content. If the concentration is too low large amount of water will be incorporated for each spray layer and this will prolong the drying process.

Spray coating is an industrial relevant technique. It is used for painting and the automotive industry already for long time. Additionally, this process is suitable for upscaling and automation to achieve precise control over barrier coating and homogeneity on 3D substrates, even with complex geometries.

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3 DECISION MATRIX

Definition of weighting (i.e., 1-5) for abovementioned criteria: prioritize criteria based on significance.

Each selected barrier system within R3PACK project has its own advantage when it comes to a certain barrier property as well as its disadvantage compared to one another. For evaluating barrier performance, the following tests are commonly applied; a first screening of Cobb, KIT, caprylic acid, followed by a deeper characterization of WVTR and OTR. While a certain system shows good water resistance, WVTR, it does not necessarily show the same good performance when it comes to OTR. All material strategies presented in this report have not been developed until the same development stage. Some strategies were not developed further for deeper characterization. This does not mean the strategies have a shortage of performance, rather promising material strategies were prioritized. However, barrier systems are being developed to reach multiple requirements simultaneously.
As described in the beginning, it requires a holistic approach to develop good packaging but at this stage of the R3PACK project, the strongest side of each barrier system is evaluated first to define which barrier system fall in which of packaging criteria region in the figure below.

Even after each barrier system completes their evolution to their best, there will be still a trade-off between conflicting properties of each barrier system. To be able to meet all necessary criteria for the packaging effectively, it is common to combine the coating systems to get the benefit from synergistical effect. By combining the coating technologies, it is possible to tailor packaging to the food specific needs and thus obtain superior overall barrier properties.

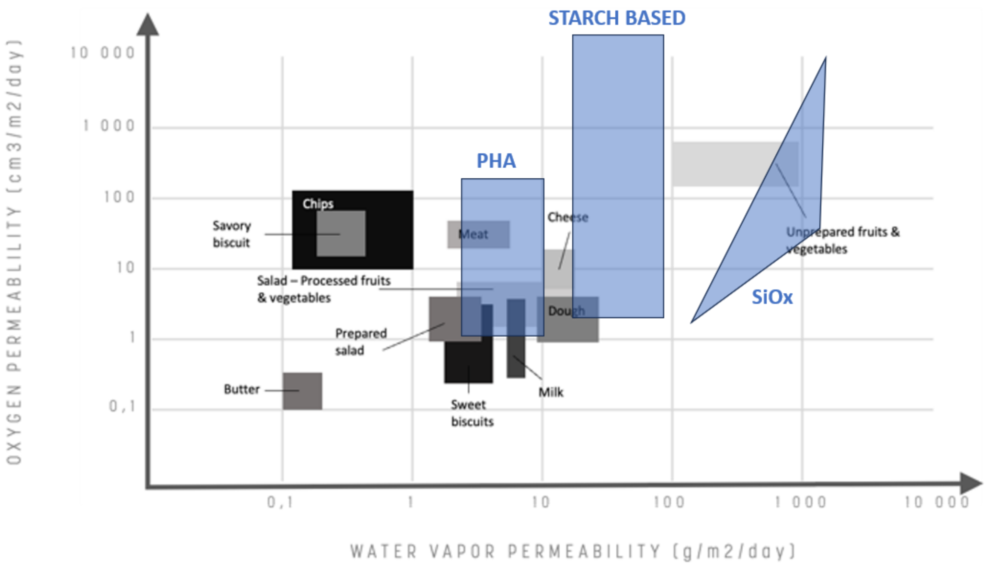

Figure 19. *A schematic overview of barrier performance for food and liquid packaging solutions in relation to barrier materials (PHA, starch and SiOx).*

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As can be seen in the figure, many food categories are covered with the strategies evaluated in this project. This was done by combining materials and using different application techniques. In order to improve the barrier properties even more, and to reach the food categories still not covered in the figure, development of each component is needed. As an example, the chemical composition of PHA can be tailored and thus would lead to a change in properties and also a potential to Improve barrier properties further.

A. Selected Materials and Barrier combinations

From each pilot, materials and technics were selected for the decision matrix, see Table below. The performance of the combinations were evaluated. and they are scored according to their performance for their selected use (each material may pass different types of packaging criteria).

Selected materials
2D pilot 1-PHA laminate 2-PHA dispersion 3-PHA suspension 4-Starch based material 5-Wax based material 6-Siox based coating
3D Pilot 1-starch based formulation 2-Chitosan formulation

B. Creation of Matrix

The data were obtained from relevant characteristics of barrier systems. 5-1 scoring criteria is applied for comparison. The results are summarized in the table below. Two different criteria are scored. Criteria 1 considers the material performance and criteria 2 considers the application performance.
What is not included for consideration is the structure of the substrate. Improvement of substrate, for instance a smoother surface, will have an impact on the barrier performance but is not taken into account here.

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SUBSTRATE	PILOT	CRITERIA 1 Selected material property (differs for each pilot)	CRITERIA 2 Level of application performance at lab scale	SUITABLE FOOD CATEGORY (Based on barrier performance on existing data)
2D PAPER W/WO MFC	PHA LAMINTE	4	5	Meat, sweet biscuits, salad, fruits, cheese
	PHA DISPERSION	4	4	Meat, sweet biscuits, salad, fruits, cheese
	PHA EMULSION	4	3	Meat, sweet biscuits, salad, fruits, cheese
	STARCH BASED	4	4	Dough, cheese
	WAX BASED	3	3	*Data not available*
	SiOx	4	4	Unprepared fruits and vegetables
3D TRAY	STARCH BASED	3	3	*Data not availbale*
	CHITOSAN BASED	3	3	*Data not availbale*

Criteria 1: 1: No promising, 2: Indication of performance 3: Promising but early development stage, 4: Has shown potential, 5: Meets all requirements.
Criteria 2: 1: No applicable, 2: Need to change the application method, 3: Need to develop current application method, 4: Need to adopt material for current application method, 5: Meets all requirements.

As an example, to review how the scoring was performed, the strategy of using PHA laminate will be reflected.
PHA in combination with MFC and an adhesion promoter has shown very good oxygen and water-vapor barrier properties at lab scale. The good barrier properties were obtained by ensuring good coverage of both PHA and MFC. The barrier properties match the requirements for liquid packaging such as stand-up pouches for milk. The barrier properties need to be confirmed also at higher humidity. It is important that adhesion between layers is maintained over time, otherwise the package will not fulfill the requirements of shelf life. There is room for Improvement of this strategy. This can be done by further tailoring the PHA and adapting the lamination parameters. The grading of Criteria 1: Selected material property was 4 for the PHA strategy.
The lamination process has shown good potential at lab scale. The grading of Criteria 2: Level of application performance at lab scale was 5 for this strategy. The lamination process brings several advantages to the product such as extra mechanical support, suitable surface for printing, making firm sealing possible. These properties need to be confirmed when scaling up the process.

4 CONCLUSION AND SHORT-TERM PERSPECTIVES WITH R3PACK DEMONSTRATOR

The trials conducted within the framework of WP4 have demonstrated the potential of various materials for the development of barrier packaging. Combining cellulosic substrates, both 2D and 3D, with these materials could enable the attainment of barrier requirements for a wide range of food products, thereby assisting in the transition to plastic-free packaging.
The next steps will involve scaling up these combinations to conduct additional tests and evaluate requirements beyond barriers, such as machinability, shelf life, sealability, and recyclability.

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These scale-up tests will allow us to confirm the potential of various combinations and precisely match them with the different products to be packaged.
Considering the required development timelines, this work package has concurrently worked on short-term solutions to anticipate the demonstration phase and address the urgent need to bring cellulose-based substrate packaging to the market.
In this context, WP4 is simultaneously addressing the machinability of commercially available papers that are promising in terms of barrier properties. These papers incorporate coatings and laminations derived from petroleum sources, with a cellulosic substrate rate superior to 85%.
Conducting trials with these commercial papers on food producer's industrial lines helps better understand the challenges associated with transitioning from plastic packaging to paper on lines initially designed for plastic packaging.
The advancements made in material development during the initial phase could potentially reduce reliance on petroleum-derived products and optimize various solutions including solutions that are already commercially available, ultimately facilitating the packaging of the entire range of products from food producers.

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