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

Grant Agreement No. 101060806

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EXECUTIVE SUMMARY

This document includes on one hand material selection and testing for barrier systems, and on the other hand the production of wet molded trays to investigate various pulp stock additives as well as process parameters, to reach out the best substrate for future barrier applications, 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 were 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. In the wet molding trials AKD, starch, PAE and a variety of combinations of those were used as additives. A wide range of process parameters were screened to understand substrate's water resistance and surface porosity/topography. 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.

ABBREVIATIONS

AKD - Alkyl Ketene Dimer

CNC – Cellulose nanocrystals

CTMP - Chemi Thermo Mechanical Pulp

DC - Dry content

HV - Hydroxyvalerate

HW - Hardwood

MFC – Microfibrillated cellulose

OTR – Oxygen transmission rate

PAE - Polyamideamine epichlorohydrin

PE - Polyethylene

PHA – Polyhydroxyalkanoate

PHBV – Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

PP - Polypropylene

PVD – Physical vapor deposition

RH – Relative humidity

SEM – Scanning electron microscopy

SiOx – Silicon oxide

SV - Surface variation

SW - Softwood

WVTR – Water vapor transmission rate

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1. R3PACK 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
- to 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,

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cost-effective technologies and reuse models allowing immediate substitution of complex multi-layer plastic packaging.

Figure 1. *Targeted food products*

Cellulosic materials inherently lack the barrier properties necessary to effectively package demanding food products **(Figure 1)**. 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 carnauba wax, microfibrillated cellulose (MFC) onto paper substrates, the processing of polyhydroxyalkanoates (PHAs), the use of starch-based formulation, chitosan, the deposition of silicon oxide (SiOx) by physical vapor deposition (PVD), 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. Also, the possibility to Improve the cellulose substrate itself, has been evaluated for wet molded trays.

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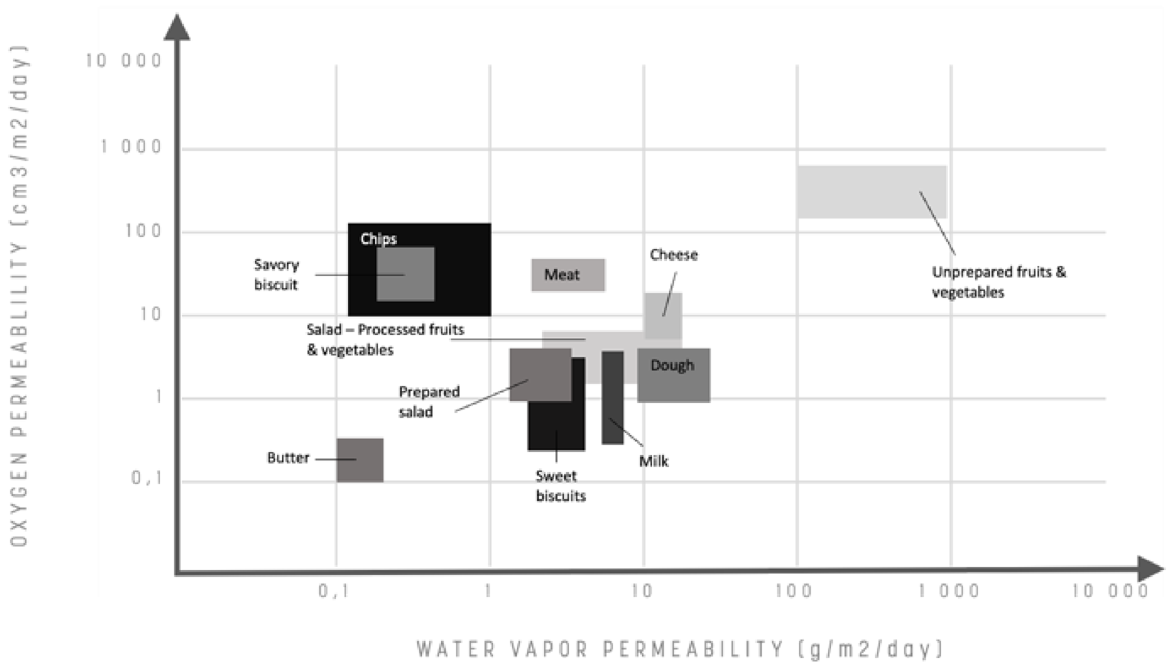

Figure 2. *Overview of R3PACK's food products barrier property's needs (OTR and WVTR) to preserve and maintain their shelf-life.*

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.
- The paper/cardboard rate of the developed packaging solutions must be higher than 85%.

WP4 INVOLVED PARTNERS	**LOGO**	**PARTNER CONTRIBUTION**
BIM KEMI	BIM	Surface analysis, preparation, formulation, deposition, evaluation

BIOEXTRAX	Bioextrax	PHA provider, PHA preparation
FIBERLEAN	FiberLean Technologies	MFC provider, surface preparation
FRAUNHOFER	Fraunhofer IVV	Deposition, machinability evaluation, shelf-life analysis
GASCOGNE	Gascogne	Paper provider, Deposition, cost optimisation
GUILLIN/THIOLAT	GUILLIN EMBALLAGES THIOLAT BY GUILLIN	Molded fiber and cardboard provider, deposition, cost optimization
INNOVHUB	INNOVHUB STAZIONI SPERIMENTALI PER L'INDUSTRIA innovazione e ricerca	Recyclability and compostability evaluation
POLIMI	POLITECNICO MILANO 1863	Financial modeling, cost optimisation
RISE	RI. SE	Surface analysis and preparation, formulation, deposition, evaluation
(RE)SET	(RE)SET	Work Package management

2. INTRODUCTION

2.1. Context and scope of this deliverable

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This document is a technical report that 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, also called strategies. 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. For 3D substate, wet molded paper tray, work has been performed to gain understanding of how the surface of the substrate can be optimized before barrier application.

This technical report summarizes all work performed within the barrier development of WP4. The main conclusions from this work have also been presented in deliverable 4.2 Decision Matrix. In this report, more detailed data will be presented and analyzed.

The desire to work with sustainable alternatives to plastics in the field of food packaging has become a paramount concern. While actual packaging 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).

Finding more environmentally friendly materials 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 feedstock to end-of-life?

Cellulose based material is a good candidate as a replacement of plastics. Cellulosic substrates can be processed by different ways, 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).

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.

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 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.

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.

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.

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.

More details of the materials used will be presented within each strategy. In next paragraph, an overview of the materials used is presented.

2.2. Overview of used materials

The work of the deliverable was based on different materials (lab formulation, commercially available materials, several grades etc.). For a better overview, the following table listed all the used materials (pulp, additive, substrate, coating, laminate etc.). In the Appendix an overview of all the different technical data sheets (if available) has been included.

Table 1. *Overview of substrates and materials used in this project*.

Material (commercial) name	Manufacturer	Composition/Specificity	Form (film, powder, granules)
Substrate			
Bleached paper	FiberLean	50 g/m^2	Paper
Unbleached paper	FiberLean	50 g/m^2	Paper
MFC coated Bleached paper	FiberLean	62 g/m^2	Coated paper
MFC coated Unbleached paper	FiberLean	62 g/m^2	Coated paper
Axello	Billerud Korsnäs	80 g/m^2	Paper
Kraft paper coated with CNC	Gascogne		Paper
Bleached Kraft (BK) paper	Neenah Coldenhove	48 g/m^2	Paper
Paper tray	Guillin	-	Tray

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Wood pulp for wet molding			
Softwood	Not known. Distributed by Guillin		Dried pulp
Hardwood	Not known. Distributed by Guillin		Dried pulp
CTMP	Not known. Distributed by Guillin		Dried pulp
Pulp additives for wet molding			
AKD Fenno Size KD-MB 574MP*	Kemira	Alkyl Ketene Dimer	Dispersion
PAE Maresin M1.0*	Mare	Polyamideamine epichlorohydrin	Solution
Starch	Roquette		Dispersion
Barrier products/materials			
PHBV 1.5*	Bioextrax	1.5 % HV	Flakes
PHBV 11.5 *	Bioextrax	11.5 % HV	Flakes
PHBV	Tianan	3% HV	Powder
PHA		Anionic semi-crylstalline polyhydroxybutylate emulsion, 38-42 %	Emulsion
MFC	FiberLean	1.3 and 3.2% DC	Suspension
Wax	Allinova	Carnauba wax. 40%DC	Dispersion
Chitosan*	AlphaChitin	Fungi based chitosan	Powder
BA85113X*	BIM KEMI	80% biobased, 30%DC	Dispersion
BA85028*	BIM KEMI	50% biobased, 40%DC	Dispersion
Siox	Fraunhofer	Inorganic/ceramic	Deposition by PVD technique

* Technical Data Sheet (TDS) available, see Appendix.

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3. DIFFERENT APPROACHES TO BRING BARRIER PROPERTIES TO PAPER 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 as substrates. The papers from FiberLean were also evaluated with or without pre-coating of microfibrillated cellulose (MFC).

3.1. Possibility of MFC pre-coating to enhance some barrier properties

MFCs are fine nanofibrils of cellulose, obtained through mechanical fragmentation of native cellulose. Their micro/nanometric structure grants them a high specific surface area and an exceptional ability to reinforce the substrates' matrix. Additionally, their 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.

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 provides barriers against moisture, oxygen, and contaminants while also ensuring food safety and compliance with regulations.

3.2. PHA family materials: the use of different materials combination and deposition strategies

3.2.1. Background

The bacterial polyesters polyhydroxyalkanoates (PHAs) are produced by a large range of microorganisms fed by organic biomass, possibly not in competition with food such as agro-residues (Laycock et al., 2014). PHA granules are stored inside the cells of the bacteria during

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the production phase and are then extracted from the cells using various methods. PHAs have gained considerable attention as they are synthetized by a biological process, biobased and biodegradable under natural conditions. Such polymers could substitute some fossil-based plastics such as polyethylene (PE) or polypropylene (PP). One of the most prominent commercially available PHA is the semicrystalline and thermoplastic copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) with varying ratio of 3-hydroxyvalerate monomers in the polymer chain. PHVB displays also excellent oxygen barrier properties, resistant to UV, oil and fat, however it is rather brittle. The modification in the 3HV monomeric composition can bring more flexibility to the material, targeting packaging application (Doineau, Perdrier et al., 2023). Furthermore, flexible packaging based on PHBV has the advantage of being more easily degradable. This is because the degree of flexibility and degradability is a function of the proportion of crystallinity.

Common PHBV based barriers deposition techniques on cellulose-based substrates for packaging application are different coating techniques and thermal film lamination. The starting material form for PHBV can be powder, granules or flakes. A pre-screening work was carried out to increase the fundamental understanding of the processability and performance at lab scale of PHBV deposition on A4 paper sheets, as film laminate, formulation, or combination of both solutions. During this work, emphasis was made on observing characteristics relevant for a potential up-scaling of research pilots, being the aim of R3PACK project.

The processing methods to produce films, lamination of paper and the application of coatings were the focus to evaluate besides the adhesion properties of film laminate on paper substrate. The mechanical properties were evaluated by the adhesion strength of the film laminated paper consisting of a hand peeling test. The z-strength of the substrate was also tested using mechanical testing equipment to give a measured value. The barrier performance was evaluated based on the results from a grease resistance test i) TAPPI T454 (a grease resistance test), ii) OTR test and iii) WVTR tests.

Investigation of different multilayer barrier structures was made step by step by RISE (see Figure 3):

- **“Barrier structure 1”:** lamination of PHBV barrier film to a base paper.
- **“Barrier structure 2”:** lamination of PHBV (Bioextrax and Tianan) barrier film to a base paper with MFC pre-coating to reinforce oxygen barrier.
- **“Barrier structure 3”:** a more complex multi-layer barrier structure consisting of both PHBV based coating formulation and laminate, in combination with MFC pre-coating.
- **“Barrier structure 4”:** the final stage with a PHBV based coating on paper with and without MFC pre-coating, and no PHBV lamination.
- **“Barrier structure 5” (BIM KEMI):** in terms of comparison, investigation of a commercial PHA emulsion and lab PHBV formulation work by BIM KEMI.

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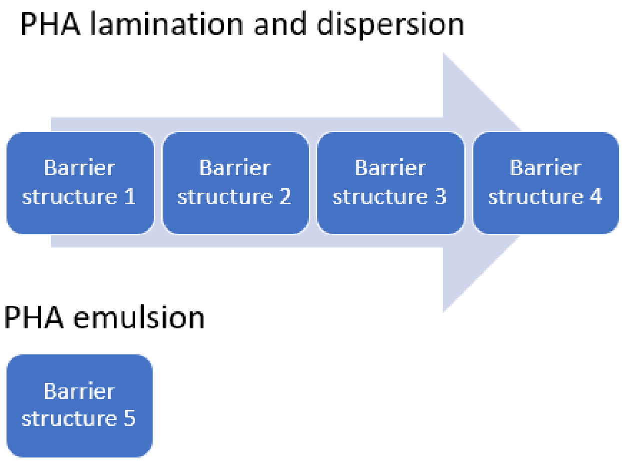

Figure 3. *Work process on PHA deposition techniques and PHA/MFC combination to investigate promising barrier multilayer structures. Barrier structure 1 to Barrier structure 4: PHBV lamination and dispersion in different combination strategies. Barrier structure 5: commercial PHA emulsion and PHBV formulation work.*

See Figure 4 as a general illustration for all PHA barrier structures presented in this section.

Figure 4. *Schematic of PHA applied on paper substrate, with or without MFC pre-coating.*

Rheology is the study of the flow and deformation of materials. For processing of thermoplastics and in this case, film making with heat and pressure of PHBV will involve the flow properties of the molten polymer. The melting temperature of the polymers exists within a range where the processing (in this case hot pressing) is possible, and this range depends on the molecular structure of the polymer. On the other hand, at an upper temperature or higher and combined with a lower crystalline melting point, this will be associated with the onset of thermal decomposition (Brewis, Briggs, & Swallowe, 1999). PHBV exhibits shear-thinning behaviour characteristic of non-Newtonian fluid. This implies pseudoplasticity where the material deviates from a linear correlation between shear stress and shear rate, indicating a complex relationship.

A decrease in **polymer viscosity** will increase the mobility of the molten polymer, which provides a viscosity that is necessary to provide the flow properties required during hot pressing. It is the temperature during pressing in the hot press and on press plates that exhibits

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the most significant effect on the film's stretch ratio and film thickness (Abbasi, Pokhrel, Coats, Guho, & McDonald, 2022). Both increasement in temperature and pressure will cause enhancement of density, crystallinity, MFI, ultimate tensile strength, and Young's modulus. However, an increase in temperature and pressure also alters the fracture mode from ductile to brittle (Younesi & Bahrololoom, 2009). Azam & Lee 2018 demonstrated the importance of the melting temperature of a thermoplastic polymer, which is one of the most important factors affecting film thickness. From the measurement, the film thickness was found to decrease when a higher melting temperature was used (Azam & Lee, 2018).

The **thickness** of laminates is important in relation to, the price, energy cost, barrier and mechanical properties and the choice of the end product. In terms of barrier capability, it is mostly desirable to avoid impregnation but instead to provide a barrier layer that covers the substrate. You may also need to consider the packaging in terms of thickness. For a more flexible packaging that will be handled often, a thinner laminate about 50 µm is preferable. Packaging with a higher risk of creases upon bending may benefit from a thicker laminate, around 100 µm.

Adhesion is the tendency of different particles or surfaces to stick together while cohesion refers to the tendency of similar or identical particles/surfaces to stick together. The forces that cause adhesion and cohesion can be divided into several types. The intermolecular forces are responsible for the function of different types of films. Adhesion falls into the categories of chemical adhesion, dispersive adhesion, and diffusive adhesion. Materials that wet each other tend to have a larger contact area than those that do not. Wetting depends on the surface energy of the materials. Besides an increase in these intermolecular forces, there will also be mechanical effects (Israelachvili, 2011, 3d Edition).

3.2.2. Materials and Methods for "Barrier Structure 1-4"

- **PHBV raw materials**

In this study a PHBV resin was produced and supplied as a fine powder by TianAn Bioploymers. PHBV (ENMAT Y1000P) displays a density of 1.25 g/cm3, a vicat softening temperature of 166°C and a melting temperature (Tm) of 170-176°C. The PHBV contained 3 mol% hydroxyvalerate (3HV) (Mara Cunha 2015).

For the main trials of film lamination, two PHBV grades were investigated from Bioextrax AB, i.e. 3HV fractions of 1.5 wt% and 11.5 wt%. These were delivered as flakes which were then ground into a fine powder using a mortar and pestle before being hot-pressed into film laminates.

Further on in this report %HV is given in a simplified way not showing if it is wt%HV or mol%HV.

Properties for all PHBV qualities are given in Table 2.

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Table 2. *Basic properties of PHBV of 1,5wt%, 3mol% and 11,5wt% of 3HV molar fraction.*

Sample	HV content (%)	Mw (g/mol)	Tm-range (°C)	Purity (gPHA/gTSS)	Producer
PHBV (ENMAT Y1000P	3 mol%		170 - 176		TianAn Bioploymers
PHBV (BX60-BVC27-BX)	1.5 wt%	604×10^3	134 - 177	0.97	Bioextrax AB
PHBV (BX60-BVC06-BX)	11.5 wt%	608×10^3	119 - 166	0.95	Bioextrax AB

- **Papers and deposited barrier coat weights**

See Table 3 for the different papers used as substrate, as well as the coating weight of MFC and/or PHBV deposited by lamination or coating technique, all well described below.

Table 3. *Specified paper grammage and analysed dry coat weights.*

Samples	**Grammage (g/m^2)**
BillerudKorsnäs bleached paper	80
FiberLean bleached base paper	70
MFC coated paper (Bleached FiberLean base paper)	75
	Dry coat weight (g/m^2)
Coatings	
1x red rod coating (PHBV 1,5%HV)	4
1x red rod coating on MFC paper (PHBV 1,5%HV + MFC layer)	7
Melt pressed coatings	
2x black rod coating (PHBV 1,5%HV)	25
Films	
PHBV 1,5% HV film (uncertain values)	105
PHBV 11,5% HV film (uncertain values)	130

- **Description of hot-pressing method for PHBV film production**

Hot-pressing of the PHBV films were carried out using an automatically operating hydraulic Hot-Press Polystat 200T equipped with two heating plates of the dimension 20 x 20 cm2.

Important factors to consider before hot-pressing were: 1) type of material (pellets, granules, or powder, 2) amount of material, 3) heating time, 4) melt temperature of the PHBV 5) pressure required to squeeze the material to a specific film area, 6) cooling time.

An assembly of PHBV powder, backing films and press plates were stacked on top of each other and placed in the hot-press. The order was as follows (Figure 5 and Figure 6): 1. Hot press plate, 2. Backing film, 3. PHBV powder sample, 4. Backing film, 5. Hot press plate.

The stepwise hot-pressing procedure was as follows:

- Weight of the PHBV powder
- Heating of the press plates
- Stacking of the assembly
- Preheating of the assembly in the hot-press (without pressure)
- Hot-pressing; pressure, temperature, and time applied settings
- Cooling in room climate on a lab bench
- Removal of the backing film from the pressed PHBV film

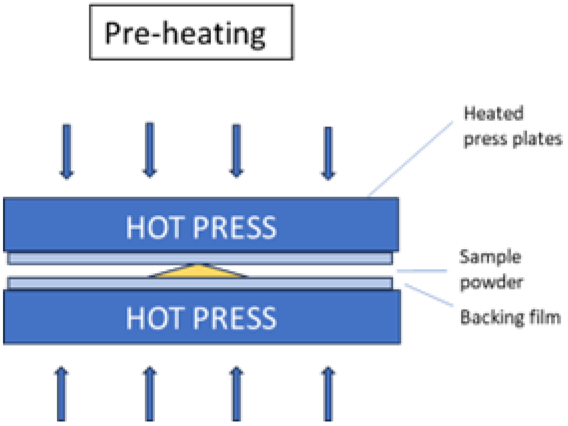

Figure 5. *Pre-heating of PHBV powder without applying pressure settings.*

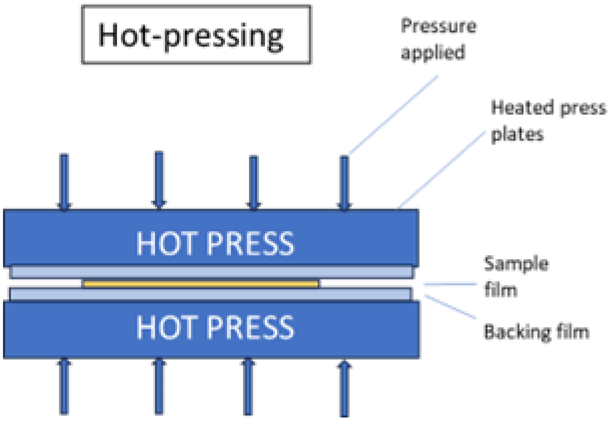

Figure 6. *Hot-pressing of a film using selected temperature, pressure, and time.*

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Two backing films were tested: Mylar PET purchased from Dupont Teijin Films Europe (thickness 100 µm) and a Polytetrafluoreten (PTFE, Teflon) purchased from Fluortek AB, Sweden (thickness 250 µm). The purpose of the backing film was mainly to function as a support but also to facilitate an easy release of the PHBV film. The backing film also avoids the risk of the PHBV film sticking to the aluminium press plates after cooling. Table 4 shows the differences in coefficient of friction and hardness for PET and Teflon respectively. Teflon has 10 times lower friction than PET.

Table 4. *Properties of backing film made of PET and Teflon*

Polymer	Coefficient of friction (µ)	Hardness (Shore D)	Reference
PET (Mylar)	0.4[a]	85 - 90[b]	a) (Dupont_Teijn_Films, 2006) DuPont Teijin Films Mylar® M813 Polyester Film, 48 Gauge b) (Omnexus, 2023)
PTFE (Teflon)	0.06 – 0.13[c]	50 - 65[d]	c) (AZO_Materials, 2023) d) (Omnexus, 2023)

- ### Description of PHBV coating material and deposition process

A semi-automatic K control coater (RK Print Coat Instruments, UK) was used for the application of layers of formulation on paper substrates before lamination. This applied to **formulation "a"**, a PHBV based formulation (adhesion promoter), and **formulation "b"**, a PHBV based dispersion coating. The number of layers and the size of the bars were varied to obtain the final coating weights.

- ### Description of PHBV film lamination

The same equipment was used for film lamination as for film production, i.e. a Polystat 200T press **(Figure 5)**. The thin film was placed on the paper with support films on both sides and on top of these two hot press plates on each side were placed. The purpose of using heated press plates from the start was to achieve a faster process. The films were allowed to melt from the very beginning, and thus allowed the contact with the paper fibers or wetting of the coating surface. Notably, the pressure should be high enough to ensure that the void content is minimal, and that the molten polymer would wet all the fibers or the barrier coating layer. The aim was to achieve a fully laminated sheet of paper. On the other hand, too high pressure and temperature would risk impregnation of the paper, which could risk reducing the barrier capacity. Several methods develop with varied conditions for temperature, pressure and time were investigated, see **Table 5** and **Table 6**.

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Table 5. *Conditions for lamination method 1-3 and A–E.*

Lamination method	Temperature (°C)	Pressure (bar)	Time (s)
D	155	10	20
C	165	10	20
E	176	10	2
B	176	20	10
A	176	20	20
2	176	100	20
1	180	20	20
3	180	100	20

Table 6. *Conditions for melt pressing method B. C. E and F.*

Melt pressing method	Temperature (°C)	Pressure (bar)	Time (s)
C	165	10	20
E	176	10	20
B	176	20	10
F	185	10	20

- ### Description of manual adhesion method

The adhesion tests were performed manually after cooling of the laminated samples. During lamination, a 1.5 cm wide film strip was placed on the substrate with dimensions 6 x (10-12) cm^2 so that the strip part protruded from the paper **(Figure 10).** The idea was to start the peeling with the protruded part. Unfortunately, it turned out that the loose protruding part was prone to break. Therefore, most peel tests were performed directly on top of the laminated film. A ranking list was created to facilitate the evaluation of the manual peeling tests see **Table *7***.

Table 7. Ranking of manual adhesion tests.

Ranking description		Ranking number
No adhesion		1
Light adhesion	No visible coating or fiber pull off strength	2
Medium adhesion	Coating pull-off strength and minor fibre tearing	3

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Strong adhesion	Risk for tearing of film laminate and large fibre tearing strength	4
Impregnation	Impregnation of molten film and unable to detach film	5

The lamination methods differed regarding the choice of temperature, pressure, and time. The remaining conditions were constant such as size of laminate strip, choice of backing film (Teflon) and cooling at room temperature, see Table 4. The actual handling of the peel tests was done by the same person and the same execution.

- **Description of barrier properties characterization methods**

Water vapor transmission rate (WVTR) measurement followed the standard method ASTM F1249, «Standard Test Method for Water Vapor Transmission Rate Through Plastic Film and Sheeting Using a Modulated Infrared Sensor». WVTR has been measured at 23°C and 50%RH with an exposure area of 5 cm^2 and with a conditioning time of 10 hours. The number of measurement cycles varied depending on when steady state was reached. The measurements were performed on instrument Permatran 3/33 and Aquatran 1MG.

Oxygen transmission rate (OTR) measurement followed the standard method ASTM-F1927 «Standard test method for determination of oxygen gas transmission rate, permeability and permeance at controlled relative humidity through barrier materials using a coulometric detector» OTR has been measured at 23°C and 50%RH with 100%O_2 and with an exposure area of 5 cm^2 and with a conditioning time of 10 hours. The number of measurement cycles varied depending on when steady state was reached. The measurements were performed on instrument Ox-Tran 2/22.

The grease test followed the standard method Tappi T454, Turpentine test for voids in glassine and grease proof paper. In accordance with the standard, a grease barrier will be approved if the penetration time for turpentine oil exceeds 30 min.

3.2.3. Barrier structure 1: Processing, results and discussions

AS A REMINDER: “Barrier structure 1” = lamination of PHBV barrier film to a base paper.

PHBV film laminates were manufactured and laminated on uncoated based paper with and without a PHBV based adhesion promotor (**Figure 7**). The PHBV films were based on a commercial PHBV 3%HV (TianAn). The laminated papers were analysed by manual peeling, WVTR measurement, grease test and SEM analysis of the cross section.

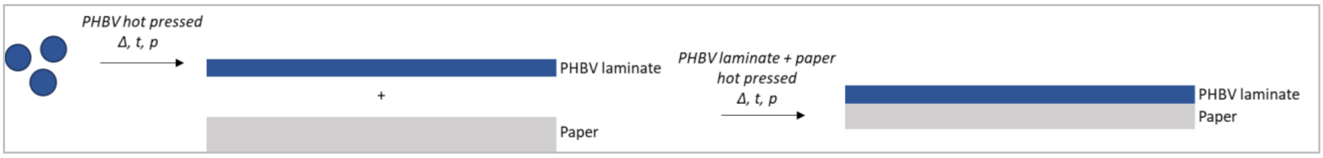

Figure 7. *Schematic representation of paper PHA lamination process*.

- **Film processing optimization of PHBV 3%HV (TianAn)**

The film processing optimization was carried out to find an indication of the magnitude of the effect of temperature and pressure on the film thickness, surface area, surface roughness and the continuity of thin polymer film, in addition to visually evaluating the alteration of the fracturing mode from ductile to brittle. There was also the requirement that the film should be easy to release from the backing film. See pictures on **Figure 8** from the PHBV powder/flakes to the film processing step.

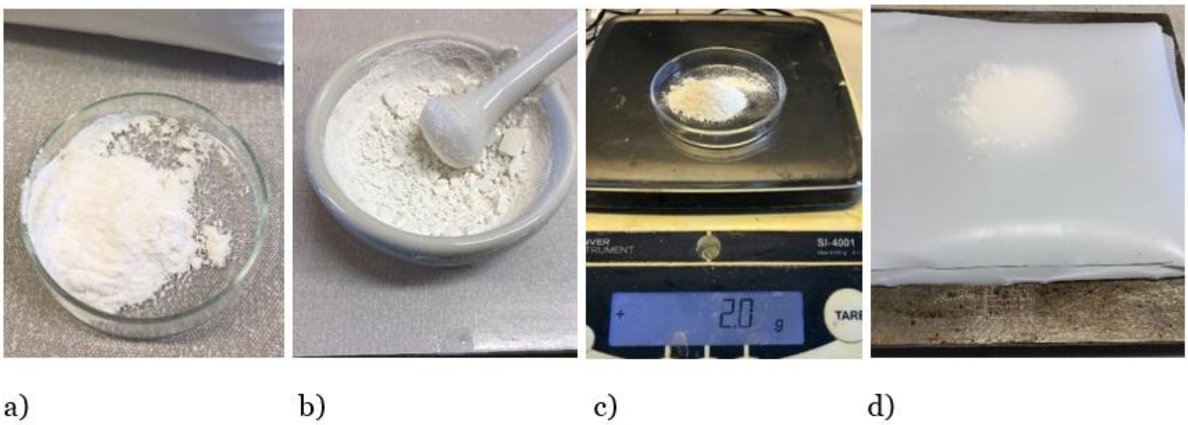

Figure 8. *PHBV from TianAn was delivered as a powder (a) while PHBV from Bioextrax was delivered as flakes which was then ground by hand in a mortar (b). The amount of powder tested for filmmaking varied between 1 - 2 grams (c) In picture (d), the powder can be seen placed in a pile between Teflon films (backing films) before hot pressing.*

The first films were made from PHBV 3%HV from TianAn as that was the available material in the lab at the time. The chosen temperatures were 175°C and 180°C and the hydraulic pressure was set to 280 and 350 bar. Hot pressing was performed at a constant pressing time of 2 min. The weight of the powder varied between 1 and 2 g between tests **(Table 8).**

Table 8. *Hot-pressing conditions for film 3, 6 and 9.*

Film pressing method	3	6	9
Weight (g)	2	1	1
Pre-heating temperature and time (°C, minutes)	(175, 2)	(180, 2)	(180, 2)
Temperature (°C)	175	180	180
Hydraulic pressure (bar)	280	350	350

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Final surface pressure (MPa)	18	22	22
Press time (min)	2	2	2
Backing film	PET (Mylar)	PET (Mylar)	PTFE (Teflon)

- **Results of film processing based on PHBV 3%HV (TianAn)**

Film 6 made from 1g was more difficult to remove from the Mylar (PET) backing film compared to films using PTFE (Teflon). The film was also clearly distinguished by its transparency **(Figure 9 b).**

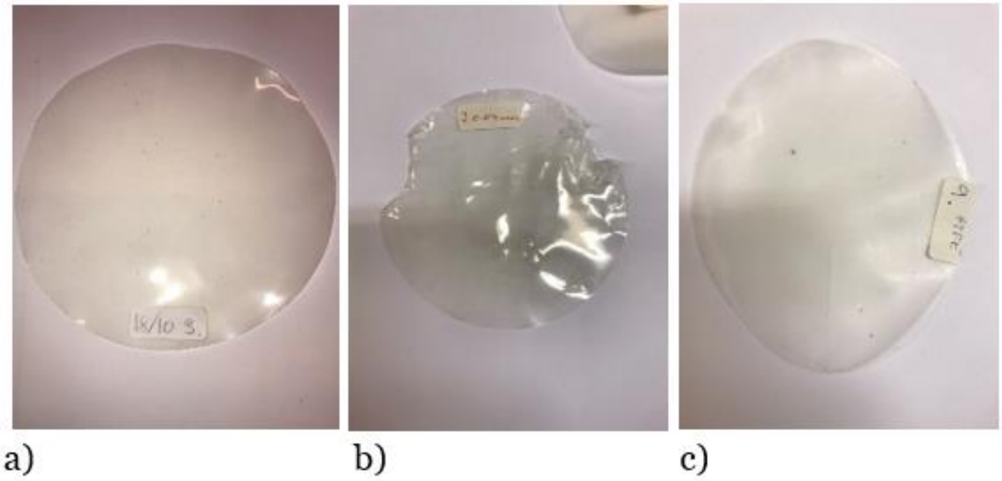

Figure 9. a) *Film 3: 2 gram, 176°C,* **b)** *Film 6: 1 gram, 180°C,* **c)** *Film 9: 1 gram, 180°C.*

Furthermore, 6 was smaller, stiffer, and not as flexible as film 9 even though both were hot pressed with the same conditions. The difference was attributed to the usage of Teflon for film 9. It should be noted that the press temperature of 180 °C exceeded the melt temperature range of 175 °C for both films. Moreover, notable differences in film properties were observed between Teflon and Mylar.

Mylar has a higher coefficient of friction (0.4) and hardness (85 - 90) compared to Teflon, which has values of (0.06 - 0.13) and (50 - 65), respectively. The stiffer, transparent nature of 6 is believed to result from a press temperature exceeding the Tm threshold, combined with the choice of Mylar film. The Mylar film was both harder and provided 10 times more friction than Teflon, giving no indication of the crystallinity of film 6 in terms of its transparent appearance. On the other hand, film 3, also hot-pressed with Mylar film, showed a semi-transparent appearance. However, this film was instead pressed at a lower temperature in the Tm range.

Film 9, pressed with a Teflon film, showed a clear opaque appearance, Indicating significant crystallinity. The degree of crystallization of the barrier material is particularly important for the oxygen barrier. Conversely, despite its high crystallinity, film 9 showed to be the most flexible film. This is in contrary to the general decrease in flexibility as crystallinity increases.

Film 3 was hot pressed with 2 g powder at 175°C within the melt temperature range for PHBV (TianAn) and the applied pressure was 280 bar. This resulted in an even semi-transparent film with quite good flexibility, positioned between the flexibility levels of film 6 and 9. There were no visual pin holes or cracks. It achieved a thickness of 0.12 mm, coupled with a diameter of 12 cm. Mylar was used as the backing film see **(Figure 9 a).**

The PHBV powder was successfully processed into polymer films with a thickness ranging from 70 to 120 µm using the hot-pressing method shown in **Table 9.** All films were even and continuous exhibiting no defects expect for film 6, which was stiffer and more difficult to release from the backing film.

Table 9. *Thickness of films made from TianAn PHBV powder at different pressing conditions.*

Film pressing method	3	6	9
Thickness (mm)	0,12	0,07	0,10

Results summary on PHBV film hot-press processing: These first test on film 3, 6 and 9 resulted in the use of Teflon film as a standard for the film making for further tests. This because films using Teflon were not adversely affected by higher temperatures in the same way as PET, besides giving rise to more crystalline films.

- **Preparation of PHBV laminated papers for adhesion tests "Barrier Structure 1"**

The overall objective was to evaluate the adhesion performance of the PHBV films (3, 6 and 9) laminated to a PHBV-based adhesion promoter coated on the base paper. A reference was also tested with PHBV laminate directly applied on the uncoated paper. The aim was also to get a first indication of the adhesiveness in relation to the thickness of the films.

Samples 1 to 3 were prepared using PHBV films with thicknesses of 0.10 mm and 0.12 mm. For the fourth sample, which was laminated onto uncoated paper **(see Table 10),** a film with a thickness of 0.12 mm was used. The lamination conditions were set according to method 1, 2 and 3 **(see Table 5).** The placement of the film laminate on the substrate is shown in **Figure 10.**

Table 10. *Film processing conditions of PHBV 3%HV lamination*

Test	Substrate	Adhesion promotor	Film laminate (sample, thickness)		Lamination method
1	FiberLean base paper	PHBV (TianAn) based formulation	9	0,10 mm	1
2	FiberLean base paper	PHBV (TianAn) based formulation	3	0,120 mm	2

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3	FiberLean base paper	PHBV (TianAn) based formulation	9	0,10 mm	3
4	FiberLean base paper	No coating	3	0,120 mm	3

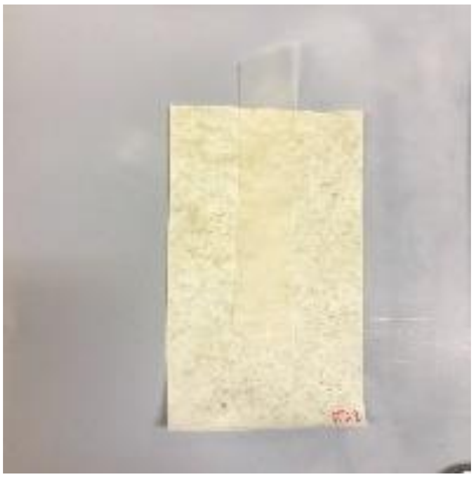

Figure 10. *Example of the placement of a 1.5 cm film strip on a 6 x 12 cm PHBV coated paper prior to lamination in hot-press.*

- **Results of adhesion test – “Barrier structure 1”**

The manual adhesion test showed that the PHBV film exhibited adhesion to the base paper at least as effectively as it did to the adhesion promoter. This was determined by visual observation that the adhesion promoter did not completely cover the paper and it was assumed that it was the paper underneath that contributed to the adhesion result. This assumption was further supported by the test on uncoated paper, which demonstrated equally good adhesion, receiving a ranking of 5 for test 4 **(see Table 11)**. Nevertheless, additional tests need to be made and the adhesion promoter needs to be investigated to draw further conclusions.

Table 11. *Adhesion tests for PHBV (TanAn) films laminated on i) basepaper with PHBV based adhesion promotor and ii) uncoated basepaper. For description of Adhesion ranking, see* ***Error! Reference source not found.****.*

Test	**Substrate**	**Film laminate (sample, thickness)**		**Lamination method**	**Adhesion test on laminated paper**		**Adhesion ranking**
1	FiberLean paper with PHBV based coating	9	0.10 mm	1			4

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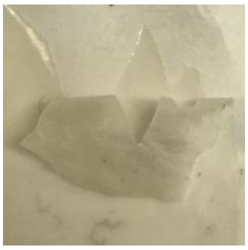
2	FiberLean paper with PHBV based coating	3	0.12 mm	2			4
3	FiberLean paper with PHBV based coating	9	0.11 mm	3			5
4	Fiber Lean base paper no coating	3	0.12 mm	3			5

An increase in the adhesion ability from ranking 3 to 5 was likely due to the increase in pressure and temperature **(Table 11),** see lamination conditions in **Table 5**. Thinner laminates that were pressed in high pressure and temperature further had the tendency to impregnate the substrate to a larger extent, indicating that pressing conditions must be tuned properly.

Results summary on adhesion test of PHBV laminated papers:

- Better adhesion by increasing pressure and temperature parameters.
- Adhesion level of ranking 4 was preferable. This resulted in sufficiently large peel strength without creating cohesion in the film laminate or causing impregnation of the paper.

- **Barrier properties results “Barrier structure 1”**

Barrier properties obtained on “Barrier structure 1” were compiled with those obtained for “Barrier structure 2” in the Section below.

3.2.4. Barrier structure 2: Processing, results and discussions

AS A REMINDER: “Barrier structure 2” = Lamination of PHBV (Bioextrax and Tianan) barrier film to a base paper with MFC pre-coating to reinforce oxygen barrier.

PHBV films were manufactured and laminated on uncoated and MFC pre-coated Fiberlean paper **(Figure 11)**. For “Barrier structure 2”, PHBV films were based on 3%HV (from TianAn), but also 1.5%HV or 11.5%HV (from Bioextrax). PHBV laminated uncoated or MFC pre-coated papers were analysed by manual peeling and grease test.

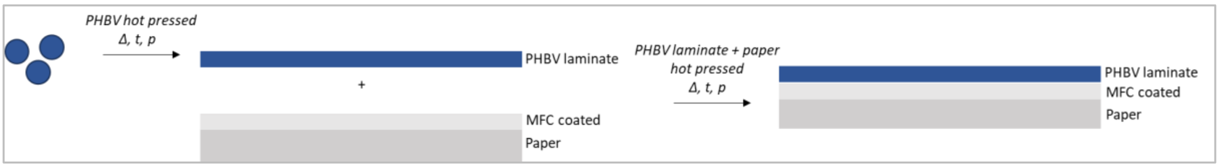


Figure 11. *Schematic of PHBV lamination process on MFC pre-coated paper.*

- **Results of film processing based on PHBV 1.5%HV and 11.5%HV (Bioextrax), and 3%HV (TianAn)**

Film processing with PHBV from Bioextrax was carried out at temperature below the melting temperature of the two grades 1.5% and 11.5% HV.

To begin, the melting temperature used for PHBV Bioextrax was the same of the reference PHBV 3%HV from TianAn. Based on results obtained from film processing of PHBV from TianAn (sub-section "Description of hot-pressing method for PHBV film production"), smaller changes were made for the film processing methods, resulting in method 8 and 11 **(Table 12).** Moreover, Bioextrax and TianAn PHBV films were made following the same method 8 and 11.

Table 12. *Hot-press conditions for film processing methods 8 and 11.*

Hot pressing (film) method	**8**	**11**
Weight (g)	2	2
Pre-heating Temperature and time (°C, minutes)	(180, 2)	(175, 2)
Temperature (°C)	180	175
Hydraulic pressure (bar)	350	280
Final surface pressure (MPa)	22	18
Press time (min)	2	2
Cooling time (min)	5	5
Backing film	Teflon	Teflon

The aim was to create a clear difference in thickness, and Teflon was used throughout these tests. See **Table 12** for remaining constant press parameters. Since Bioextrax PHBV were available in two different grades, i.e. 1.5%HV and 11.5%HV, the two film pressing conditions (methods) were applied for each PHBV grade (see **Table 13**).

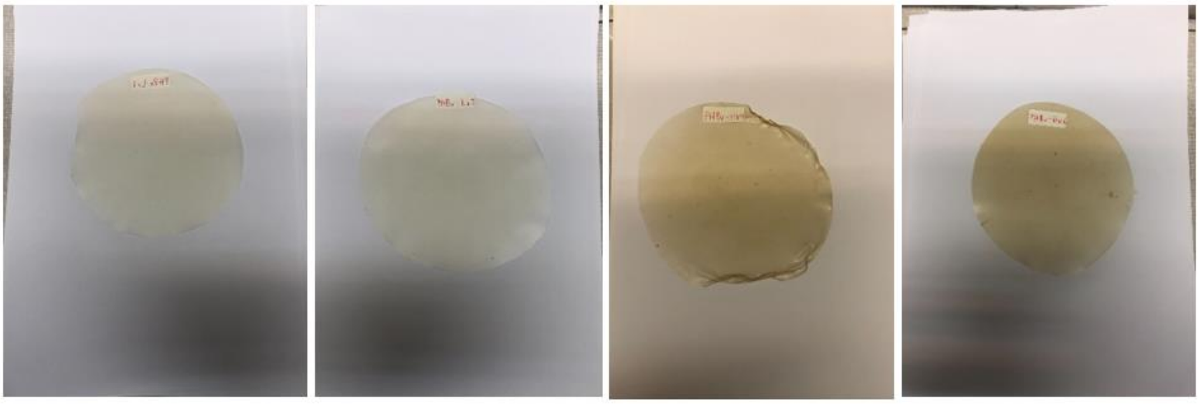
Table 13. *Film pressing of two different film thicknesses using methods 8 and 11, for PHBV 1.5% and 11.5%HV (Bioextrax) and 3%HV (TianAn).*

Film	**%HV from PHBV**	**Film pressing method**	**Thickness (mm)**
A	1.5	8	0.08
B	1.5	11	0.12

C	11.5	8	0.08
D	11.5	11	0.12
E	3	8	0.08
F	3	11	0.12

The PHBV films A, C and E, i.e. with 1.5%HV, 11.5HV% and 3%HV respectively, were pressed at higher temperature and pressure to obtain thinner thickness (0.08 mm), compared to B, D and F (0.12 mm) (see **Table 13**).

PHBV films were evaluated regarding thickness, homogeneity, and ease of handling. The visual appearance of the films is shown below in **Figure 12.**



A) (T, p) (180 °C, 350 bar) B) (T, p) (175 °C, 280 bar) C) (T, p) (180 °C, 350 bar) D) (T,p) (175 °C, 280 bar)

Figure 12: *A) Film A: Bioextrax 1.5%HV (0.08 mm); B) Film B: Bioextrax 1.5%HV (0.12 mm); C) Film C: Bioextrax 11.5%HV (0.08 mm); D) Film D: Bioextrax 11.5%HV (0.12 mm).*

First, all films showed good film-forming properties and were uniform except for PHBV 11,5%HV processed at 180°C and 350bar (thickness 0.08 mm), which was difficult to handle due to excessive film flexibility. Such hot-pressing conditions seem to be too harsh for this grade of PHBV. However, the melting temperatures of Bioextrax PHBV were unknown at this time, which meant that it was not immediately possible to set the right temperature to avoid damaging PHBV. So, the same temperature was used as for PHBV 3%HV from TianAn: the settings for film production methods 8 and 11 was 180 °C/ 350 bar and 175 °C/ 280 bar respectively.

The colour appearance differed between films made from 1.5% and 11.5%HV respectively, showing a whiter colour for 1.5% while 11.5% had a darker yellow-brown colour. The difference may be due to an effect of different degree of purity for 1.5% and 11.5% HV. Moreover, this colour may be due to thermal degradation of the PHBV, which is very often observed at excessively high temperatures (Bossu et al, 2021).

Table 14. *Film pressing temperature in comparison with specified Tm-range. Temperature marked with bold Indicate higher temperature than the specified melting temperature.*

Sample	%HV content	T_m - range (°C)	Film hot-pressing method

			11 (thick film)	8 (thin film)
			Films B, D and F	Films A, C and E
			Press temp (°C)	Press temp (°C)
PHBV	3	170 - 176	175	**180**
	1.5	134 - 177	175	**180**
	11.5	119 - 166	**175**	**180**

Indeed, films A, C and E made from 1,5%, 11,5% and 3%HV PHBV respectively were all hot-pressed at 180˚C, which was above the specified Tm range **(see Table 14).** Film A and E (1,5% and 3% HV) were hot-pressed at 4 and 3 degrees above the range while film C made from 11,5% HV was hot-pressed at 14 degrees above the range. Regarding films processed with milder hot-press conditions (175°C, 280bar), only PHBV 11.5%HV (film D) exceeded the melt temperature range of 119-166°C, so from 9 degrees.

Results summary on PHBV film hot-press processing:

PHBV films with 1,5%HV and 3%HV were processed close to Tm range (3 and 4 °C respectively) and were still cohesive with an even surface and there were no major differences in thickness within each film compared to the usual appearance. Films were easily released and handled.

However, PHBV film D processed at 14°C above the Tm range, resulted in a less even structure with difficulty to separate from the Teflon film. It was clear that the 11.5%HV film had begun to break down due to too harsh hot-pressing conditions.

- **Preparation of adhesion tests and results of PHBV laminated papers for "Barrier Structure 2"**

The overall purpose was to laminate PHBV film to MFC pre-coating base paper to create or improve oxygen and grease barriers. Two different PHBV film's thicknesses were obtained, i.e. thin film with 0.08 mm and thick film with 0.12 mm and laminated to uncoated or MFC pre-coated paper **(Table 15).**

Lamination method 3 with a higher pressure of 100 bar was used despite the indication from previous tests that a lower pressure was preferable. Indeed, a higher pressure was chosen until clear adhesion could be observed during testing.

Table 15. *PHBV laminated both uncoated baseboard and MFC paper for adhesion test, based on PHBV 1.5, 3 and 11.5%HV.*

Adhesion test samples	Film	Thickness (mm)	Substrate (FiberLean)	Lamination method	**Adhesion performance**
5	A C	0.08	(uncoated)	3	**5** **5**
6	B D	0.12	(uncoated)	3	**4** **4**
9	TianAn	0.08 0.12	(uncoated)	3	**5** **4**

7	A C	0.08	MFC coated paper	3	**No adhesion** **No adhesion**
8	B D	0.12	MFC coated paper	3	**No adhesion** **No adhesion**
10	TianAn	0.08 0.12	MFC coated paper	3	**No adhesion** **No adhesion**

No significant difference was found for adhesion between thin and thicker PHBV films, except for TianAn films where the thin film showed the largest adhesion strength (ranking 5) and was impossible to peel off. All films showed very high adhesion strength to the uncoated Fiberlean paper.

However, the presence of MFC pre-coating on Fiberlean paper induced no more adhesion between PHBV laminate film and paper substrate **(Table 15, Figure 13** - **Tests 7, 8 and 10).** This behaviour could be explained by a closer structure of the MFC layer instead of uncoated base paper, making it more difficult to impregnate the paper with PHBV and so, decreasing the mechanical anchoring between PHBV laminate film and base paper.

Test 5 Test 6 Test 7 Test 8 Test 9 Test 10

Figure 13. Test 5) *Thin films of 1.5%HV(left) and 11.5%HV(right),* ***Test 6)*** *thick films of 1.5%HV(left) and 11.5%HV(right),* ***Test 7)*** *thin films of 11.5%HV(left) and 1.5%HV(right) on MFC pre-coated paper,* ***Test 8)*** *thick films of 1.5%HV(left) and 11.5%HV(right) on MFC pre-coated paper,* ***Test 9)*** *thick (left) and thin (right) films of 3%HV,* ***Test 10)*** *thick (left) and thin (right) films of 3%HV on MFC pre-coated paper. Thin stands for film thickness 0.08mm and thick for 0.12mm.*

Results summary on adhesion test of PHBV laminated papers:

- No huge difference between laminate films at 0.08 or 0.12 mm thick, with adhesion ranks from 4 to 5.

- The presence of MFC pre-coating on Fiberlean paper prevents the adhesion between the PHBV laminated film and the base paper.

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- **Barrier properties results “Barrier structure 2”**

First, barrier properties results were obtained for “Barrier structure 1” and are presented in **Table 16.** The PHBV film obtained by the hot-pressing film processing method 3 showed very promising water vapor barrier (23°C, 50%RH) from 0.9 to 4.3 g/m^2/d depending on %HV content, but no oxygen barrier (fail).

Regarding results of PHBV laminated uncoated Fiberlean paper using lamination method 3, a strong water vapor barrier (23°C, 50%RH) from 3.2 to 5.8 g/m^2/d was obtained, very similar to PHBV films. Moreover, an oxygen barrier was observed with OTR (23°C, 50%HR) around 90 cc/m^2/d, compared to PHBV films showing no oxygen barrier. However, no grease barrier was observed for both PHBV films and PHBV laminated Fiberlean papers.

Table 16. *Barrier properties obtained for “Barrier structure 1”.*

Barrier sample	Substrate	Film laminate	Film processing method	Adhesion method	WVTR (g/m^2/day) 23°C, 50%RH	OTR (cc/m^2/day) 23°C, 50%RH	Grease test (approved >1800 s)
1	PHBV film	1,5% PHBv*	3		0,9	Fail	No grease barrier (1 s)
2	PHBV film	11,5% PHBv*	3		4,3	Fail	No grease barrier (1 s)
3	FiberLean baspaper	1,5% PHBv*	3	3	3,2	87	No grease barrier (1 s)/grease barrier
4	FiberLean baspaper	11,5% PHBv*	3	3	5,8		

Fail = Upper measurement limit >2000 cc/m2/day

*At this time, testing of Bioextrax PHBV 1.5% and 11.5% HV had begun

Results summary on barrier properties of PHBV film and laminated uncoated paper: WVTR values of PHBV film was not damaged by the lamination on paper substrate, with values around 3 to 6 g/m^2/d. Moreover, oxygen barrier was observed on the structure PHBV laminate/Fiberlean paper substrate compared to PHBV film. No grease barrier was observed in “Barrier structure 1”.

To obtain an oxygen barrier, a multilayer structure based on a commercial MFC coated paper from FiberLean was used, called “Barrier structure 2”. However, there was no adhesion when PHBV film was laminated to MFC pre-coated paper, for all PHBV grades, i.e. 1.5, 3 and 11.5 %HV.

Results summary on barrier properties of PHBV laminated MFC pre-coated paper: Thus, no qualitative laminated samples with MFC pre-coated paper were obtained to investigate barrier properties. Instead, a grease test was performed on the commercial MFC pre-coated paper from Fiberlean, showing no grease barrier, probably due to the presence of pinholes.

In order to investigate barrier properties of PHBV barrier deposited on MFC pre-coated paper, a new strategy was considered, called “Barrier structure 3”.

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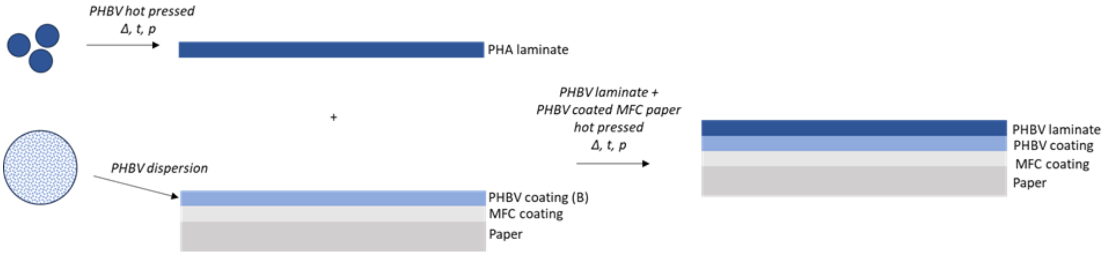
3.2.5. Barrier structure 3: Processing, results, and discussions

AS A REMINDER: “Barrier structure 3” = a more complex multi-layer barrier structure consisting of both PHBV based coating formulation and laminate, in combination with MFC pre-coating.

PHBV films were manufactured and laminated on uncoated paper from Billerud Korsnäs, and MFC pre-coated paper from FiberLean. Before lamination, a PHBV-based dispersion coating was applied to both papers (**Figure 14).** PHBV films were prepared, with PHBV 1.5%HV or 11.5%HV from Bioextrax. Finally, PHBV coated and laminated papers were tested by manual peeling, WVTR, OTR, grease barrier and SEM.



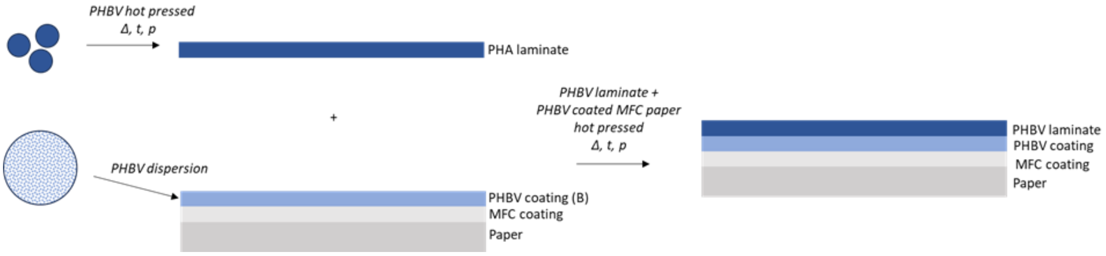


Figure 14. *Schematic representation of PHA laminate on MFC-coated paper, pre-coated with a PHA coating layer.*

- **Preparation of PHBV coated and laminated papers, and results for adhesion test “Barrier structure 3”**

Additional lamination methods A, B, C, D and E **(Table 4)** were tested. Furthermore, because of the adhesion test on “Barrier structure 2”, showing lack of adhesion of PHBV film laminate with MFC pre-coated paper, a PHBV dispersion coating was now added to the MFC pre-coated paper. At this stage, PHBV dispersion coating was slightly optimized. The adhesion strength was tested by manual peeling and the samples were visually examined regarding occurrence of impregnation. The square sized laminated substrates were prepared to perform barrier properties measurements. Thus, WVTR and OTR tests were not included.

Two lamination methods B and D were investigated with water vapor barrier measurements. Lamination method B (T = 176°C, P = 20bar) was performed using harsher hot-pressing conditions, while method D (T = 155 °C, P = 10bar) used milder conditions **(Table 17).** Results of the adhesion tests are also included in **Table 17**, i.e. the adhesion ranking.

Table 17. *Preparation and results for adhesion tests of PHBV films (1.5%HV and 11.5%HV) laminated on uncoated base paper and MFC pre-coated paper, including a PHBV pre-coating layer.*

Sample	PHBV, HV content	Film making method /thickness (mm)		Lamination method	PHBV 1.5wt%HV (1x red rod) coating	MFC coated paper	BK paper	**Adhesion ranking**
3	1.5%	8	0.08	B	x	x		**4**
6				B *	x	x		**4**
7				B	x	x		**3**
4				C	x	x		**3**
5				D*	x	x		**2**
11				B	x		x	**4**
14				B *	x		x	**4**
15				D	x		x	**3**
1	11.5%	11	0.12	A	x	x		**4**
2		8	0.08	A	x	x		**4**
9				B *	x	x		**4**
10				B	x	x		**4**
8				D	x	x		**3**
12				B	x		x	**4**
13				B *	x		x	**4**
16				D	x		x	**3**

*) The laminate films were square shaped with the aim of being tested for barrier properties WVTR and OTR. The remaining films had the shape of a 2 cm wide strip. Sample 7 is not included in the pictures (**Figure 15**).

Optimization of the lamination yielded to different methods, i.e. A to E methods. Peeling tests showed method B the most relevant, with respect to good adhesion strength characterized by fiber tearing behaviour, but no tearing of the film laminate itself, corresponding to an adhesion ranking 4. This was observed for both uncoated and MFC pre-coated substrates.

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Lamination method B (P = 20 bar) induced a small expansion of the film during pressing, and so a quasi no impregnation into the substrate (**Figure 15**).

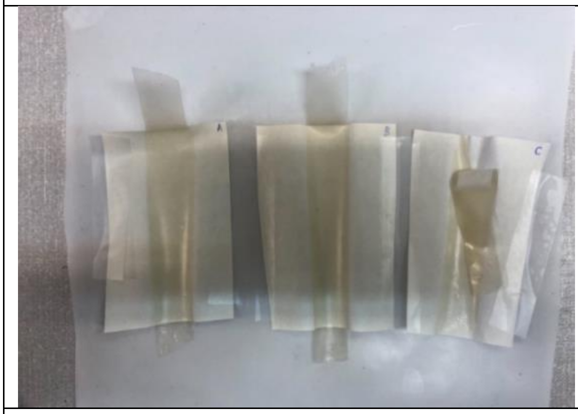
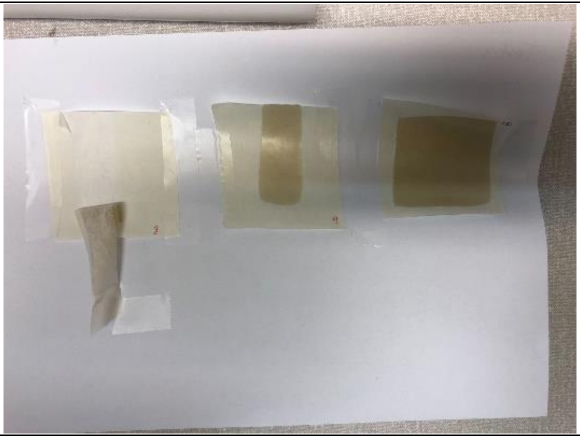
	
Samples 1 (left), 2 (middle) 3 (right)	**Samples 4 (left), 5 (middle), 6 (left)**
	
Samples 8 (left), 9 (middle), 10 (right)	**Samples upper row: 11 (left, 12(middle), 13 (right); lower row: 14 (right), 15 (middle), 16 (right)**

Figure 15. *PHBV laminate/PHBV pre-coating/base paper and PHBV laminate/ PHBV pre-coating/BK paper were tested for adhesion strength. Also, square dimensional samples were produced for WVTR measurement and grease tests.*

Ranking of the adhesion ability for the different laminated papers are detailed in **Table 17**. The PHBV laminates produced with lamination method B showed very good adhesion with fiber tearing (ranking 4) while laminates prepared with lamination method D (milder hot-pressing conditions) showed weaker adhesion (ranking 3), whatever the PHBV %HV.

A comparative WVTR measurement was carried out on samples 5 and 6 having the same conditions but different lamination methods D and B respectively.

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Figure 16. *Test sample 6: 1.5%HV, lamination method B, thin film.*

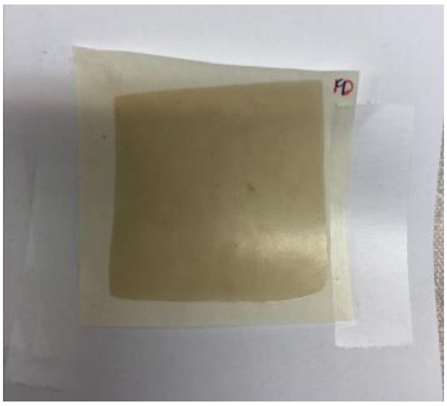

Figure 17. *Test sample 9: 11.5%H, lamination method B, thin film.*

PHBV film laminated on MFC pre-coated paper including a PHBV pre-coating with the same pressing conditions (**Figure 16**) was compared with **Figure 17**, where the only difference was HV content, i.e. 1.5%HV in **Figure 16** and 11.5%HV in **Figure 17** respectively.

After one month, a significant difference in adhesion behaviour was observed. PHBV 1.5%HV laminated paper resulted in blisters and bubbles, while no change occurred for PHBV 11.5%HV. Although PHBV 11.5%HV was processed 14 °C above its melt temperature range, the sample remain stable in macroscopic aspect.

Furthermore, adhesion tests resulted in fiber tearing, indicating that the adhesion strength was stronger than the paper strength. Thus, the z-strength was measured, and the results are given in **Table 18Error! Reference source not found.**. The adhesion strength of the PHBV film against the paper exceeds the measured z-strength of the paper given as ZD tensile strength**.**

Table 18. *Adhesion strength of PHBV film against paper by measuring ZD tensile strength of the paper.*

Quality	ZD Tensile Strength						
	1	2	3	4	Mean [MPa]	Std. Dev. [MPa]	CoV [%]
Axello (Billerud Korsnäs)	2.08	1.89	1.57	1.78	**1.83**	0.22	11.75

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MFC pre-coated Fiberlean paper	1.16	0.92	0.82	1.02	**0.98**	0.14	14.56
Uncoated Fiberlean paper	1.20	1.13	1.41	1.28	**1.26**	0.12	9.69

Results summary on adhesion test of PHBV laminated on PHBV and MFC pre-coated papers: By combining optimized hot-pressing conditions (lamination method B; T = 176°C, P = 20 bar) and PHBV dispersion coating as adhesive promoter, the adhesion of the multilayers was improved, even with the presence of MFC pre-coating on the surface of paper.

- **Barrier properties results "Barrier structure 3"**

Successfully, the multilayer structure was not over-pressed, preventing the total impregnation of PHBV within cellulosic fibres to maintain the barriers. Films of PHBV with both 1.5% and 11.5% HV, laminated to MFC pre-coated Fiberlean paper by lamination method B, showed a good ambient water vapor barrier, i.e. WVTR (23°C, 50%RH) = 3.5 and 4.5 respectively, besides remaining the grease barrier **(Table 19).** Film laminated MFC coated paper following lamination method B gave a WVTR of 4.5 while instead using lamination method D gave a poor WVTR of 94.

Table 19. *Barrier results for "Barrier structure 3"*

Substrate	PHBV dispersion coating as adhesion promoter	PHBV %HV (film)	Hot-pressing method	Laminate method	WVTR (g/m2/day) 23°C; 50%RH	OTR (cc/m2/day) 23°C; 50%RH	Grease test (approved >1800 s)
MFC pre-coated Fiberlean paper	1.5%HV PHBV $(7\ g/m^2)$	1.5	8	B	3.5	9760	Grease barrier
		11.5			4.5		Grease barrier
		1.5		D *poor adhesion*	94		
Bleached kraft (BK) paper	1.5%HV PHBV $(4\ g/m^2)$	1.5	8	B	3.2		Grease barrier
	1.5%HV PHBV $(4\ g/m^2)$	11.5			2.0		Grease barrier
Optimized pressing method with calendering							
MFC pre-coated	1.5%HV PHBV $(25\ g/m^2)$	1.5	8	B		0.6	

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Fiberlean paper							

PHBV laminated uncoated bleached kraft (BK) paper without MFC pre-coating (hot-pressing method 8) showed very good WVTR values (23°C, 50%RH) of 2.0 to 3.1 g/m2/d depending on %HV content, and diplayed a grease barrier. The OTR barrier has not yet been measured for all structures, even if it is known that MFC pre-coating contributes to oxygen barrier. However, oxygen barrier appears very low for PHBV laminated MFC pre-coated Fiberlean paper (hot-pressing method 8) with OTR (23°C, 50%RH) = 9760 cc/m^2/d.

In order to improve the oxygen barrier, calendaring process of MFC pre-coated paper was implemented to the "Barrier structure 3", changing the PHBV based dispersion coating regarding g DS from 30 wt% to 20 wt% (inducing 25gsm coat weight instead of 7gsm), but keeping the hot-pressing conditions and lamination method. This improved the oxygen barrier with OTR below 1 (**Table 19**).

Results summary on barrier properties of PHBV coated and laminated on MFC pre-coated paper:

- high OTR barrier was obtained by optimizing the dry content of PHBV coating and by implementing a calendaring step. PHBV coated (25gsm) and laminated on MFC pre-coated Fiberlean paper displayed OTR (23°C, 50%RH) below 1.
- water vapor barrier was also obtained on "Barrier structure 3" with 7gsm PHBV adhesion promoter coat weight and without calendaring, i.e. WVTR (23°C, 50%RH) = 2.0 to 3.1 g/m2/d, as well as grease barrier.

3.2.6. Barrier structure 4: Processing, results and discussions

AS A REMINDER: The final stage with a PHBV-based coating on paper with and without MFC pre-coating, and no PHBV lamination.

The barrier performance of PHBV dispersion coating was evaluated on both MFC pre-coated and uncoated paper, prepared with a deposition of one or several layers (**Figure 18**).

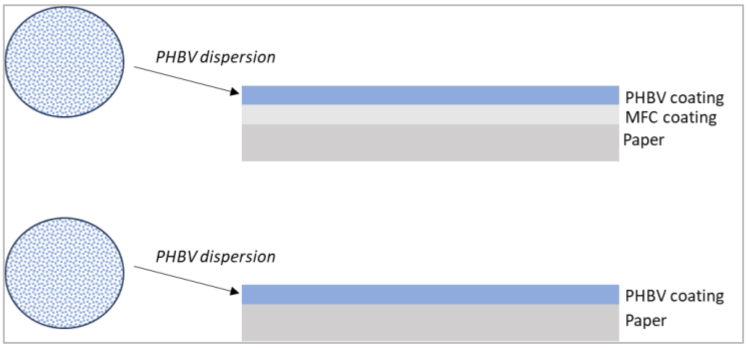

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Figure 18. *Schematic representation of PHBV dispersion coated paper with and without MFC pre-coating..*

Considering complexity to obtain high oxygen barrier, different optimisation strategies were investigated to improve OTR values by tuning the structure of the substrate, i.e., **calendaring of MFC pre-coated paper** as well as **melt-pressing of PHBV/MFC-coated paper**.

- **Dispersion coating formulation and application technique**

Solid PHBV flakes were produced by Bioextrax. PHA was ground into a fine powder and then dispersed in water with a binder (PVOH) and a dispersion agent.

PHBV-based coating formulation was deposited by a laboratory bench coater, used with wire wound rods of varied sizes for different number of layers. The coated papers were dried 105 ˚C, 5 minutes.

- **Barrier properties results “Barrier structure 4”**

The material has shown a good water vapor barrier with WVTR = 7 to 10 g/m2/day at 23°C, 50%RH. Grease test was performed on PHBV dispersion coated MFC pre-coated Fiberlean paper and revealed the presence of a grease barrier. Moreover, the optimized MFC pre-coated paper showed a very good oxygen barrier with OTR = 6.9 cc/m2/d. It has to be noticed that the presence of a grease barrier does not always lead to a good oxygen barrier **(Table 20).**

The multilayer structure without MFC was not over pressed. There is otherwise a risk at higher temperature and pressure conditions that the PHBV melt impregnates the cellulose fibers with a decreased barrier capacity consequently. However, this was not the case here, the barrier layer remained on top of the substrate **(Figure 19).**

Table 20. *Barrier results for Barrier structure 4*

Substrate	Adhesion promoter (PHBV based dispersion coating)	Hot-pressing method	WVTR (g/m2/day) 23°C 50%RH	OTR (cc/m2/day) 23°C 50%RH	Grease test (approved >1800 s)

FiberLean paper	1.5%HV PHBV (25 g/m^2)	E	12.3		No grease barrier (5 min)
MFC pre-coated Fiberlean paper			11.4		Grease barrier
FiberLean paper	1.5%HV PHBV (25 g/m^2)	B	7.0		
MFC pre-coated Fiberlean paper			12.3		
Optimized pressing method					
MFC pre-coated Fiberlean paper	1.5%HV PHBV (25 g/m^2)	F		6.9	

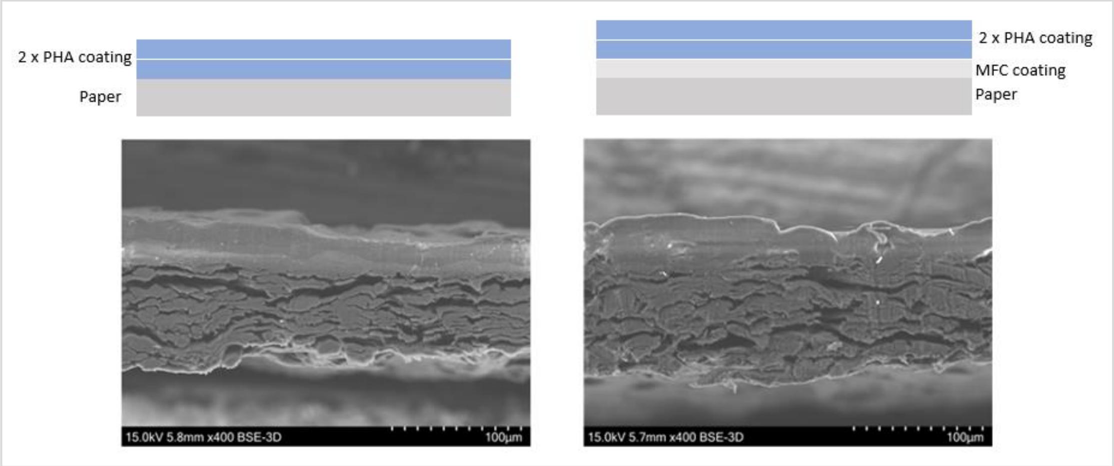

Figure 19. *SEM images at 300x magnitude of a cross-section of a) base paper coated with double layers of PHBV based dispersion and b) MFC paper coated with double layers of PHBV based dispersion.*

3.2.7. Summary Barrier Structure 1-4

A summary of barrier properties (WVTR, OTR and grease barrier), adhesion performance and barrier layer weight for barrier structure 1, 2 3 and 4 is shown in Table 21.

- It was shown that tougher pressing conditions regarding pressure and temperature resulted in a thinner film using method 8 as compared to a thicker film using method 11. In most of the tests these samples were used.
- Teflon film was used as the standard backing film in film production and lamination. This is because films using Teflon were not negatively affected by higher temperatures in the same way as with PET. In addition, the use of Teflon was shown to contribute to

more crystalline films with an opaque appearance. The degree of crystallization of the barrier material is particularly important for the oxygen barrier.

- The conditions for lamination i.e. pressure and temperature are important factors for the adhesion performance but also influencing the risk for delamination.
- To avoid delamination a lamination temperature at the upper range of the melting point was necessary.
- The delamination influenced the barrier properties measured with water vapor after delamination 98 vs 3.5 without.
- The MFC paper did not show any grease barrier property.
- To achieve adhesion properties on the MFC coated paper, there was a need for a PHBV based pre-coating.
- The 11.5% PHBV containing film showed better durability than 1.5% when observing the delamination after 30 days. Note that this was for a film with 11.5% PHBV pressed above its Tm range thus resulting in the risk of degradation of polymer chains.
- The most influential factors for improving the oxygen barrier were the optimization for the PHBV laminated MFC paper (using a PHBV based adhesion promoter with increased DS) and the PHBV coated MFC coated paper (using tougher melt pressing conditions utilizing the thermoplastic properties of the PHBV coating). In both cases the MFC paper was calendered (Table 24).

Table 21. *Barrier properties (WVTR, OTR and grease barrier), adhesion performance and Barrier layer weight for barrier structure 1, 2, 3 and 4.*

	Barrier structure 1 - 4	**Barrier layer weight (g/m^2)**	**Adhesion test by hand**	**Grease test (Tappi T454)**	**WVTR (g/m^2/day) 23°C 50%RH**	**OTR (cc/m^2/day) 23°C 50%RH**
	Lamination of PHBV					
1	**PHBV films** Hot pressing of PHBV powder into films	100 - 140 µm		Fail	0,9 - 4,3	
	PHBV laminates FL Lamination of PHBV films onto paper, FL = FiberLean paper		Approved	Fail	3 - 6	87
2	**PHBV laminated MFC paper FL** Lamination of PHBV films onto MFC coated paper (FL)		Fail			
3	**PHBV laminated BK (BillerudKorsnäs) paper coated paper with PHBV dispersion coating**	4 - 7 (coating layer)	Approved	Approved	2 - 3	Fail
	PHBV laminated MFC coated paper with PHBV dispersion coating	4 - 7 (coating layer)	Approved	Approved	3.5 - 4.5	**0.43**
	MFC paper	15 (MFC layer)		Fail		
	Bar coating following melt pressing					

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4	**Melt pressed PHBV coated paper**	25		Fail	11	Fail
	Melt pressed PHBV coated MFC paper	25		Approved	7	**6,93**

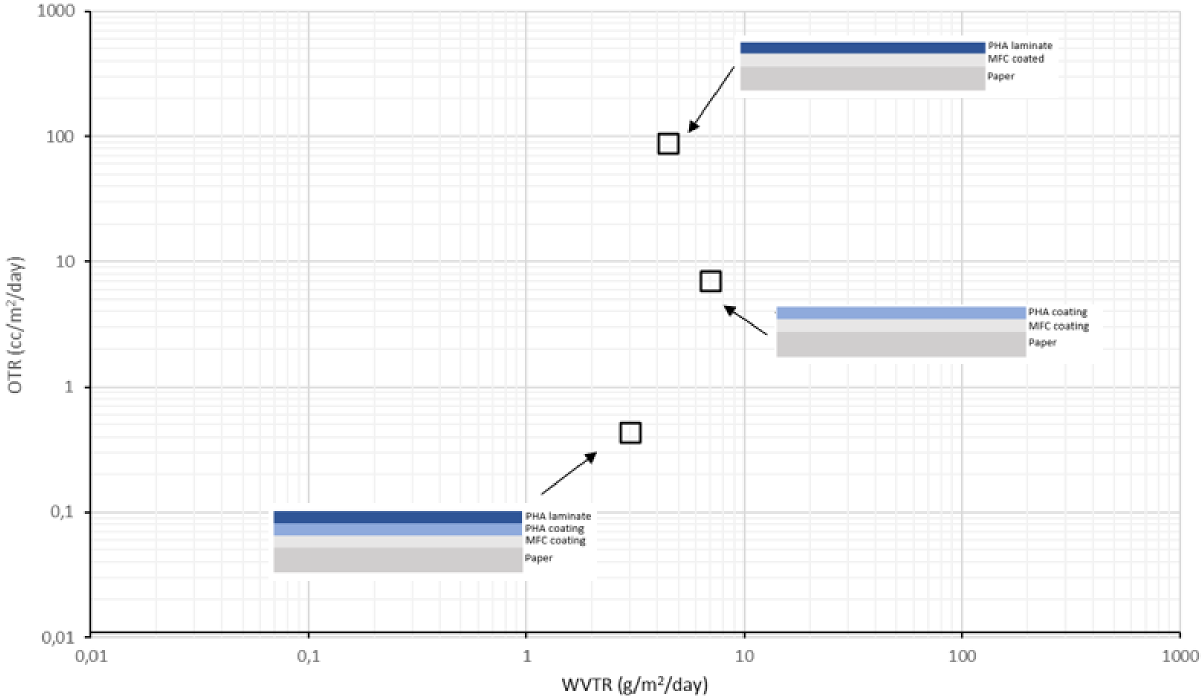

Figure 20. *OTR and WVTR measured for three different material combinations of PHA deposition on paper substrate, performed at 23°C and 50% RH.*

3.2.8. Barrier Structure 5: Processing, results and discussions

AS A REMINDER: in terms of comparison, investigation of a commercial PHA emulsion and lab PHBV formulation work by BIM KEMI.

- **Raw materials**

For dispersion coating trials on different substrates, two PHBV grades were investigated from Bioextrax AB, i.e. 3HV molar fractions of 1.5 % and 11.5 %. These were delivered as flakes which were then ground into a fine powder using a mortal before being dispersed in formulations. Moreover, a PHA emulsion from CJ Biomaterials was also evaluated as a dispersion barrier coating. Following PHA materials were used:

- PHA Emulsion from CJ Biomaterials. The dry content was 40 %.
- PHA from Bioextrax AB
- BX60-BVC27-BX" Pure PHBV 1.5% valerate 97% purity"
- BX60-BVC06-BX" Pure PHBV 11.5% valerate 95% purity"

Following paper substrates were used as substrate:

- Fiberlean uncoated and unbleached paper

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- Fiberlean uncoated and bleached paper
- Fiberlean MFC precoated and unbleached paper
- Fiberlean MFC precoated and bleached paper
- Neenah Coldenhove bleached Kraft 48 gsm

The PHBV qualities from Bioextrax AB was prepared in formulations and the PHA emulsion from CJ Biomaterials was used as it is, one or two layers of the different formulations were applied by bar-coating on the different substrates, i.e., MFC-coated and uncoated papers **(Figure 21).**

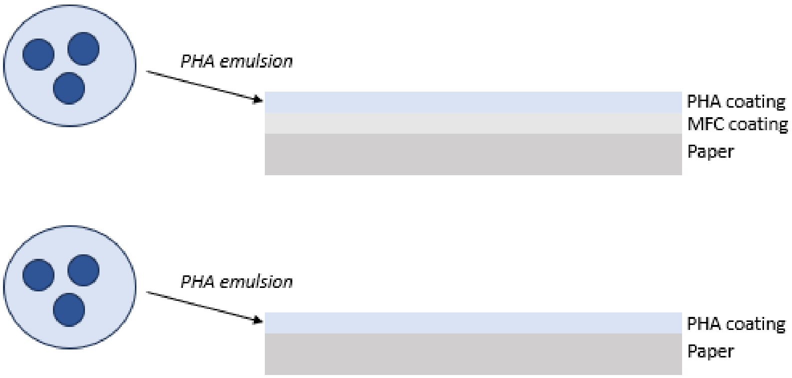

Figure 21. *Schematic of PHA emulsion coated paper with and without MFC.*

The different PHA/PHBV formulations were deposited on different substrates at one or two layers of coating. Two layers showed better results of liquid water and fat resistance compared to one layer. WVTR values obtained with this strategy were between 36 and 55,2 g/m^2/day at 23°C and 75% RH.

- **Coating of PHA emulsion and PHBV dispersion**

A RK Control coater was used with wire rod bars for application of the PHA emulsion and the PHBV formulations. A conveyor oven was used for drying the coated papers, see picture below in **Figure 22**. An IR lamp was used at the opening of the oven giving a temperature of above 200℃ followed by 100 °C in the oven, and the drying time was 1.5 min. An IR lamp was used at the opening of the oven giving a temperature of above 200 °C followed by 100 °C in the oven, and the drying time was 1.5 min. Test were also made without the IR lamp, instead a temperature of 180-200 *℃* was used in the oven. The paper substrates were coated with one or two layers of PHA/PHBV. To be able to coat the second layer, the first layer needed to be hot, coming directly out of the oven. Before conducting any surface analysis, the substrates are acclimatized to RH 50 % and 23 °C. The coating weight is gravimetrically measured by weighing of the coated sample and withdrawing of the weight of the uncoated reference sample.

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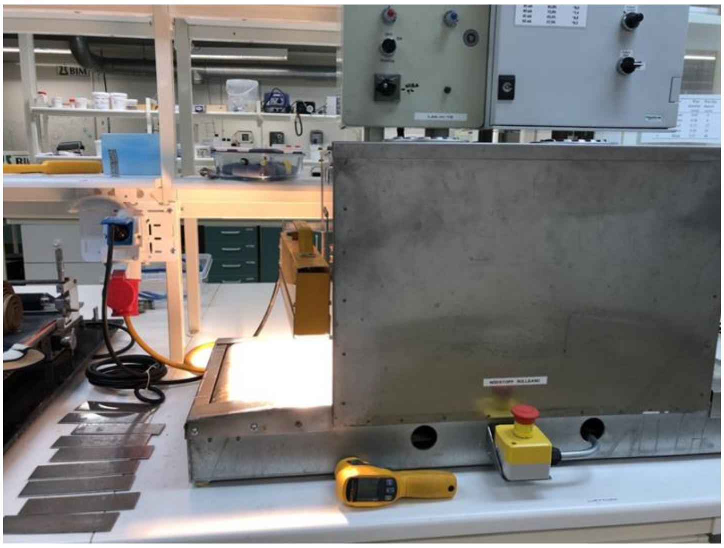

Figure 22. *Picture of IR Lamp and conveyor oven*

- **Description of barrier properties characterization**

The coated substrates were tested for liquid water, moisture, and grease resistance.

The COBB-test (standard: ISO 535:2014) is used to determine the quantity of water that can be absorbed by the surface of paper or board during a given time. The samples are evaluated for a set time, normally between 60 seconds and 30 minutes. The time in seconds is included in the methods name, for example a 30 minutes test is called COBB1800.

Grease resistance is measured with KIT-test (TAPPI T-559 pm-96). The test consists of organic solvents with different degree of aggressivity on a range from 0-12, with 12 being the most aggressive. The different solvents are applied to the test specimen for 15 seconds. The KIT-test solution with highest number that does not affect the base paper is noted as the grease resistance KIT-number.

WVTR (standard ASTM E96/E96M-16) measures the permeability of barrier materials by using diffusion. The sample is sealed between a wet chamber and a dry environment. The water vapor that permeates through the barrier is absorbed by a hygroscopic salt and the amount is gravimetrically measured. The test can be done at different conditions, from temperate (23 °C, RH 75 %) to tropical (38 °C, RH 90 %).

- **Barrier properties results "Barrier structure 5"**

The PHA emulsion was evaluated on different substrates at one or two layers of coating. Two layers of PHA emulsion showed better results of water and fat resistance compared to one layer. The coated PHA emulsion dried with IR lamp showed better barrier properties compared to the coated PHA emulsion dried in oven at 180-200 °C.

The PHBV dispersions were formulated and coated in two layers. Two types of grades of PHBV powder were used, either 1,5 or 11,5 % of hydroxyvalerate, for the PHBV dispersions. Of each

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PHBV grade, two types of formulations were made with different dry contents, 30 and 40 % respectively. There were no big differences observed between the different hydroxyvalerate types. However, to verify the significance of the results more testing would be needed.

The substrates with a precoating of MFC gave better fat resistance, nevertheless the water resistance was decreased. Overall, PHA emulsion and PHBV dispersion showed good potential regarding their barrier properties. An obstacle worth noting is that the drying of the PHA and PHBV barrier requires much higher temperatures compared to a classical dispersion barrier. Another obstacle is that the second layer of coating needs to be applied when the first layer still is hot, otherwise the second layer will bead on the surface.

The barrier performance of PHA emulsion coated on FiberLean unbleached paper, dried with IR lamp is presented in Tables below (**Table 22**, **Table 23**). Results for PHA emulsion coated on Kraft and FiberLean bleached paper, dried with IR lamp, is presented in Appendix.

The barrier performance of PHA emulsion coated on FiberLean unbleached paper, dried with IR lamp is presented in Tables below. Results for PHA emulsion coated on Kraft and FiberLean bleached paper, dried with IR lamp, is presented in Appendix.

Table 22. *PHA emulsion coated on FiberLean uncoated and unbleached paper.*

PHA emulsion coated on FiberLean uncoated and unbleached paper			
Number of coating layers	1	2	2
Coating weight [g/m^2]	9	16	44
KIT	fail	6	10
Cobb1800 [g/m^2]	43	40	5
WVTR (g/m^2*day) at 23°C & 75%RH	-	-	46

Table 23. *Results obtained of PHA emulsion coated on FiberLean MFC coated and unbleached paper, PHA coating dried with IR lamp.*

PHA emulsion coated on FiberLean MFC pre-coated and unbleached paper			
Number of coating layers	1	2	2
Coating weight [g/m2]	7	17	45
KIT	12	12	12
Cobb1800 [g/m2]	90	35	6
WVTR (g/m2*day) at 23°C & 75%RH	-	-	36

The barrier performance of PHA emulsion coated on kraft and FiberLean MFC pre-coated unbleached paper, dried with 180-200 °C in oven, is presented in Figures below (**Figure 23**, **Figure 24**).

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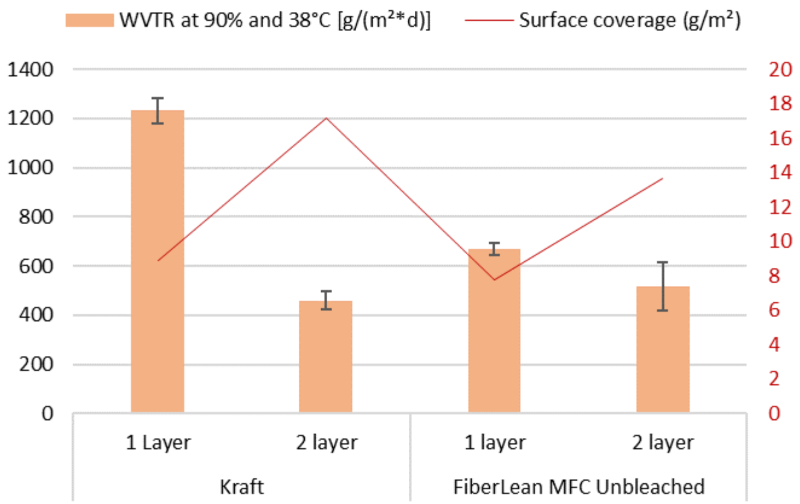

Figure 23. *WVTR at 90% RH and 38 °C (g/(m^2*d)) and surface coverage of PHA emulsion on kraft paper and FiberLean MFC unbleached paper. PHA coating dried at 180 - 200 °C in oven.*

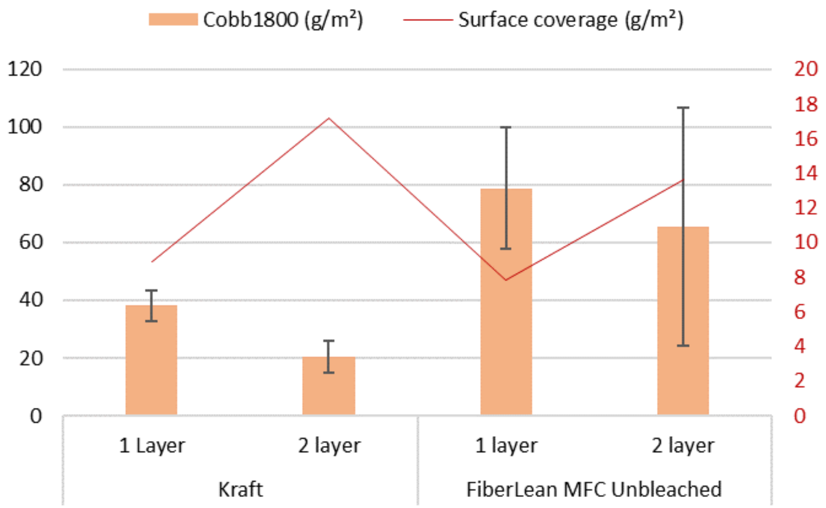

Figure 24. *Cobb1800 (g/m^2) and surface coverage of PHA emulsion on kraft paper and FiberLean MFC unbleached paper. PHA coating dried at 180 - 200 °C in oven.*

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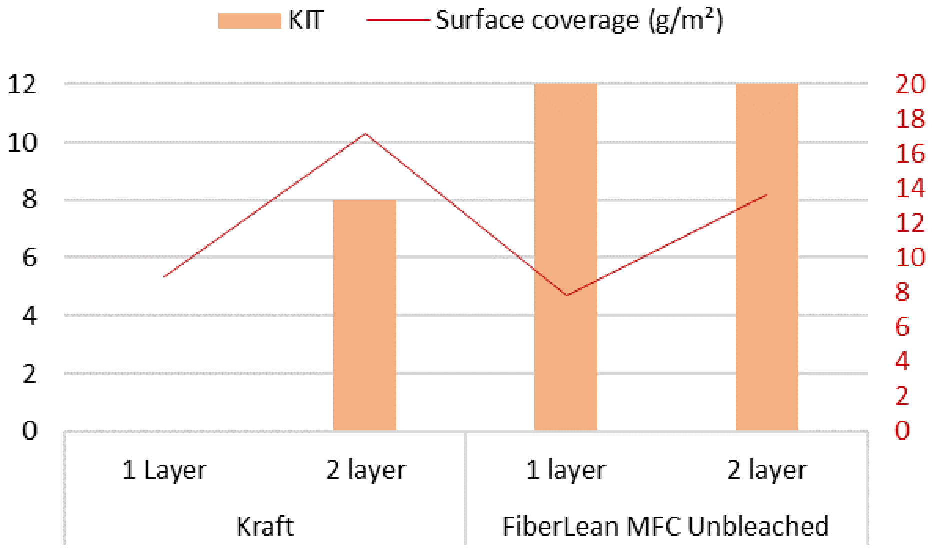

Figure 25. *KIT and surface coverage of PHA emulsion on kraft paper and FiberLean MFC unbleached paper. PHA coating dried at 180 - 200 °C in oven.*

The barrier performance of PHBV dispersion (1.5 % HV) coated 2 layers on kraft paper, dried with IR lamp is presented in **Figure 26**.

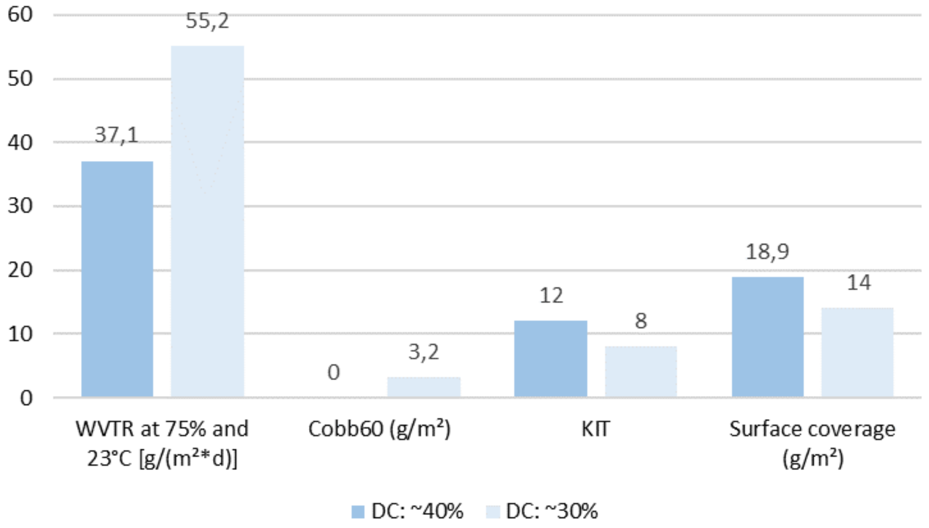

Figure 26. *WVTR 75% RH and 23 °C (g/(m2*d)), Cobb60 (g/m2), KIT and Surface coverage (g/m2) for 2 layers of PHBV dispersion of* 1.5 % HV, 30 or 40 % dry content*, coated on kraft paper.*

The barrier performance of PHBV dispersion coated 2 layers on FiberLean unbleached paper, dried with IR lamp, is presented in the Figures below (**Figure 27**, **Figure 28**).

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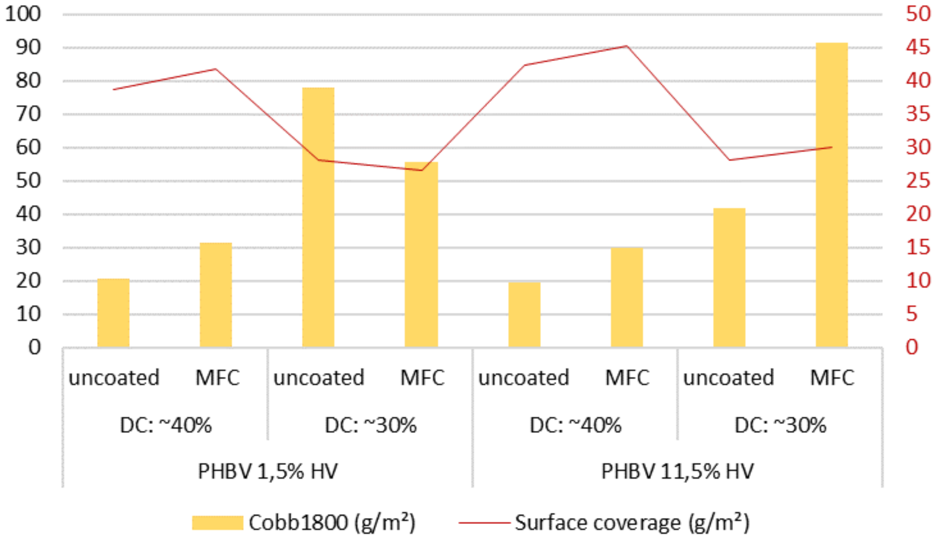

Figure 27. *Cobb1800 (g/m2) for 2 layers PHBV dispersion, 1.5 or 11.5 % HV, 30 or 40 % dry content*, coated on FiberLean *MFC coated or uncoated* unbleached paper

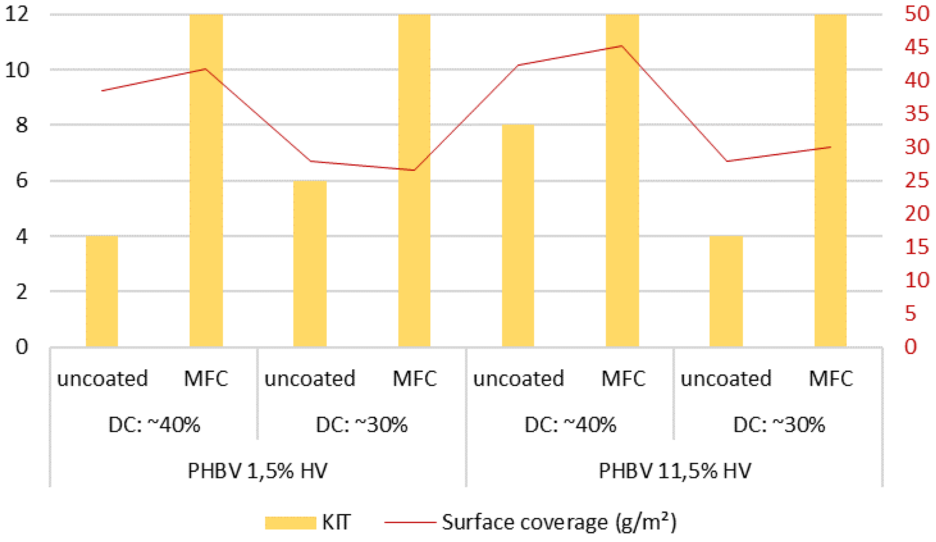

Figure 28. *KIT for 2 layers PHBV dispersion, 1.5 or 11.5 % HV, 30 or 40 % dry content, coated on FiberLean MFC coated or uncoated unbleached paper*.

3.2.9. 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 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 Regulation, 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 an ability to be reused.

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3.3. Starch-based solutions

3.3.1. Background

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).

Starch-based and partly fossil free coatings were applied on MFC-coated or uncoated paper substrates (**Figure 29**) and the barrier properties and performance of multilayer structures were evaluated.

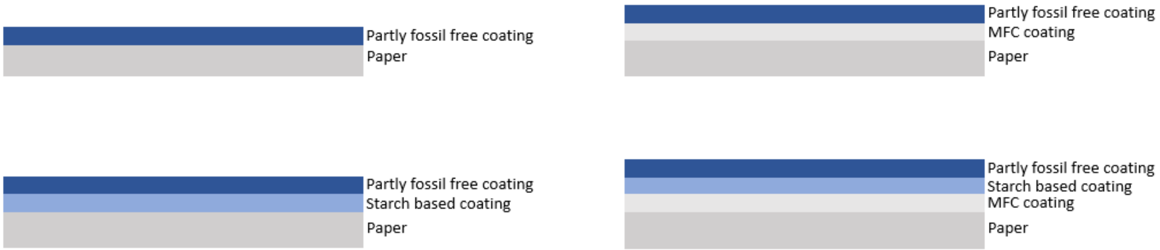

Figure 29. Schematic of partly fossil free and starch-based coatings deposited on MFC-coated or uncoated paper.

3.3.2. Material and methods

- **Description of the material**

A starch-based barrier formulation, BIM BA 85113X, was used as barrier and as a primer layer. A partly fossil free barrier formulation, BIM BA 85028, was used as a top coating.

BIM BA 85113X is a development product from BIM Kemi, dry content ~30 %. It is a barrier with intended use in food packaging. Focused resistance against fat and grease. The barrier is starch based and 80 % fossil free of solid content. No animalic content.

BIM BA 85028 is a development product from BIM Kemi BA 85028, dry content ~40 %. It is a barrier with intended use in food packaging with good resistance against water, moisture, fat and grease. The barrier is partly biobased and 50 % fossil free of solid content. No animalic content.

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

- **Description of preparation method**

The starch-based barrier coating (BIM BA 85113X) was used as a primer with the partly fossil free barrier (BIM BA 85028) 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.

A RK Control coater was used with wire rod bars. A conveyor oven was used for drying of the coated papers. A temperature of 120 °C was used and the drying time was 1.5 min. Before conducting any surface analysis, the substrates are acclimatized to RH 50 % and 23 °C. The coating weight is gravimetrically measured by weighing of the coated sample and withdrawing of the weight of the uncoated reference sample.

- **Description of characterization method**

The coated substrates were tested for liquid water, moisture, oxygen and grease resistance.

The COBB-test (standard: ISO 535:2014) is used to determine the quantity of water that can be absorbed by the surface of paper or board during a given time. The samples are evaluated for a set time, normally between 60 seconds and 30 minutes. The time in seconds is included in the methods name, for example a 30 minutes test is called COBB1800.

Grease resistance is measured with KIT-test (TAPPI T-559 pm-96). The test consists of organic solvents with different degree of aggressivity on a range from 0-12, with 12 being the most aggressive. The different solvents are applied to the test specimen for 15 seconds. The KIT-test solution with highest number that does not affect the base paper is noted as the grease resistance KIT-number.

WVTR (standard ASTM E96/E96M-16) measures the permeability of barrier materials by using diffusion. The sample is sealed between a wet chamber and a dry environment. The water vapor that permeates through the barrier is absorbed by a hygroscopic salt and the amount is gravimetrically measured. The test can be done at different conditions, from temperate (23 °C, RH 75%RH) to tropical (38 °C, RH 90%RH).

The determination of the oxygen permeation (OTR) of the samples was performed according to DIN 53 380-3 (oxygen specific carrier gas method) with an Oxtran Twin (Mocon) at a temperature of 23 °C with pure oxygen and a relative humidity of 50%RH. The samples were tested in a double determination.

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3.3.3. Results and discussions

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 (**Error! Reference source not found.**-**Error! Reference source not found.**). 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.

The barrier performance was measured on samples with partly fossil free barrier alone or in combination with starch-based barrier. The extent of surface coverage on the paper substrates varied. The WVTR was less than 53 g/m^2/day for all samples except for the sample with primer layer BIM BA 85113X and top coating BIM BA 85028 on FiberLean uncoated bleached paper. The barriers showed good water resistance. Cobb1800 was less than 37 g/m^2 for all samples. The sample with both primer layer and top coating on FiberLean MFC coated unbleached paper showed the best performance in Cobb, 0.6 g/m^2, it also had the highest surface coverage, 22 g/m^2. All barriers showed good fat resistance. The KIT value was 12 for all except for the samples with BIM BA 85028 alone on FiberLean uncoated papers.

The barrier performance was measured on samples with partly fossil free barrier alone or in combination with starch-based barrier. The extent of surface coverage on the paper substrates varied. The WVTR was less than 53 g/m2/day for all samples except for the sample with primer layer BIM BA 85113X and top coating BIM BA 85028 on FiberLean uncoated bleached paper. The barriers showed good water resistance. Cobb1800 was less than 37 g/m2 for all samples. The sample with both primer layer and top coating on FiberLean MFC coated unbleached paper showed the best performance in Cobb, 0.6 g/m2, it also had the highest surface coverage, 22 g/m2. All barriers showed good fat resistance. The KIT value was 12 for all except for the samples with BIM BA 85028 alone on FiberLean uncoated papers.

The barrier performance for primer layer BIM BA 85113X and top coating BIM BA 85028, as well as BIM BA 85028 alone, are presented in the Figures below **(Figure 30, Figure 31, Figure 32, Figure 33).**

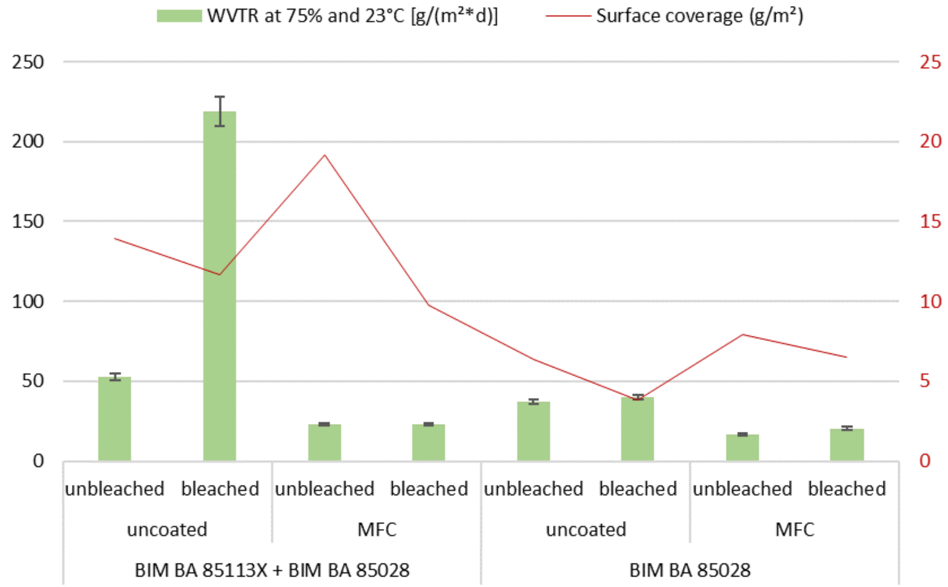

Figure 30. *WVTR at 75% RH and 23 °C (g/(m^2*d)) and surface coverage (g/m^2) of BIM BA 85028 alone or in combination with BIM BA 85113X. Different substrates from FiberLean used, coated/uncoated with MFC on bleached or unbleached paper.*

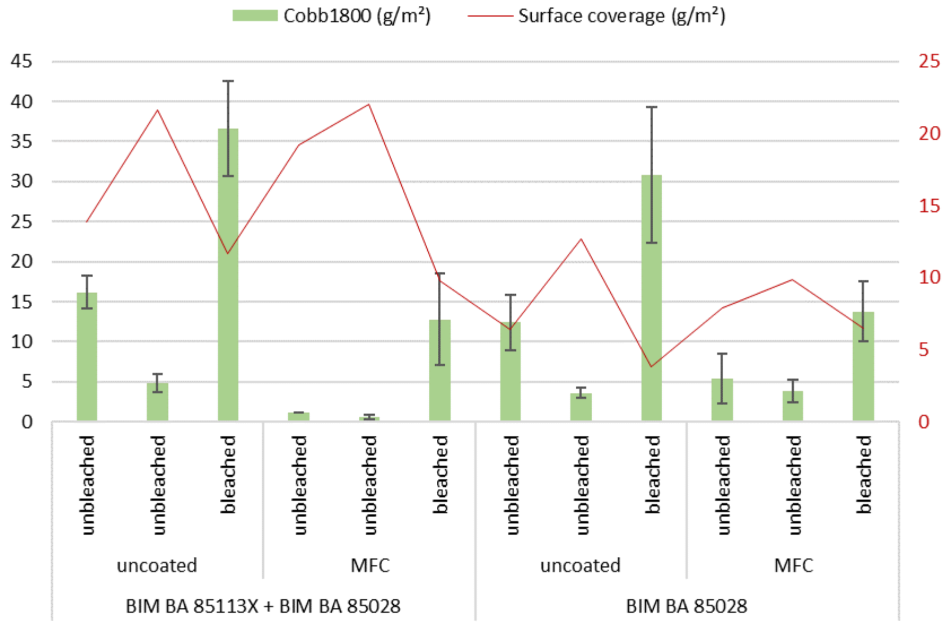

Figure 31. *Cobb1800 (g/m^2) and surface coverage of BIM BA 85028 alone or in combination with BIM BA 85113X. Different substrates from FiberLean used, coated/uncoated with MFC on bleached or unbleached paper.*

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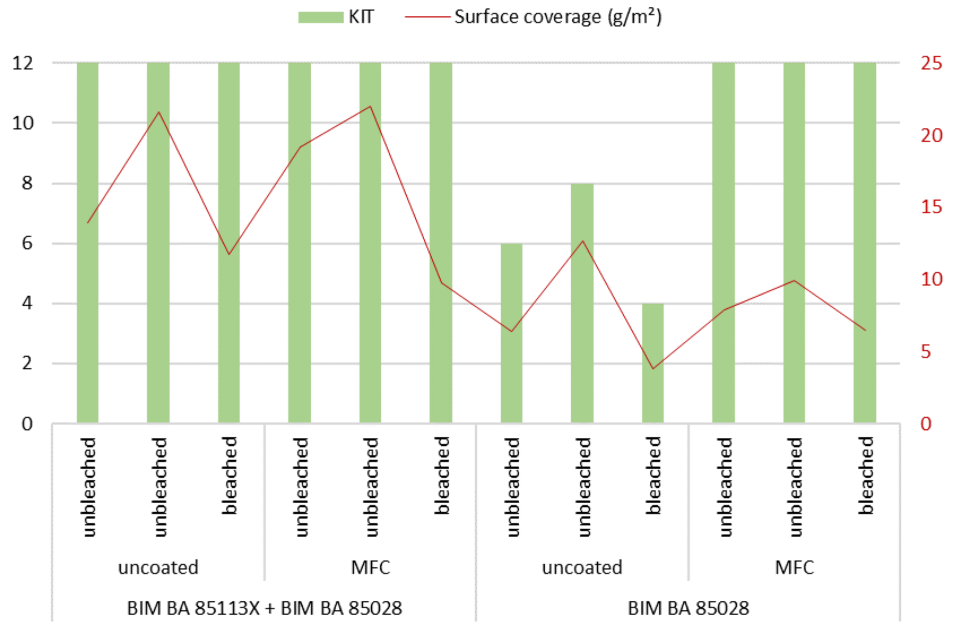

Figure 32. *KIT and surface coverage (g/m^2) of BIM BA 85028 alone or in combination with BIM BA 85113X. Different substrates from FiberLean used, coated/uncoated with MFC on bleached or unbleached paper.*

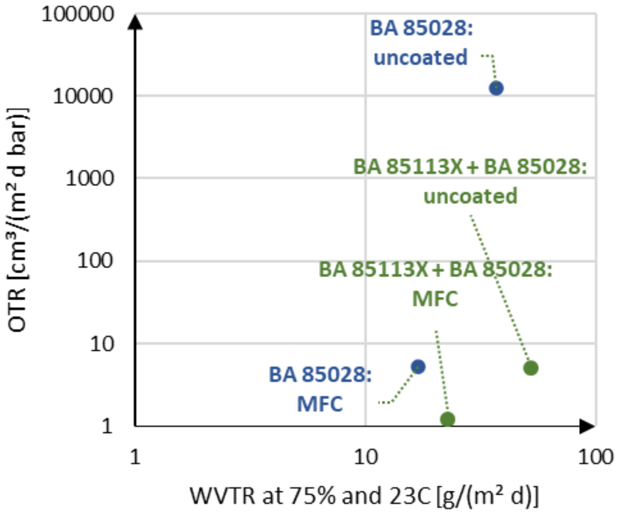

Figure 33. *OTR and WVTR measured for BIM BA 85028 alone or in combination with BIM BA 85113X coated on FiberLean unbleached papers, MFC coated or uncoated.*

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.

Results summary on starch-based pilot: The starch-based barrier showed promising barrier properties in combination with the partly fossil based barrier. This material will be further evaluated in a scaled-up process.

3.4. Wax based strategy

3.4.1. Background

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).

The method of obtaining a waxy layer that is appropriate as a barrier for packaging can vary where either i) melted wax is used directly through application on the packaging surface or ii) formulation of an emulsion prior to application with certain coating technique. The second alternative lends itself well as the control of coating layer is more straightforward and is compatible with techniques such as rod-coating, in contrary to the former alternative. Wax formulations can further be differentiated based on the presence or absence of solvents. In solvent-based formulation the wax is dissolved and will thus form the coating layer upon removal of solvent from the freshly applied coating. For dispersions without the presence of solvents the wax has to be melted and emulsified (while in a liquid state). After this the wax droplets should be stable as they will harden and form a solid-in-water dispersion. Given the environmental drawbacks of solvent-based systems we only consider dispersions without solvents in this project.

The possibility to use carnauba wax as a barrier was evaluated. The wax was added as a dispersion coating on paper or in combination with other materials. Different barrier formulations were tested, using different combinations of carnauba wax together with other components of formulations such as chitosan and/or PHA emulsion, see **Figure 34**.

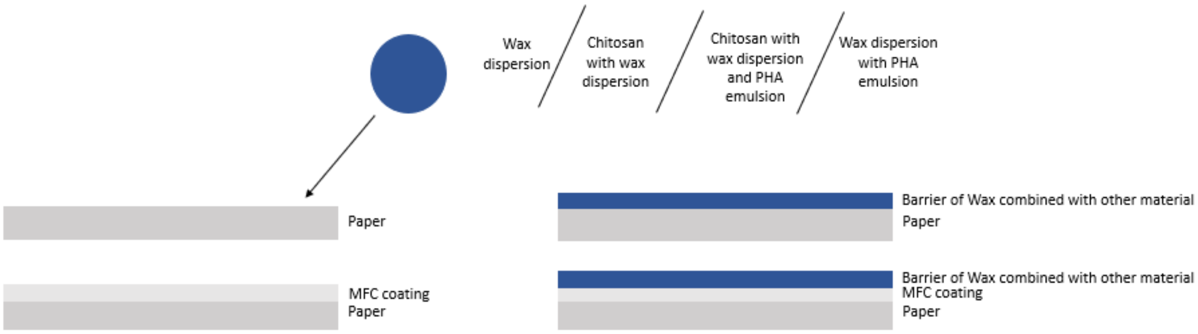

Figure 34. *Schematic of different combinations of wax-based barrier formulations coated on MFC-precoated or uncoated paper.*

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One of the materials explored together with wax was 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.

3.4.2. Material and methods

- **Description of the material**

Following material was used as components in barrier formulation:

- Carnauba wax dispersion (Innospers CWSF) supplied from Allinova. The dry content was 40 %.
- Chitosan (PREC+AA, 220607-GHL) was supplied from Alpha Chitin.
- PHA Emulsion from CJ Biomaterials. The dry content was 40 %.

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
- Neenah Coldenhove bleached Kraft 48 gsm

- **Description of preparation method**

Different barrier formulations were prepared with the different raw materials. Formulations with approximate dry content:

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- Carnauba wax with chitosan, ~40 %
- Carnauba wax with chitosan and PHA, five formulations A-E, ~27-37 %
- Carnauba wax with PHA, three formulations A-C, ~40 %

The prepared formulations were coated on the different substrates in one and two layers. See Figure below for example picture, carnauba wax with chitosan formulation coated on kraft paper 1 or 2 layers.

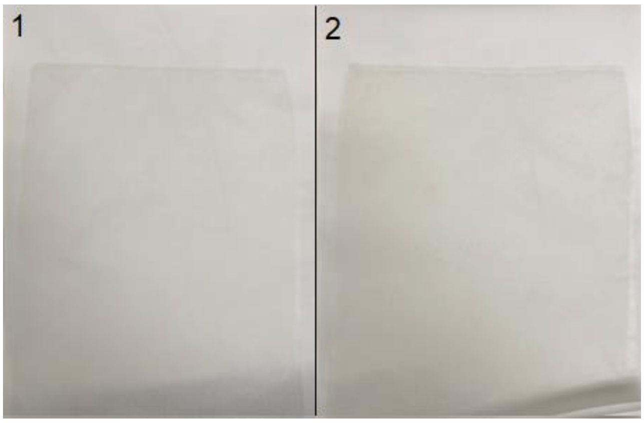

Figure 35. *Pictures of carnauba wax with chitosan formulation coated on kraft paper, 1 and 2 layers.*

A RK Control coater was used with wire rod bars. A conveyor oven was used for drying of the coated papers. Most often a temperature of 120 °C was used and the drying time was 1.5 min. Depending on the coating materials need, usage of an IR-lamp, other temperatures and other drying times were used. Before conducting any surface analysis, the substrates are acclimatized to RH 50 % and 23 °C. The coating weight is gravimetrically measured by weighing of the coated sample and withdrawing of the weight of the uncoated reference sample.

- **Description of characterization method**

The coated substrates were tested for liquid water and grease resistance.

The COBB-test (standard: ISO 535:2014) is used to determine the quantity of water that can be absorbed by the surface of paper or board during a given time. The samples are evaluated for a set time, normally between 60 seconds and 30 minutes. The time in seconds is included in the methods name, for example a 30-minute test is called COBB1800.

Grease resistance is measured with KIT-test (TAPPI T-559 pm-96). The test consists of organic solvents with different degree of aggressivity on a range from 0-12, with 12 being the most aggressive. The different solvents are applied to the test specimen for 15 seconds. The KIT-test solution with highest number that does not affect the base paper is noted as the grease resistance KIT-number.

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3.4.3. Results and discussions

Carnauba wax dispersion was coated on bleached kraft paper. The dispersion was added in one layer. The Cobb60 value was 47 g/m2 (see **Table 24**).

Table 24. *Results of carnauba wax dispersion coated on bleached Kraft paper 48 gsm.*

Carnauba wax dispersion coated on Kraft paper	
Number of coating layers	1
Coating weight [g/m2]	6
KIT	2
Cobb60 [g/m2]	47

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 (see **Table 25**).

Table 25. *Results of carnauba wax with chitosan formulation.*

Carnauba wax with chitosan formulation										
Paper substrates	Bleached Kraft		FiberLean Uncoated Unbleached		FiberLean Uncoated Bleached		FiberLean MFC Unbleached		FiberLean MFC Bleached	
Coating Layers	1	2	1	2	1	2	1	2	1	2
Coating weight [g/m^2]	6	11	8	15	5	12	9	15	9	12
KIT	4	6	4	6	4	6	12	12	12	12
Cobb60 [g/m^2]	40	20	27	18	33	52	6	2	3	1

The formulation of carnauba wax with chitosan and PHA were coated on bleached kraft paper. The Cobb60 values were between 3-13 g/m2. See Table below.

Table 29. *Results of carnauba wax with chitosan and PHA formulation on bleached kraft paper, dried with IR lamp.*

Carnauba wax with chitosan and PHA formulations on **kraft** paper										
Different formulations	A		B		C		D		E	
DC of formulation (%)	32		35		37		30		27	
Coating Layers	1	2	1	2	1	2	1	2	1	2

Coating weight [g/m2]	3	8	3	8	4	9	2	6	1	6
KIT	2	6	2	6	fail	8	4	6	4	6
Cobb60 [g/m2]	11	6	12	3	9	3	12	8	13	8

The formulation of carnauba wax and PHA were coated on bleached kraft paper. The Cobb60 values were between 7-24 g/m^2. KIT failed for most of the tested samples. See Table below.

Table 26. *Results of carnauba wax with PHA formulation on bleached kraft paper, dried with 180* °C in oven or with *IR lamp.*

PHA, carnauba formulations on bleached Kraft paper									
Different formulations	A			B			C		
Drying	180 °C		IR	180 °C		IR	180 °C		IR
Coating Layers	1	2	1	1	2	1	1	2	1
Coating weight [g/m^2]	5	10	5	6	11	5	5	9	4
KIT	fail	2	fail	fail	6	fail	fail	4	2
Cobb60 [g/m^2]	21	11	13	24	7	17	31	11	19

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 more investigations. Due to lack of raw materials of chitosan and the low performance, no further tests were made with carnauba wax material.

Results summary on starch-based pilot: Carnauba wax in combination with other film forming material showed promising barrier properties. Carnauba wax itself showed not good results in terms of water and grease resistance.

3.5. SiOx ceramic nanolayer deposition by PVD

3.5.1. Background

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) since it offers a very thin, transparent barrier layer which is unproblematic during recycling. It is important to note that SiOx alone does not provide barrier properties but rather enhances pre-existing ones. SiOx

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can be deposited as a thin layer onto cellulosic substrates to further improve their already existing barrier properties from coatings or pretreatments on the paper (**Figure 36**). 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 provides an eco-friendly solution to optimize and bolster existing barrier properties while reducing reliance on plastics in food packaging.

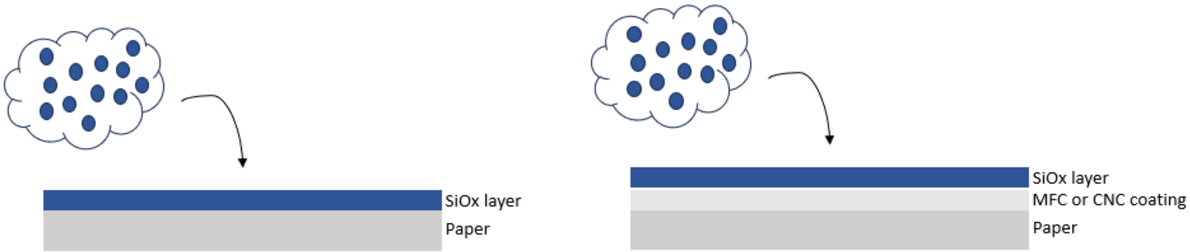

Figure 36. *Schematic of SiOx deposition on MFC-, CNC-coated or uncoated paper.*

Physical vapor deposition (PVD) is a vacuum-based coating process, in which the evaporated material, such as aluminium, or in this case transparent 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.

3.5.2. Material and methods

- **Description of the material**

A 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.

- **Description of preparation method**

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 as they are.

PVD is a vacuum-based coating process, in which the evaporated material, such as aluminium, or in this case transparent 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. This is controlled

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by a quartz thickness monitor (QCM). SiOx was applied as an inorganic barrier layer. A sintered SiOx target was used for the PVD.

The machine used at Fraunhofer IVV is an adapted plant from Leybold, see **Figure 37**.

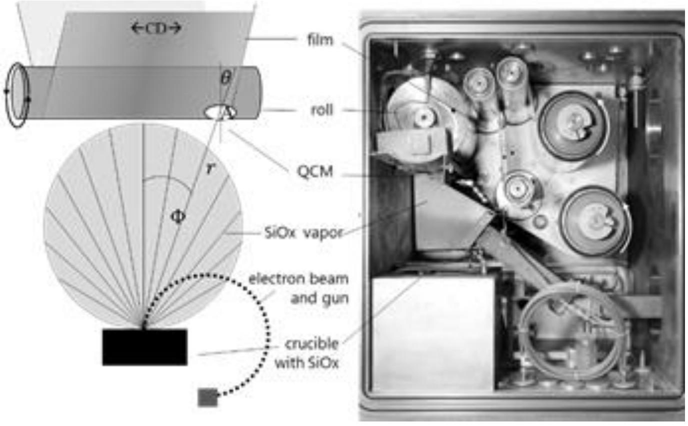

Figure 37. *Vacuum web coating at Fraunhofer IVV*

The Vacuum deposition was conducted with process parameters listed in **Table 27**.

Table 27: *Vacuum deposition process parameters*

Temperature of process roll [°C]	-8
Pressure recipient [mbar]	$4*10^{-5}$
Current [mA]	80
Process pressure [mbar]	$7*10^{-5}$
Evaporation rate [Å/s]	200
Web speed [m/min]	5

- **Description of characterization method**

The determination of the oxygen permeation (OTR) of the samples was performed according to DIN 53 380-3 (oxygen specific carrier gas method) with an Oxtran Twin (Mocon) at a temperature of 23°C with pure oxygen and a relative humidity of 50 % r.h. The samples were tested in a double determination.

The determination of the water vapour permeability (WVTR) was performed according to DIN 53122-1 (gravimetric method) at a temperature of 23 °C and a gradient of relative humidity from 85 % r.h. to 0 % r.h.. The measurement was performed using four specimens of each sample.

To test the water-repellent properties, a COBB-Test (DIN EN ISO 535) was performed. The coating weight was determined gravimetrically.

The coating thickness of the Inorganic layer was determined indirect using a quartz microbalance (QCM) with which the evaporation rate is monitored. Considering the coating speed and geometrical constraints under which the QCM, the evaporation source and the substrate are arranged, the coating thickness can be calculated.

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.

3.5.3. Results and discussions

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 aforementioned substrates are suitable for SiOx deposition. 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 hygroexpansion 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 fibers expand again and can lead to tension and cracks in the inflexible inorganic surface. Therefore, a paper with a minimal hygroexpansion is preferred.

WVTR was measured at 23 °C and 85%RH, OTR at 23 °C and 50%RH (**Table 28**). The WVTR was not measured for substrates without SiOx since no barrier properties from MFC or CNC itself could be expected.

Table 28. *Results of SiOx deposition on different substrates.*

BASE SUBSTRAT	GSM	PRE-COATING	GSM	Inorganic COATING	thickness [nm]	WVTR 1 [g/m^2*d] (23°C-85%RH)	WVTR 2 [g/m^2*d] (23°C-85%RH)	WVTR 3 [g/m^2*d] (23°C-85%RH)	WVTR 4 [g/m^2*d] (23°C-85%RH)	OTR 1 [cm^3/m^2*d *bar] (23°C-50% RH)	OTR 2 [cm^3/m^2*d *bar] (23°C-50% RH)	WATER COBB 60 [g/m^2]
kraft paper (Gascogne)	70	CNC (2 layers)	10							3.03	0.253	38.3
kraft paper (Gascogne)	70	CNC (2 layers)	10	SiOx	60	85.4	166	83.6	167	7.55	4.59	38.3
bleached paper (Fiberlean)	60.5											28.2
bleached paper (Fiberlean)	60.5	MFC	16.6							8386	24700	39.5
bleached paper (Fiberlean)	60.5	MFC	16.6	SiOx	60	1170	1137	1125	1110	26.7	6937	39.5
unbleached paper (Fiberlean)	59.9											27.4
unbleached paper (Fiberlean)	59.9	MFC	16.4							15151	19643	40.3

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unbleached paper (Fiberlean)	59.9	MFC	16.4	SiOx	60	869	872	837	827	17935	1538	40.3

The kraft paper from Gascogne with CNC coating (approximately 10 g/m^2 coating weight) had a good oxygen without the SiOx layer, but the coating was quite inhomogeneous, as the double determination showed (3,03 cm^3/m^2*d*bar versus 0,25 cm^3/m^2*d*bar). The water vapour was around 125,5 g/m^2*d also with variations. COBB60 is at 38,3 g/m^2. 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 around 16,5 g/m^2 could not be improved with SiOx coating. The water vapour barrier was between 850 and over 1000 g/m^2*d with SiOx coating. Except for one sample with 26,7 cm^3/m^2*d*bar, there was almost no oxygen barrier noticeable. Furthermore, it could be noticed, that the MFC increased the COBB60 for the bleached as well as the unbleached paper (from 28,2 g/m^2 to 39,5 g/m^2 and from 27,4 g/m^2 to 40,3 g/m^2).

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.

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.

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.

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 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.

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

Results summary on Siox-based pilot: These results lead to the conclusion that the papers with their respective pre-coatings are not yet suitable for SiOx deposition. Improvements can be made by choosing substrates with a smoother surface and low hygroexpansion, but also by

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selecting a precoating that forms a more plane underground and has some barrier performance itself which can be improved by the inorganic layer. Additionally, an upscaled process is often less susceptible to variations in the coating procedure than coating in single batches in lab scale.

4. DIFFERENT APPROACHES TO BRING BARRIER PROPERTIES TO 3D WET MOLDED TRAYS

Not only has the barrier properties of papers been evaluated in this project. Another part of the work package was to apply barrier with the multilayer strategy on paper trays. The barrier materials were applied with spray coating technique (**Figure 38**). The process of forming the trays has also been investigated with the aim to obtain suitable substrate for barrier application.

Figure 38: Schematic of single or multilayer spray-coated cellulosic tray substrate

4.1 Multilayer spray coating on 3D trays

4.1.1 Background

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

Materials with barrier properties were spray coated on cellulosic tray. Different combinations of materials and different coating weights were evaluated. The benefits of using MFC (see previous section 3.1) as pre-coating was also evaluated for 3D substrates. Materials used as barrier were, chitosan and two different barrier products from Bim Kemi.

The advantage of using chitosan has been presented in previous section, however one also need to consider the challenges with this polysaccharide, due to its chemical nature, biodiversity, and availability in large scale production.

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

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barriers were applied with spray coating technique which made it necessary to prepare the barriers with special physical properties.

4.1.2 Material and methods

- **Description of the material**

Low and high solid content MFC from Fiberlean (approximately 1.3% and 3.2%, respectively) were employed for spray coating paper-based trays.

The chitosan (160822-PREC-GHL) was supplied by Alpha Chitin. The supplied chitosan was dispersed at dry content ~20% in 1% acetic acid solution in water prior to the spray coating.

A starch-based barrier formulation (BIM BA 85113X) was used as barrier or as a primer layer. BIM BA 85113X is a development product from BIM Kemi, dry content ~30%. It is a barrier with intended use in food packaging. Focused resistance against fat and grease. The barrier is starch based and 80 % fossil free of solid content. No animalic content.

A partly fossil free barrier formulation (BIM BA 85028) was used as a top coating. BIM BA 85028 is a development product from BIM Kemi BA 85028, dry content ~40%. It is a barrier with intended use in food packaging with good resistance against water, moisture, fat, and grease. The barrier is partly biobased and 50 % fossil free of solid content. No animalic content.

Additionally, BA 85117 and BA 85884 products from BIM Kemi was also used for top-coating layers on the MFC primer layer. These barriers also intended use in food packaging with good resistance against water, moisture, fat, and grease.
Paper based trays from Guillin were used (**Figure 39**).

Figure 39. *Paper trays from Guillin after spray coating.*

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- **Description of preparation method**

A suspension with an appropriate sprayable concentration was prepared for each material before spraying. Each layer of spray coating had a surface coating ranging from 5 to 40 g/m^2. Specifically, for MFC, to achieve higher coating grammages of MFC (>10 g/m^2), the material was applied in multiple layers of coatings.

The Graco GX FF mobile spray unit, equipped with a 310 nozzle (green), was utilized for the spray application. Tray samples were positioned horizontally within a fume hood, secured with a clamp to a rack on the back wall. The spray gun was directed towards the window, positioned at the same level as the center of the tray, maintaining 40 to 50 cm between the spray gun nozzle and the tray's bottom. The spray pressure was adjusted to 50 bar.

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.

- **Description of barrier properties characterization methods**

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

The COBB-test (standard: ISO 535) is used to determine the quantity of water that can be absorbed by the surface of paper or board during a given time. The samples were evaluated for 60 seconds.

In this quick oil test procedure, a single drop of olive oil is applied to the center of a 4 x 4 cm sample using a 5 ml plastic Pasteur pipette. After 5 minutes, the diameter of the wetted area is measured, and the sample is examined for penetration through the material on its backside. If a visible stain is detected with backlighting, the test fails; otherwise, it passes.

The KIT test (Tappi 559) is based on the ISO 16532-2 and TAPPI 559 standards for assessing how resistant paper and paperboard are to grease. This test takes place in a room kept at a temperature of 23°C ± 1ºC and a relative humidity of 50% ± 2%. Test solutions with different penetrating abilities (KIT ratings) are created using castor oil, toluene, and n-heptane. The solution with the lowest KIT rating (KIT=1) is pure castor oil, and the one with the highest KIT rating (KIT=12) is a mix of toluene and heptane in roughly equal amounts. In the test, the KIT solution is dropped from a height of about 10 mm onto the surface, left for 15 seconds, and then the surface is visually inspected. The KIT value for the surface is determined by identifying the test solution that doesn't cause any darkening.

The Caprylic acid test is employed to assess oil and grease resistance. A volume of Caprylic acid is placed in contact with the surface for an extended period (24 hours). Any darkening in the contact area between the Caprylic acid and the surface is observed over time.

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4.1.3 Results and discussions

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 (**Table 29**). Depending on multilayer coating weight, the spray coated trays also showed grease resistance (**Table 30**, **Table 31**, **Table 32**).

Table 29. *Results of Cobb60 (g/m^2) on trays spray coated with different coatings.*

COATING 1st layer	GSM	COATING 2nd layer	GSM	COATING 2nd layer	GSM	WATER COBB 60 $[g/m^2]$ (Tray Bottom)	WATER COBB 60 $[g/m^2]$ (Tray Wall)
---	---	---	---	---	---	56.9 ± 8.3	32.3 ± 0.2
MFC	10	---	---	---	---	51.6 ± 4.0	35.0 ± 0.4
Chitosan	10	---	---	---	---	20.5 ± 0.5	17.1 ± 1.2
BA 85117	10	---	---	---	---	4.8 ± 0.7	6.2 ± 2.2
BA 85884	10	---	---	---	---	11.1 ± 1.2	9.7 ± 1.7
MFC	10	Chitosan	10	---	---	27.7 ± 0.7	21.7 ± 0.2
MFC	10	Chitosan	10	BA 85117	10	**0.0 ± 0.0**	**0.2 ± 0.2**
MFC	10	Chitosan	10	BA 85884	10	**0.0 ± 0.0**	**1.8 ± 2.5**
MFC	10	Chitosan	10	BA 85028	10	**0.0 ± 0.0**	**1.8 ± 2.5**
MFC	5	Chitosan	5	BA 85117	5	1.2 ± 1.7	2.3 ± 2.2
MFC	5	Chitosan	5	BA 85028	5	**0.0 ± 0.0**	9.9 ± 6.0
MFC	20	BA 85117	20	---	---	1.9 ± 0.2	0.5 ± 0.7
MFC	40	BA 85117	10	---	---	2.5 ± 2.5	2.7 ± 1.7

Table 30: *Results of Quick Oil barrier test on tray spray coated with different coatings.*

COATING 1st layer	GSM	COATING 2nd layer	GSM	COATING 2nd layer	GSM	Quick oil barrier test (Tray Bottom)	Quick oil barrier test (Tray Wall)
---	---	---	---	---	---	Fail	Fail
MFC	**10**	---	---	---	---	**Pass**	**Pass**
Chitosan	**10**	---	---	---	---	Fail	Fail
BA 85117	**10**	---	---	---	---	Fail	Fail
BA 85884	**10**	---	---	---	---	Fail	Fail
MFC	**10**	**Chitosan**	**10**	---	---	**Pass**	Fail
MFC	**10**	**Chitosan**	**10**	**BA 85117**	**10**	**Pass**	**Pass**
MFC	**10**	**Chitosan**	**10**	**BA 85884**	**10**	**Pass**	Fail
MFC	**10**	**Chitosan**	**10**	**BA 85028**	**10**	**Pass**	**Pass**
MFC	**5**	**Chitosan**	**5**	**BA 85117**	**5**	Fail	Fail
MFC	**5**	**Chitosan**	**5**	**BA 85028**	**5**	Fail	Fail
MFC	**20**	**BA 85117**	**20**	---	---	**Pass**	**Pass**
MFC	**40**	**BA 85117**	**10**	---	---	**Pass**	**Pass**

Table 31. *Results of KIT on trays spray coated with different coatings.*

COATING 1st layer	GSM	COATING 2nd layer	GSM	COATING 2nd layer	GSM	KIT (Tray Bottom)	KIT (Tray Wall)
---	---	---	---	---	---	< 9	< 9
MFC	**10**	---	---	---	---	**12**	**12**
Chitosan	**10**	---	---	---	---	< 9	< 9
BA 85117	**10**	---	---	---	---	< 9	< 9
BA 85884	**10**	---	---	---	---	< 9	< 9

MFC	**10**	**Chitosan**	**10**	---	---	12	12
MFC	**10**	**Chitosan**	**10**	**BA 85117**	**10**	12	12
MFC	**10**	**Chitosan**	**10**	**BA 85884**	**10**	12	12
MFC	**10**	**Chitosan**	**10**	**BA 85028**	**10**	12	12
MFC	**5**	**Chitosan**	**5**	**BA 85117**	**5**	< 9	< 9
MFC	**5**	**Chitosan**	**5**	**BA 85028**	**5**	< 9	< 9
MFC	**20**	**BA 85117**	**20**	---	---	12	12
MFC	**40**	**BA 85117**	**10**	---	---	12	12

Table 32. *Results of Caprylic acid test on trays spray coated with different coatings.*

COATING 1st layer	GSM	COATING 2nd layer	GSM	COATING 2nd layer	GSM	Caprylic acid test (Tray Bottom)	Caprylic acid test (Tray Wall)
---	---	---	---	---	---	Fail	Fail
MFC	**10**	---	---	---	---	Pass	Fail
Chitosan	**10**	---	---	---	---	Fail	Fail
BA 85117	**10**	---	---	---	---	Fail	Fail
BA 85884	**10**	---	---	---	---	Fail	Fail
MFC	**10**	**Chitosan**	**10**	---	---	Pass	Fail
MFC	**10**	**Chitosan**	**10**	**BA 85117**	**10**	Pass	Pass
MFC	**10**	**Chitosan**	**10**	**BA 85884**	**10**	Pass	Pass
MFC	**10**	**Chitosan**	**10**	**BA 85028**	**10**	Pass	Pass
MFC	**5**	**Chitosan**	**5**	**BA 85117**	**5**	Fail	Fail
MFC	**5**	**Chitosan**	**5**	**BA 85028**	**5**	Fail	Fail

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MFC	**20**	**BA 85117**	**20**	**---**	**---**	**Pass**	**Pass**
MFC	**40**	**BA 85117**	**10**	**---**	**---**	**Pass**	**Pass**

Spray coating is a technique with significant industrial relevance, having been employed in the painting and automotive industries for an extended period. Moreover, this process is highly amenable to upscaling and automation, facilitating precise control over barrier coating and uniformity on 3D substrates, including those with complex geometries. To effectively execute this barrier coating process, materials must be sprayable, necessitating attention to their rheological properties and dry content. If the concentration is too low, it results in the incorporation of a large amount of water for each spray layer, which, in turn, extends the drying process.

It's essential to emphasize that all materials supplied by our project partners and subjected to testing have demonstrated remarkable stability for spray-coating. Furthermore, they have displayed relatively consistent coverage on 3D tray geometries, with minimal deviation in barrier test results observed between the tray bottoms and walls. This underscores the industrial feasibility of coating complex 3D structures and achieving superior barrier performance, particularly through the application of multilayer barrier coatings that feature biobased primer layers and readily available top layers. With the strategies explored above, we anticipate effectively addressing intricate challenges in barrier coatings, especially for food contact packaging, by incorporating more sustainable and biobased barrier layers synergistically.

Results summary on "multilayer spray-coating deposition on 3D trays": By spray coating barrier materials in a multilayer structure, the water resistance was significantly reduced. Grease resistances were obtained for some samples, and this was dependant on the coating weight.

4.2 Wet molding

4.2.1 Background

The production trial at the wet molding lab line has been carried out by considering the variables that affect the tray quality and by following the recipe to reach out to the best substrate quality. The aim is to yield the best substrates for coating applications for wet strength.

Unlike flat paper making, due to the different forming type, fibers in 3D molded substrate are oriented in all directions. Using fiber mixture can result in smoother and more uniform surface finish. For obtaining bulkier web, it is preferred to use stiffer pulp type, i.e. high yield pulp. Lignin in CTMP provides stiffer nature and 40 % of the pulp mixture in this study consists of CTMP. Using long fibers (SW) provides better tensile strength, short fibers (HW) contribute to

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compressive strength, that’s why the rest of the pulp mixture consists of 30% SW and 30% HW.

A screening study on type and amount of paper additives and process parameters, to produce RISE trays, was carried out to produce the best substrate ready for after treatment-barrier coating. The goal is to achieve the highest COBB60 value, to investigate surface topology (OptiTopo) and to explore the relationship between these two characteristics. The substrate should not undergo potential structural and functional changes after water exposure which will take place during the barrier coating process. Over the course of trials, the substrates were evaluated through a first glimpse to stickiness (to the mold), 3D structure defects, sturdiness, discoloration, and surface smoothness. The test samples were chosen according to this first evaluation. This is an exploratory study; the results cannot be compared with reference materials since this data is not available in literature.

4.2.2 Materials and Methods

- **Description of the material**

Guillin fiber mix (40% CTMP, 30% BSWKP, 30% BHWKP) was used for wet forming trials. PAE (Polyamideamine epichlorohydrin), Maresin M1.0 was supplied by MARE. AKD (Alkyl Ketene Dimer), Fenno Size KD-MB 574MP (21.7 – 22.7 % dry content) was supplied from Kemira. Starch was cooked from Roquette starch at 110-115 °C with an industrial jet cooker that depends on flow rate pipe length and pipe diameter. %DC was 40 %. Stock volume: 1 IBC; Stock consistency: 0.2%: Stock concentration: 2g/L.

- **Description of preparation method**

Substrate trays were prepared at the wet molding lab line in RISE that consist of forming step, forming press, thermopress and calibration press **(Figure 40, Figure 41).**

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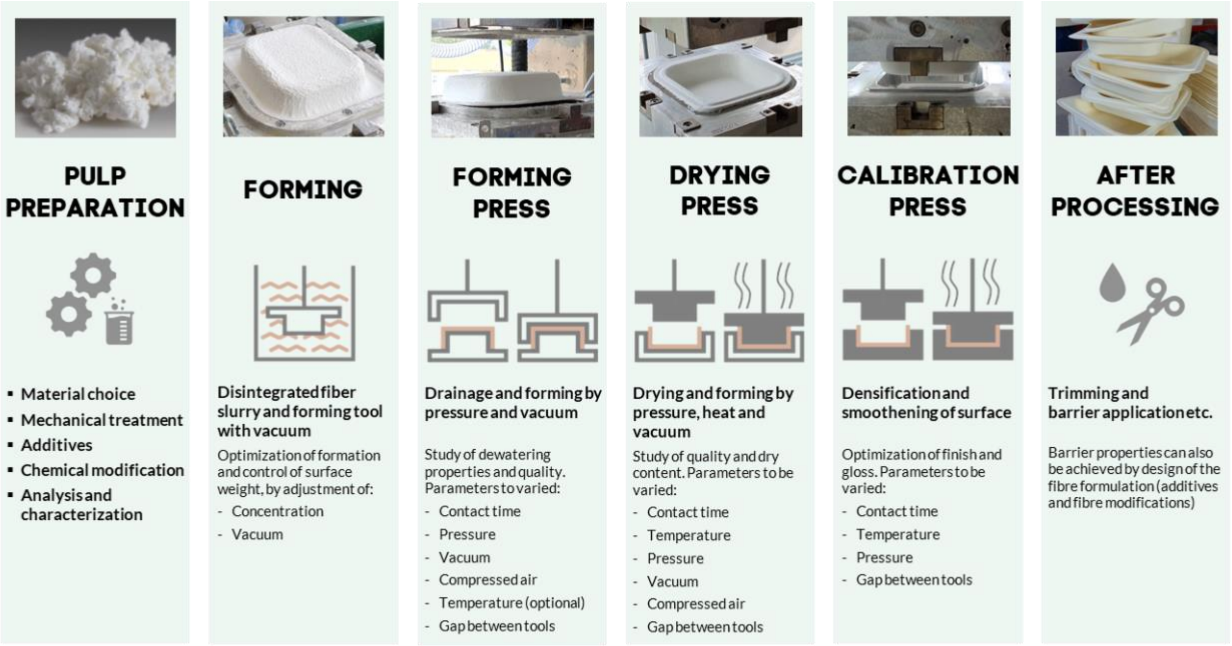

Figure 40. *Demonstration of wet molding process stages and adjustments.*

Figure 41. *Image of paper tray produced at RISE.*

The screening study for additives type (AKD, PAE, starch) and amount was performed as well as the process parameters. Briefly, wet molding process starts with slushing pulp, adding additives, forming step in the tank, forming press, thermo press, calibration press and eventually post-treatment (in the oven at 105°C for 20 min). The additive’s amounts were predefined (**Table 33**), but process parameters were adjusted according to the material's response during process (**Table 34**). Namely, weight of the tray (even after each press), dryness, surface defects, failures in the sturdiness of tray, stickiness to tools were monitored during the process.

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Table 33. *Stock additives composition.*

Entry	AKD % (wt)	PAE % (wt)	Starch % (wt)
Batch 1 (1-28)	1.5	-	-
Batch 2.1 (29-48)	2.5	-	-
Batch 2.2S (49-56)	2.5	-	1
Batch 3 (57-74)	5	-	-
Batch 3S (75-82)	5	-	1
Batch 4 (96-132)	1.5	2.5	-
Batch 5 (133-169)	2.5	2.5	-
Batch 6 (177-208)	5	2.5	-
B7 (209-239)	1.5	1	-
B7.S (240-251)	1.5	1	1
B8 (252-285)	2.5	1	-
B8.S (286-303)	2.5	1	1

Table 34. *Summary of wet molding process parameters*

Variables	Entry
Forming time, s	4-10
Thermopress time, s	30-80
Thermopress (drying) pressure, ton	2.5 or 6.5
Calibration (precision) press pressure, ton	3 or 8.5
Thermopress temperature, °C	160-205
Calibration press temperature, °C	160-220
Stop blocks*	with and without

*Without stop blocks there is no gap between the plates

- ### Description of characterization method

Cobb60 values were determined with distilled water on the samples cut from bottom inside of 3D molded substrates and performed as per ISO 535:2014.

Surface roughness was determined by **OptiTopo** instrument. Hardware: L&W OptiTopo device from ABB/Lorentsen & Wettre (developed together with RISE). Software: OptiTopo Expert software developed by RISE. The samples were conditioned in 23 C, RH 50% +/-3% for min 24h.

Four 32x32 mm sample cut from bottom inside of the trays (total area: 41 cm2). Resolution is x/y: 15.6 um, z: < 0.1 um. Surface roughness (standard deviation) in spatial wavelengths; Fine: Interval 0.0625-0.5 mm, Medium: Interval 0.5-2 mm, Large: Interval 2-8 mm. Crater and hill; crater and hill fine: amount craters and hills deeper/higher than -/+ 1.5

um, Crater and hill medium: amount craters and hills deeper/higher than -/+ 3 um, Crater and hill coarse: amount craters and hills deeper/higher than -/+ 5 um.

4.2.3 Results and discussions

Several tray samples were manufactured under varying conditions in wet molding lab line. The samples from each batch with good and stable 3D structure were tested.

Table 35 summarizes COBB60 value of the trays prepared with different additives in the wet end with CTMP, BSWKP and BHWKP pulp mixture.

Starch was used further to improve the dry strength. AKD was added as an emulsion also improved the strength and dramatically improved the hydrophobicity. PAE was used as wet strength agent.

Pulp concentration (by dry weight measurements), formation time in formation tank, time of vacuum suction after exit from formation tank until heat press (water drainage), vacuum level during suction after exit from formation tank, temperature during hot pressing, time of hot pressing, temperature during calibration press, time of calibration pressing, and pressure during both pressing are process variables directly affect the resulting material property.

Table 35. *Cobb60 value for pulp molded trays.*

Sample no	Tray no	Weight, g/m²	Thickness, µm	Density, kg/m³	Cobb 60, g/m²
B1-911	2	572.3	980.2	583.8	16.28
B1-911	4	573.8	962.0	596.5	16.08
B1-911	6	568.1	952.5	596.5	15.63
B1-911	8	570.2	930.9	612.6	15.85
B1-912	9	563.9	922.6	611.2	16.93
B1-912	13	544.2	922.6	589.8	16.98
B1-912	18	534.6	922.9	579.3	16.95
B1-912	22	553.5	886.0	624.7	18.43
B1-912	25	565.0	881.5	641.0	20.33
B1-912	27	531.3	876.3	606.2	18.55
B1-913	31	595.0	898.6	662.1	14.88
B1-913	33	584.6	896.5	652.1	14.50
B1-913	35	603.4	903.6	667.8	14.60
B1-913	37	589.5	904.9	651.5	14.58
B1-913	39	599.3	894.4	670.0	14.68
B1-913	41	593.2	889.6	666.8	14.78
B1-913	43	566.5	875.4	647.2	14.68

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B2.2-913	45	587.9	891.2	659.7	14.40
B2.2-913	47	577.2	864.8	667.4	16.93
B2.2S-913	49	559.0	899.9	621.2	14.48
B2.2S-913	52	547.8	880.5	622.2	14.20
B2.2S-914	53	565.9	916.9	617.2	14.63
B2.2S-914	55	567.3	887.0	639.5	13.53
B3-0918	57	572.7	885.5	646.8	14.50
B3-0918	59	569.7	888.3	641.4	14.70
B3-0918	67	584.6	886.5	659.5	13.50
B3-0918	69	589.8	886.1	665.6	13.48
B3-0918	73	572.5	863.3	663.2	11.45
B3.S 918	75	573.1	872.3	657.0	14.00
B3.S 918	77	582.3	893.8	651.5	14.48
B3.S 918	79	567.8	861.7	659.0	13.13
B3.S 918	81	569.0	881.3	645.6	13.38
B3 S 919	85	569.1	685.3	830.4	12.48
B3 S 919	86	572.5	692.4	826.8	11.90
B3 S 919	92	539.5	669.3	806.0	11.12
B4 919	97	572.0	933.4	612.8	14.90
B4 919	99	572.3	956.4	598.3	15.17
B4 919	101	562.8	923.9	609.2	14.33
B4 919	103	545.0	945.3	576.5	14.50
B4 919	110	543.5	869.8	624.9	14.32
B4 919	112	571.5	878.7	650.3	14.32
B4-920	115	546.5	835.8	653.9	14.58
B4-920	117	527.4	853.0	618.3	14.45
B4-920	120	547.6	886.6	617.7	14.48
B4-920	122	574.2	880.8	651.9	14.63
B4-920	124	574.2	848.9	676.4	14.35
B4-920	126	568.7	856.0	664.4	14.03
B4-920	129	568.8	671.5	847.1	13.23
B4-920	131	559.5	680.2	822.6	13.30
B5-920	133	580.6	907.2	640.0	14.95
B5-920	135	575.5	881.5	652.9	14.30
B5-921	139	572.1	917.1	623.8	14.30
B5-921	140	572.8	897.3	638.4	13.98
B5-921	141	565.8	894.4	632.6	13.85
B5-921	142	555.0	899.8	616.8	13.80
B5-921	144	560.5	895.5	625.8	13.60
B5-921	145	581.6	921.2	631.4	13.70
B5-921	147	593.5	909.4	652.7	13.88
B5-921	148	581.6	902.7	644.4	13.47
B5-921	149	567.2	916.7	618.7	13.88

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B5-921	150	573.5	910.4	630.0	13.63
B5-921	151	569.7	896.6	635.4	11.85
B5-921	152	568.5	915.7	620.9	13.55
B5-921	153	563.3	850.3	662.5	12.55
B5-921	154	577.3	851.3	678.1	12.85
B5-921	155	556.5	894.5	622.2	12.90
B5-921	156	569.4	893.1	637.5	12.98
B5-921	157	577.7	918.0	629.3	13.05
B5-921	158	577.5	915.4	630.8	13.83
B5-921	159	596.8	905.8	658.9	12.93
B5-921	160	590.5	912.3	647.3	14.40
B5-921	161	564.1	844.2	668.2	12.75
B5-921	162	537.1	857.9	626.0	12.90
B5-921	163	571.8	882.4	648.0	13.10
B5-921	164	557.3	859.5	648.4	13.18
B5-921	165	561.8	706.3	795.5	12.72
B5-921	166	569.1	681.9	834.6	12.28
B5-921	168	581.0	688.0	844.5	11.88
B5-921	169	564.4	685.3	823.5	12.80
B6-921	170	562.5	920.9	610.9	13.47
B6-921	171	574.5	938.2	612.3	13.52
B6-921	172	543.5	953.0	570.2	13.30
B6-921	173	585.1	951.7	614.8	13.63
B6-921	174	583.0	948.2	614.8	13.33
B6-921	175	585.2	961.4	608.7	13.30
B6-921	176	564.5	949.8	594.3	13.27
B6-921	177	584.2	938.6	622.4	13.33
B6-925	178	564.5	876.1	644.4	14.17
B6-925	180	602.5	931.2	647.0	14.03
B6-926	183	568.3	872.6	651.2	13.55
B6-926	185	552.9	887.2	623.2	13.70
B6-926	189	549.2	903.0	608.2	13.47
B6-926	191	571.0	911.3	626.5	13.53
B6-926	194	535.1	883.8	605.5	13.65
B6-926	196	535.8	900.7	594.9	13.55
B6-926	200	544.6	869.1	626.7	13.02
B6-926	202	546.9	862.2	634.3	13.23
B7-927	210	589.7	948.5	621.7	15.27
B7-927	212	561.6	917.4	612.2	14.40
B7-927	216	571.2	627.3	910.5	12.55
B7-927	220	576.6	686.1	840.5	12.78
B7-927	226	570.2	619.0	921.2	10.85
B7-927	228	574.9	647.8	887.5	14.18

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B7S-928	240	578.7	940.2	615.5	13.93
B7S-928	242	574.5	943.8	608.7	14.15
B7S-928	244	574.0	691.0	830.7	12.52
B7S-928	246	568.5	730.7	777.9	13.27
B7S-928	248	562.6	692.6	812.4	11.98
B7S-928	250	564.7	880.7	641.2	12.50
B8-928	252	615.7	615.7	932.9	14.10
B8-928	254	567.9	567.9	948.2	14.00
B8-928	256	547.8	547.8	966.8	14.18
B8-928	260	562.5	562.5	675.9	13.15
B8-929	269	597.7	597.7	640.8	10.52
B8-929	271	596.7	596.7	638.5	10.65
B8-929	275	586.4	586.4	968.0	13.95
B8-929	279	588.7	588.7	885.7	12.28
B8-929	281	574.2	574.2	689.8	10.55
B8-929	283	557.6	557.6	575.7	14.50
B8S-102	286	507.9	507.9	981.6	15.13
B8S-102	288	658.6	658.6	897.3	13.18
B8S-102	290	532.5	532.5	646.3	12.65
B8S-102	292	592.6	592.6	686.9	12.73
B8S-102	294	610.2	610.2	639.0	11.50
B8S-102	296	595.5	595.5	634.5	10.95
B8S-102	298	609.7	609.7	706.7	12.00
B8S-102	302	596.7	604.3	887.4	18.50

The samples with value in red have shown remarkable COBB60 results when compared to the rest of the samples. It has been demonstrated that by a good stock design it is possible to considerably lower COBB value. One another striking finding here is that the process parameters have a great effect on the resulting material property. Within the same series, which means the stock additives composition is constant, COBB60 value differs quite much with varying process parameters. It is noteworthy to note that for the exploration of the best stock design and process parameters, it is crucial to carry out multivariant screening work. This is the first screening work that allows us to define the working range for the future trials. MFC in the wet end is not evaluated yet. During the next trial, MFC incorporation with different strategies will be evaluated.

To investigate the effect of AKD amount on water resistance of the substrate, the trays were prepared with pulp stocks containing 1.5, 2.5, and 5 % AKD. For batch 2 and 3, there are trays that were prepared also with 1% starch.

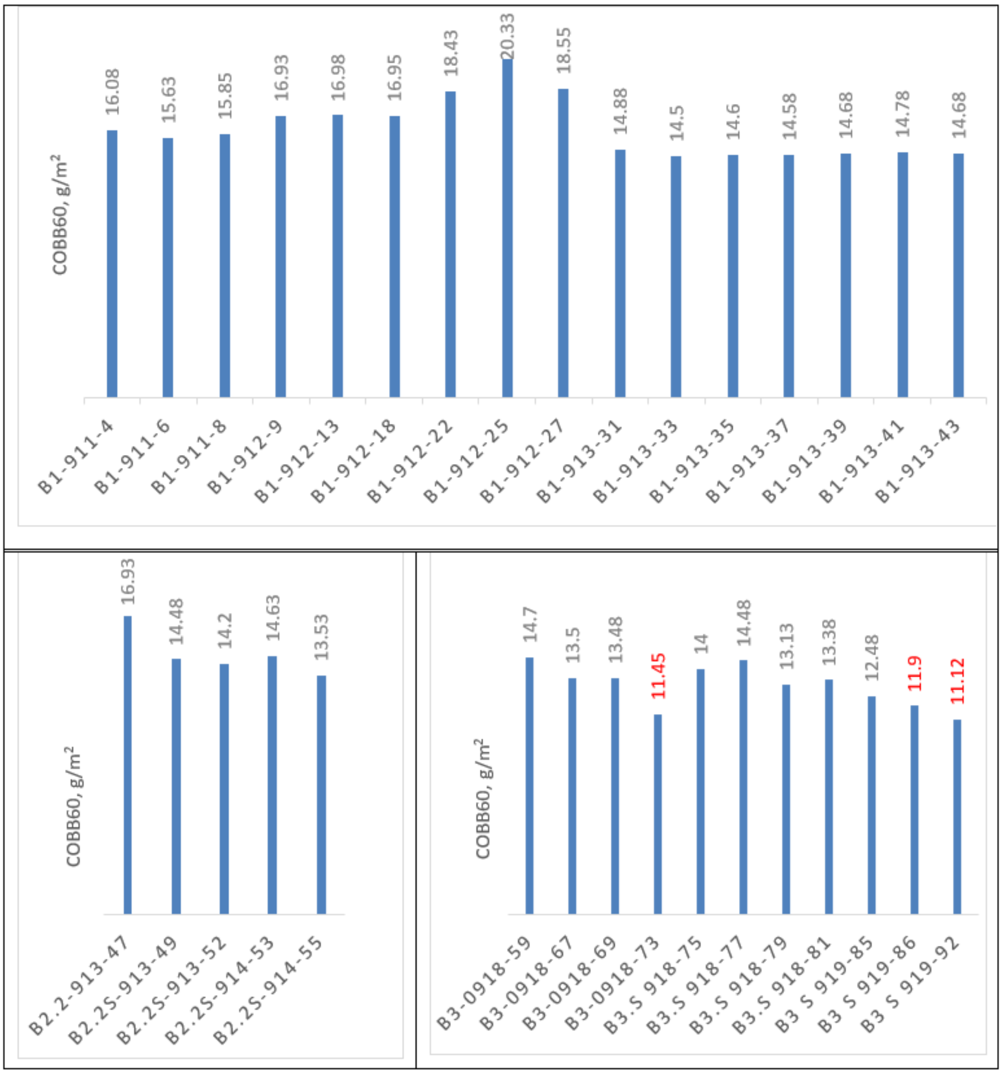

Figure 42. *The effect of AKD amount on COBB60. The starch addition effect. B1 has 1.5 % AKD: graph on top, B2 (2.5 % AKD) and B2S (2.5%AKD and 1 % starch):in bottom left, and B3 (5 % AKD) and 3S (5%AKD and 1 % starch): in bottom right.*

As can be seen in **Figure 42**, low COBB60 was obtained for the trays with 5% AKD both with and without starch. Variables for these 3 samples was process parameters (see **Table 34**). There is no data for starch addition to Batch1 and for Batch2 there is not enough data to conclude on it.

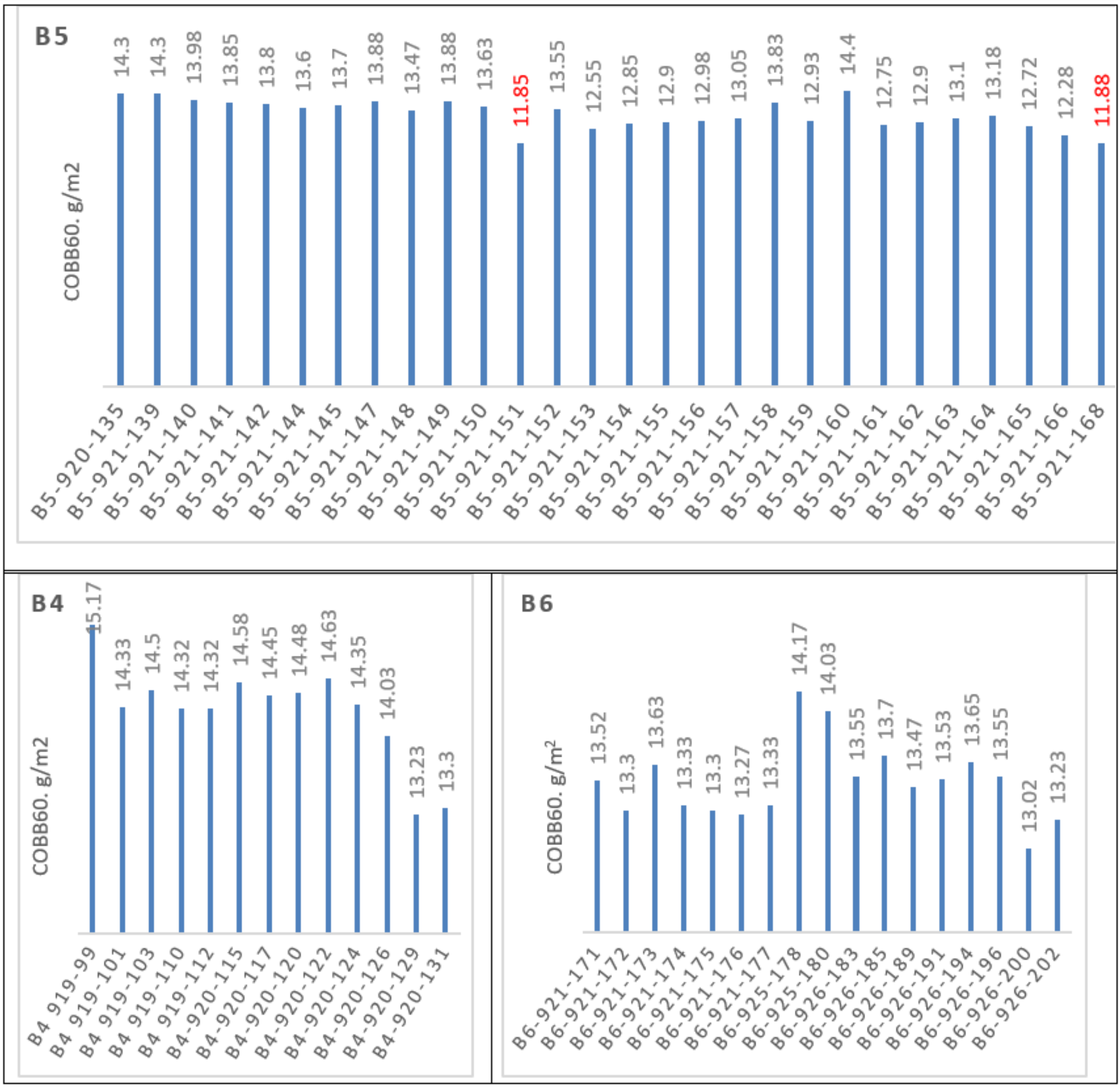

Figure 43. *The effect of PAE (2.5%) with varying AKD amount on COBB60. B5 has 2.5 % AKD: graph on top, B4 (1.5 % AKD): on bottom left and B6 (5 % AKD) in bottom right.*

The best PAE effect on COBB60 was observed on Batch 5 at which AKD was 2.5%. The COBB values were rather lower in B6 (5% AKD) when compared to B4 (1.5% AKD). Note that stock composition is not the only decisive factor but also process parameters, for water resistance of material.

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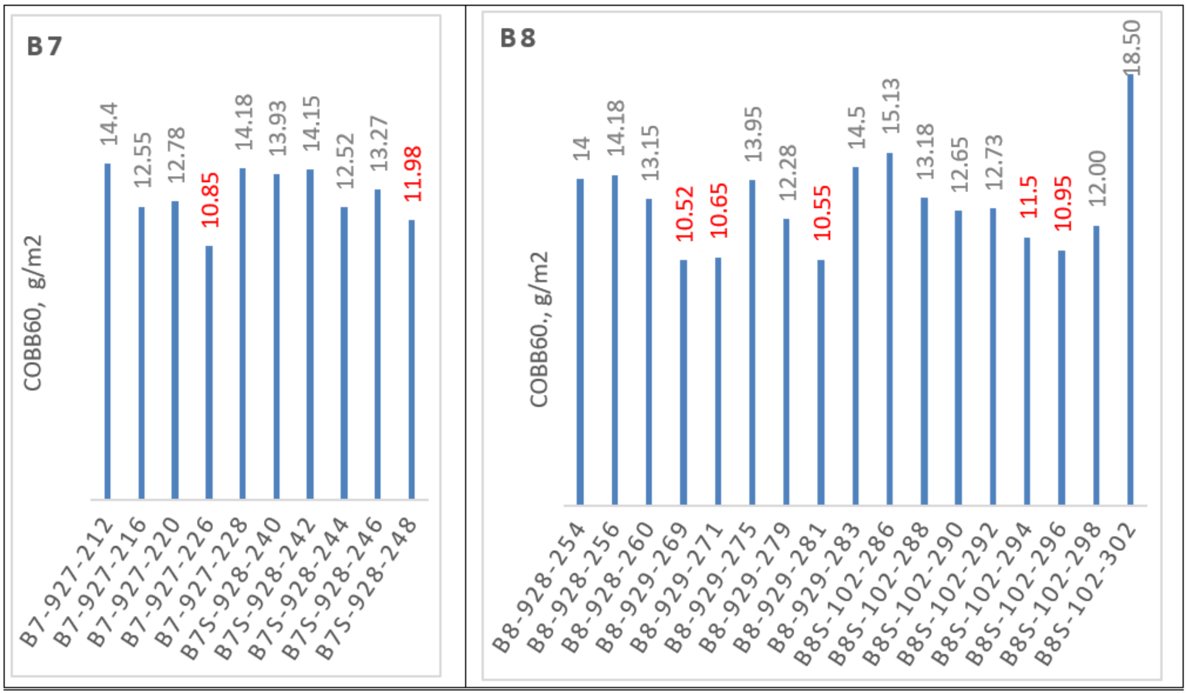

Figure 44. *The effect of PAE (1%) with varying AKD amount on COBB60. The starch addition effect. B7 (1.5 % AKD and 1% PAE), and B7S (1.5 % AKD, 1% PAE and 1% starch), to the left. B8(2.5 % AKD) and B8S (2.5%AKD and 1 % starch), to the right.*

It has been shown that with lower PAE amounts (1%) the lowest COBB60 ever (**Figure 44**) for this trial has been reached, with a value of 10.52. All the additives have a function in the pulp stock, but it is not an easy task to define in which combination and in which amounts they are needed to get the best result. This, together with process conditions, controls the resulting material's water barrier level. This screening work allowed us to narrow down the additives and process parameters that yield the best performing substrate in terms of water resistance, but the evaluation criteria is not limited to the COBB60 evaluation. The number one goal was to obtain the best substrate for the following barrier coating steps. In most cases, the barrier application includes vast amount of inevitable water addition especially in case of spray coating. This requires, first a certain water resistance, so that over the course of coating application and during drying as well, the material would keep its integrity and other micro properties.

There are no such criteria for COBB to be under (or above) a certain limit to define the suitable substrate for a better barrier coating application or a better substrate that allows a barrier system to show the best performance of it. It is a question that remains to be answered during the future work period in which coating and testing will also be introduced. The first trial was carried out to find an answer to the abovementioned fundamental questions, regarding the stock preparation and wet molding process.

There should be correlation between surface variation and COBB60 value since water uptake behavior of the substrate is also related to surface roughness. On the other hand, surface roughness should be in a range that allows to apply barrier coating in the most efficient way.

To investigate the relationship between Opti Topo (surface topography) and COBB60 (water uptake) results, a comparative study was carried out and the results are presented below.

- **Effect of additives and process parameters**

To investigate the correlation, OptiTopo and COBB60 results are summarized in the figures below.

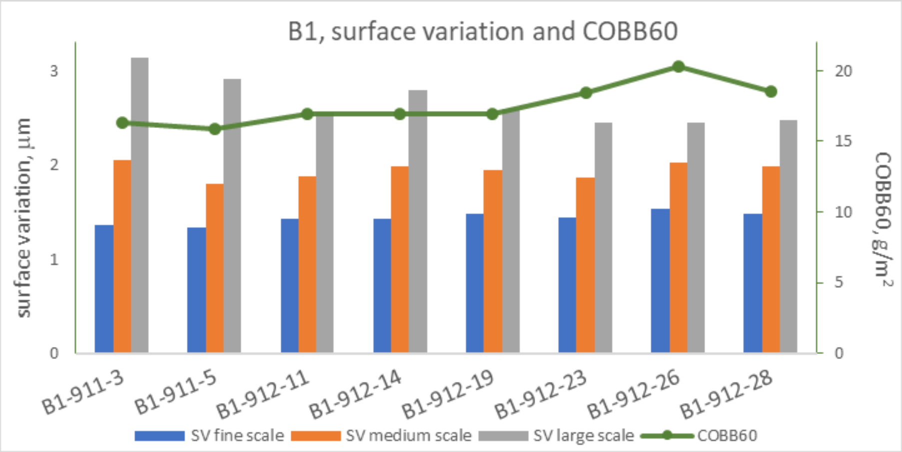

Figure 45. *Opti Topo-surface variation and COBB60 for Batch1.*

In all cases, there is a trend for the surface variation value and scale namely fine scale has the lowest value while large scale has the highest. However, these data do not allow for capturing a constant rate of increase or decrease in surface variation (SV) within all three SV scales.

In this series, each substrate has a high COBB value and high roughness in all scales and does not differ much from each other. That is why, it is not possible to draw a conclusion and be able to claim for any trend between water resistance and surface roughness.

For further information craters and hills (OptiTopo) data were analyzed (**Figure 46**).

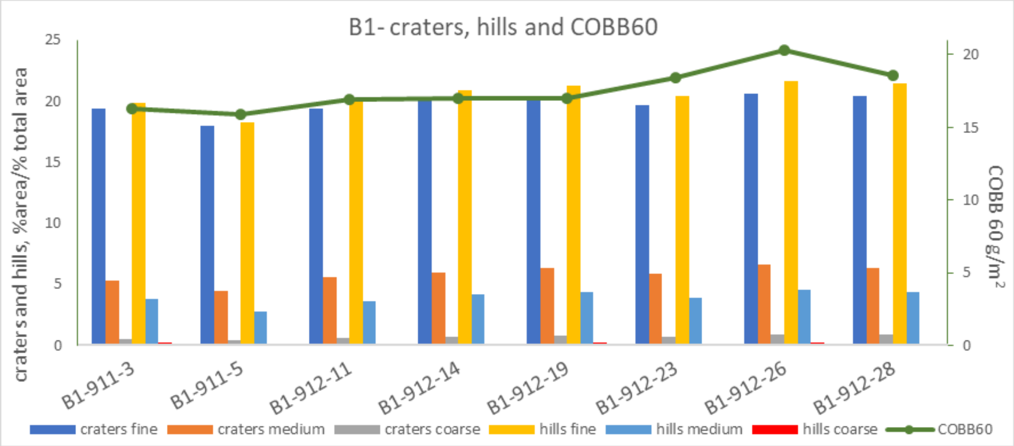

Figure 46. *OptiTopo- craters and hills and COBB60 for Batch1*

Unlike surface variation vs COBB60, it is easy to see the trend between water resistance and craters (and hills). When the crater value decreases COBB60 value decreases. The increase or

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decrease ratio of these values looks the same from the graphs. But there needs to be further data analysis for expressing this behavior quantitively.

Again, unlike surface variation values, all 3 ranges for craters and hills increase or decrease with the same ratio that make is easy to confirm once one defines a trend for fine grade it is also valid for medium and coarse grade.

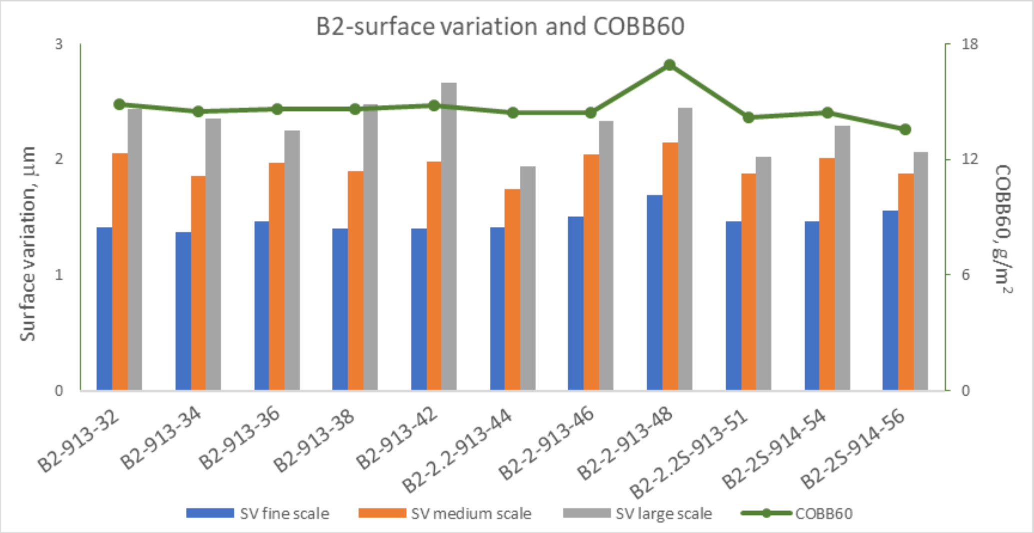

Figure 47. *Opti Topo-surface variation and COBB60 for Batch 2*

In this series (**Figure 47**), if we follow the substrate with highest COBB60 value (sample 48) and the lowest (sample 56) it is possible to mark the correlation between a decreasing COBB60 value with a decreasing roughness (see medium and large scale to follow). But at the same time there are samples that have shown a low COBB60 value (sample 38,42) when compared to sample number 48 (highest COBB60 value) that has the same surface roughness degree. To explore the relationship between COBB60 and surface roughness there is a need to get more reproducible results. (The next trial will allow to reproduce interesting series of substrates.)

For further understanding see craters and hills graph in **Figure 48**.

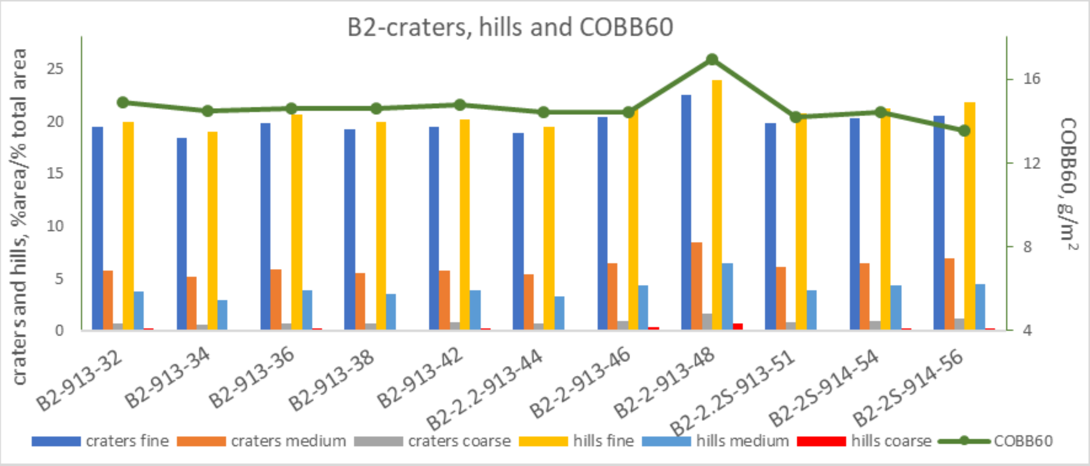

Figure 48. *OptiTopo-craters and hills and COBB60 for Batch2*

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Just like the first phase, the trend that we could not monitor with surface variation is quite clear in craters and hills graph. There is a correlation with the increasing COBB60 value, and crater and hills values.

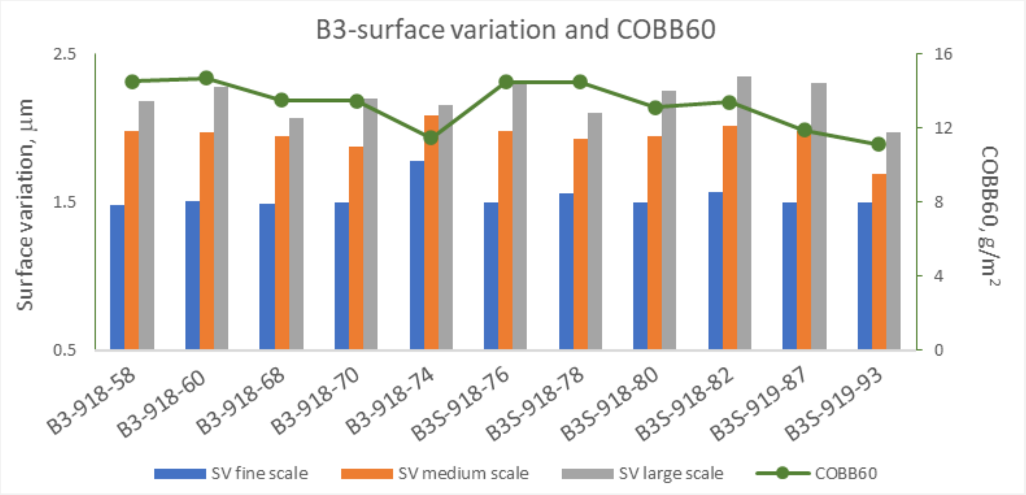

Figure 49. *Opti Topo-surface variation and COBB60 for Batch 3*

In this series (B3, see Figure 49) COBB60 does not seem to follow surface variation, in general. From sample 68 to 70, COBB60 value remains the same while large scale SV increases. But at the same time medium scale SV decreases. On the other side, for sample 93, it is expected that the lowest COBB value was reached out at the smoothest surface with lowest SV at all scales.

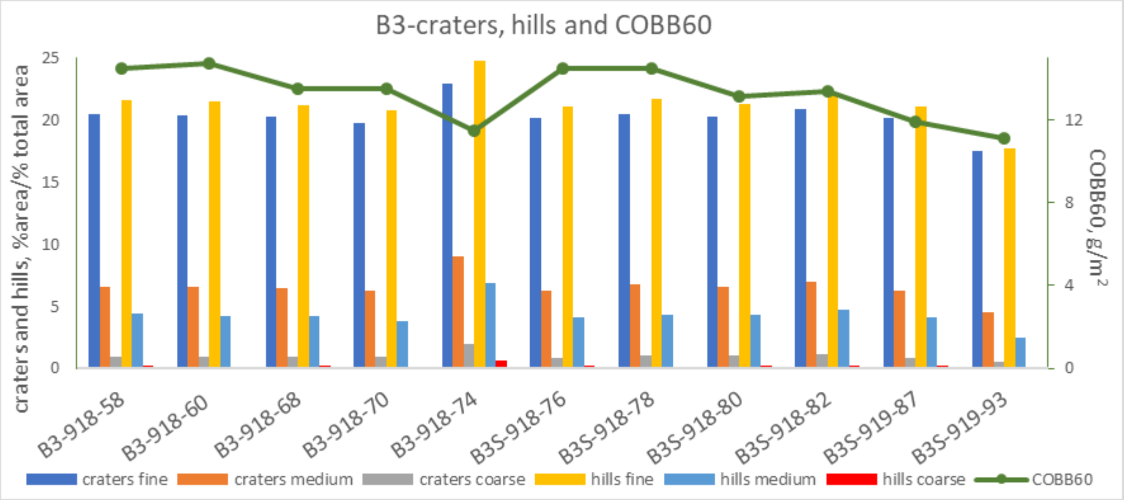

Figure 50. *OptiTopo-craters and hills and COBB60 for Batch3*

In craters and hills graph of B3 series, it is again hard to follow a trend but the lowest COBB60 value was reached out with the smoothest sample 93.

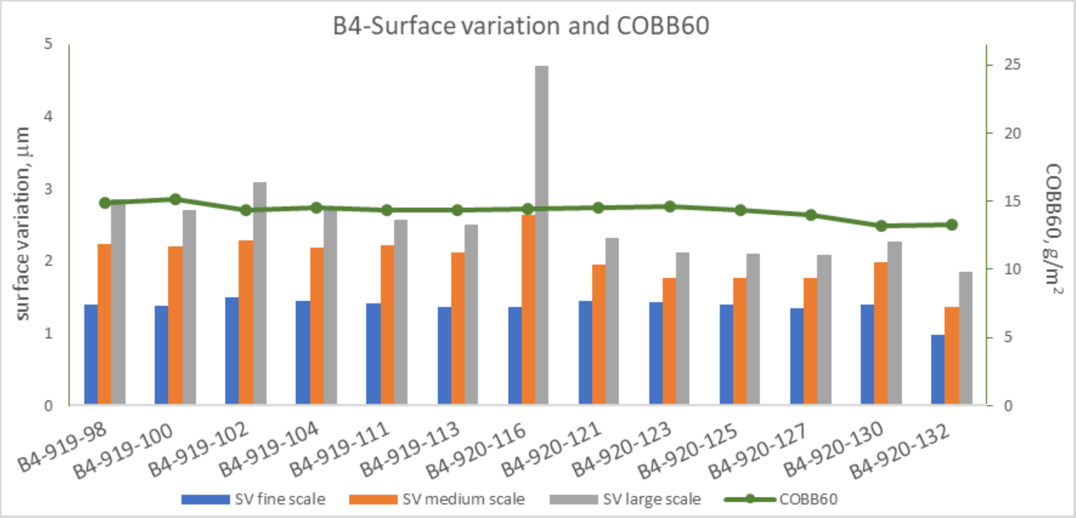

Figure 51. *Opti Topo-surface variation and COBB60 for Batch4*

In batch 4, even though there is not a trend between COBB60 and surface roughness in all cases, for most cases it is possible to follow large scale surface variation value decrease when COBB60 decreases also.

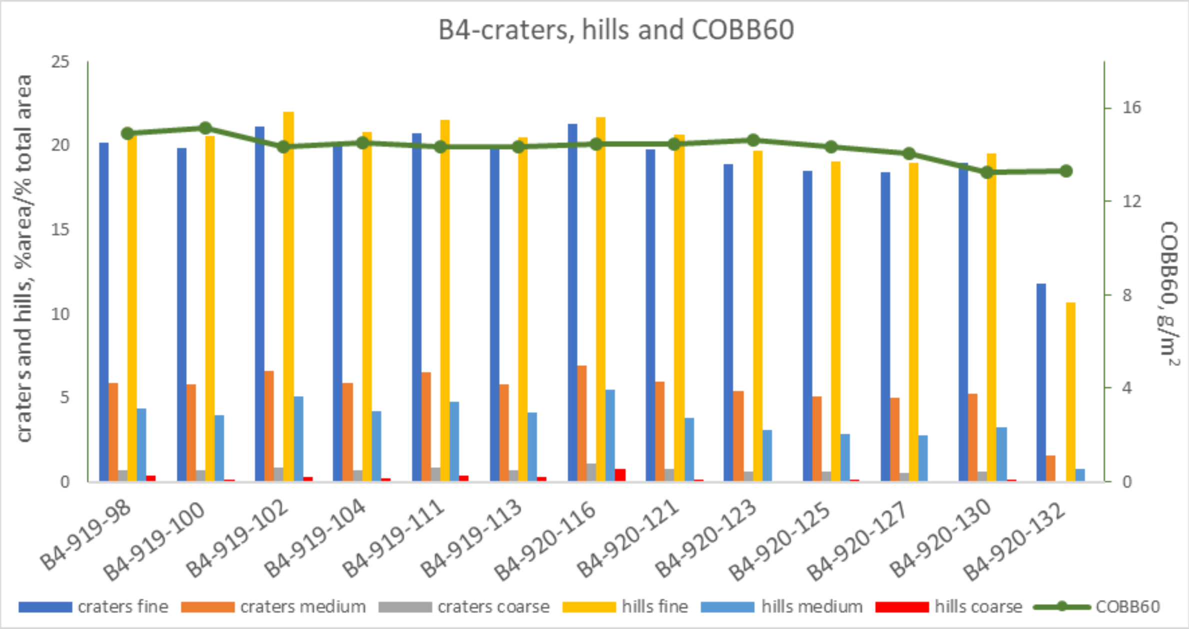

Figure 52. *OptiTopo-craters and hills and COBB60 for Batch4*

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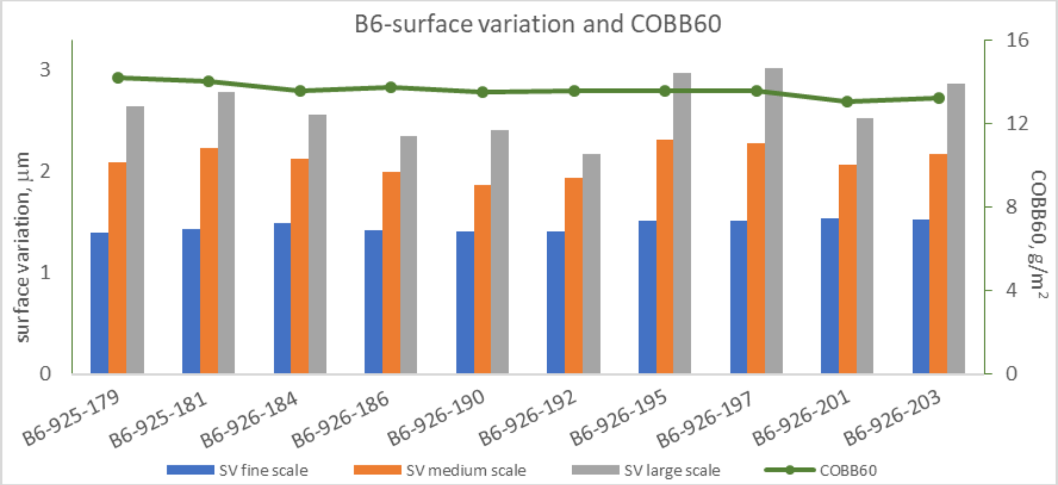

Figure 53. *Opti Topo-surface variation and COBB60 for Batch6*

Batch 6 SV graph does not indicate any trend, but craters and hills graph show that if there is no significant difference between COBB60 values, it is because there is no difference between craters and hills.

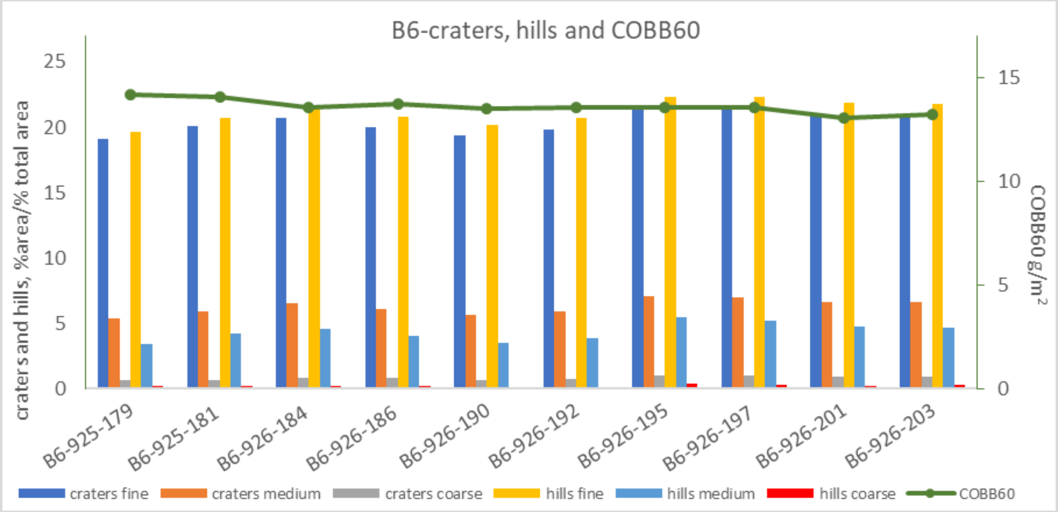

Figure 54. *OptiTopo-craters and hills and COBB60 for Batch6*

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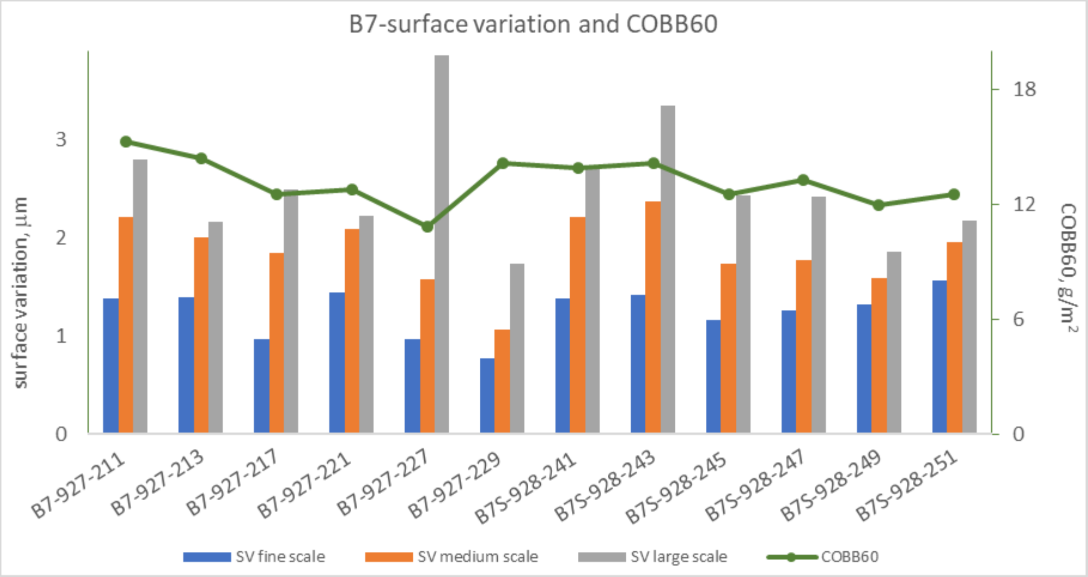

Figure 55. *Opti Topo-surface variation and COBB60 for Batch7*

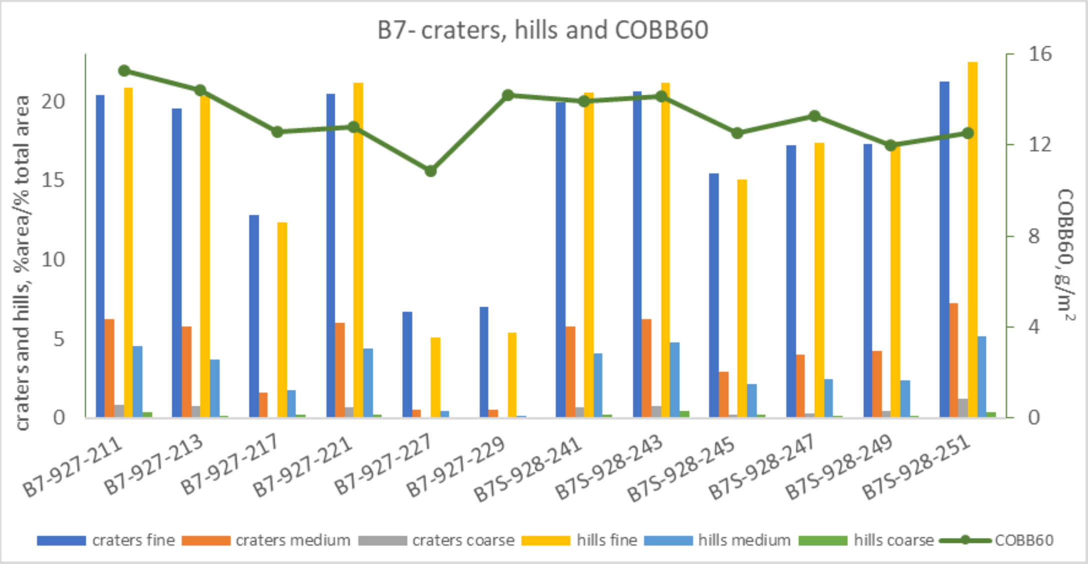

Figure 56. *OptiTopo-craters and hills and COBB60 for Batch7*

For B7 from sample 211 to 213 craters fine and hills fine decreases while COBB60 value also decreases. If we include samples 217 and 227, there is bigger difference in craters and hills in all scales and this explains the lower COB60 value for both samples. Sample 221 and 229 are out of trend and they require some more tests to understand their behavior.

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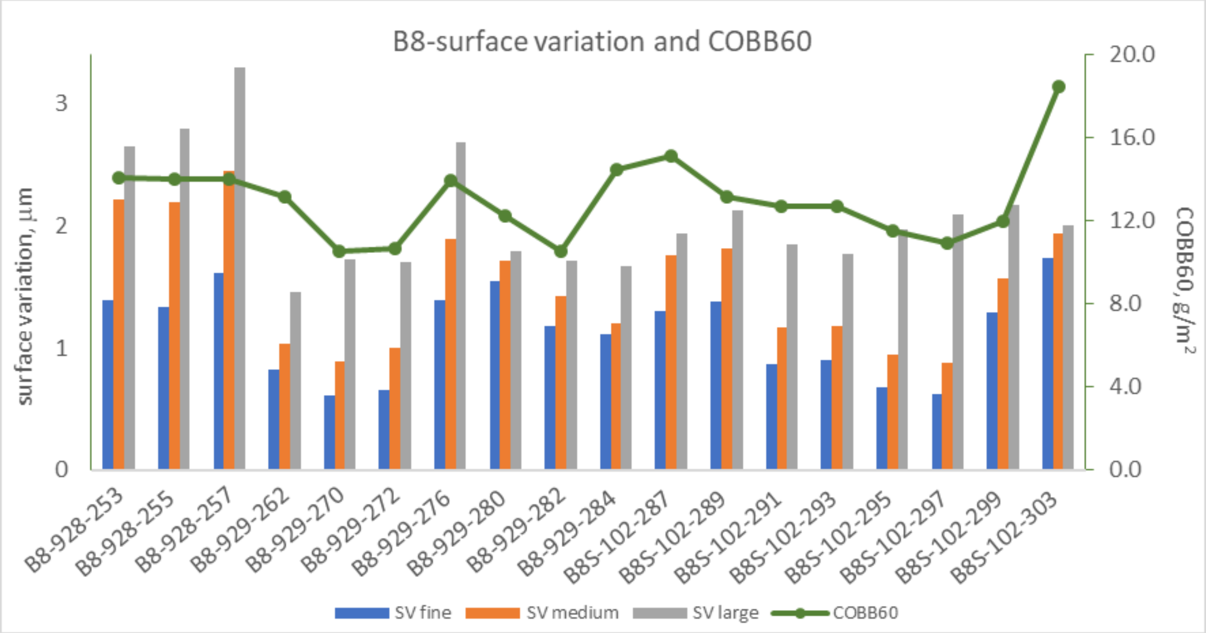

Figure 57. *Opti Topo-surface variation and COBB60 for Batch8*

In series B8, it is easier to see how COBB values differ with varying surface properties, even though there is not consistent trend within the entire series. It is again hard to explain high COBB60 value with low SV (sample 303). But in the craters and hills graph there is a trend that COBB60 value increases with increasing craters and hills values, in general.

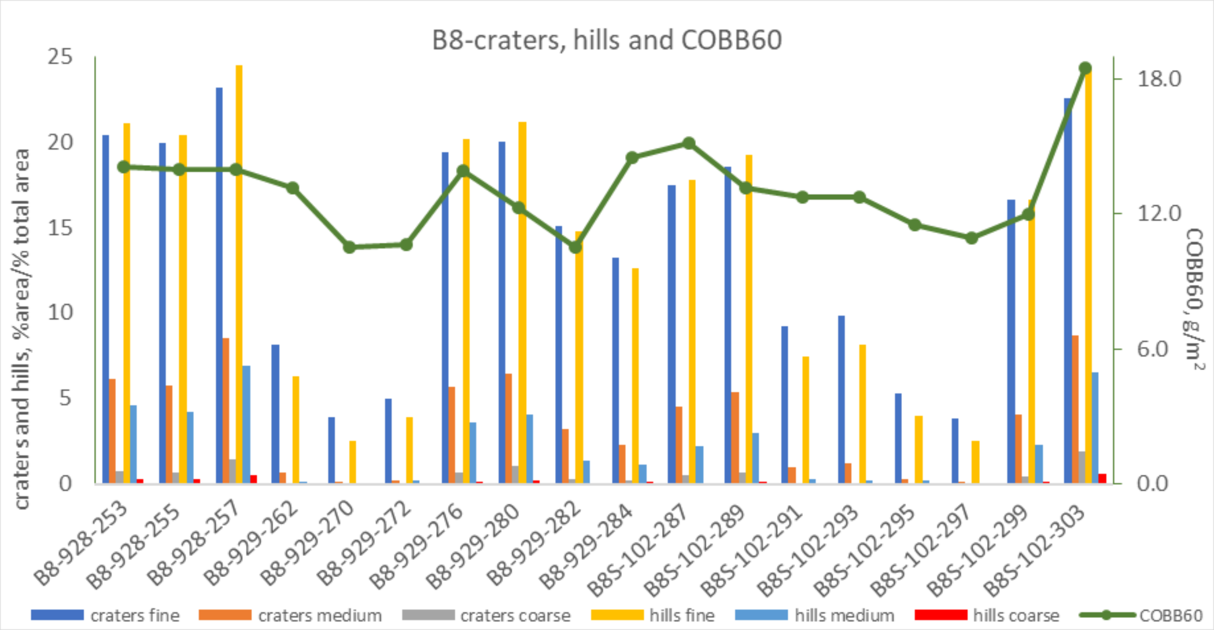

Figure 58. *OptiTopo-craters and hills and COBB60 for Batch8*

- **Effect of additives and varying process parameters on selected substrates**

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To understand if there is the same correlation between COBB60 values from the materials through different series (or to see this relationship is valid only the same stock is used-within), a comparative data analysis was carried out (Figure 55-Figure 56). For this evaluation, the materials with good COBB60 value were selected (up till 12). Note that process parameters are another variable here. So, if there is a trend between COBB60 and surface property due to the variation in the additive types it may be hard to follow from this graph. In the same way, if there is an effect of added additives, it might be hard to follow if it is because of process variable or additive variables. The conclusion is based on good water resistance. The selected material's next property in question is surface roughness and how they relate to each other. And then the best stock composition was defined according to these two properties, in this section.

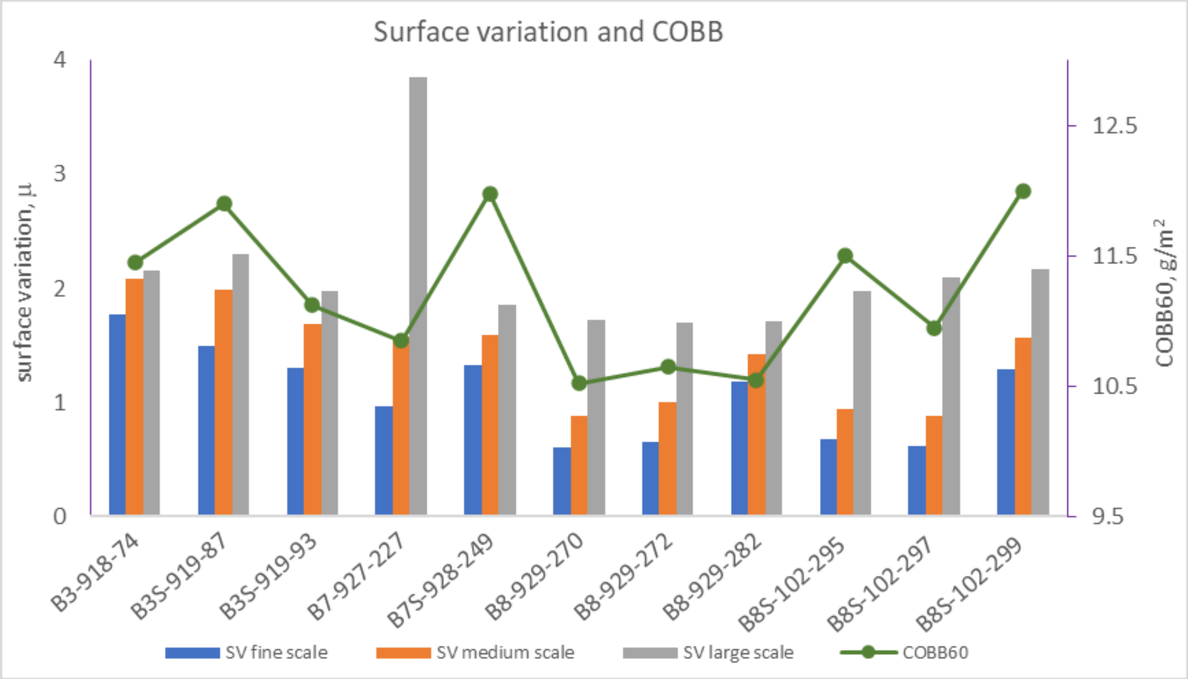

Figure 59. *OptiTopo-surface variation and COBB60 for selected materials from all batches*

On the other hand, it is not an unexpected behavior if there is no trend between surface roughness and COBB60 values since, in this case, the materials generated from different stocks (varying additive type and amount) are being compared and thus not only the surface topography is decisive factor for material's behavior against water but also the surface chemistry. Here (Figure 55), it is possible to see the effect of the stock additives on the resulting material's surface properties and water resistance.

For film lamination application, the substrate should have a certain porosity so that it allows the vacuum lamination. Therefore, the samples with high roughness might be also considered as better substrate for lamination while the same substrate might not good one for spray coating. Instead of defining a surface roughness value in general and rejecting the substrates

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outside this range, the substrates would be grouped according to their suitability for each coating application method in the future studies.

Results summary on wet moulding process optimization: Depending on additives and process parameters, the water resistance and the porosity/topography of the substrate can be tailored. By varying the surface topography, the substrate will be suitable for different barrier application techniques. The next phase of the wet molding part will be the application of the barrier systems on produced 3D substrate and investigate the effect of barrier by comparing COBB60 and surface porosity/topography results.

5. GENERAL SUMMARY AND CONCLUSIONS

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.

With the **PHA** strategy, desired barrier properties were obtained only after a certain deposition of barrier. This means that the aim to have >85% paper content needs further optimization or other substrates can be considered. As a proof of concept, barrier performance was obtained by different application strategies.

The **starch-based barrier** showed promising barrier properties in combination with the partly fossil based barrier. This material will be further evaluated in a scaled-up process.

Carnauba wax in combination with other film forming material showed promising barrier properties. Carnauba wax itself showed not good results, compared to other barriers in this project and was not prioritized further.

SiOx depositions were investigated on different substrates with and without pre coating. However, at this stage in the project, the substrates were not smooth enough. Improvement of substrate surface can make it possible to gain benefits of SiOx deposition.

For 3D substrates, the spray coating technique has been evaluated and barriers have been deposited in a multilayer structure. Water resistance significantly reduced, and grease resistance were obtained for some samples by applying this technique and the results were dependant on the coating weight. Trays produced at RISE have shown low Cobb value, down to 10-11 g/m2 by varying the process parameters and additives. These trays will be used for different barrier strategies.

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.

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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7. APPENDIX

7.1 Supplementary Information

Table A 1. *Results obtained of PHA emulsion coated on kraft paper, PHA coating dried with IR lamp.*

PHA emulsion coated on Kraft paper					
Number of coating layers	1	1	2	2	2
Coating weight [g/m^2]	6	13	13	21	36
KIT	fail	2	10	12	12
Cobb60 [g/m^2]	6	-	0,8	-	-
Cobb1800 [g/m^2]	-	25	-	11,2	4
WVTR (g/m^2*day) at 23 °C & 75 % humidity	-	-	-	-	48

Table A 2. *Results obtained of PHA emulsion coated on FiberLean uncoated and bleached paper, PHA coating dried with IR lamp.*

PHA emulsion coated on FiberLean uncoated and bleached paper			
Number of coating layers	1	2	2
Coating weight [g/m^2]	8	13	40
KIT	fail	2	12
Cobb1800 [g/m^2]	40	33	4
WVTR (g/m^2*day) at 23 °C & 75 % humidity	-	-	52

Table A 3. *Results obtained of PHA emulsion coated on FiberLean MFC coated and unbleached paper, PHA coating dried with IR lamp.*

PHA emulsion coated on FiberLean MFC coated and bleached paper			
Number of coating layers	1	2	2
Coating weight [g/m^2]	6	12	35
KIT	12	12	12

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Cobb1800 [g/m^2]	70	42	5
WVTR (g/m^2 *day) at 23 °C & 75 % humidity	-	-	46

Table A 4. *Results obtained of PHA emulsion coated on kraft paper, PHA coating dried with IR lamp.*

PHA emulsion coated on bleached Kraft paper 48 gsm					
Number of coating layers	1	1	2	2	2
Coating weight [g/m2]	6	13	13	21	36
KIT	Fail	2	10	12	12
Cobb60 [g/m2]	6	-	0,8	-	-
Cobb1800 [g/m2]	-	25	-	11,2	4
WVTR (g/m2*day) at 23 °C & 75 % humidity	-	-	-	-	48

Table A 5. *Results obtained of PHA emulsion coated on FiberLean uncoated and unbleached paper, PHA coating dried with IR lamp.*

PHA emulsion coated on FiberLean uncoated and unbleached paper			
Number of coating layers	1	2	2
Coating weight [g/m2]	9	16	44
KIT	Fail	6	10
Cobb1800 [g/m2]	43	40	5
WVTR (g/m2*day) at 23 °C & 75 % humidity	-	-	46

Table A 6. *Results obtained of PHA emulsion coated on FiberLean uncoated and bleached paper, PHA coating dried with IR lamp.*

PHA emulsion coated on FiberLean uncoated and bleached paper			
Number of coating layers	1	2	2
Coating weight [g/m2]	8	13	40
KIT	Fail	2	12
Cobb1800 [g/m2]	40	33	4
WVTR (g/m2*day) at 23 °C & 75 % humidity	-	-	52

Table A 7. *Results obtained of PHA emulsion coated on FiberLean MFC coated and unbleached paper, PHA coating dried with IR lamp.*

PHA emulsion coated on FiberLean MFC coated and bleached paper			
Number of coating layers	1	2	2
Coating weight [g/m2]	6	12	35
KIT	12	12	12
Cobb1800 [g/m2]	70	42	5

WVTR (g/m2*day) at 23 °C & 75 % humidity	-	-	46

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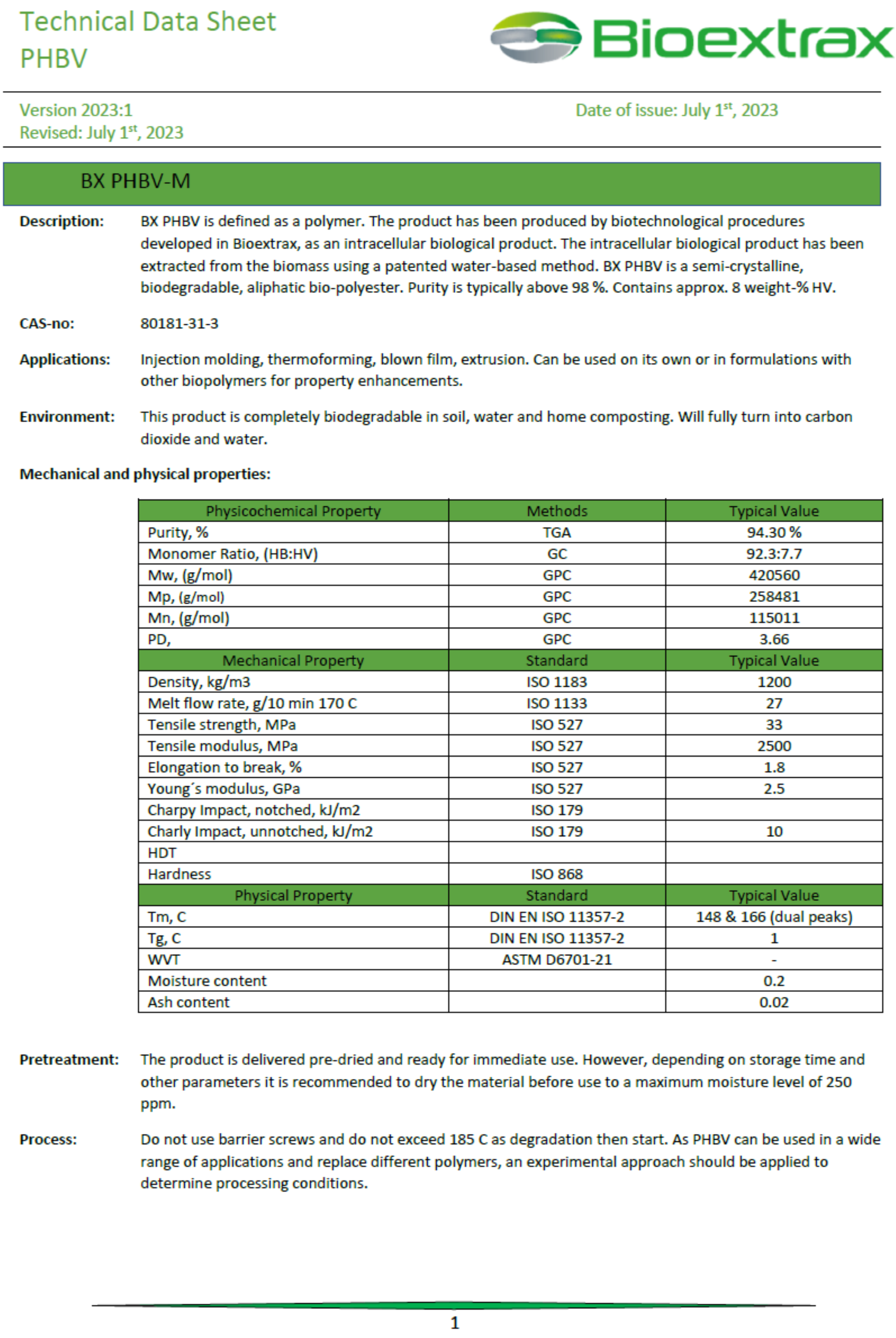
7.2 Technical Data Sheets



Technical Data Sheet
PHBV

Version 2023:1
Revised: July 1st, 2023

Date of issue: July 1st, 2023

BX PHBV-M

Description: BX PHBV is defined as a polymer. The product has been produced by biotechnological procedures developed in Bioextrax, as an intracellular biological product. The intracellular biological product has been extracted from the biomass using a patented water-based method. BX PHBV is a semi-crystalline, biodegradable, aliphatic bio-polyester. Purity is typically above 98 %. Contains approx. 8 weight-% HV.

CAS-no: 80181-31-3

Applications: Injection molding, thermoforming, blown film, extrusion. Can be used on its own or in formulations with other biopolymers for property enhancements.

Environment: This product is completely biodegradable in soil, water and home composting. Will fully turn into carbon dioxide and water.

Mechanical and physical properties:

Physicochemical Property	Methods	Typical Value
Purity, %	TGA	94.30 %
Monomer Ratio, (HB:HV)	GC	92.3:7.7
Mw, (g/mol)	GPC	420560
Mp, (g/mol)	GPC	258481
Mn, (g/mol)	GPC	115011
PD,	GPC	3.66
Mechanical Property	Standard	Typical Value
Density, kg/m3	ISO 1183	1200
Melt flow rate, g/10 min 170 C	ISO 1133	27
Tensile strength, MPa	ISO 527	33
Tensile modulus, MPa	ISO 527	2500
Elongation to break, %	ISO 527	1.8
Young´s modulus, GPa	ISO 527	2.5
Charpy Impact, notched, kJ/m2	ISO 179	
Charly Impact, unnotched, kJ/m2	ISO 179	10
HDT		
Hardness	ISO 868	
Physical Property	Standard	Typical Value
Tm, C	DIN EN ISO 11357-2	148 & 166 (dual peaks)
Tg, C	DIN EN ISO 11357-2	1
WVT	ASTM D6701-21	-
Moisture content		0.2
Ash content		0.02

Pretreatment: The product is delivered pre-dried and ready for immediate use. However, depending on storage time and other parameters it is recommended to dry the material before use to a maximum moisture level of 250 ppm.

Process: Do not use barrier screws and do not exceed 185 C as degradation then start. As PHBV can be used in a wide range of applications and replace different polymers, an experimental approach should be applied to determine processing conditions.

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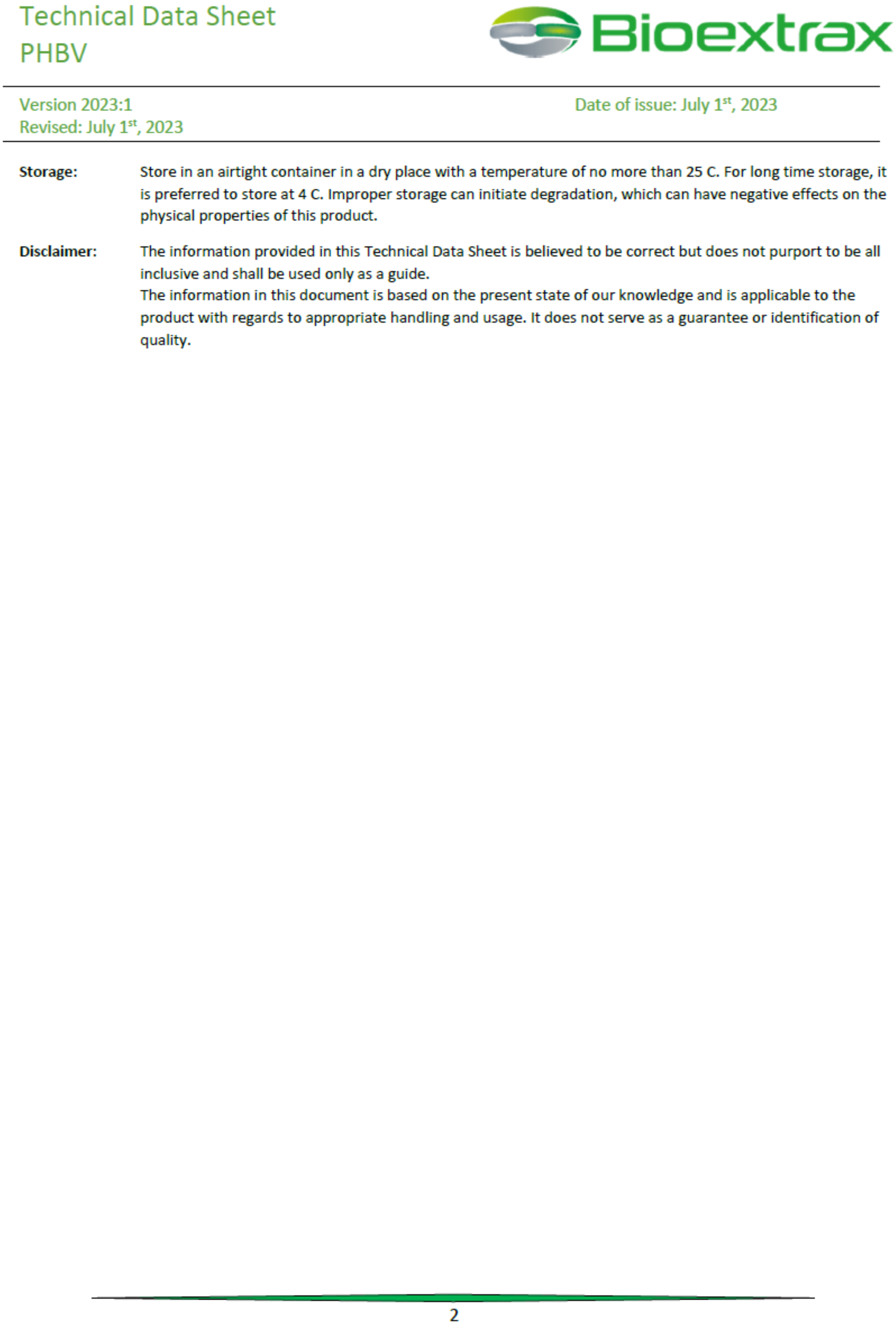

Technical Data Sheet
PHBV

Version 2023:1
Revised: July 1st, 2023
Date of issue: July 1st, 2023

Storage: Store in an airtight container in a dry place with a temperature of no more than 25 C. For long time storage, it is preferred to store at 4 C. Improper storage can initiate degradation, which can have negative effects on the physical properties of this product.

Disclaimer: The information provided in this Technical Data Sheet is believed to be correct but does not purport to be all inclusive and shall be used only as a guide.
The information in this document is based on the present state of our knowledge and is applicable to the product with regards to appropriate handling and usage. It does not serve as a guarantee or identification of quality.

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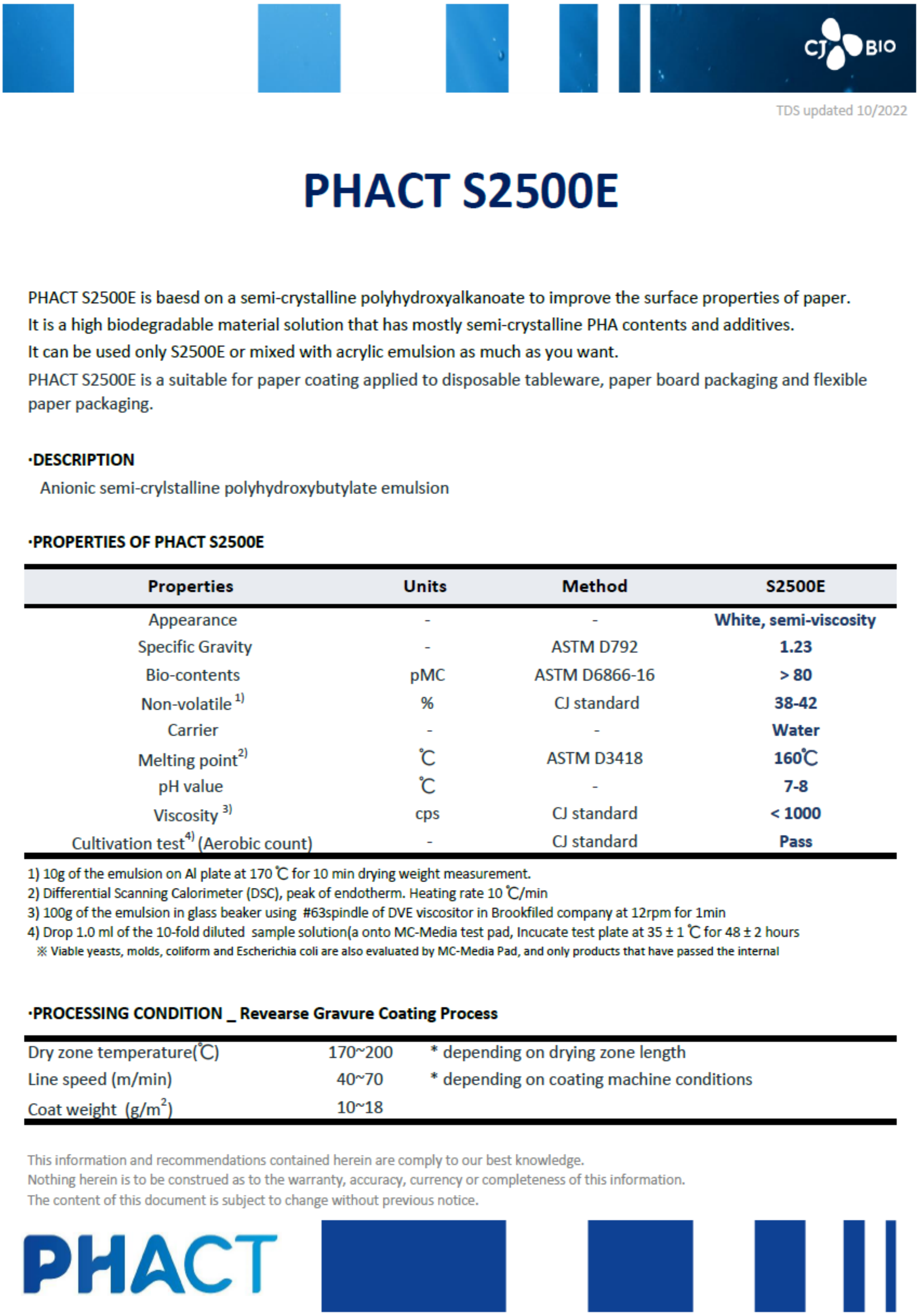

CJ BIO

TDS updated 10/2022

PHACT S2500E

PHACT S2500E is baesd on a semi-crystalline polyhydroxyalkanoate to improve the surface properties of paper.
It is a high biodegradable material solution that has mostly semi-crystalline PHA contents and additives.
It can be used only S2500E or mixed with acrylic emulsion as much as you want.
PHACT S2500E is a suitable for paper coating applied to disposable tableware, paper board packaging and flexible paper packaging.

·DESCRIPTION

Anionic semi-crylstalline polyhydroxybutylate emulsion

·PROPERTIES OF PHACT S2500E

Properties	Units	Method	S2500E
Appearance	-	-	**White, semi-viscosity**
Specific Gravity	-	ASTM D792	**1.23**
Bio-contents	pMC	ASTM D6866-16	**> 80**
Non-volatile[1]	%	CJ standard	**38-42**
Carrier	-	-	**Water**
Melting point[2]	℃	ASTM D3418	**160℃**
pH value	℃	-	**7-8**
Viscosity[3]	cps	CJ standard	**< 1000**
Cultivation test[4] (Aerobic count)	-	CJ standard	**Pass**

1) 10g of the emulsion on Al plate at 170 ℃ for 10 min drying weight measurement.
2) Differential Scanning Calorimeter (DSC), peak of endotherm. Heating rate 10 ℃/min
3) 100g of the emulsion in glass beaker using #63spindle of DVE viscositor in Brookfiled company at 12rpm for 1min
4) Drop 1.0 ml of the 10-fold diluted sample solution(a onto MC-Media test pad, Incucate test plate at 35 ± 1 ℃ for 48 ± 2 hours
※ Viable yeasts, molds, coliform and Escherichia coli are also evaluated by MC-Media Pad, and only products that have passed the internal

·PROCESSING CONDITION _ Revearse Gravure Coating Process

Dry zone temperature(℃)	170~200	* depending on drying zone length
Line speed (m/min)	40~70	* depending on coating machine conditions
Coat weight (g/m^2)	10~18	

This information and recommendations contained herein are comply to our best knowledge.
Nothing herein is to be construed as to the warranty, accuracy, currency or completeness of this information.
The content of this document is subject to change without previous notice.

PHACT

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PROVISIONAL DATA SHEET

Innospers CWSF

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Description

Innospers CWSF is a small particle size, non-ionic Carnauba wax emulsion, developed as a slip additive for coating applications. Apart from the biocide, all components have food additive status. All raw materials, including the surfactants, are of vegetable origin.

Intended Applications

Innospers CWSF is used as a slip modifier and anti-blocking agent for coatings, especially for heat-sealable coatings on film. It can also be used to enhance the hydrophobicity of water based coatings.

Usage Recommendation

Innospers CWSF should be added to the formulation whilst stirring and is typically used at addition levels of between 3 and 10% to achieve the desired performance. The product has good general compatibility with other formulatory components, but it is still advised to check stability at a lab scale before commercial use.

Storage & Shelf Life

Innospers CWSF is delivered in 150 litre drums or 1000 litre IBC's.

Property	Target Value
Solids content (%)	40%
pH	7.0
Appearance	Beige liquid
Viscosity (mPa.s @ 23°C)	250
Bio based content	100%

Innospers CWSF exhibits good shelf-life stability of at least 6 months. Since this is an aqueous dispersion, the product should be stored under cool but frost-free conditions (between 5°C and 25°C) out of direct sunlight. Stock rotation should be practised and stirring is advised before use.

Safety

Material Safety Data Sheets are available for all Innospers products. Please contact our technical service personnel for the latest version. Our Material Safety Data Sheets contain important information that you might need to protect your employees against any known health and safety hazards.

Development Status

Innospers CWSF is a developmental product. As a result the recipe and target properties may be subject to change in the future and commercial supply cannot be guaranteed at the present date.

Disclaimer

Information and details given in this document, particularly any recommendations for application and use of our products are based on careful laboratory tests and prevailing practical experience and are believed to be correct at time of publication. The information is not binding, which is also generally true for our practical customer service, given verbally, in writing and by tests. Due to (possibly varying) conditions of transport, storage, process, substrate use or product application (which are beyond our knowledge and control), it is the responsibility of the user to carry out sufficient tests in order to ensure that our products are suitable for the intended processes and applications. Whilst proper care has been taken in the preparation of this document, no liability for damage or injury resulting from its use is accepted, other than the limited liability which may arise towards a contractual party on the basis of Allinova's conditions of sale (a copy of these conditions is available on request). Allinova's acceptance of any orders for this product is expressly conditional upon purchaser's assent to these conditions of sale. No information contained in this document (nor any information given verbally, in writing and by tests) is to be construed as permission, recommendation or inducement by Allinova or its officers, employees or affiliates, to use any product or process so as to infringe upon or conflict with any patent. Allinova does not attest or guarantee that the use of its products or processes will not infringe upon any patent; user is responsible for verifying its freedom to operate in any jurisdiction.

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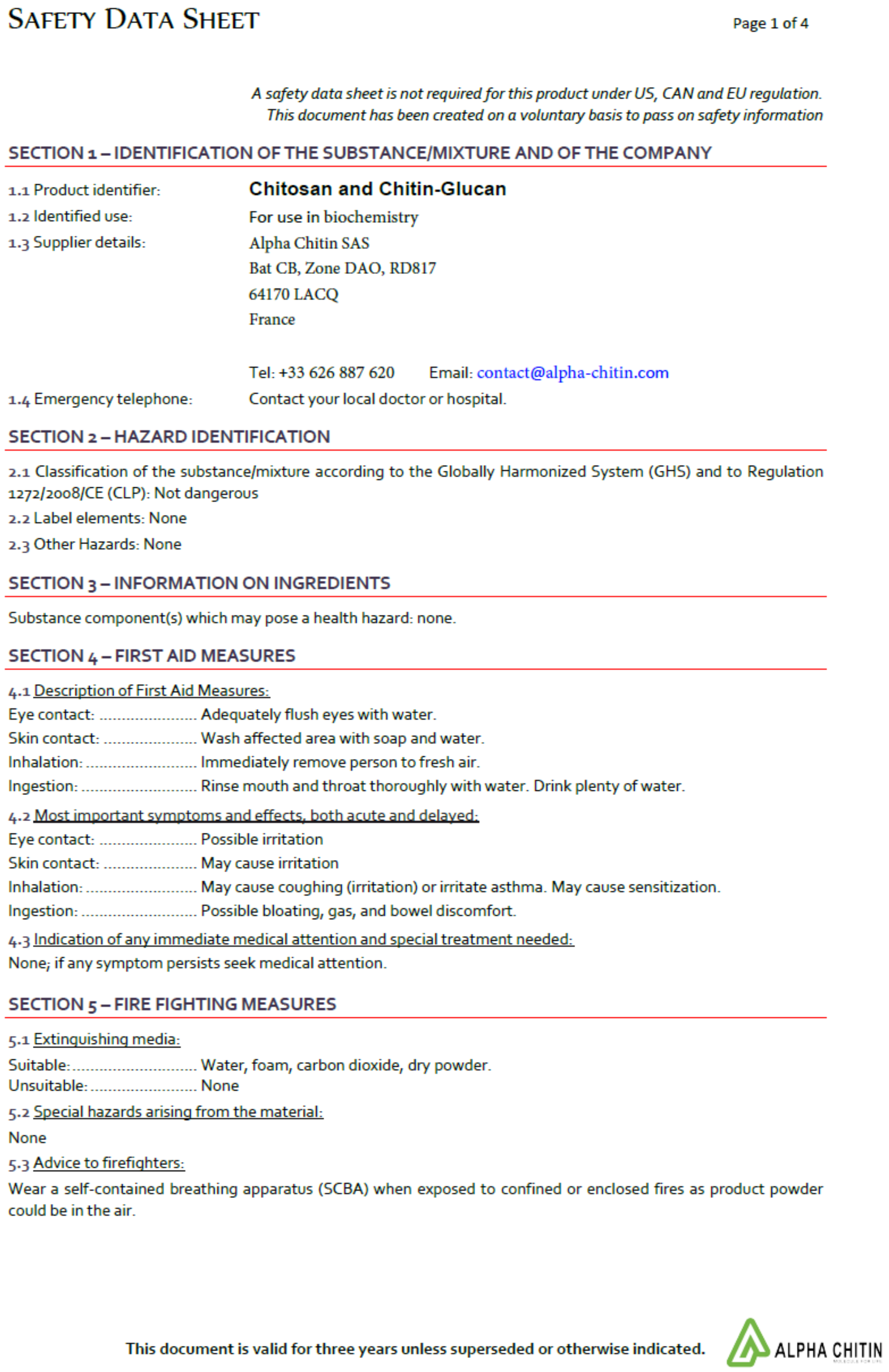

SAFETY DATA SHEET

Page 1 of 4

A safety data sheet is not required for this product under US, CAN and EU regulation.
This document has been created on a voluntary basis to pass on safety information

SECTION 1 – IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY

1.1 Product identifier:	**Chitosan and Chitin-Glucan**
1.2 Identified use:	For use in biochemistry
1.3 Supplier details:	Alpha Chitin SAS Bat CB, Zone DAO, RD817 64170 LACQ France Tel: +33 626 887 620 Email: contact@alpha-chitin.com
1.4 Emergency telephone:	Contact your local doctor or hospital.

SECTION 2 – HAZARD IDENTIFICATION

2.1 Classification of the substance/mixture according to the Globally Harmonized System (GHS) and to Regulation 1272/2008/CE (CLP): Not dangerous

2.2 Label elements: None

2.3 Other Hazards: None

SECTION 3 – INFORMATION ON INGREDIENTS

Substance component(s) which may pose a health hazard: none.

SECTION 4 – FIRST AID MEASURES

4.1 Description of First Aid Measures:
Eye contact: .... Adequately flush eyes with water.
Skin contact: .... Wash affected area with soap and water.
Inhalation: .... Immediately remove person to fresh air.
Ingestion: .... Rinse mouth and throat thoroughly with water. Drink plenty of water.

4.2 Most important symptoms and effects, both acute and delayed:
Eye contact: .... Possible irritation
Skin contact: .... May cause irritation
Inhalation: .... May cause coughing (irritation) or irritate asthma. May cause sensitization.
Ingestion: .... Possible bloating, gas, and bowel discomfort.

4.3 Indication of any immediate medical attention and special treatment needed:
None; if any symptom persists seek medical attention.

SECTION 5 – FIRE FIGHTING MEASURES

5.1 Extinguishing media:
Suitable: .... Water, foam, carbon dioxide, dry powder.
Unsuitable: .... None

5.2 Special hazards arising from the material:
None

5.3 Advice to firefighters:
Wear a self-contained breathing apparatus (SCBA) when exposed to confined or enclosed fires as product powder could be in the air.

This document is valid for three years unless superseded or otherwise indicated. ALPHA CHITIN

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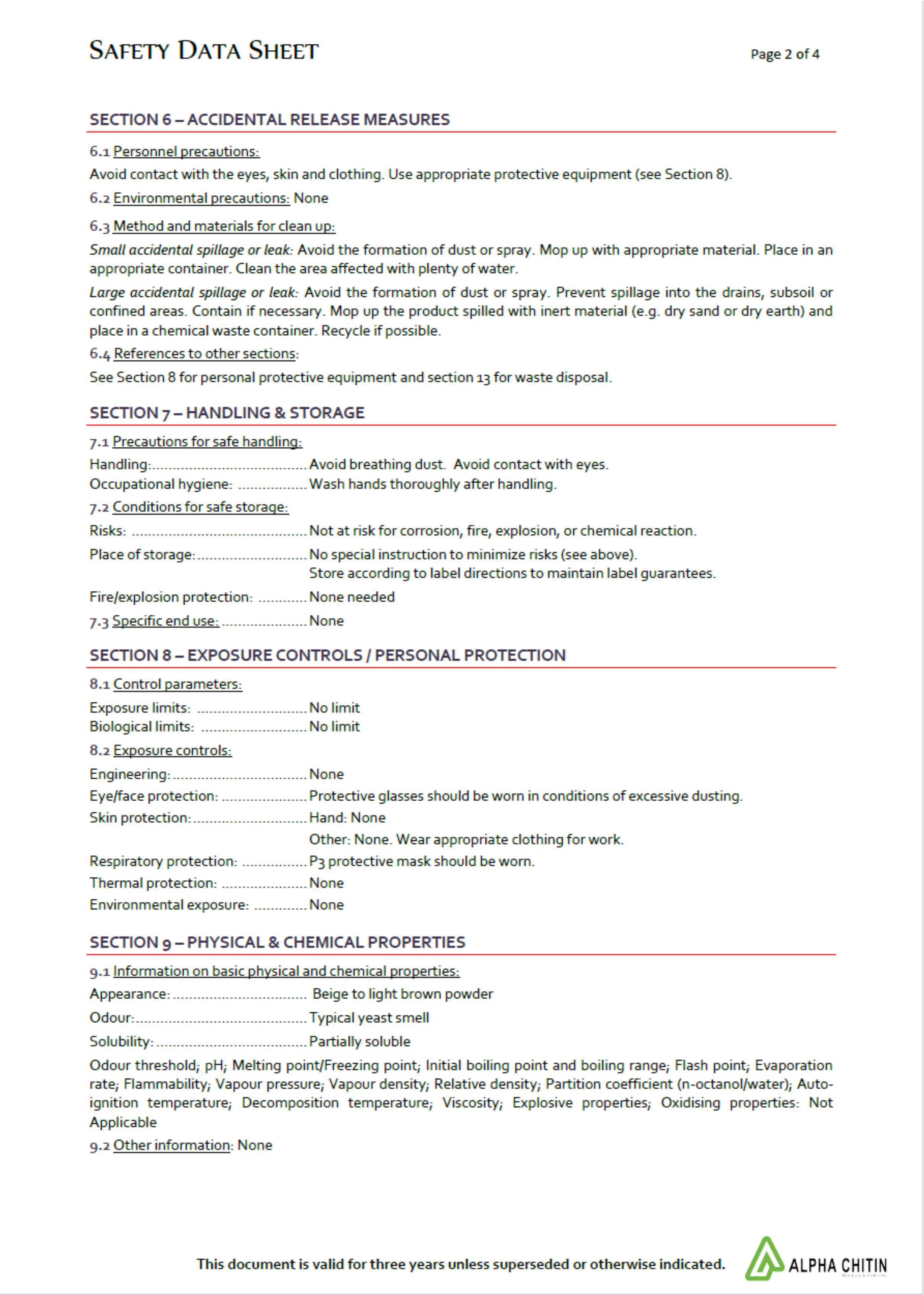

SAFETY DATA SHEET

Page 2 of 4

SECTION 6 – ACCIDENTAL RELEASE MEASURES

6.1 Personnel precautions:

Avoid contact with the eyes, skin and clothing. Use appropriate protective equipment (see Section 8).

6.2 Environmental precautions: None

6.3 Method and materials for clean up:

Small accidental spillage or leak: Avoid the formation of dust or spray. Mop up with appropriate material. Place in an appropriate container. Clean the area affected with plenty of water.

Large accidental spillage or leak: Avoid the formation of dust or spray. Prevent spillage into the drains, subsoil or confined areas. Contain if necessary. Mop up the product spilled with inert material (e.g. dry sand or dry earth) and place in a chemical waste container. Recycle if possible.

6.4 References to other sections:

See Section 8 for personal protective equipment and section 13 for waste disposal.

SECTION 7 – HANDLING & STORAGE

7.1 Precautions for safe handling:

Handling:	Avoid breathing dust. Avoid contact with eyes.
Occupational hygiene:	Wash hands thoroughly after handling.

7.2 Conditions for safe storage:

Risks:	Not at risk for corrosion, fire, explosion, or chemical reaction.
Place of storage:	No special instruction to minimize risks (see above). Store according to label directions to maintain label guarantees.
Fire/explosion protection:	None needed
7.3 Specific end use:	None

SECTION 8 – EXPOSURE CONTROLS / PERSONAL PROTECTION

8.1 Control parameters:

Exposure limits:	No limit
Biological limits:	No limit

8.2 Exposure controls:

Engineering:	None
Eye/face protection:	Protective glasses should be worn in conditions of excessive dusting.
Skin protection:	Hand: None Other: None. Wear appropriate clothing for work.
Respiratory protection:	P3 protective mask should be worn.
Thermal protection:	None
Environmental exposure:	None

SECTION 9 – PHYSICAL & CHEMICAL PROPERTIES

9.1 Information on basic physical and chemical properties:

Appearance:	Beige to light brown powder
Odour:	Typical yeast smell
Solubility:	Partially soluble

Odour threshold; pH; Melting point/Freezing point; Initial boiling point and boiling range; Flash point; Evaporation rate; Flammability; Vapour pressure; Vapour density; Relative density; Partition coefficient (n-octanol/water); Auto-ignition temperature; Decomposition temperature; Viscosity; Explosive properties; Oxidising properties: Not Applicable

9.2 Other information: None

This document is valid for three years unless superseded or otherwise indicated.

ALPHA CHITIN

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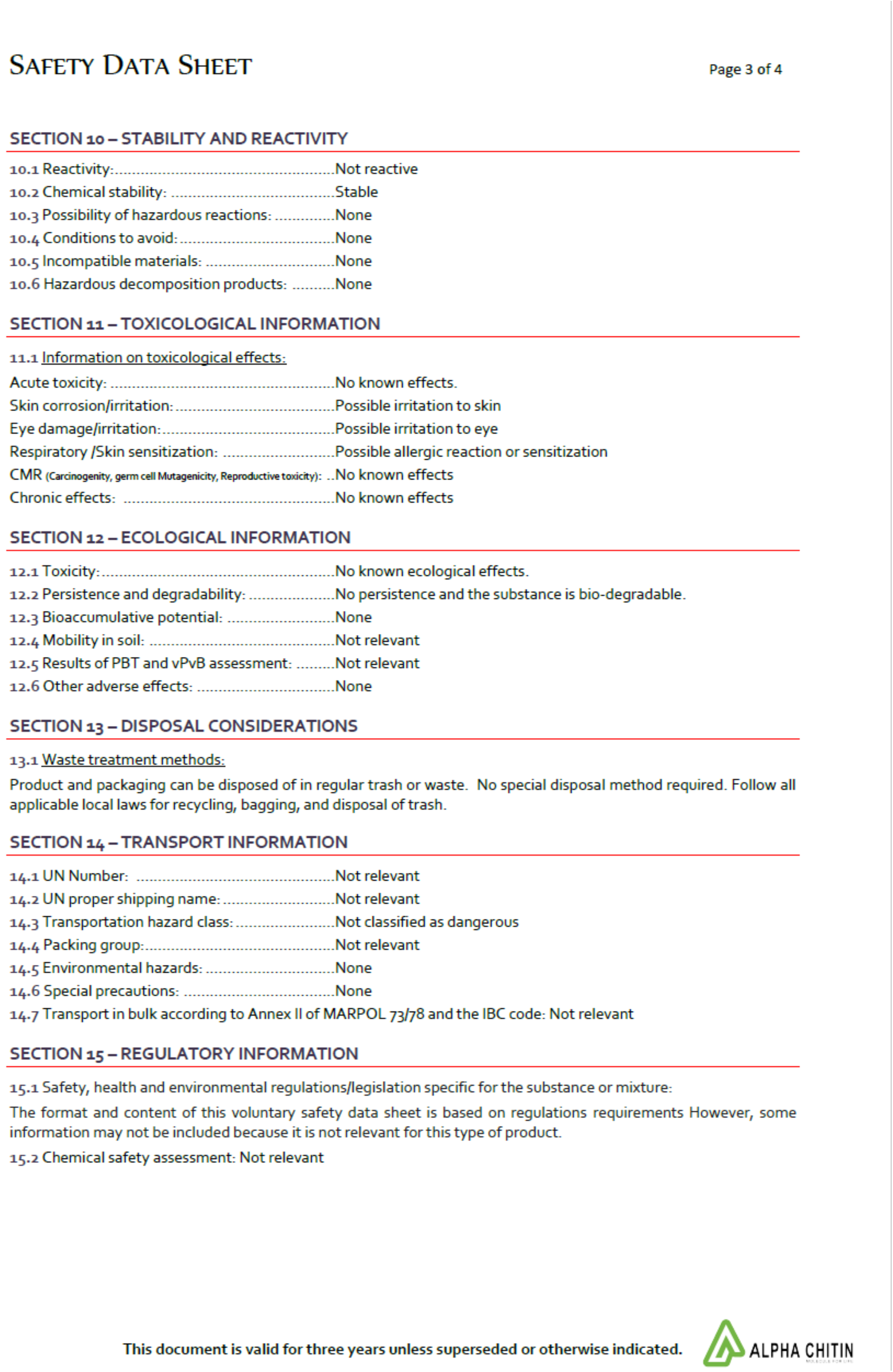

SAFETY DATA SHEET

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SECTION 10 – STABILITY AND REACTIVITY

10.1 Reactivity:..........Not reactive
10.2 Chemical stability: ....Stable
10.3 Possibility of hazardous reactions: ....None
10.4 Conditions to avoid: ....None
10.5 Incompatible materials: ....None
10.6 Hazardous decomposition products: ....None

SECTION 11 – TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects:

Acute toxicity: ....No known effects.
Skin corrosion/irritation: ....Possible irritation to skin
Eye damage/irritation: ....Possible irritation to eye
Respiratory /Skin sensitization: ....Possible allergic reaction or sensitization
CMR (Carcinogenity, germ cell Mutagenicity, Reproductive toxicity): ..No known effects
Chronic effects: ....No known effects

SECTION 12 – ECOLOGICAL INFORMATION

12.1 Toxicity: ....No known ecological effects.
12.2 Persistence and degradability: ....No persistence and the substance is bio-degradable.
12.3 Bioaccumulative potential: ....None
12.4 Mobility in soil: ....Not relevant
12.5 Results of PBT and vPvB assessment: ....Not relevant
12.6 Other adverse effects: ....None

SECTION 13 – DISPOSAL CONSIDERATIONS

13.1 Waste treatment methods:

Product and packaging can be disposed of in regular trash or waste. No special disposal method required. Follow all applicable local laws for recycling, bagging, and disposal of trash.

SECTION 14 – TRANSPORT INFORMATION

14.1 UN Number: ....Not relevant
14.2 UN proper shipping name: ....Not relevant
14.3 Transportation hazard class: ....Not classified as dangerous
14.4 Packing group: ....Not relevant
14.5 Environmental hazards: ....None
14.6 Special precautions: ....None
14.7 Transport in bulk according to Annex II of MARPOL 73/78 and the IBC code: Not relevant

SECTION 15 – REGULATORY INFORMATION

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture:

The format and content of this voluntary safety data sheet is based on regulations requirements However, some information may not be included because it is not relevant for this type of product.

15.2 Chemical safety assessment: Not relevant

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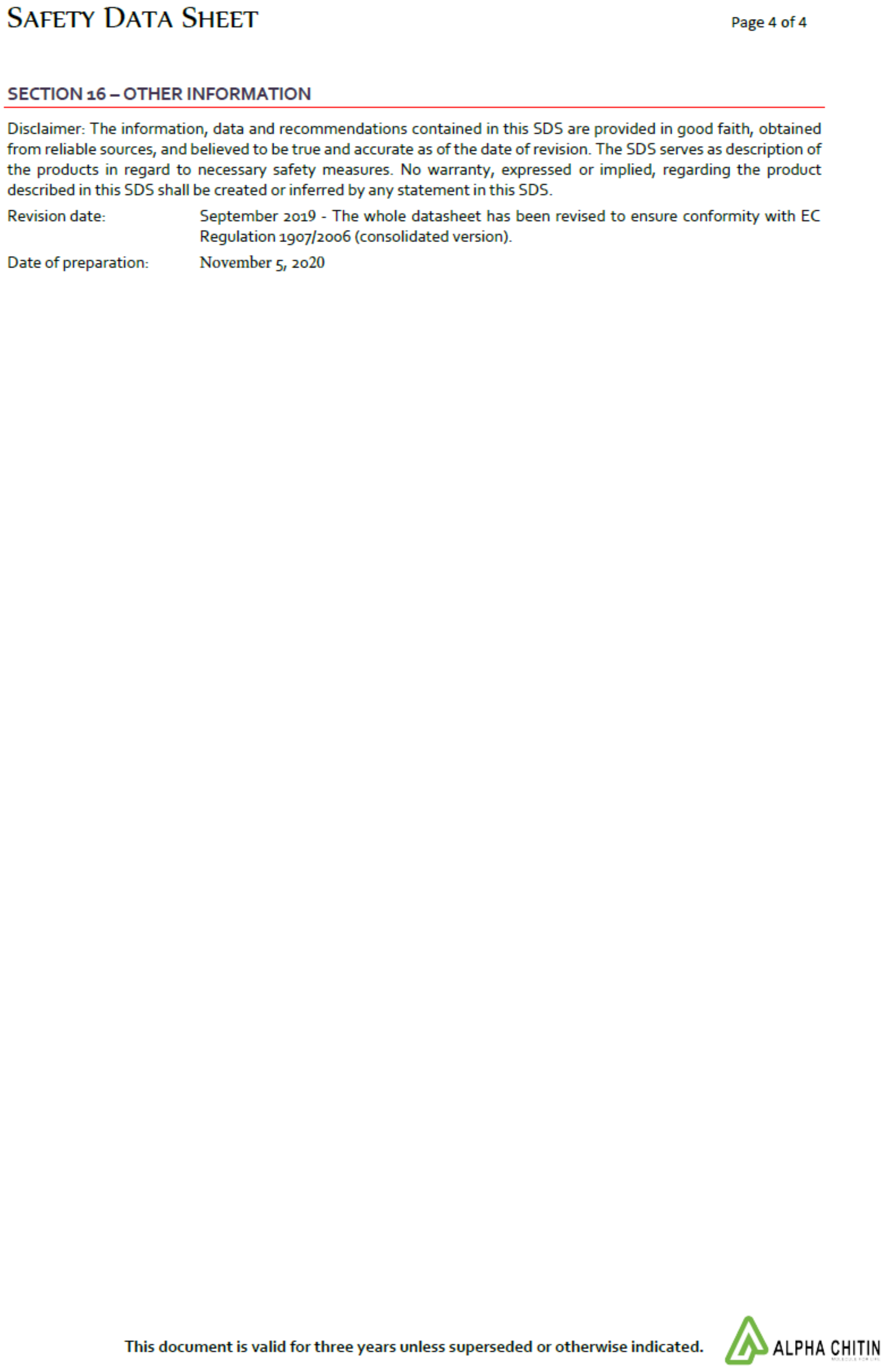

SAFETY DATA SHEET

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SECTION 16 – OTHER INFORMATION

Disclaimer: The information, data and recommendations contained in this SDS are provided in good faith, obtained from reliable sources, and believed to be true and accurate as of the date of revision. The SDS serves as description of the products in regard to necessary safety measures. No warranty, expressed or implied, regarding the product described in this SDS shall be created or inferred by any statement in this SDS.

Revision date:	September 2019 - The whole datasheet has been revised to ensure conformity with EC Regulation 1907/2006 (consolidated version).
Date of preparation:	November 5, 2020

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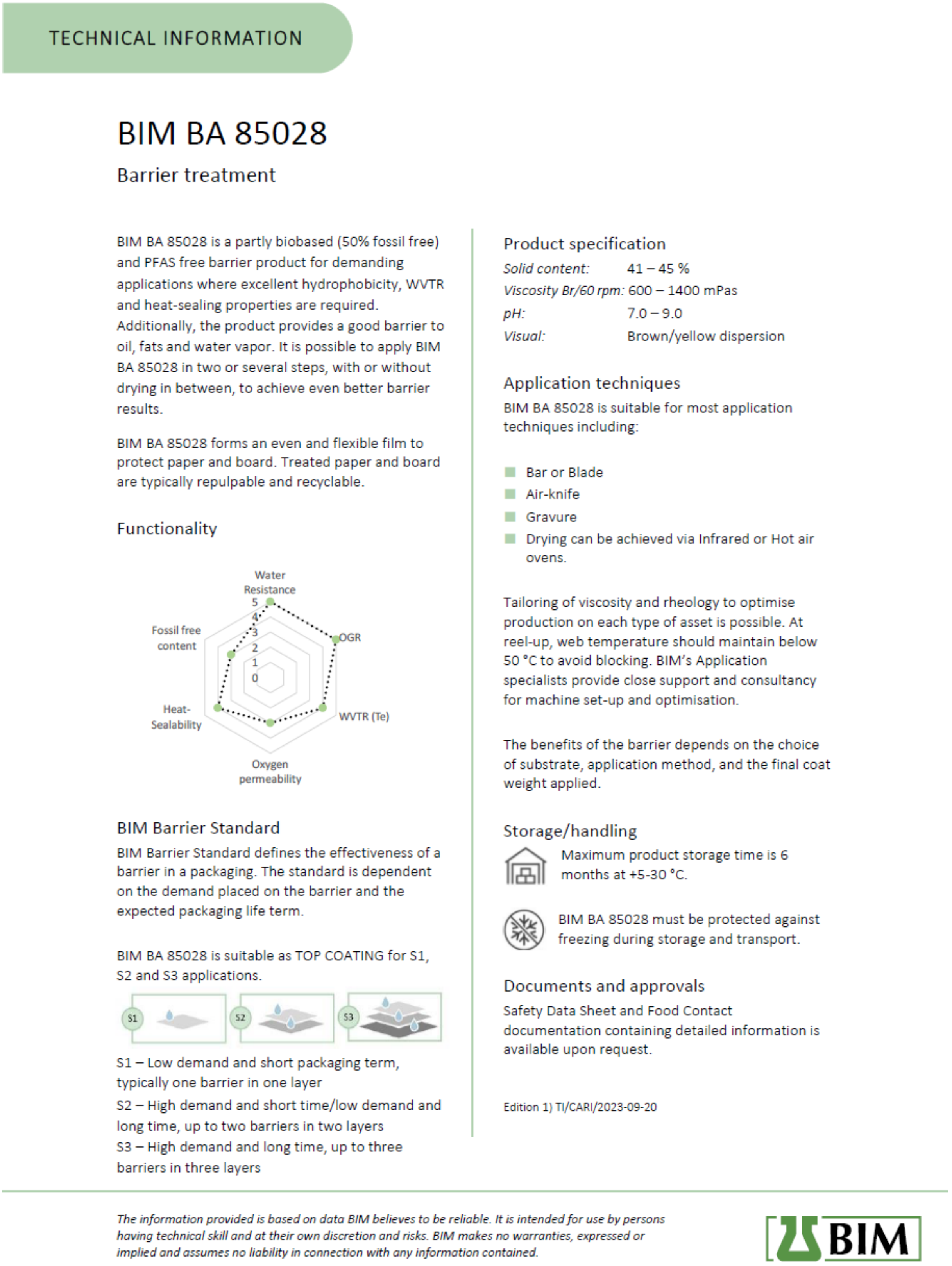

TECHNICAL INFORMATION

BIM BA 85028

Barrier treatment

BIM BA 85028 is a partly biobased (50% fossil free) and PFAS free barrier product for demanding applications where excellent hydrophobicity, WVTR and heat-sealing properties are required. Additionally, the product provides a good barrier to oil, fats and water vapor. It is possible to apply BIM BA 85028 in two or several steps, with or without drying in between, to achieve even better barrier results.

BIM BA 85028 forms an even and flexible film to protect paper and board. Treated paper and board are typically repulpable and recyclable.

Functionality

BIM Barrier Standard

BIM Barrier Standard defines the effectiveness of a barrier in a packaging. The standard is dependent on the demand placed on the barrier and the expected packaging life term.

BIM BA 85028 is suitable as TOP COATING for S1, S2 and S3 applications.

S1 – Low demand and short packaging term, typically one barrier in one layer

S2 – High demand and short time/low demand and long time, up to two barriers in two layers

S3 – High demand and long time, up to three barriers in three layers

Product specification

Solid content:	41 – 45 %
Viscosity Br/60 rpm:	600 – 1400 mPas
pH:	7.0 – 9.0
Visual:	Brown/yellow dispersion

Application techniques

BIM BA 85028 is suitable for most application techniques including:

- Bar or Blade
- Air-knife
- Gravure
- Drying can be achieved via Infrared or Hot air ovens.

Tailoring of viscosity and rheology to optimise production on each type of asset is possible. At reel-up, web temperature should maintain below 50 °C to avoid blocking. BIM's Application specialists provide close support and consultancy for machine set-up and optimisation.

The benefits of the barrier depends on the choice of substrate, application method, and the final coat weight applied.

Storage/handling

Maximum product storage time is 6 months at +5-30 °C.

BIM BA 85028 must be protected against freezing during storage and transport.

Documents and approvals

Safety Data Sheet and Food Contact documentation containing detailed information is available upon request.

Edition 1) TI/CARI/2023-09-20

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TECHNICAL INFORMATION

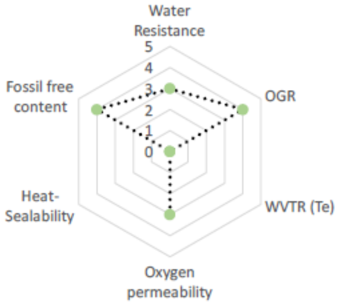
BIM BA 85113 X

Barrier treatment

BIM BA 85113 X is a 80 % fossil free barrier with high biocontent. It is mainly used for improving grease resistance of grease proof paper. BA 85113 X is PFAS free.

BIM BA 85113 X forms an even and flexible film to protect paper and board. Treated paper and board are typically repulpable and recyclable.

Functionality



BIM Barrier Standard

BIM Barrier Standard defines the effectiveness of a barrier in a packaging. The standard is dependent on the demand placed on the barrier and the expected packaging life term.

BIM BA 85113 X is suitable as TOP COATING for S1 and PRE COATING for S2 and S3 applications.

S1 – Low demand and short packaging term, typically one barrier in one layer

S2 – High demand and short time/low demand and long time, up to two barriers in two layers

S3 – High demand and long time, up to three barriers in three layers

Product specification

Solid content: 30 – 31 %
Viscosity Br/60 rpm: 450 – 550 mPas
pH: 5.0 – 7.0
Visual: Slighly beige dispersion

Application techniques

BIM BA 85113 X is suitable for most application techniques including:

- Bar or Blade
- Air-knife
- Gravure
- Drying can be achieved via Infrared or Hot air ovens.

Tailoring of viscosity and rheology to optimise production on each type of asset is possible. At reel-up, web temperature should maintain below 50 °C to avoid blocking. BIM's Application specialists provide close support and consultancy for machine set-up and optimisation.

The benefits of the barrier depends on the choice of substrate, application method, and the final coat weight applied.

Storage/handling

Maximum product storage time is 6 months at +5-30 °C. Stirring is required before taking product in use.

BIM BA 85113 X must be protected against freezing during storage and transport.

Documents and approvals

Safety Data Sheet and Food Contact documentation containing detailed information is available upon request.

Edition 1) TI/CARI/2023-09-21

BIM

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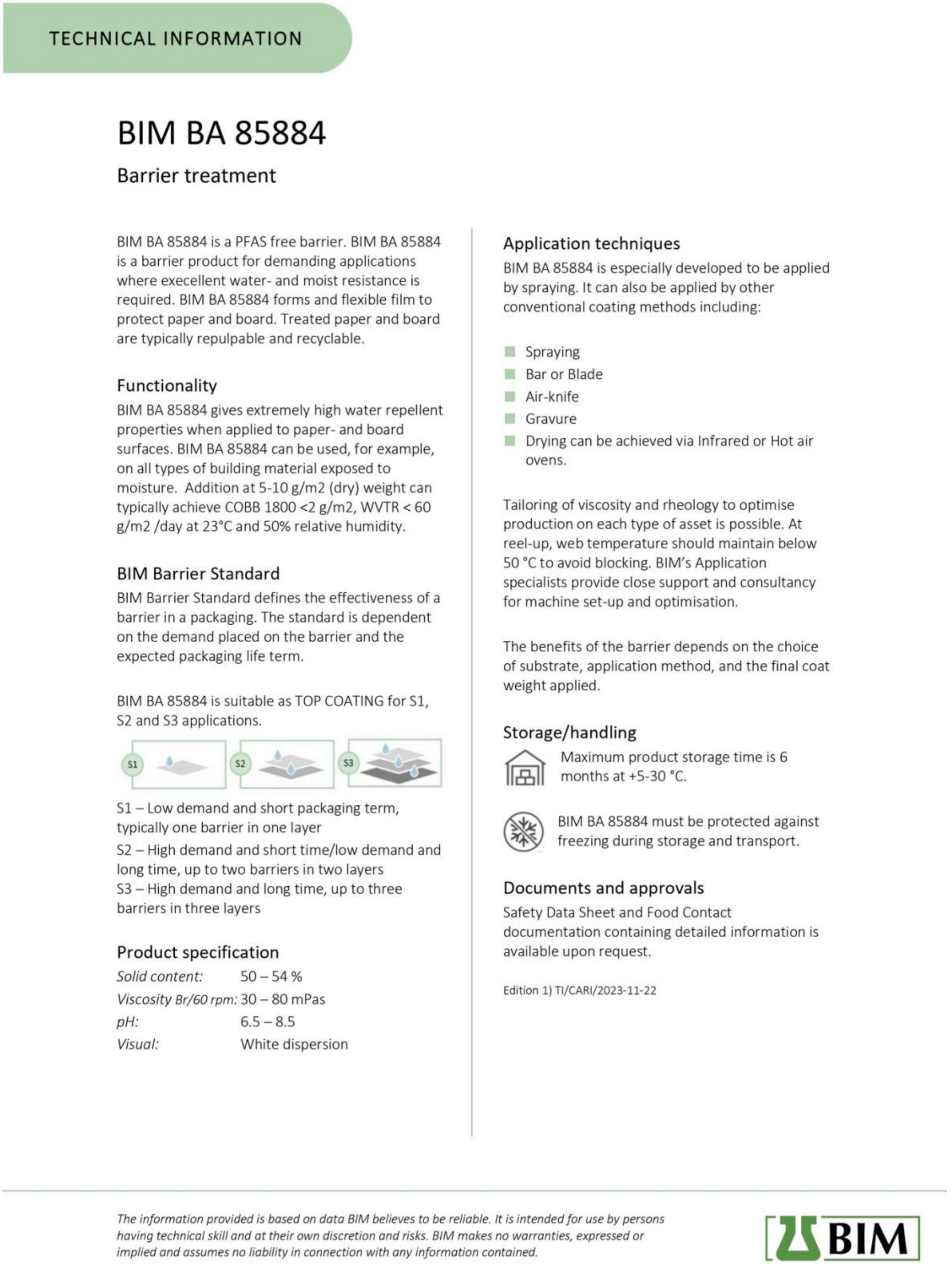

TECHNICAL INFORMATION

BIM BA 85884

Barrier treatment

BIM BA 85884 is a PFAS free barrier. BIM BA 85884 is a barrier product for demanding applications where execellent water- and moist resistance is required. BIM BA 85884 forms and flexible film to protect paper and board. Treated paper and board are typically repulpable and recyclable.

Functionality

BIM BA 85884 gives extremely high water repellent properties when applied to paper- and board surfaces. BIM BA 85884 can be used, for example, on all types of building material exposed to moisture. Addition at 5-10 g/m2 (dry) weight can typically achieve COBB 1800 <2 g/m2, WVTR < 60 g/m2 /day at 23°C and 50% relative humidity.

BIM Barrier Standard

BIM Barrier Standard defines the effectiveness of a barrier in a packaging. The standard is dependent on the demand placed on the barrier and the expected packaging life term.

BIM BA 85884 is suitable as TOP COATING for S1, S2 and S3 applications.

S1 – Low demand and short packaging term, typically one barrier in one layer

S2 – High demand and short time/low demand and long time, up to two barriers in two layers

S3 – High demand and long time, up to three barriers in three layers

Product specification

Solid content:	50 – 54 %
Viscosity Br/60 rpm:	30 – 80 mPas
pH:	6.5 – 8.5
Visual:	White dispersion

Application techniques

BIM BA 85884 is especially developed to be applied by spraying. It can also be applied by other conventional coating methods including:

- Spraying
- Bar or Blade
- Air-knife
- Gravure
- Drying can be achieved via Infrared or Hot air ovens.

Tailoring of viscosity and rheology to optimise production on each type of asset is possible. At reel-up, web temperature should maintain below 50 °C to avoid blocking. BIM's Application specialists provide close support and consultancy for machine set-up and optimisation.

The benefits of the barrier depends on the choice of substrate, application method, and the final coat weight applied.

Storage/handling

Maximum product storage time is 6 months at +5-30 °C.

BIM BA 85884 must be protected against freezing during storage and transport.

Documents and approvals

Safety Data Sheet and Food Contact documentation containing detailed information is available upon request.

Edition 1) TI/CARI/2023-11-22

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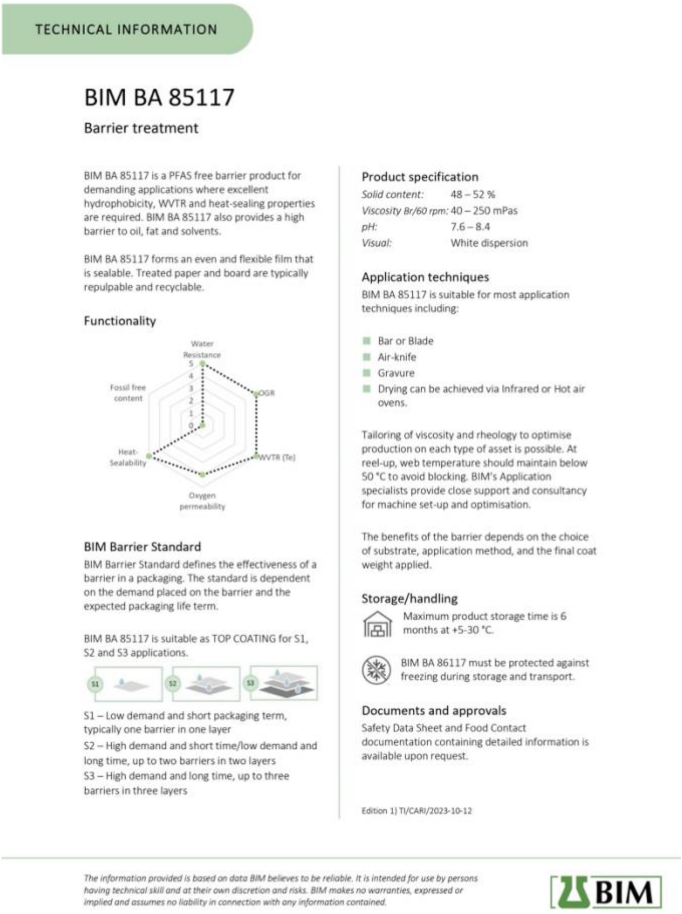


TECHNICAL INFORMATION

BIM BA 85117

Barrier treatment

BIM BA 85117 is a PFAS free barrier product for demanding applications where excellent hydrophobicity, WVTR and heat-sealing properties are required. BIM BA 85117 also provides a high barrier to oil, fat and solvents.

BIM BA 85117 forms an even and flexible film that is sealable. Treated paper and board are typically repulpable and recyclable.

Functionality

BIM Barrier Standard

BIM Barrier Standard defines the effectiveness of a barrier in a packaging. The standard is dependent on the demand placed on the barrier and the expected packaging life term.

BIM BA 85117 is suitable as TOP COATING for S1, S2 and S3 applications.

S1 – Low demand and short packaging term, typically one barrier in one layer
S2 – High demand and short time/low demand and long time, up to two barriers in two layers
S3 – High demand and long time, up to three barriers in three layers

Product specification

Solid content:	48 – 52 %
Viscosity Br/60 rpm:	40 – 250 mPas
pH:	7.6 – 8.4
Visual:	White dispersion

Application techniques

BIM BA 85117 is suitable for most application techniques including:

- Bar or Blade
- Air-knife
- Gravure
- Drying can be achieved via Infrared or Hot air ovens.

Tailoring of viscosity and rheology to optimise production on each type of asset is possible. At reel-up, web temperature should maintain below 50 °C to avoid blocking. BIM's Application specialists provide close support and consultancy for machine set-up and optimisation.

The benefits of the barrier depends on the choice of substrate, application method, and the final coat weight applied.

Storage/handling

Maximum product storage time is 6 months at +5-30 °C.

BIM BA 86117 must be protected against freezing during storage and transport.

Documents and approvals

Safety Data Sheet and Food Contact documentation containing detailed information is available upon request.

Edition 1) TI/CARI/2023-10-12

FennoSize™ KD-MB 574MP

Sizing agent for paper and board with RSPO accreditation

FennoSize KD-MB 574MP is an alkylketendimer (AKD) based wax dispersion for hydrophobation of paper and board. The product uses RSPO Mass Balance certified AKD wax .

The product is developed to give efficient, fast and evenly spread sizing in high-quality paper and board in the neutral-to-slightly alkaline pH range.

FennoSize KD-MB 574MP is especially well suited for sizing of liquid packaging board.

Application

To ensure uniform sizing, we recommend that FennoSize KD-MB 574MP is added to a point with good mixing. The best performance is achieved by optimizing the dosing individually for each machine.

Typical Product Properties*

Dry Content	21.7 – 22.7 %
Viscosity	< 100 mPa.s (25°C)
pH	3.2 – 4.2
Ionicity	cationic
Density	ca 1000 kg/m³
Appearance	Off-white liquid

***This information only indicates a typical property of the product and must not be taken as a specification**

Product Safety and Regulatory Compliance

Please refer to the Safety Data Sheet for material usage and handling.

Approvals and dosage limitations for paper and board for food contact can be found in Product Compliance Sheet.

Delivery

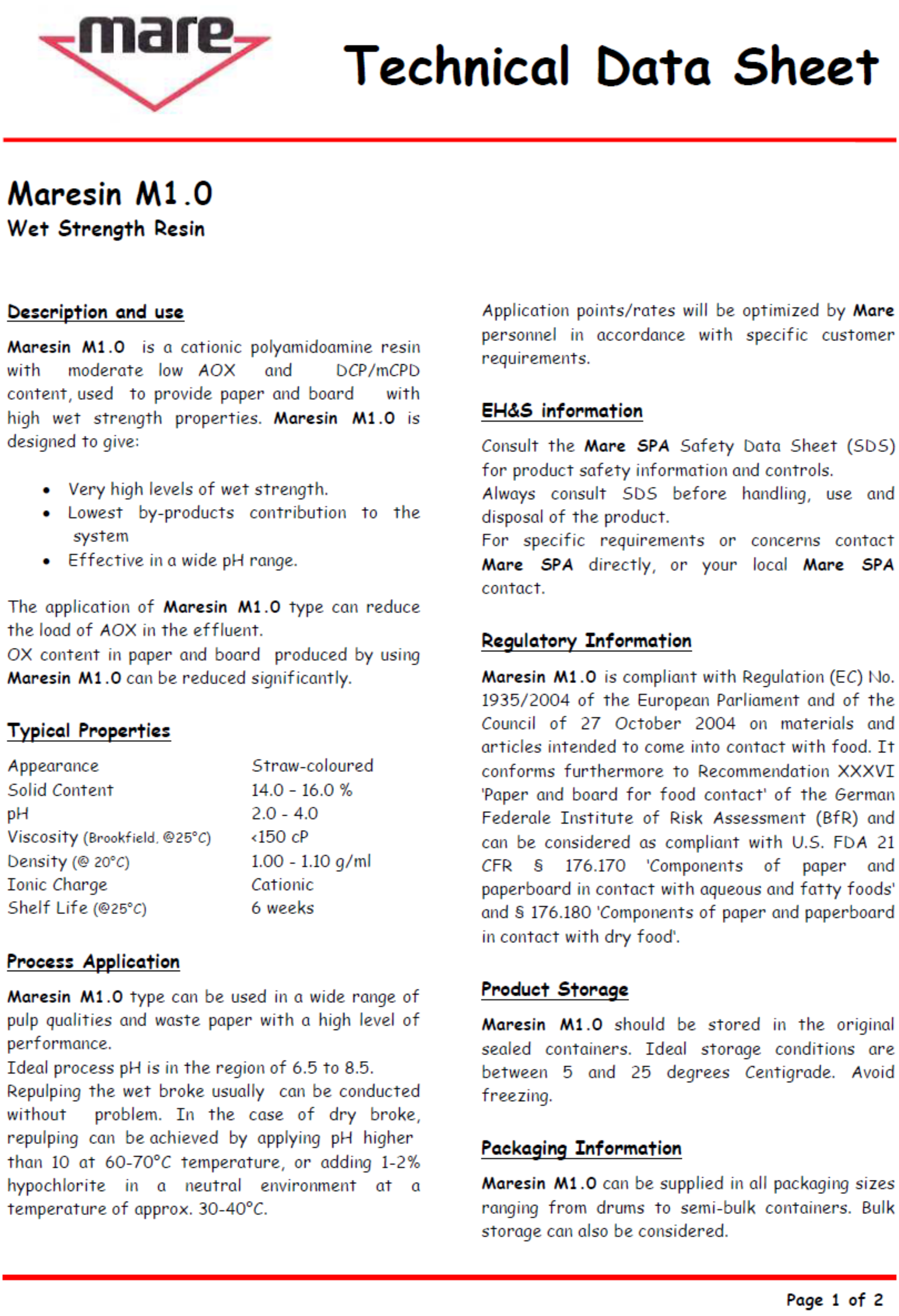
FennoSize KD-MB 574MP is delivered by tank lorry or in 1 ton containers.

Storage

The stability of the dispersion decreases with increasing storage time and temperature. Therefore storage in a cool place is recommended, bearing in mind that the product must not be allowed to freeze. Freezing, as well as heavy mechanical stress, can destroy the dispersion.

The dispersion can be stored for several weeks at room temperature.

Storage temperatures above +30°C are not recommended.



Technical Data Sheet

Maresin M1.0

Wet Strength Resin

Description and use

Maresin M1.0 is a cationic polyamidoamine resin with moderate low AOX and DCP/mCPD content, used to provide paper and board with high wet strength properties. **Maresin M1.0** is designed to give:

- Very high levels of wet strength.
- Lowest by-products contribution to the system
- Effective in a wide pH range.

The application of **Maresin M1.0** type can reduce the load of AOX in the effluent.
OX content in paper and board produced by using **Maresin M1.0** can be reduced significantly.

Typical Properties

Appearance	Straw-coloured
Solid Content	14.0 - 16.0 %
pH	2.0 - 4.0
Viscosity (Brookfield. @25°C)	<150 cP
Density (@ 20°C)	1.00 - 1.10 g/ml
Ionic Charge	Cationic
Shelf Life (@25°C)	6 weeks

Process Application

Maresin M1.0 type can be used in a wide range of pulp qualities and waste paper with a high level of performance.
Ideal process pH is in the region of 6.5 to 8.5.
Repulping the wet broke usually can be conducted without problem. In the case of dry broke, repulping can be achieved by applying pH higher than 10 at 60-70°C temperature, or adding 1-2% hypochlorite in a neutral environment at a temperature of approx. 30-40°C.

Application points/rates will be optimized by **Mare** personnel in accordance with specific customer requirements.

EH&S information

Consult the **Mare SPA** Safety Data Sheet (SDS) for product safety information and controls.
Always consult SDS before handling, use and disposal of the product.
For specific requirements or concerns contact **Mare SPA** directly, or your local **Mare SPA** contact.

Regulatory Information

Maresin M1.0 is compliant with Regulation (EC) No. 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food. It conforms furthermore to Recommendation XXXVI 'Paper and board for food contact' of the German Federale Institute of Risk Assessment (BfR) and can be considered as compliant with U.S. FDA 21 CFR § 176.170 'Components of paper and paperboard in contact with aqueous and fatty foods' and § 176.180 'Components of paper and paperboard in contact with dry food'.

Product Storage

Maresin M1.0 should be stored in the original sealed containers. Ideal storage conditions are between 5 and 25 degrees Centigrade. Avoid freezing.

Packaging Information

Maresin M1.0 can be supplied in all packaging sizes ranging from drums to semi-bulk containers. Bulk storage can also be considered.

Page 1 of 2

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