PFAS and Molded fiber: Challenges and Opportunities

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Table of Contents

1. Executive Summary

Per- and polyfluoroalkyl substances (PFAS) are widely added to food packaging materials, especially molded fiber, in order to easily and cheaply achieve water and oil barrier properties. However, PFAS are associated with high environmental and human health hazards, and are subject to a FDA phase out. Safer alternatives are urgently needed for molded fiber, and thorough research into their potential hazards are necessary to avoid introduction of a regrettable substitute. Strategy 1 alternatives, sourced externally from the paper industry, include rhamnolipids and pectin. Strategy 2 alternatives, sourced from within the paper industry, are cellulose nanocrystals and lignin. We highly valued selected alternatives' ability to be incorporated into the molded fiber production process and level of compostability. While all alternatives show potential in their technical capability and health assessments, lignin was found to be both the most versatile, as well as the current most viable alternative material.

Acknowledgments

2. Background

2.1 Problem Landscape

Food packaging manufacturers are currently faced with a multitude of challenges: modern, environmentally conscious consumers demand less single-use plastic, and current compostable bioplastics are not widely accepted by composting facilities. Paper-based food packaging offers a solution: it has the potential to be more sustainably produced and it degrades faster than its plastic counterparts. Additionally, it has a natural look and feel that appeals to consumers. However, fiber materials require additives and further processing in order to achieve barrier properties required for food packaging. PFAS dominate the paper food packaging industry as a fast, cheap, and versatile additive to instantly impart water and oil repellency to fiber food contact materials (FCMs). However, this convenience comes at a high cost to human and environmental safety (1).

2.2 PFAS Health Concerns

The health hazards of PFAS are well known for longer-chain PFAS compounds perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). These compounds were phased out in the U.S. between 2000 and 2015 (2), but continue to persist in soil, water, air and biota, including humans (3). Intentionally adding PFAS into food packaging leads to the contamination of food through migration into food, and the environment at the product's end-of-life. As a result, PFAS in the food industry market invariably leads to human exposures, and the ubiquity of these hazardous chemicals are impermissible. As a class, PFAS toxicants are associated with a broad range of adverse health outcomes, kidney and testicular cancer, elevated cholesterol, liver disease, decreased fertility, thyroid problems, hormone dysregulations, immunosuppression, and adverse developmental effects (4). Additionally, PFAS food packaging additives contaminate the cycle of food production through multiple, interrelated pathways (Figure 2.1): from additives in direct contact with food, indirect contamination of drinking water sources after food packaging disposal, and through contaminated soil, sediment, or compost used to grow new crops.

Fluorinated hydrocarbons in food packaging have faced increasingly stringent regulations in the last two decades, beginning with a ban on long-chain PFAS, which led food packaging producers to seek side-chain PFAS as a convenient substitute. Regulators and producers

assumed that reducing the chain length of carbon-fluorine tails would confer the nonstick properties they desired while minimizing toxicity hazards (4). However, toxicological evidence suggested otherwise. The shift to side-chain PFAS primarily involved polymer manufacture with 6:2 fluorotelomer alcohol as the starting material for polymeric formulations used in existing chemicals. Side-chain PFAS is associated with high degrees of persistence, volatilization, and degradation to a perfluoroalkyl acid perfluorohexanoic acid (PFHxA), which can partly explain the environmental ubiquity of PFAS compounds in the remote regions of the globe (5). PFHxA is an established toxicant (6), and the direct and indirect release of side-chain PFAS in the manufacture, use, and end-of-life of food packaging materials constitutes a national and global health concern.

Figure 2.1. The effects of PFAS release are cyclical in food packaging. Image derived from DTSC (5).

In 2020, the U.S. Food and Drug Administration (FDA) announced a voluntary phase-out of shorter-chain PFAS that includes 6:2 fluorotelomer alcohol (6:2 FTOH). The food packaging industry urgently needs an alternative to PFAS with lower health hazards, acceptable technical performance, and compatibility with current fiber manufacturing processes.

2.3 Background References

(1) Wang, Z., Dewitt, J. C., Higgins, C. P., & Cousins, I. T. (2017). A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? Environmental Science and Technology, 51(5), 2508–2518. https://doi.org/10.1021/acs.est.6b04806

(2) Schaider, L. A., Balan, S. A., Blum, A., Andrews, D. Q., Strynar, M. J., Dickinson, M. E., Lunderberg, D. M., Lang, J. R., & Peaslee, G. F. (2017). Fluorinated Compounds in U.S. Fast Food Packaging. Environmental Science & Technology Letters, 4(3), 105–111. https://doi.org/10.1021/acs.estlett.6b00435

(3) Crone, B. C., Speth, T. F., Wahman, D. G., Smith, S. J., Abulikemu, G., Kleiner, E. J., & Pressman, J. G. (2019b). Occurrence of Per- and Polyfluoroalkyl Substances (PFAS) in Source Water and Their Treatment in Drinking Water. Critical Reviews in Environmental Science and Technology, 49(24), 2359–2396. https://doi.org/10.1080/10643389.2019.1614848

(4) Kwiatkowski, C. F., Andrews, D. Q., Birnbaum, L. S., Bruton, T. A., DeWitt, J. C., Knappe, D. R. U., Maffini, M. V., Miller, M. F., Pelch, K. E., Reade, A., Soehl, A., Trier, X., Venier, M., Wagner, C. C., Wang, Z., & Blum, A. (2020). Scientific Basis for Managing PFAS as a Chemical Class. Environmental Science & Technology Letters, 7(8), 532–543. https://doi.org/10.1021/acs.estlett.0c00255

(5) Department of Toxic Substance Control. (2020). Product-Chemical Profile for Food Packaging Containing Perfluoroalkyl or Polyfluoroalkyl Substances. https://dtsc.ca.gov/scp/food-packaging-containing-pfass/

(6) Agency for Toxic Substances and Disease Registry (ATSDR). 2018. Toxicological profile for Perfluoroalkyls. (Draft for Public Comment). Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

3. Approach

3.1 Project Scope

3.1.1 Paper-based Packaging
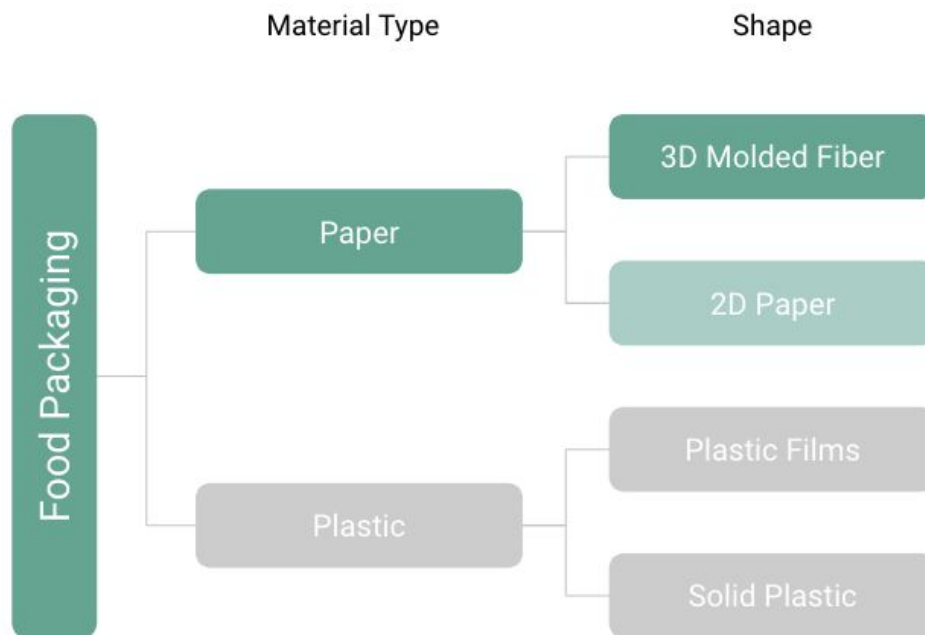
Figure 3.1. *Food packaging is divided into several broad categories. Our project focuses on 3D molded fiber packaging.*

Food packaging products include a wide variety of materials, processes, and shapes made for foods with diverse barrier needs. We first narrowed our scope to paper packaging materials because plastic materials generally have sufficient barrier properties without the use of PFAS. Within the realm of paper packaging, existing reports on the transition away from fluorochemicals tend to focus on 2D paper and paperboard packaging, while upholding biopolymers (e.g., polylactic acid [PLA]) as the most effective choice for mitigating PFAS use. However, many biopolymers are confronted with challenges surrounding their degradability in compost, and use as a composting feedstock (1). 3D molded fiber materials have been consistently shown to contain high levels of PFAS (2), but have potential in their degradability and overall sustainability, making molded fiber an ideal focus for this report.

3.1.2 Molded Fiber
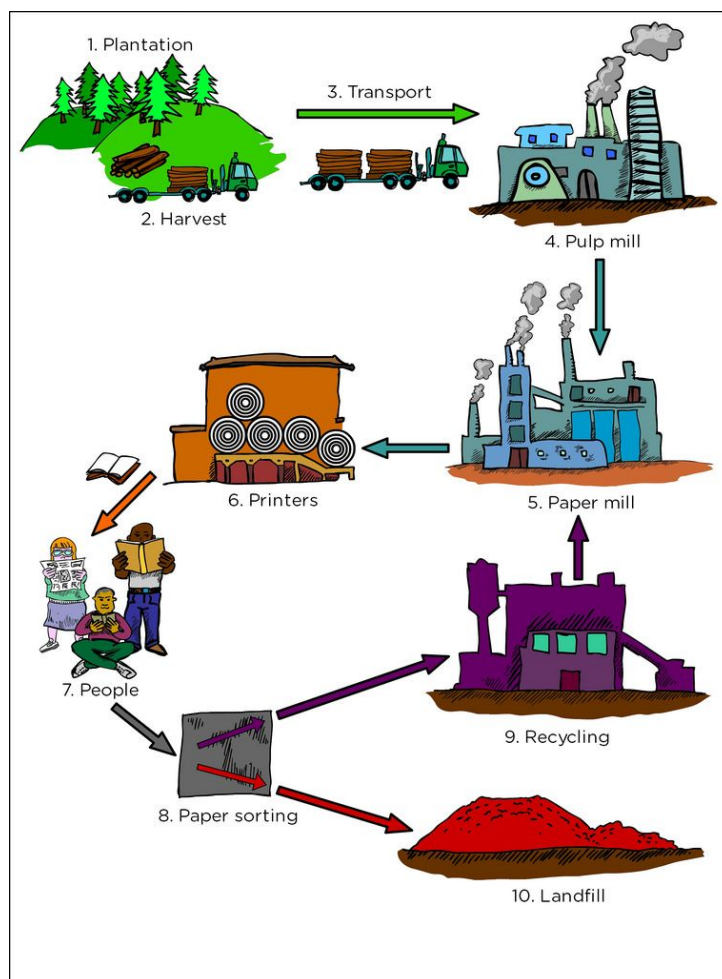
Figure 3.2. Schematic of paper production and life-cycle (6).

Molded fiber as a whole has many favorable qualities: it has a seamless shape that prevents leaks and the ability to be customized based on the needs of the client. It can also be made from a recycled feedstock, and the pulp fibers degrade readily in compost. However, the use of PFAS in molded fiber negates many of these positive attributes. As mentioned earlier (Section 2.2), PFAS containing materials cannot be safely composted due to potential uptake into plants grown from the contaminated compost. PFAS-containing molded fiber can also leach fluorinated byproducts into the environment if landfilled, or can accumulate in the paper system if recycled. Replacing PFAS with a benign and degradable alternative would greatly improve the end-of-life, even introducing the possibility of closing the loop for molded fiber production if compost produced from molded fiber is used to grow new paper trees.
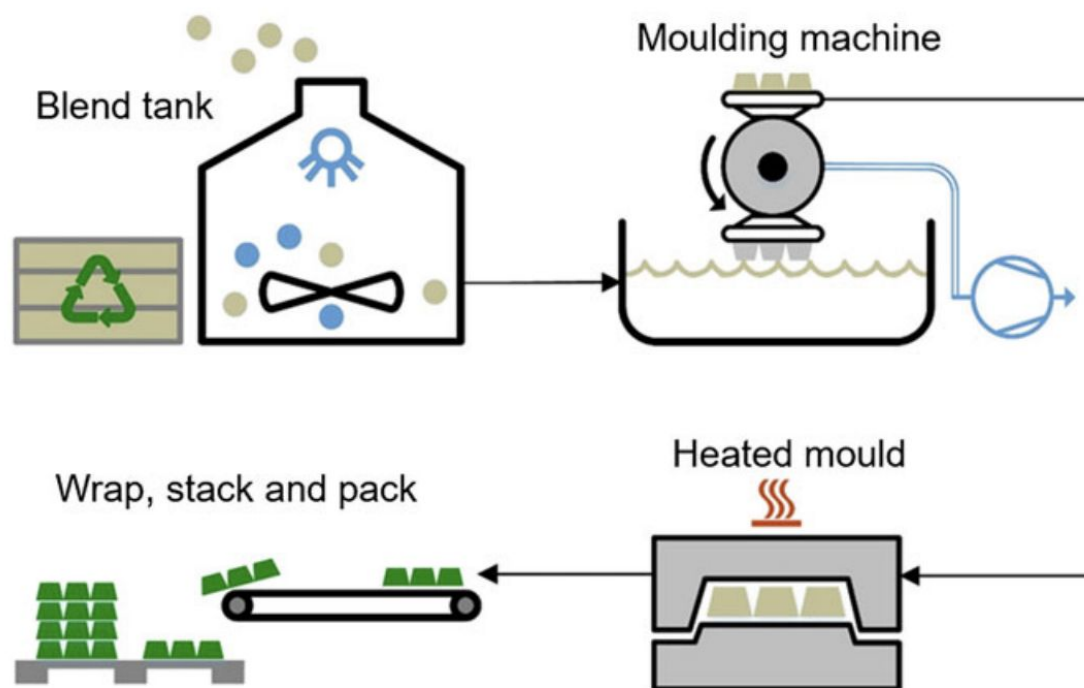
Figure 3.3. *Schematic of the molded fiber production process (3).*

In a recent study conducted by Safer Chemicals Healthy Families, 100% of molded fiber products surveyed contained PFAS, and those products "showed the highest levels of fluorine out of all items tested in [the] study," (2). Pulp fiber materials were also among the food contact materials containing the highest levels of fluorotelomer alcohols (FTOHs) (4). These factors are likely due to the specific manufacturing constraints surrounding molded fiber. Paper-type products are generally produced in a flat sheet, then folded into a three dimensional shape, such as a cup, bag, or bowl. They are therefore able to be treated by plastic lamination or spray coating while they are flat (5). These factors make PFAS-free solutions more widely available for 2D paper products. In contrast, molded fiber undergoes the production process outlined in Figure 3.3, starting as bulk pulp fibers suspended in water in a blend tank, which are then molded and dried in an oven, and packed for shipping. Molded fiber food packaging takes on a three dimensional, organic shape that is difficult to coat evenly once dried, rendering most dry-end processes prohibitively costly. Solutions applied in the form of films and sprays are difficult to adapt into a 3D molded fiber manufacturing process. Production of 3D molded fiber materials often rely exclusively on the addition of PFAS into the blend tank(known as "wet-end" treatment). PFAS alternatives at the wet end of the manufacturing process are far less developed, and very few are commercially available. The 3D molded fiber industry is ripe for both innovation and intervention: new approaches are needed to replace perfluorinated

compounds, and this is an important opportunity to prevent regrettable substitutes through careful hazard assessment.

In summary, the foodservice molded fiber industry emerged as a need in packaging for more sustainable options, so our goal is to identify chemical solutions that would support the promise of molded fiber. As a result, we aim to identify safer and degradable chemicals that would be added on the wet-end of the molded fiber forming process to achieve water and oil repellency.

3.2 Technical Criteria

3.2.1 Defining Properties Evaluated

Table 3.1: Definitions of the properties included in the technical assessment. Note that dispersibility and degradability definitions are not industry standards, but rather are based on the data available.

	Relevant Property	Definition
Barrier Properties	grease resistance	Measured in kit value, a relative score of paper to absorb a series of oil-containing reagents
	water contact angle	The angle between the surface of the liquid and the outline of the contact surface
	water vapor permeability	The mass of water vapor at a certain pressure that permeates a material (with a certain thickness and surface area) over time
Surface Properties	porosity (oxygen permeability)	The volume of oxygen that permeates a material's surface area over time
Thermal Properties	thermal resistance	The temperature at which there is large drop in a material's weight relative to its original weight
	temperature dependence	The temperature required for synthesis or formation of a material
Chemical Properties	dispersability	Yes/No on whether the material can disperse in cellulose slurry
Mechanical Properties	tensile strength	The maximum load a material can support without fracture divided by its original cross-sectional area
End-of-Life Properties	degradability	The amount of time for at least 70% of a material to break down in soil at ambient temperature containing no targeted microbes

Table 3.1 defines the technical properties used to describe the performance of our alternatives. To determine these properties, we consider the needs of consumers, manufacturers, and composters (both facilities and at-home). Consumers are most concerned with usability, which is strongly tied to food leakage and preservation. This is best represented by barrier and surface properties. Kit value measures the degree of repellence or anti-wicking of paper and boards (7) (Figure 3.4 a). This measurement was developed specifically for fluorine containing papers, and ranges from 1 to 12.
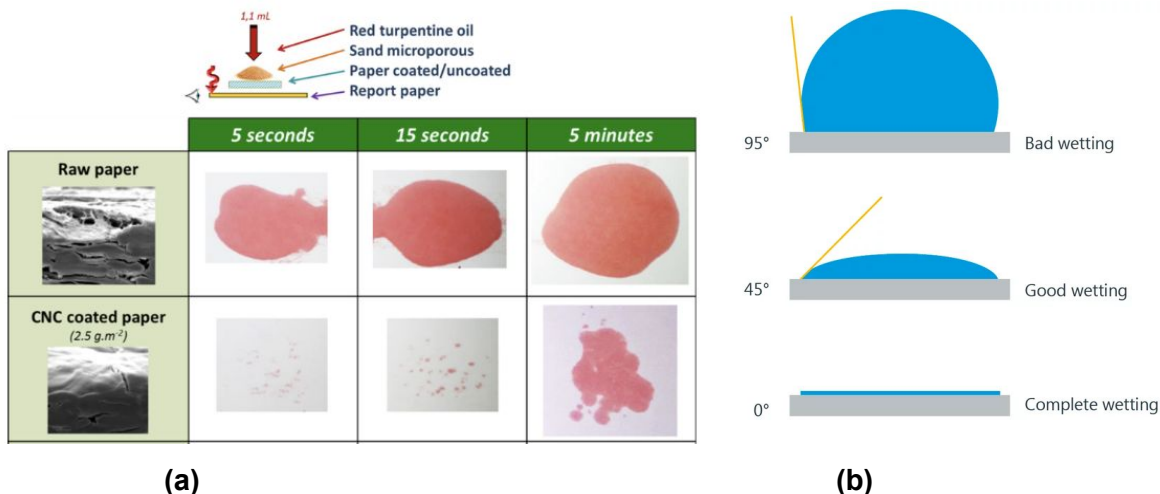
Figure 3.4. *(a) An example kit test comparing raw paper and cellulose nanocrystal (CNC) coated paper (14). (b) The association between contact angle and wettability (8). Materials with bad wetting are hydrophobic.*

Water contact angle indicates how well a droplet deposited on a solid substrate spreads out. Figure 3.4 displays the water contact angle test. If a droplet angle is above 90 degrees, the material is considered hydrophobic; below 90 degrees, the material is considered hydrophilic (8). Water vapor permeability (WVP) refers to water resistance in relation to humidity of the environment. A low WVP indicates better resistance and means the end product does not need an extremely dry environment for storage. The one surface property, porosity, indicates how close and strongly the fibers are bound together. Here it is measured in oxygen permeability, where a lower value indicates lower porosity and therefore a more densely packed material. A low oxygen permeability could also provide a slower rate of food decay when the product is in use.

In addition to barrier properties, manufacturers prioritize the thermal, chemical, and mechanical properties. Table 3.1 defines the difference between thermal resistance and temperature dependence. Thermal resistance provides information on the final product's ability to withstand high temperatures. The data provided indicate the temperature the material breaks down, but it is important to note that the temperature it can withstand during use is lower. The temperature dependence predicts whether the alternative can undergo any necessary reactions while withstanding temperatures up to 100˚C. This is because the alternative is added at the wet end, where the cellulose slurry, on average, is mixed at 100˚C.

The chemical property included is dispersibility, which is also due to the wet-end limitation. In order to fully be incorporated into molded fiber, the alternative must be able to evenly disperse

in cellulose slurry. This may require a dispersing agent. Mechanical properties are important to consider for transport, storage, and rigidity during use. A higher tensile strength means the product can be compact during transport and carry a larger food load.

Finally, our end-of-life property is degradability, which gauges compostability. These data were difficult to standardize across the alternatives, but degradation up to at least 70% was found for them all. Many materials are normally composted at high temperatures or with targeted microorganisms, but the data included were at ambient soil temperatures and no targeted microbes. This is intended not only to standardize the data, but also to find alternatives that have the capacity to be composted in more basic facilities or even in consumer's homes.

3.2.2 Approach to Technical Assessment

Baseline for Comparison

For the technical assessments, we have chosen polylactic acid (PLA) as our baseline for comparison rather than PFAS-based molded fiber products. PLA is a common compostable bioplastic that is used to coat paper and molded fiber products. We are not considering it for our project because it is only compostable in industrial composting facilities that are able to treat their compost at high temperatures (10). As mentioned in our scope, our solutions are limited to those that are highly degradable.

PLA is used as our baseline because it is much more realistic for our alternatives to strive towards. PFAS-based products, on the other hand, overperform by making molded fiber highly hydrophobic and oleophobic. PFOA on cellulose, for example, has a water contact angle of 160°, which is almost double of the 75°- 85° range listed for PLA (9). For the purposes of food packaging, which spend a short amount of time in use, this level of barrier resistance is not necessary.

Table 3.2: Technical assessment of all discussed alternatives. All sources from this table can be found in Appendix B.

	Application of Data Source	Barrier Properties			Surface Properties	Thermal Properties		Chemical Properties	Mechanical Properties	End-of-Life Properties
Relevant Property	film or within molded fiber matrix	grease resistance	water contact angle	water vapor permeability (WVP)	porosity (oxygen permeability)	thermal resistance (temp at major % weight loss)	temperature dependence (manufacture temp 100˚C)	dispersability	tensile strength	degradability (at least 70% in soil)
Units	--	kit value	degrees	g.mm/m2.kPa.day	cm3/m2/24hr	˚C	˚C	--	MPa	days
PLA	Films	12+ (1)	75 - 85 (2)	0.161-0.237 (1)	38-42 (3)	335˚C (4)	52.5-150˚C (2)	DG	27-35 (5)	> 150 (6)
Rhamnolipid (Proxy: Palmitic Acid & minerals)	Fiber Matrix and Films	DG	120-140 (7)	DG	DG	240˚C (8)	90-120˚C (7)	Yes (7)	DG	8-12 (9)
Pectin	Films	DG	47-87 (10)	2.26 - 2.83 (11)	DG	174-180°C (12)	5 - 35˚C (13)	Yes (14)	7.10 ± 0.22 (11)	4 (15)
Cellulose Nanocrystals	Films	11 (16)	65 (16)	9 (17)	DG	250˚C (18)	30-60˚C (18)	Yes (18)	15.6 (18)	2 (19)
Lignin	Fiber Matrix and Films	12 (20)	89 (21)	5.3 ± 0.1 (20)	26.6 ± 0.5 (20)	260-290˚C (22)	85˚C (22)	Yes, with agent (22)	20.3 (21)	23 (23)

Rankings are relative *to each other:*   Idea   Moderate   Non-ideal   DG = data gap

Table 3.2 lists all the technical data collected to compare our alternatives to PLA. Each row contains data on a single material from several references. It is important to note that each reference uses the material at different conditions. Some have been applied on a very thick layer of cellulose, some have been applied on cellulose with specific additives, and some have used the material for an entirely different application. To the best of our ability, we have used data that is representative of solely the material, or the material on cellulose (important for barrier and surface properties). The first column also indicates whether the sources applied the alternative as a film, or integrated the alternative within a fiber matrix. Note that some information on rhamnolipids, for which data was scarce, comes from a proxy material whose data are input in red. The ranking of properties for each alternative are indicated by the color of the box. Green is ideal, yellow is moderate, red is non-ideal, and in gray are data gaps. These rankings are relative to each other, which means that a green box does not necessarily indicate the best option, but indicates the most ideal amongst the listed alternatives.

3.3 Human and environmental health criteria

We assessed hazards of candidate alternatives with a method adapted from GreenScreen for Safer Chemicals (11). We assessed 15 endpoints in human health, between Group I and II endpoints, and 2 endpoints in environmental fate and toxicity (Table 3.3). The general process in collecting hazard information started with authoritative lists from Pharos, then data compiled by the European Chemical Agency (ECHA) or literature review, followed by predictive modeling

using EPA CompTox and ToxTree. Any remaining data not found was collected from Material Safety Data Sheets, administrative reports, and expert judgment based on the physical-chemical profiles of existing and alternative chemicals.

Table 3.3 GreenScreen hazard endpoint definitions. Adapted from Clean Production Action (2018).

Endpoint	Abbr.	Definition
Group I human health endpoints		
Carcinogenicity	C	Capable of increasing the incidence of malignant neoplasms, reducing their latency, or increasing their severity or multiplicity.
Mutagenicity	M	Agents which alter that structure, information content, or segregation of DNA, including those which cause DNA damage by interfering with normal replication.
Reproductive toxicity	R	The occurrence of biologically adverse effects on the reproductive systems of females or males that may result from exposure to environment agents.
Developmental toxicity	D	Adverse effects in the developing organism that may result from exposure prior to conception (either parent), during prenatal development, or postnatally to the time of sexual maturation.
Endocrine toxicity	E	An exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes health effects in an intact organism, or its progeny, or (sub)populations
Group II human health endpoints		
Acute mammalian toxicity	AT	Adverse effects occurring from oral or dermal administration of a single dose of substance, or multiple doses given within 24 hours, or an inhalation exposure of 4 hours
Systemic toxicity & organ effects (incl. immunotoxicity)	ST	Includes all significant non-lethal effects in a single organ that can impair function, both reversible and irreversible, immediate and/or delayed, not otherwise covered by any other endpoint; or generalized changes of a less severe nature involving several organs. *Note:* ST resulting from repeated exposures were prioritized in this hazard assessment.
Neurotoxicity	N	An adverse change in the structure or function of the central and/or peripheral nervous system following exposure to a chemical, or a physical or biological agent. *Note*: only acute neurotoxicity was considered during assessment here.
Skin sensitization	SnS*	A skin sensitizer is a substance that will lead to an allergic response after skin contact

Respiratory sensitization	SnR*	Hypersensitivity of the airways following inhalation of a substance or mixture
Skin irritation	IrS	The production of reversible damage to the skin following the application of a test substance or mixture for up to 4 hours
Eye irritation	IrE	The production of changes in the eye following the application of a test substance to the anterior surface of the eye, which are fully reversible within 21 days of application
Environmental fate and toxicity		
Acute and chronic aquatic toxicity	AA/CA	The intrinsic property of a substance to be injurious to an organism in a short-term, aquatic exposure to that substance, or in relation to the life-cycle of the organism
Persistence	P	The length of time the chemical can exist in the environment before being destroyed (i.e., transformed) by natural processes.

We assessed the confidence level of hazard scores as high or low after evaluating the reliability of data sources. Briefly, a score received high confidence if information came from an authoritative list, or expert reviewed assays. A score received low confidence if measured data were conflicting or incomplete, or came from *in silico* analyses without lab assays. All scores from MSDS, administrative reports, or expert judgment received a low confidence rating. We adopted the method described by Faludi et al. (2016) to translate GreenScreen Hazard scores (Very High, High, Moderate, Low, very Low) to category scores from 1 to 4 (12). For simplicity in interpretation, we color-coded 1 as very high hazard, 2 as high hazard, 3 as moderate hazard, and 4 as low hazard, where the difference between integer scores represents an order of magnitude difference in relative hazard.

We selected two fluorinated chemicals and one non-fluorinated methacrylate to represent the existing polymeric additives:

- Tridecafluorohexylethyl methacrylate (6:2 FTMAC) [CAS No.: 2144-53-8]
- 2-(N,N-Diethylamino)ethyl methacrylate [CAS No.: 105-16-8]
- 6:2 FTOH [CAS No.: 678-39-7]

Table 3.4. Summary hazard table. More details on the hazard assessment included in the respective sections and Supplementary Information.

Legend. 1: Very High Hazard, 2: High Hazard, 3: Moderate Hazard, 4: Low Hazard, UNK: Data gap. **Bold:** High confidence, *italicized*: low confidence.

	Chemicals	Group I endpoints					Group II and II* endpoints							Ecotox and fate	
		C	M	R	D	E	AT	ST*	N	SnS*	SnR*	IrS	IrE	AA/CA	P*
Existing chemicals	6:2 Fluorotelomer methacrylate	2	3	2	2	1	3	2	UNK	3	3	2	2	1	1
	6:2 Fluorotelomer alcohol	2	3	3	2	1	3	2	UNK	3	3	2	2	1	**1**
	2-(N,N-Diethylamino)ethyl methacrylate	3	3	**1**	2	UNK	2	UNK	UNK	1	UNK	**1**	**1**	1	4
Alternative 1	Rhamnolipid	3	4	UNK	UNK	UNK	4	UNK	UNK	3	UNK	UNK	**1**	4	4
Alternative 2	Pectin	3	3	3	3	UNK	4	4	UNK*	2	2	4	4	4	4
	Calcium carbonate	4	4	3	4	UNK	4	4	4	2	UNK	4	4	4	**1***
	Ethylene glycol	4	4	2	1	3	3	3	2	3	3	3	3	4	4
Alternative 3	Cellulose nanocrystals	3	3	3	3	UNK	4	3	UNK	3	2	4	3	3	4
	Sulfuric acid	3	4	3	3	UNK	1	**1**	UNK	3	1	**1**	**1**	2	1**
Alternative 4	Lignin														
	Xylan														
	Sulfuric acid	3	4	3	3	UNK	1	**1**	UNK	3	1	**1**	**1**	2	1**
	1-Allyl-3-methylimidazolium chloride	3	3	UNK	UNK	3	3	2	UNK	3	UNK	2	2	UNK	4

* Persistent scores reflect integrated information about the fate of degradation products.

** All inorganic compounds are persistent, and listed chemicals were categorized based on EC-CEPA Domestic Substances List (DSL).

More than half of the currently used side-chain PFAS packaging additives contain a 6:2 FTMAC copolymer, and seven of the 17 contain a copolymers acrylate. 6:2 FTOH is a fluorotelomer alcohol used in the synthesis of the fluorinated methacrylate and a degradation product of 6:2 FTMAC commonly detected among food and consumer packaging surveys (4). By virtue of their highly fluorinated chemical composition, both compounds are associated with very high levels of environmental toxicity and persistence. As mentioned above, the terminal degradation product of 6:2 FTMAC and 6:2 FTOH is PFHxA, which is a very persistent toxicant, widespread in the natural and built environment. The persistence of these fluorinated compounds not only imply widespread human exposure, but also represents a safety concern with respect to the known and potential hazards (13). As a result, we believe these compounds represent the inherent hazards present in the manufacturing, use, and end-of-life of molded fiber.

The fluorinated compounds and methacrylate have known and potential human health hazards that range from moderate to high acrossGroup I and II/II* endpoints (Table 3.4). These hazards represent the hazard baseline against which we compare each alternative strategy chemical in more detail in the sections below. In terms of health and environmental health performance, our minimum criteria for a safer substitute for side-chain PFAS are 1) logarithmically lower human health hazards for known Group I and Group II/II* endpoints compared to the three bad actors, and 2) minimal environmental toxicity and low levels of persistence

3.4 Approach References

(1) Vasile, C., Pamfil, D., Râpă, M., Darie-Niță, R. N., Mitelut, A. C., Popa, E. E., … Popa, M. E. (2018). Study of the soil burial degradation of some PLA/CS biocomposites. Composites Part B: Engineering, 142, 251–262. https://doi.org/https://doi.org/10.1016/j.compositesb.2018.01.026

(2) Packaged in Pollution: Are food chains using PFAS in packaging? (n.d.). Retrieved November 12, 2020, from https://saferchemicals.org/packaged-in-pollution/

(3) Didone, M., Saxena, P., Brilhuis-Meijer, E., Tosello, G., Bissacco, G., Mcaloone, T. C., Pigosso, D. C. A., & Howard, T. J. (2017). Moulded Pulp Manufacturing: Overview and Prospects for the Process Technology. In Packaging Technology and Science (Vol. 30, Issue 6, pp. 231–249). John Wiley and Sons Ltd. https://doi.org/10.1002/pts.2289

(4) Yuan, G., Peng, H., Huang, C., & Hu, J. (2015). Ubiquitous Occurrence of Fluorotelomer Alcohols in Eco-Friendly Paper-Made Food-Contact Materials and Their Implication for Human Exposure. https://doi.org/10.1021/acs.est.5b03806

(5) Khwaldia, K., Arab-Tehrany, E., & Desobry, S. (2010). Biopolymer Coatings on Paper Packaging Materials. In Comprehensive Reviews in Food Science and Food Safety (Vol. 9, Issue 1, pp. 82–91). John Wiley & Sons, Ltd. https://doi.org/10.1111/j.1541-4337.2009.00095.x

(6) Why We Should Recycle Paper [Image] Northdene Media Centre. https://northdenemediacentre.wordpress.com/2017/03/06/why-we-should-recycle-paper/

(7) Taylor, M. Paper Testing- Surface Properties: Grease Resistance. *Smithers.*

(8) Contact Angle. *Kruss Scientific.* https://www.kruss-scientific.com/en/know-how/glossary/contact-angle

(9) Khanjani, P., W. T. King, A., J. Partl, G., Johansson, L.-S., A. Kostiainen, M., & H. A. Ras, R. (2018). Superhydrophobic Paper from Nanostructured Fluorinated Cellulose Esters. ACS Applied Materials & Interfaces, 10(13), 11280–11288. https://doi.org/10.1021/acsami.7b19310

(10) Vasile, C., Pamfil, D., Râpă, M., Darie-Niță, R. N., Mitelut, A. C., Popa, E. E., … Popa, M. E. (2018). Study of the soil burial degradation of some PLA/CS biocomposites. Composites Part B: Engineering, 142, 251–262. https://doi.org/https://doi.org/10.1016/j.compositesb.2018.01.026

(11) Clean Production Action. (2018). The GreenScreen for Safer Chemicals.

(12) Faludi, J., Hoang, T., Gorman, P., & Mulvihill, M. (2016). Aiding alternatives assessment with an uncertainty-tolerant hazard scoring method. Journal of Environmental Management, 182, 111–125. https://doi.org/10.1016/j.jenvman.2016.07.028

(13) Department of Toxic Substance Control. (2020). Product-Chemical Profile for Food Packaging Containing Perfluoroalkyl or Polyfluoroalkyl Substances.

(14) Gicquel, E., Martin, C., Yanez, J., & Bras, J. (2017). Cellulose nanocrystals as new bio-based coating layer for improving fiber-based mechanical and barrier properties. *Journal of Materials Science*, *52*. https://doi.org/10.1007/s10853-016-0589-x

# 4. Sourced Externally from Paper Industry

4.1 Strategy 1: Introduction

Our first strategy is compounds or materials that need to be synthesised or extracted from an external source before entering the wet-end of molded fiber production system at the paper mill stage. PFAS, for example, would fit into this category. Such externally sourced solutions can be purchased from a trusted manufacturer. This traditional method of procuring additives does not incur the cost of adding new production steps or performing in-house material modification. The two alternatives, rhamnolipids and pectin, come from microbes and plants respectively, and both are *added* to the paper manufacturing process.

4.2 Rhamnolipids

4.2.1 Background

Inspiration for Rhamnolipids

Rhamnolipids are a type of biosurfactant—an amphiphilic biological compound produced extracellularly or as a part of the cell membrane by a variety of yeast, bacteria, and filamentous fungi from substances including sugars and oils. Rhamnolipids are produced from bacteria of the genus *Pseudomonas,* and their structure is composed of rhamnose and 3-hydroxy fatty acids, which can be potentially used for surface chemical works (1). The sugar groups provide attraction to water, while the fatty acids help the surfactants repel water. Rhamnolipids are currently used in eco-friendly alternatives to commercial cleaning products, pesticides, and antifungal agents (1). A unique facet of our strategy is that rhamnolipids could be used to form a barrier as opposed to breaking down a barrier. When PFAS was first added in molded fiber it was added at the wet-end in its surfactant form. This is what inspired the use of a biosurfactant to improve barrier properties in molded fiber. Although rhamnolipids are usually used to break the water-oil barrier, their structure shows promise in chemically binding to cellulose and acting as a hydrophobic barrier (Figure 4.1 a).
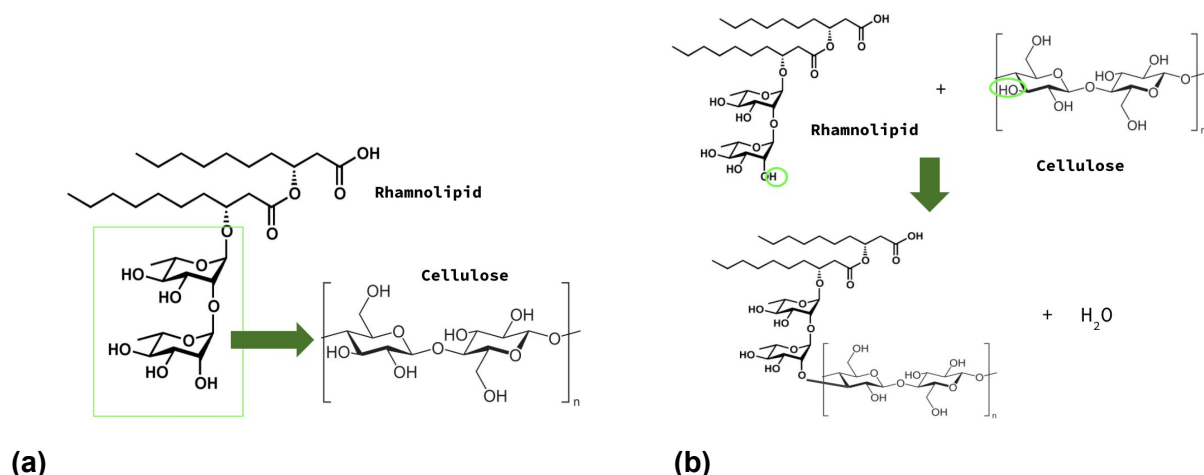
Figure 4.1 *(a) Rhamnolipid heads have a structure very similar to that of cellulose. (b) How rhamnolipids can attach via dehydration synthesis. This process requires an added agent such as a strong acid (e.g. sulfuric acid) or alumina.*

Method of Incorporation

Rhamnolipids are produced at scale by farmed microbes, typically *pseudomonas aeruginosa*. These microbes have been shown to accept a wide variety of substrates (feedstocks), from sugars to vegetable oils, in order to produce rhamnolipids of tunable and predictable tail lengths (3).

Cellulose and the rhamnolipids could bind together by using their hydroxyl groups as agents for dehydration synthesis,where a water molecule is lost when two molecules bind together. A schematic of this process is shown in Figure 4.1 b. On the hydrophobic side of the rhamnolipid is a carboxylic acid, which can be used to bind together other hydrophobic tails. This potentially forms a hydrophobic polymeric structure within the molded fiber structure. It could also serve as a binding point for another additive, possibly one that provides grease resistance.
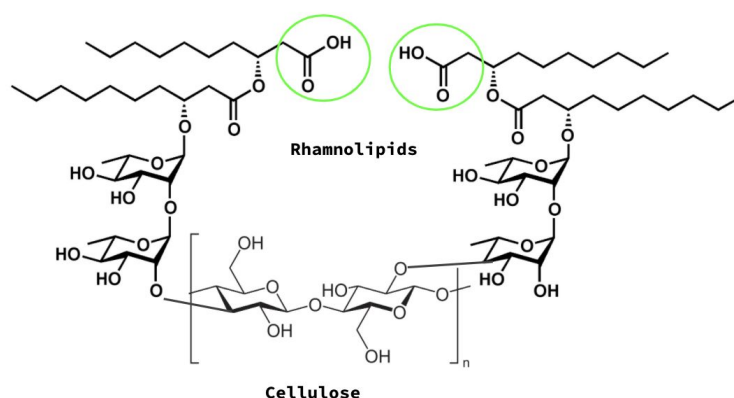
Figure 4.2. *Once the rhamnolipids' heads are bound to cellulose particles, their tails could bind together to give a hydrophobic polymeric structure to the molded fiber product.*

The efficiency of this process will be improved if a protecting group is invoked. Given its structure, the carboxylic acid group could also bind with cellulose unless it is protected by an added chemical during the rhamnolipids initial introduction into the wet-end slurry. Once the hydrophilic end is bound to cellulose molecules, the protecting group would have to be removed. More research will have to be done to determine the precise additives necessary to achieve optimum efficiency for this overall synthesis.

4.2.2 Technical Performance

Table 4.1: Technical assessment of rhamnolipids. For sources see Appendix B.

	Application of Data Source	Barrier Properties			Surface Properties	Thermal Properties		Chemical Properties	Mechanical Properties	End-of-Life Properties
Relevant Property	film or within molded fiber matrix	grease resistance	water contact angle	water vapor permeability (WVP)	porosity (oxygen permeability)	thermal resistance (temp at major % weight loss)	temperature dependence (manufacture temp 100˚C)	dispersability	tensile strength	degradability (at least 70% in soil)
Units	--	kit value	degrees	g.mm/m2.kPa.day	cm3/m2/24hr	˚C	˚C	--	MPa	days
PLA	Films	12+ (1)	75 - 85 (2)	0.161-0.237 (1)	38-42 (3)	335˚C (4)	52.5-150˚C (2)	DG	27-35 (5)	> 150 (6)
Rhamnolipid (Proxy: Palmitic Acid & minerals)	Fiber Matrix and Films	DG	120-140 (7)	DG	DG	240˚C (8)	90-120˚C (7)	Yes (7)	DG	8-12 (9)

Table 4.1 compares rhamnolipid properties to that of PLA. Of all the alternatives discussed, rhamnolipids have the most data gaps in technical properties. This is due to it traditionally being used as a surfactant as opposed to a barrier. To perform a more thorough technical assessment, palmitic acid was used as a proxy. This is viable because palmitic acid is analogous to the hydrophobic fatty acid tail of rhamnolipid, and once it is bound to cellulose, exhibits a similar total structure to rhamnolipids (4). Data derived from the proxy is indicated with red text. Note that this proxy solution has minerals added to the product, however, the

properties that have been included are representative of how rhamnolipids would perform in molded fiber. Due to the listed high water contact angle, which is significantly higher than that of PLA, the proxy indicates that rhamnolipids could serve as excellent water barriers. The temperature dependence and dispersibility show potential that they will spread evenly at the wet-end end phase of molded fiber production. Data from rhamnolipids themselves show that they could be used to serve hot foods, and the decomposition shows promising compostability.

4.2.3 Health and Environmental Performance

Table 4.2: Summary hazard table for rhamnolipids.

Legend. 1: Very High Hazard, 2: High Hazard, 3: Moderate Hazard, 4: Low Hazard, UNK: Data gap. **Bold:** High confidence, *italicized*: low confidence.

	Chemicals	Group I endpoints					Group II and II* endpoints							Ecotox and fate	
		C	M	R	D	E	AT	ST*	N	SnS*	SnR*	IrS	IrE	AA/CA	P*
Existing chemicals	6:2 Fluorotelomer methacrylate	*2*	*3*	**2**	**2**	*1*	*3*	**2**	UNK	*3*	*3*	**2**	**2**	*1*	*1*
	6:2 Fluorotelomer alcohol	*2*	*3*	**3**	**2**	*1*	*3*	**2**	UNK	*3*	*3*	**2**	**2**	*1*	*1*
	2-(N,N-Diethylamino)ethyl methacrylate	*3*	*3*	**1**	**2**	UNK	*2*	UNK	UNK	*1*	UNK	**1**	**1**	*1*	*4*
Alternative 1	Rhamnolipid	*3*	*4*	UNK	UNK	UNK	*4*	UNK	UNK	*3*	UNK	UNK	**1**	*4*	*4*

* Persistent scores reflect integrated information about the fate of degradation products.
** All inorganic compounds are persistent, and listed chemicals were categorized based on EC-CEPA Domestic Substances List (DSL).

Compared to current PFAS polymer mixtures, rhamnolipids are safer on various orders of magnitude for carcinogenicity, mutagenicity, acute mammalian toxicity, and skin sensitization. While overall safer compared to 6:2 FTMAC, 6:2 FTOH, and DEAE-MAC, rhamnolipids may cause severe eye tissue damage (IrE), a Group II endpoint that predominantly concerns select worker populations exposed to aqueous rhamnolipid solutions. Rhamnolipids are classified as an eye irritant under authoritative lists based on results from *in vivo* toxicity assays at 100%, 50%, 9.5%, and 1.0% w/w concentrations with decreasing levels of irritation when exposed to more dilute concentrations (6)(7). These data suggest the rhamnolipid concentration matters in evaluating the relative health risks of rhamnolipids during manufacture. These hazards could be effectively minimized by proper workplace safety controls and consumer applications. Identifying a feasible concentration of rhamnolipids to achieve technical performance while minimizing hazards will be a constraint with this solution.

Hazard data gaps exist for rhamnolipids after ingestion *in vivo*, a gap that may prohibit the use of biosurfactants in food applications (8).The FDA classifies rhamnose sugar as food grade, and the hydrocarbon chains as omnipresent in the natural environment, but the nature of rhamnolipids is also associated with opportunistic pathogenicity. Surface structure modification or use of a non-pathogenic microbial feedstock may overcome these limitations if they arise (8). Resolving these uncertainties would enable more confidence in this alternative solution as a safer surface-treatment additive.
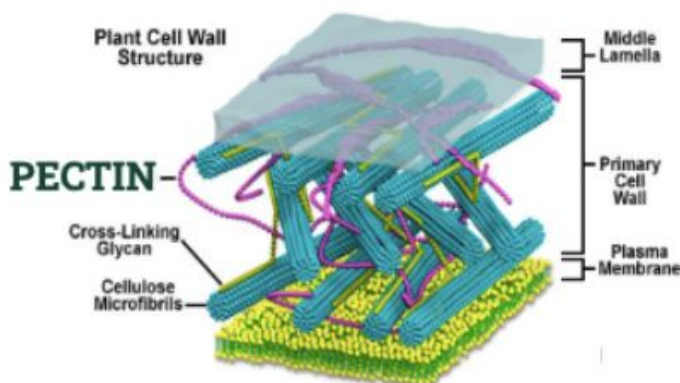
4.3 Pectin

4.3.1 Background

Inspiration for Pectin

Pectin is a biopolymer that occurs naturally in the starch of ripening fruits such as apples, citrus, cranberries, gooseberries, and plums to name a few. This branched heteropolysaccharide consists of long-chain galacturonan segments and other neutral sugars such as rhamnose, arabinose, galactose, and xylose (9). It forms a matrix with cellulose and hemicelluloses and contributes to plant cell structure (Figure 4.3). The word 'pectin' comes from the Greek word pektos which means firm and hard, reflecting pectin's ability to form hard gels due to the structures it can assimilate.

Figure 4.3. A cross section of the plant cell wall structure. The branched structure (pink) of pectin provides the plant cell with structures by forming a matrix with celluloses and the rest of the cell (12).

This material is one of the most significant renewable natural polymers which is ubiquitous in nature. Pectin can be sourced from a number of easily available horticulture crops as well (9).Due to its flexibility, pectin and its derivatives are used in many biodegradable packaging materials that serve as barriers towards moisture, oil, and aroma.

Method of Incorporation

Generally, hard pectin gels are formed in the presence of divalent cations such as Ca^{2+} (Figure 4.4). The required pH value ranges from 2 to 6 and sugar is not necessary for gel formation. An increase in ionic strength determines the lower concentration of Ca^{2+}, which is required for gelation. An increase in pH from 3.5 to 8.5 resulted in an increase of gel hardness, which was

connected with an increase in the degree of dissociation of galacturonic acid residues and next the de-esterification of pectin.
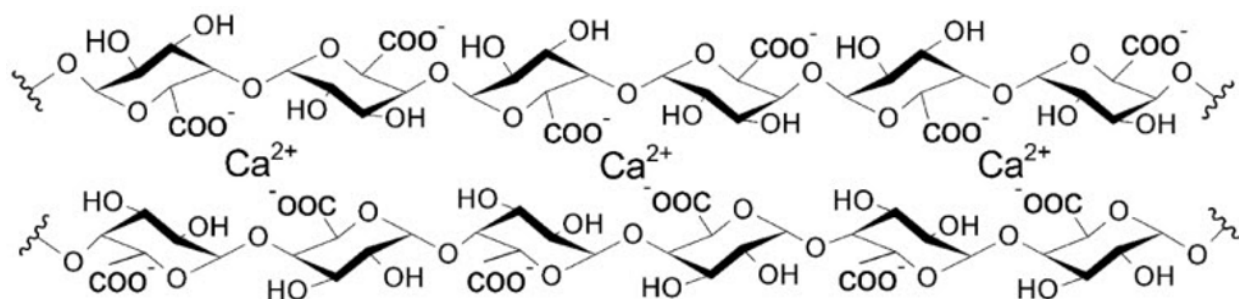
Figure 4.4. Scheme of the interactions of the pectin biopolymer and Ca²⁺ ions via the oxygen atoms in the carboxylate group of the pectin biopolymer (10).

The mechanism of pectin gelation is built upon pectin and alginate interactions. X-ray and EXAFS studies have indicated that the interaction of calcium ions with polygalacturonate chains may occur via oxygen atoms in the carboxylate group, in the ring, and in the glycosidic bond and in the hydroxyl group of the next residue (10).

The expected mechanism of action at the wet-end in addition to the cross-linking of pectin during the manufacturing process would be a reduction in fiber porosity. As a result, barrier properties would increaseWe conclude pectin is also a promising starting material towards creating alternative food packaging barriers and we recommend further study in regards to the application of this strategy.

4.3.2 Technical Performance

Table 4.3: Technical assessment of pectin. For sources see Appendix B.

	Application of Data Source	Barrier Properties			Surface Properties	Thermal Properties		Chemical Properties	Mechanical Properties	End-of-Life Properties
Relevant Property	film or within molded fiber matrix	grease resistance	water contact angle	water vapor permeability (WVP)	porosity (oxygen permeability)	thermal resistance (temp at major % weight loss)	temperature dependence (manufacture temp 100˚C)	dispersability	tensile strength	degradability (at least 70% in soil)
Units	--	kit value	degrees	g.mm/m2.kPa.day	cm3/m2/24hr	˚C	˚C	--	MPa	days
PLA	Films	12+ (1)	75 - 85 (2)	0.161-0.237 (1)	38-42 (3)	335˚C (4)	52.5-150˚C (2)	DG	27-35 (5)	> 150 (6)
Pectin	Films	DG	47-87 (10)	2.26 - 2.83 (11)	DG	174-180°C (12)	5 - 35˚C (13)	Yes (14)	7.10 ± 0.22 (11)	4 (15)

Out of all of the alternatives, pectin is the least favorable in regards to thermal and mechanical properties. It is therefore unfavorable for heavier food loads at high temperatures. Although it is easily dispersible, it may degrade during the cellulose slurry due to its low temperature during synthesis. Its low storage temperature is also a disadvantage to manufacturers since it will

increase cost of transport. On the other hand pectin shows great capability as a water barrier, as indicated by its high water contact angle and low water vapor permeability.

4.3.3 Health and Environmental Performance

Table 4.4: Summary hazard table for pectin.

Legend. 1: Very High Hazard, 2: High Hazard, 3: Moderate Hazard, 4: Low Hazard, UNK: Data gap. **Bold:** High confidence, *italicized*: low confidence.

	Chemicals	Group I endpoints					Group II and II* endpoints							Ecotox and fate	
		C	M	R	D	E	AT	ST*	N	SnS*	SnR*	IrS	IrE	AA/CA	P*
Existing chemicals	6:2 Fluorotelomer methacrylate	*2*	*3*	*2*	*2*	*1*	*3*	*2*	UNK	*3*	*3*	2	2	*1*	*1*
	6:2 Fluorotelomer alcohol	*2*	*3*	*3*	*2*	*1*	*3*	*2*	UNK	*3*	*3*	2	2	*1*	**1**
	2-(N,N-Diethylamino)ethyl methacrylate	*3*	*3*	**1**	*2*	UNK	*2*	UNK	UNK	*1*	UNK	**1**	**1**	*1*	4
Alternative 2	Pectin	*3*	*3*	*3*	*3*	UNK	*4*	*4*	UNK*	2	2	4	4	4	4
	Calcium carbonate	4	4	3	4	UNK	4	4	4	2	UNK	4	4	4	**1****
	Ethylene glycol	4	4	2	*1*	*3*	3	3	3	*3*	*3*	3	3	4	4

* Persistent scores reflect integrated information about the fate of degradation products.
** All inorganic compounds are persistent, and listed chemicals were categorized based on EC-CEPA Domestic Substances List (DSL).

Pectin is a constituent of a normal healthy diet with increasing pharmaceutical and food packaging applications (11), which reflects the overall safer profile compared to existing chemicals (Table 4.4). As an industrial chemical, pectin's form as a dry, odorless powder likely led to the hazard trade-offs among sensitization endpoints. We assigned pectin with a category score 2 for respiratory sensitization because of two authoritative listings for pectin as an asthmagen, and for skin sensitization, a positive structural alert identified pectin with a Schiff base formation.

In addition, calcium carbonate ($CaCO_3$) is a carbonic salt of calcium used in pectin gel formation to crosslink pectin molecules. Ethylene glycol is a recognized green solvent and bio-plasticizer that enables brittle carbohydrate-based packaging to become malleable. These compounds were included in a hazard assessment to represent the potential suite of chemicals that would be included in a potential pectin strategy.

Potential trade offs also exist among Group I reproductive and developmental endpoints for ethylene glycol. One authoritative list, US NIH Reproductive and Developmental Monographs, identified ethylene glycol, likely due to assays in which investigators observed toxicities at large doses (>1000 mg/kg/d) among vertebrate mammals. Interpretation with these results should be cautioned because oral ingestion of ethylene glycol is very unlikely.

The biodegradability of pectin is well-defined among researchers and manufacturers, and the environmental fate of pectin and other constituents are safer than PFAS. Candidate chemicals had strong evidence of no aquatic toxicity, persistence, or bioaccumulation. While $CaCO_3$ is listed by EC-CEPA Domestic Substances List (DSL) with a very high hazard score due its

inorganic nature, the terminal degradation products Ca^{2+} ions are safe in expected concentrations with proposed use.

Data gaps and uncertainties in hazards exist among candidate chemicals in this strategy, although pectin is unlikely to pose significant health risks among consumers or worker populations when appropriate safety and health controls are available.

4.4 Strategy 1: References

(1) Chong, H., & Li, Q. (2017). Microbial production of rhamnolipids: opportunities, challenges and strategies. *Microbial cell factories*, *16*(1), 137. https://doi.org/10.1186/s12934-017-0753-2

(2) Buck, R. C., Franklin, J., Berger, U., Conder, J. M., Cousins, I. T., de Voogt, P., Jensen, A. A., Kannan, K., Mabury, S. A., & van Leeuwen, S. P. (2011). Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. *Integrated environmental assessment and management*, *7*(4), 513–541. https://doi.org/10.1002/ieam.258

(3) Tan, Y.N., Li, Q. Microbial production of rhamnolipids using sugars as carbon sources.*Microb Cell Fact* 17, 89 (2018). https://doi.org/10.1186/s12934-018-0938-3

(4) Izadyar, S., Aghabozorgi, M., & Azadfallah, M. (2020). Palmitic acid functionalization of cellulose fibers for enhancing hydrophobic property. *Cellulose*, *27*(10), 5871–5878. https://doi.org/10.1007/s10570-020-03174-x

(5) Banat, Ibrahim & Makkar, Randhir & Cameotra, Swaranjit. (2000). Potential Commercial Applications of Microbial Surfactants. Applied microbiology and biotechnology. 53. 495-508. 10.1007/s002530051648.

(6) *Rhamnolipids: Fermentation products of glucose... - Registration Dossier - ECHA*. (n.d.). Retrieved December 16, 2020, from https://echa.europa.eu/et/registration-dossier/-/registered-dossier/20930/2/1

(7) US EPA Office of Pesticides Program. (n.d.). Rhamnolipid Biosurfactant (PC Code 110029). Retrieved December 16, 2020, from https://www3.epa.gov/pesticides/chem_search/reg_actions/registration/decision_PC-110029_11-May-04.pdf

(8) Nitschke, Marcia & Silva, Sumária. (2017). Recent Food Applications of Microbial Surfactants. Critical Reviews in Food Science and Nutrition. 58. 631-638. 10.1080/10408398.2016.1208635.

(9) T. Vanitha, M. Khan, Role of Pectin in Food Processing and Food Packaging. February 22nd 2019.doi:10.5772/intechopen.83677

(10) Gawkowska, D., Cybulska, J., & Zdunek, A. (2018). Structure-Related Gelling of Pectins and Linking with Other Natural Compounds: A Review. *Polymers*, *10*(7), 762. https://doi.org/10.3390/polym10070762

(11) Antony, Allwyn. (2012). A Review on Pectin: Chemistry due to General Properties of Pectin and its Pharmaceutical Uses. Scientific Reports. 1. 1- 3. 10.4172/scientificreports.553.

(12) Davidson, M. W. (2015, November 13). The Plant Cell Wall.

      https://micro.magnet.fsu.edu/cells/plants/cellwall.html

5. Sourced Internally from Paper Industry

5.1 Strategy 2: Introduction

Our second strategy consists of materials that *are already part of* the molded fiber production system. This includes material that is considered waste as well as material already being recycled and used in the system. Alternatives in this strategy have the potential to be made in-house by molded fiber manufacturers, giving them even more control over the physical properties of their product and reducing the environmental impact of transporting materials. The two alternatives we have chosen can be sourced from within the paper industry—cellulose nanocrystals (CNC) and lignin.

5.2 Cellulose Nanocrystals (CNC)

5.2.1 Background

Inspiration for CNC
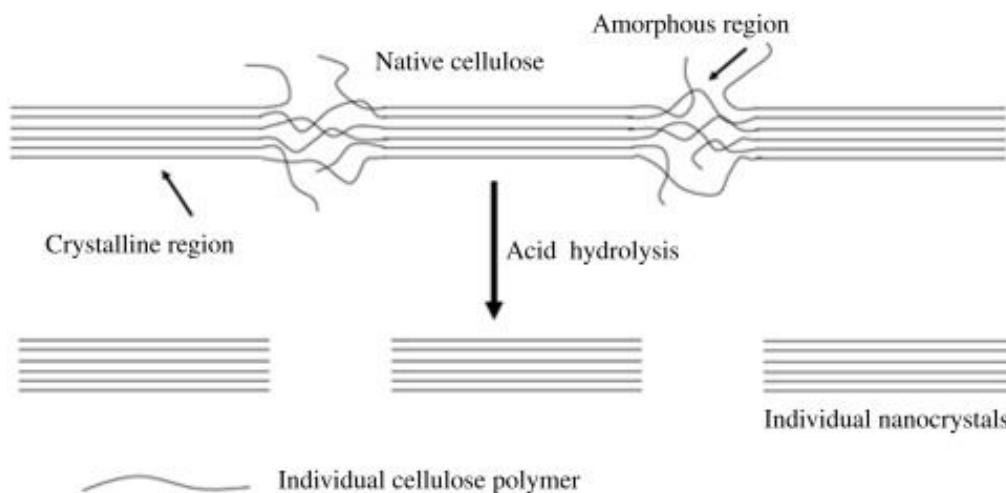
Figure 5.1. Scheme of natural cellulose transformation into cellulose nanocrystals (1).

Cellulose, in its bulk form, is the primary material used to make paper products, and the most abundant natural polymer on Earth. In its natural form, cellulose is made up of both amorphous

and crystalline regions (2). When the crystalline regions of natural cellulose are isolated and recrystallized at the nano-scale, cellulose gains hydrophobic properties without loss of degradability. CNC are widely studied as stabilizers for improving structural stability of bio-composite films (3)(4)(5). They can be made from a wide variety of plant sources and have many desirable properties when used in film contexts.

Method of Incorporation

Bulk cellulose fiber or paper pulp is first digested in acid to hydrolyze bonds in natural cellulose, break down the amorphous regions of the polymer, and form CNC (5). These CNC have the same chemical composition as natural cellulose, but take on a more rigid and hydrophobic crystal structure (2). Following production, we propose that CNC can be directly added to the pulp fiber blend tank. While the dispersibility of CNC depends on the polarity and purity of the mixture, which varies between manufacturers, some reports have shown successful incorporation into films without any added dispersing agent (5). The CNC could be produced in-house by molded fiber manufacturers, from the same bulk fiber used in molded fiber. This method has great potential especially for manufacturers that use recycled paper for their pulp feedstock. Not only can cellulose nanocrystals be prepared using recycled paper, they have the added advantage of adding stability to shorter fibers that are often a disadvantage of using recycled paper materials (6). In-house production of CNC by manufacturers could cut costs of purchasing external additives, improve sustainability from reduced transport of materials, and provide control over the specific properties of the CNC. However, this would require investment into the infrastructure to support a new acid-digestion processing step. Purchase of CNC from an external supplier is also a potential pathway.

5.2.2 Technical Performance

Table 5.1: Technical assessment of cellulose nanocrystals. For sources see Appendix B.

Relevant Property	Application of Data Source	Barrier Properties			Surface Properties	Thermal Properties		Chemical Properties	Mechanical Properties	End-of-Life Properties
Relevant Property	film or within molded fiber matrix	grease resistance	water contact angle	water vapor permeability (WVP)	porosity (oxygen permeability)	thermal resistance (temp at major % weight loss)	temperature dependence (manufacture temp 100˚C)	dispersability	tensile strength	degradability (at least 70% in soil)
Units	--	kit value	degrees	g.mm/m2.kPa.day	cm3/m2/24hr	˚C	˚C	--	MPa	days
PLA	Films	12+ (1)	75 - 85 (2)	0.161-0.237 (1)	38-42 (3)	335˚C (4)	52.5-150˚C (2)	DG	27-35 (5)	> 150 (6)
Cellulose Nanocrystals	Films	11 (16)	65 (16)	9 (17)	DG	250˚C (18)	30-60˚C (18)	Yes (18)	15.6 (18)	2 (19)

Technical data available for CNC are largely for film systems (Table 5.2), so the values may not be the same when incorporated into a fiber matrix. Nonetheless, we observe that relative to PLA, CNC films perform well in the grease resistance category, having a kit value comparable to

PLA and moderate water contact angle (7). In terms of water vapor permeability, its performance is much worse than PLA. The value of 9 g.mm/m2.kPa.day indicates that a significant amount of water vapor is able to escape through the film, though this value is also strongly influenced by the type of film that the study is performed on. Incorporation of CNC into the molded fiber matrix shows promise from its dispersibility but may be of concern during wet-end processing due its lower temperature dependence. If CNC slightly degrades due to the cellulose slurry temperature, this may affect mechanical properties of the final molded fiber product.

5.2.3 Health and Environmental Performance

Table 5.2 Summary hazard table for CNC.

Legend. 1: Very High Hazard, 2: High Hazard, 3: Moderate Hazard, 4: Low Hazard, UNK: Data gap. **Bold:** High confidence, *italicized*: low confidence.

	Chemicals	Group I endpoints					Group II and II* endpoints							Ecotox and fate	
		C	M	R	D	E	AT	ST*	N	SnS*	SnR*	IrS	IrE	AA/CA	P*
Existing chemicals	6:2 Fluorotelomer methacrylate	*2*	*3*	*2*	*2*	*1*	*3*	**2**	UNK	*3*	*3*	**2**	**2**	*1*	*1*
	6:2 Fluorotelomer alcohol	*2*	*3*	*3*	*2*	*1*	*3*	**2**	UNK	*3*	*3*	**2**	**2**	*1*	**1**
	2-(N,N-Diethylamino)ethyl methacrylate	*3*	*3*	**1**	*2*	UNK	*2*	UNK	UNK	*1*	UNK	**1**	**1**	*1*	**4**
Alternative 3	Cellulose nanocrystals	*3*	*3*	*3*	*3*	UNK	*4*	*3*	UNK	*3*	*2*	*4*	*3*	*3*	*4*
	Sulfuric acid	*3*	**4**	*3*	*3*	UNK	*1*	**1**	UNK	*3*	*1*	**1**	**1**	*2*	**1****

* Persistent scores reflect integrated information about the fate of degradation products.
** All inorganic compounds are persistent, and listed chemicals were categorized based on EC-CEPA Domestic Substances List (DSL).

To the best of our knowledge, CNC hazard information from authoritative lists were unavailable and the need to adapt a hazard evaluation method for emerging nanomaterials has been expressed. Despite this, a preliminary hazard assessment for wood-derived CNCs can still be performed based on expert judgment and peer-reviewed toxicity studies of CNCs from Shatkin et al., (2016)(8), Roman (2015)(9), and Shatkin & Kim (2015)(10).

The parent compound of CNCs is cellulose, which is overall benign; however, the acid treatment and resulting decrease in particle size as well as changes in physicochemical characteristics of nanomaterials slightly shift the hazard profiles of CNCs.. The particle dimensions of CNCs are 130 ± 67 nm in length by 5.9 ± 1.8 nm in width, which increase the surface area to volume ratio (8). The hazard overview indicates that CNC would improve the relative safety of most known Group I and II/II* endpoints by an average of one order of magnitude, except for respiratory sensitization, where one occupational epidemiology study identified an association to reduced lung function with repeated exposures (10).

According to Shatkin et al. (2016), the environmental performance of CNC is relatively sufficiently known, where aquatic toxicity assays among zebrafish indicate low toxicity (8). CNCs are not known or expected to persist in the environment, although the bioaccumulation potential of CNCs isunknown, and available predictive modeling would not be applicable to estimate this

endpoint. A better approximation of bioaccumulation would entail adapting traditional predictive methods and physicochemical characterization beyond the scope of this hazard assessment (11).

Finally, CNC manufacture and incorporation relies on dissolving cellulose fiber in sulfuric acid. The partial esterification of hydroxyl groups on the CNC imparts a slight acidity but may be considered minimal against the buffering capacities of mammalian organisms (9). Among molded fiber manufacturers intended to adopt this process, cellulose acidification represents a hazardous step that already exists in the papermaking process though are presumed to be minimized by effective management controls.
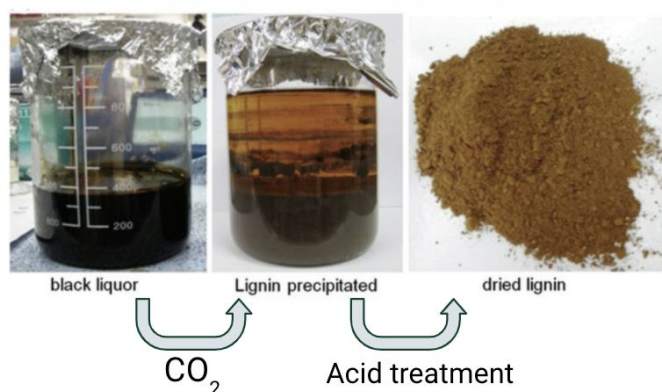
5.3 Lignin

5.3.1 Background

Inspiration for Lignin

Lignin is a biopolymer that composes 15-40% of plant biomass, depending on the species of plant it is extracted from. It is most abundant in the cell walls, and is the primary source of cell wall rigidity (12). Lignin is removed as a waste product when cellulose is isolated from raw wood chips during the paper-making process, due to its insolubility in the cellulose slurry and its ability to clump cellulose fibers together through cross-linking. In the paper industry, 70 million tons per year of lignin is disposed of as waste. It is also a common waste product in other industries, such as ethanol production. Once isolated, lignin forms a black liquor, which is often used as an internal energy input for the pulping process. Its chemical properties, however, make this an insufficient use of this biopolymer (12). Since it is known to bind so well to cellulose and provide structure in plants, it makes sense that this waste product could both be well incorporated in and provide rigidity to molded fiber.

Figure 5.2. Lignin extraction process from black liquor (14).

In order to be incorporated into the molded fiber, lignin must be extracted from the black liquor using carbon dioxide and acid treatment. Traditionally, this process uses a strong acid like sulfuric acid, which is also utilized during the stripping process in paper-making. However, there is evidence showing this aggressive chemical could be replaced with non-toxic chemicals such as potassium aluminum sulfate (15). When added to the molded fiber wet-end slurry, Lewis et al. 2016 (13) reports that adding an ionic liquid suspends the lignin—dispersing it more evenly and preventing fiber clumping. Incorporation of other plant materials like xylan, can improve molded fiber porosity (13).

Another method of incorporating lignin into molded fiber is through light delignification. As mentioned earlier, lignin is extracted from raw materials in order to form a cellulose slurry during paper making. Instead of fully removing the lignin content from the raw material, it can be partially removed, so the bonds between the original lignin and cellulose are preserved. It is important to note that this process is only possible if the molded fiber is manufactured from virgin material as opposed to recycled paper. For manufacturers that produce their molded fiber products in this way, molded fiber produced from light-delignified cellulose has been successfully achieved by Wang et. al. (16), though not in a food packaging context.

5.3.2 Technical Performance

The data collected in Table 5.3 comes primarily from data sources where lignin is applied within the molded fiber matrix. Relative to the rest of our alternatives in this report, lignin has the best technical performance. Under barrier properties we see that its Kit value and water contact angle are comparable to that of PLA. In fact the water contact angle is slightly higher meaning lignin is slightly more hydrophobic. The WVP is significantly higher, which means the final

product may require less humid storage conditions. Oxygen resistance is slightly lower, but should not cause a significantly less porous material.

Table 5.3: Technical Assessment of Lignin. For sources see Appendix B.

	Application of Data Source	Barrier Properties			Surface Properties	Thermal Properties		Chemical Properties	Mechanical Properties	End-of-Life Properties
Relevant Property	film or within molded fiber matrix	grease resistance	water contact angle	water vapor permeability (WVP)	porosity (oxygen permeability)	thermal resistance (temp at major % weight loss)	temperature dependence (manufacture temp 100˚C)	dispersability	tensile strength	degradability (at least 70% in soil)
Units	--	kit value	degrees	g.mm/m2.kPa.day	cm3/m2/24hr	˚C	˚C	--	MPa	days
PLA	Films	12+ (1)	75 - 85 (2)	0.161-0.237 (1)	38-42 (3)	335˚C (4)	52.5-150˚C (2)	DG	27-35 (5)	> 150 (6)
Lignin	Fiber Matrix and Films	12 (20)	89 (21)	5.3 ± 0.1 (20)	26.6 ± 0.5 (20)	260-290˚C (22)	85˚C (22)	Yes, with agent (22)	20.3 (21)	23 (23)

Lignin's thermal resistance indicates that it is suitable for hot foods, but will break down faster than PLA when in contact. Its temperature during manufacture appears to be compatible with molded fiber pulp slurry, so there is little concern that it will break down at the wet-end and additional heat will not be necessary. As mentioned earlier, lignin normally causes clumping when in the cellulose slurry, however if added back in with a dispersing agent like an ionic liquid, it can be evenly distributed. Finally, the tensile strength of lignin is very close to that of PLA and its degradability is significantly improved. Although lignin takes the longest of our alternatives to degrade, this time shortens when it is exposed to fungi and bacteria commonly found in temperate soils (17).

5.3.3 Health and Environmental Performance

Table 5.4: Summary hazard table for lignin.

Legend. 1: Very High Hazard, 2: High Hazard, 3: Moderate Hazard, 4: Low Hazard, UNK: Data gap. **Bold:** High confidence, *italicized*: low confidence.

	Chemicals	Group I endpoints					Group II and II* endpoints							Ecotox and fate	
		C	M	R	D	E	AT	ST*	N	SnS*	SnR*	IrS	IrE	AA/CA	P*
Existing chemicals	6:2 Fluorotelomer methacrylate	*2*	*3*	**2**	**2**	*1*	*3*	**2**	UNK	*3*	*3*	**2**	**2**	*1*	*1*
	6:2 Fluorotelomer alcohol	*2*	*3*	**3**	*2*	*1*	*3*	**2**	UNK	*3*	*3*	**2**	**2**	*1*	**1**
	2-(N,N-Diethylamino)ethyl methacrylate	*3*	*3*	**1**	*2*	UNK	**2**	UNK	UNK	*1*	UNK	**1**	**1**	*1*	4
Alternative 4	Lignin														
	Xylan														
	Sulfuric acid	*3*	*4*	**3**	**3**	UNK	*1*	**1**	UNK	*3*	*1*	**1**	**1**	**2**	**1****
	1-Allyl-3-methylimidazolium chloride	*3*	*3*	UNK	UNK	*3*	*3*	**2**	UNK	*3*	UNK	**2**	**2**	UNK	4

* Persistent scores reflect integrated information about the fate of degradation products.
** All inorganic compounds are persistent, and listed chemicals were categorized based on EC-CEPA Domestic Substances List (DSL).

Lignin is intrinsically safe. The U.S. EPA evaluated lignin under the Safer Choice program and it is listed under the "Safer Chemical Ingredient List" after experimental and modeled data verified low concern (18). Additional studies identify lignin as an anti-toxicant (19), exhibiting medicinal roles against non-communicable diseases like cancer and obesity. As a result, in our hazard

assessment (Table 5.4), we categorized lignin as benign. The implication therefore is that all hazards in each endpoint are minimized compared to the baseline.

Three additional chemical-level hazards were evaluated. Xylan is a hemicellulose conferring tensile strength, sulfuric acid is an existing chemical used in the papermaking process and used again to recover lignin waste, the ionic liquid 1-allyl-3-methylimidazolium is a potential dispersing agent used to prepare and re-incorporate lignin. A preliminary hazard assessment of these compounds suggests a similar hazard profile compared to existing baseline, although we recommend caution in interpretation here. These chemicals represent the chemicals present in the manufacturing process of this strategy, and are not expected to be present in any meaningful amount in the final molded fiber product. Similarly, sulfuric acid is an existing chemical within the papermaking industry with relatively fewer occupational risks compared to different industry sectors due to minimal workplace exposure and appropriate workplace controls.

Lignin is found in the natural environment and a product of the cellulose treatment process, which confers significant advantages in health and environmental performance in contrast to PFAS mixtures. In terms of environmental performance, lignin outperforms fluorinated compounds due to its chemically inert fate in the environment as a major component of soil organic matter[17][20]. This preliminary health assessment concludes that addition of lignin to molded fiber is one of the safest strategies in our recommendations.

5.4 Strategy 2: References

(1) Bhat, A. H., Dasan, Y. K., Khan, I., Soleimani, H., & Usmani, A. (2017). Application of nanocrystalline cellulose: Processing and biomedical applications. In *Cellulose-Reinforced Nanofibre Composites: Production, Properties and Applications* (pp. 215–240). Elsevier Inc. https://doi.org/10.1016/B978-0-08-100957-4.00009-7

(2) Mohamed, M. A., Salleh, W. N. W., Jaafar, J., Asri, S. E. A. M., & Ismail, A. F. (2015). Physicochemical properties of "green" nanocrystalline cellulose isolated from recycled newspaper. RSC Advances, 5(38), 29842–29849. https://doi.org/10.1039/c4ra17020b

(3) Liu, D., Zhong, T., Chang, P. R., Li, K., & Wu, Q. (2010). Starch composites reinforced by bamboo cellulosic crystals. Bioresource Technology, 101(7), 2529–2536. https://doi.org/10.1016/j.biortech.2009.11.058

(4) Reddy, J. P., & Rhim, J. W. (2014). Characterization of bionanocomposite films prepared with agar and paper-mulberry pulp nanocellulose. Carbohydrate Polymers, 110, 480–488. https://doi.org/10.1016/j.carbpol.2014.04.056

(5) Agustin, M. B., Ahmmad, B., De Leon, E. R. P., Buenaobra, J. L., Salazar, J. R., & Hirose, F. (2013). Starch-based biocomposite films reinforced with cellulose nanocrystals from garlic stalks. Polymer Composites, 34(8), 1325–1332. https://doi.org/10.1002/pc.22546

(6) Campano, C., Miranda, R., Merayo, N., Negro, C., & Blanco, A. (2017). Direct production of cellulose nanocrystals from old newspapers and recycled newsprint. Carbohydrate Polymers, 173, 489–496. https://doi.org/10.1016/j.carbpol.2017.05.073

(7) Gicquel, E., Martin, C., Yanez, J., & Bras, J. (2017). Cellulose nanocrystals as new bio-based coating layer for improving fiber-based mechanical and barrier properties. *Journal of Materials Science*, *52*. https://doi.org/10.1007/s10853-016-0589-x

(8) Shatkin, J. A., Ong, K. J., Ede, J. D., Wegner, T. H., & Goergen, M. (2016). Toward cellulose nanomaterial commercialization: Knowledge gap analysis for safety data sheets according to the globally harmonized system. TAPPI Journal. 15(6): 425-437., 15(6), 425–437.

(9) Roman, M. (2015). Toxicity of Cellulose Nanocrystals: A Review. Industrial Biotechnology, 11(1), 25–33. https://doi.org/10.1089/ind.2014.0024

(10) Shatkin, J. A., & Kim, B. (2015). Cellulose nanomaterials: Life cycle risk assessment, and environmental health and safety roadmap. Environmental Science: Nano, 2(5), 477–499. https://doi.org/10.1039/C5EN00059A

(11) Camarero-Espinosa, S., Endes, C., Mueller, S., Petri-Fink, A., Rothen-Rutishauser, B., Weder, C., Clift, M. J. D., & Foster, E. J. (2016). Elucidating the Potential Biological Impact of Cellulose Nanocrystals. Fibers, 4(3), 21. https://doi.org/10.3390/fib4030021

(12) Tribot, A., Amer, G., Abdou Alio, M., de Baynast, H., Delattre, C., Pons, A., … Dussap, C.-G. (2019). Wood-lignin: Supply, extraction processes and use as bio-based material. *European Polymer Journal*, *112*, 228–240. https://doi.org/https://doi.org/10.1016/j.eurpolymj.2019.01.007

(13) Lewis, A., Waters, J. C., Stanton, J., Hess, J., & Salas-De La Cruz, D. (2016). Macromolecular interactions control structural and thermal properties of regenerated tri-component blended films. *International Journal of Molecular Sciences*, *17*(12), 9–12. https://doi.org/10.3390/ijms17121989

(14) Luong, N.D., Binh, N.T.T., Duong, L.D. *et al.* (2012). An eco-friendly and efficient route of lignin extraction from black liquor and a lignin-based copolyester synthesis. *Polym. Bull.* 68, 879–890. https://doi.org/10.1007/s00289-011-0658-x

(15) Yang, J., Ching, Y.C.,& Chuah, C. H. (2019). Applications of Lignocellulosic Fibers and Lignin in Bioplastics: A Review. *Polymers*, *11*(5), 751.

(16) Wang, Q., Xiao, S., Shi, S. Q., & Cai, L. (2018). Effect of light-delignification on mechanical, hydrophobic, and thermal properties of high-strength molded fiber materials. *Scientific Reports*, *8*(1), 1–10. https://doi.org/10.1038/s41598-018-19623-4

(17) Datta R, Kelkar A, Baraniya D, Molaei A, Moulick A, Meena RS, Formanek P. (2017). Enzymatic Degradation of Lignin in Soil: A Review. *Sustainability*. 9(7):1163.

(18) US EPA, O. (2013, December 11). Safer Chemical Ingredients List [Data and Tools]. US EPA. https://www.epa.gov/saferchoice/safer-ingredients

(19) Vinardell, M. P., & Mitjans, M. (2017). Lignins and Their Derivatives with Beneficial Effects on Human Health. International Journal of Molecular Sciences, 18(6). https://doi.org/10.3390/ijms18061219

(20) Janusz, G., Pawlik, A., Sulej, J., Świderska-Burek, U., Jarosz-Wilkołazka, A., & Paszczyński, A. (2017). Lignin degradation: Microorganisms, enzymes involved, genomes analysis and evolution. FEMS Microbiology Reviews, 41(6), 941–962. https://doi.org/10.1093/femsre/fux049

6. Conclusion

6.1 Technical Comparison

6.1.1 Molded-Fiber Incorporation

Of the data collected, only those from lignin and the rhamnolipid proxy, palmitic acid, were from sources where the material was incorporated within the fiber matrix. All other sources applied the alternatives as films on a surface. By including temperature dependence and dispersibility in our assessment, we have attempted to evaluate whether the films could be applied within a cellulose fiber matrix. In terms of dispersibility, all the alternatives show promise of spreading evenly in the wet-end cellulose slurry, although lignin requires an additive to achieve this. The temperature of the slurry may be of concern for pectin and CNC. Since these alternatives are synthesized at a significantly lower temperature from the slurry, they may break down before they are able to reach the dry-end phase.

Table 6.1: The complete technical assessment of all discussed alternatives (Table 3.2 reproduced for convenience). For sources see Appendix B.

	Application of Data Source	Barrier Properties			Surface Properties	Thermal Properties		Chemical Properties	Mechanical Properties	End-of-Life Properties
Relevant Property	film or within molded fiber matrix	grease resistance	water contact angle	water vapor permeability (WVP)	porosity (oxygen permeability)	thermal resistance (temp at major % weight loss)	temperature dependence (manufacture temp 100˚C)	dispersability	tensile strength	degradability (at least 70% in soil)
Units	--	kit value	degrees	g.mm/m2.kPa.day	cm3/m2/24hr	˚C	˚C	--	MPa	days
PLA	Films	12+ (1)	75 - 85 (2)	0.161-0.237 (1)	38-42 (3)	335˚C (4)	52.5-150˚C (2)	DG	27-35 (5)	> 150 (6)
Rhamnolipid (Proxy: Palmitic Acid & minerals)	Fiber Matrix and Films	DG	120-140 (7)	DG	DG	240˚C (8)	90-120˚C (7)	Yes (7)	DG	8-12 (9)
Pectin	Films	DG	47-87 (10)	2.26 - 2.83 (11)	DG	174-180°C (12)	5 - 35˚C (13)	Yes (14)	7.10 ± 0.22 (11)	4 (15)
Cellulose Nanocrystals	Films	11 (16)	65 (16)	9 (17)	DG	250˚C (18)	30-60˚C (18)	Yes (18)	15.6 (18)	2 (19)
Lignin	Fiber Matrix and Films	12 (20)	89 (21)	5.3 ± 0.1 (20)	26.6 ± 0.5 (20)	260-290˚C (22)	85˚C (22)	Yes, with agent (22)	20.3 (21)	23 (23)

Rankings are relative *to each other:*   Idea   Moderate   Non-ideal   DG = data gap

Further research into applying these alternatives in a cellulose fiber matrix is required. Pectin, for example, forms by gelling with other pectin molecules. When introduced into the cellulose matrix, this gelling may weaken, and the technical properties could change. The full capability of pectin could still be achieved through better process design or chemical additives but further work is needed.

6.1.2 Food Type

Table 6.2: Assignment of food type for each alternative based off of technical assessment (1)(2)(3).

Possible Alternatives	Pectin	Rhamno lipids	Nano cellulose	Lignin	Nano cellulose	Lignin	Rhamno lipids	Lignin
Food Type								
Temperature	Room Temperature				Hot		Hot	
Water Content	Medium				Low		Medium	
Oil Content	Low				High		Medium	

Table 6.2 displays three types of foods that are commonly stored in molded fiber: room temperature foods with low barrier needs (e.g. salad), hot and oil-heavy foods (e.g. fries and burgers), and hot foods with moderate oil and water content (e.g. pasta). Based on the technical assessments, each alternative was categorized for which food types they would best serve.

All alternatives could possibly be applied to molded fiber salad bowls, because of the low temperature and limited barriers requirements.

Nanocellulose and lignin are suitable for use in packing greasier foods, since their kit values are very close to that of PLA and display medium levels of thermal resistance. It should be noted that the high thermal resistance of PLA may not be necessary at the temperature of hot foods. This high resistance most likely overperforms for its purpose and may contribute to its long degradation time.

The high temperature and medium barrier requirements for foods like pasta match well with the technical capabilities of rhamnolipids and lignin. Both have a high water contact angle and break down at relatively high temperatures. These foods also tend to be heavier, which is suitable for lignin since its tensile strength is very close to that PLA.

6.1.3 Sustainability

A large emphasis in our search was placed on finding alternatives that were sustainability disposed of and sourced. This led to our degradation criteria and two strategy breakdowns, respectively. As demonstrated by the degradability section of the technical assessment, all our alternatives are able to decompose without the influence of temperature or added microbes in under a month. This shows great promise that they could be composted both in a home setting and likely any composting facility. In terms of sourcing, categorizing our alternatives as those sourced internally and externally from the paper industry helped emphasize how sustainable alternatives can be reached through either strategy.

Rhamnolipids and pectin, sourced from outside the paper industry, are extracted from plants and microbes as opposed to nonrenewable sources. Their processing, however, introduces use of more energy and material. 10-30% of the cost of producing rhamnolipids comes from the material used to feed the microbes that make them. Their material and energy efficiency, however, can be controlled by their feedstock. Commonly, oils are used as the carbon source, but more sustainable sources, such as sugars in agro-industrial crop residues, are possible alternatives (4). Extraction of pectin from citrus peels requires a high amount of pressure and temperature, but recent research has found that enzymatic extraction could reduce these requirements (5). Finding new ways of incorporating these alternatives could help make them more sustainable options.

The benefit of the second strategy alternatives, which are sourced from within the paper industry, is that they have less added processing energy and materials. Lignin does require processing from its waste form, but by utilizing a waste product there is little new material added. Energy normally during wastewater treatment can also be redirected back into the production line. CNC introduces no new materials, but does involve extra processing that creates more acidic waste. The acid required for both these processes are already used in the papermaking process.

6.2 Hazard Comparison

Table 6.3 Summary hazard table of alternative strategies.

Legend. 1: Very High Hazard, 2: High Hazard, 3: Moderate Hazard, 4: Low Hazard, UNK: Data gap. **Bold:** High confidence, *italicized*: low confidence.

	Chemicals	Group I endpoints					Group II and II* endpoints							Ecotox and fate	
		C	M	R	D	E	AT	ST*	N	SnS*	SnR*	IrS	IrE	AA/CA	P*
Existing chemicals	6:2 Fluorotelomer methacrylate	2	3	2	2	1	3	2	UNK	3	3	2	2	1	1
	6:2 Fluorotelomer alcohol	2	3	3	2	1	3	2	UNK	3	3	2	2	1	1
	2-(N,N-Diethylamino)ethyl methacrylate	3	3	1	1	UNK	2	UNK	UNK	1	UNK	1	1	1	4
Alternative 1	Rhamnolipid	3	4	UNK	UNK	UNK	4	UNK	UNK	3	UNK	UNK	1	4	4
Alternative 2	Pectin	3	3	3	3	UNK	4	4	UNK*	2	2	4	4	4	4
	Calcium carbonate	4	4	3	4	UNK	4	4	4	2	UNK	4	4	4	1**
	Ethylene glycol	4	4	2	1	3	3	3	2	3	3	3	3	4	4
Alternative 3	Cellulose nanocrystals	3	3	3	3	UNK	4	3	UNK	3	2	4	3	3	4
	Sulfuric acid	3	4	3	3	UNK	1	1	UNK	3	1	1	1	2	1**
Alternative 4	Lignin														
	Xylan														
	Sulfuric acid	3	4	3	3	UNK	1	1	UNK	3	1	1	1	2	1**
	1-Allyl-3-methylimidazolium chloride	3	3	UNK	UNK	3	3	2	UNK	3	UNK	2	2	UNK	4

* Persistent scores reflect integrated information about the fate of degradation products.
** All inorganic compounds are persistent, and listed chemicals were categorized based on EC-CEPA Domestic Substances List (DSL).

Hazard reductions among Group I endpoints: Candidate chemicals overall had orders of magnitude improvements in safety among known Group I endpoints, a significant advantage of fluorinated chemicals which pose impermissible risks to human health at low doses.

Although most known Group II endpoints were reduced, some alternative chemical hazards scores under sensitization and irritation endpoints in Group II/II* were equivalent to the existing chemicals or represented trade-offs primarily due to the powder forms industrial chemicals take during manufacture. These ultimate risks posed by these chemicals correspond to select worker populations that could be mitigated by effective management controls.

All chemicals improved the environmental performance compared to the PFAS polymer baseline because chemicals had at least one endpoint. This has a significant advantage over side-chain PFAS in that as data gaps and uncertainties become resolved, the potential of hazard discovery as toxicological data emerges becomes minimal. This minimizes the potential for a regrettable substitution, and a stark contrast to the way side-chain PFAS is used in industry today.

Data gaps and uncertainties, primarily for rhamnolipids and CNC, point to opportunities for further research. In silico and high throughput methods by EPA CompTox provided a relatively easy way of detecting structural alerts, but more work is needed to corroborate results and interpret them.

6.3 Next Steps

To continue the search for safer alternatives against PFAS among molded fiber products, we have identified three broad next steps for researchers and molded fiber manufacturers.

(1) **Continue research and testing of alternatives in a molded fiber context.** Since many of these alternatives are novel, they have not been implemented for molded fiber, but are worth investigating. The strategies listed here may also be combined synergistically which may be the focus of future study, for example: lignin-containing nanocellulose (6), CNC reinforced pectin (7), incorporation of metal ions to bind biosurfactants (8), and so on. Similarly, toxicity studies along the oral ingestion route are necessary if these strategies are adopted and come into contact with food.

(2) **The second step is the creation of a common language and standard tests in the food packaging industry**. A need for this became prominent through observations of the roadblocks faced by molded fiber companies in their response to the FDA phase-out of PFAS materials and the challenges that surfaced through the technical assessments—research data varied wildly in the parameters tested and base materials used, causing discrepancies and data gaps. While some technical performance parameters were standard (e.g. water contact angle), other metrics for performance, such as oil resistance and porosity, were measured using a variety of tests that could not be compared.

(3) **The third step is to take further action for further green innovation**. Green innovation does not end with replacing PFAS. The paper and molded fiber production process involves a host of secondary materials and treatments. Traditional manufacturing chemicals like strong acids could be substituted through a similar iterative search for chemical alternatives via technical and hazards assessments.

6.5 Conclusion References

(1) PLA16 [Image] Shopify. https://cdn.shopify.com/s/files/1/0586/2193/products/PLA19__41_R_d8f756ae-f01e-4d68-812b-205bf32a94c9_grande.jpg?v=1574283722

(2) Takeout fiber tray for meals [Image] https://www.brenmarco.com/wp-content/uploads/2020/10/takeout-fiber-tray-for-meals-620026-1.jpg

(3) Sweet Green Bowls [Image] Fast Company. https://images.fastcompany.net/image/upload/w_1153,ar_16:9,c_fill,g_auto,f_auto,q_auto,fl_lossy/wp-cms/uploads/2020/03/p-2-90472838-sweetgreen.jpg

(4) Tan, Y.N., Li, Q. Microbial production of rhamnolipids using sugars as carbon sources. *Microb Cell Fact* 17, 89 (2018). https://doi.org/10.1186/s12934-018-0938-3

(5) Naghshineh, M., Olsen, K., & Georgiou, C. A. (2013). Sustainable production of pectin from lime peel by high hydrostatic pressure treatment. *Food Chemistry*, *136*(2), 472–478. https://doi.org/https://doi.org/10.1016/j.foodchem.2012.08.036

(6) Ewulonu, C. M., Liu, X., Wu, M., & Yong, H. (2019). Lignin-Containing Cellulose Nanomaterials: A Promising New Nanomaterial for Numerous Applications. *Lignin-Containing Cellulose Nanomaterials: A Promising New Nanomaterial for Numerous Applications*, *4*(1), 3–10. https://doi.org/10.21967/jbb.v4i1.186

(7) Chaichi, M., Hashemi, M., Badii, F., & Mohammadi, A. (2017). Preparation and characterization of a novel bionanocomposite edible film based on pectin and crystalline nanocellulose. *Carbohydrate Polymers*, *157*, 167–175. https://doi.org/10.1016/j.carbpol.2016.09.062

(8) Izadyar, S., Aghabozorgi, M., & Azadfallah, M. (2020). Palmitic acid functionalization of cellulose fibers for enhancing hydrophobic property. *Cellulose*, *27*(10), 5871–5878. https://doi.org/10.1007/s10570-020-03174-x

7. Appendix

7.1 Author Bios

Minerva Teli is a first year PhD student in the Environmental Engineering program at UC Berkeley. She studies materials for water treatment under Prof. Baoxia Mi and holds an undergraduate degree in Chemistry and Chemical Biology from Northeastern University. For this project she has focused on the technical criteria, assessments, and comparison as well as group coordination.

Aaron Maruzzo. Aaron is a MPH student at the Environmental Health Science program at UC Berkeley School of Public Health. He is interested in developing community-based research and action to confront environmental health challenges like the health effects of perfluorinated chemical pollution and climate change that disproportionately harm overlooked communities in the Western Pacific region. He focused on the environmental health criteria for this project.

Anna Kurianowicz is a fourth year undergraduate Biochemistry & Molecular Biology student at UC Berkeley and holds a minor in Journalism from the UC Berkeley Graduate School of Journalism. She is also a part of the Wildsoet Myopia Lab Group in the UC Berkeley School of Optometry and does additional public health work for the UCSF Pediatric Ophthalmology Clinic. For this project, she focused on identifying alternative solutions in literature and the understanding of desired properties.

Kelly Chou is a fourth year undergraduate Chemistry major at UC Berkeley. She researches green chemistry education and curriculum development as part of the Baranger group, and is affiliated with the Berkeley Center of Green Chemistry Greener Partnerships program. For this project, she focused on literature review, alternatives identification, and background on the food packaging and molded fiber industry.

7.3 Appendix B: Technical Assessment References

(1) Sánchez Aldana, D., Villa, E., De Dios, M., Hernández, D., Gonzalez, G., Rascon-Cruz, Q., … Ballinas, M. (2014). Barrier Properties of Polylactic Acid in Cellulose Based Packages Using Montmorillonite as Filler. Polymers, 6, 2386–2403. https://doi.org/10.3390/polym6092386

(2) Baran, E. H., & Erbil, H. Y. (2019). Surface Modification of 3D Printed PLA Objects by Fused Deposition Modeling: A Review. Colloids and Interfaces, 3(2). https://doi.org/10.3390/colloids3020043

(3) http://www.alphap.com/bottle-basics/plastics-comparison-chart.php

(4) Fortunati, E., Puglia, D., Kenny, J., Haque, M., & Pracella, M. (2013). Effect of ethylene-co-vinyl acetate-glycidylmethacrylate and cellulose microfibers on the thermal, rheological and biodegradation properties of poly(lactic acid) based systems. Polymer Degradation and Stability, 98. https://doi.org/10.1016/j.polymdegradstab.2013.10.007

(5) Ghasemi, S., Behrooz, R., Ghasemi, I., Yassar, R., & Long, F. (2017). Development of nanocellulose-reinforced PLA nanocomposite by using maleated PLA (PLA-g-MA). Journal of Thermoplastic Composite Materials, 089270571773460. https://doi.org/10.1177/0892705717734600

(6) Vasile, C., Pamfil, D., Râpă, M., Darie-Niță, R. N., Mitelut, A. C., Popa, E. E., … Popa, M. E. (2018). Study of the soil burial degradation of some PLA/CS biocomposites. Composites Part B: Engineering, 142, 251–262. https://doi.org/https://doi.org/10.1016/j.compositesb.2018.01.026

(7) Izadyar, S., Aghabozorgi, M. & Azadfallah, M. Palmitic acid functionalization of cellulose fibers for enhancing hydrophobic property. Cellulose 27, 5871–5878 (2020). https://doi.org/10.1007/s10570-020-03174-x

(8) Khademolhosseini, R., Jafari, A., Mousavi, S. M., Hajfarajollah, H., Noghabi, K. A., & Manteghian, M. (2019). Physicochemical characterization and optimization of glycolipid biosurfactant production by a native strain of Pseudomonas aeruginosa HAK01 and its performance evaluation for the MEOR process. RSC Adv., 9(14), 7932–7947. https://doi.org/10.1039/C8RA10087J

(9) Renfro, T. D. (2013). Rhamnolipid Biosurfactant Transport in Agricultural Soils. Florida State University Libraries.

(10) Sriamornsak, P., Wattanakorn, N., Nunthanid, J., & Puttipipatkhachorn, S. (2008). Mucoadhesion of pectin as evidence by wettability and chain interpenetration. Carbohydrate Polymers, 74, 458-467.

(11) Chambi, Hulda Noemi Mamani, & Grosso, Carlos Raimundo Ferreira. (2011). Mechanical and water vapor permeability properties of biodegradables films based on

methylcellulose, glucomannan, pectin and gelatin. Food Science and Technology, 31(3), 739-746. https://dx.doi.org/10.1590/S0101-20612011000300029

(12) Einhorn-Stoll, Ulrike & Kunzek, Herbert & Dongowski, Gerhard. (2007). Thermal analysis of chemically and mechanically modified pectins. Food Hydrocolloids - FOOD HYDROCOLLOID. 21. 1101-1112. 10.1016/j.foodhyd.2006.08.004.

(13) Cardoso SM, Coimbra MA, Silva JALd. Temperature dependence of the formation and melting of pectin–Ca2+ networks: a rheological study Food hydrocolloids.. 2003 Nov;17(6):801-807. DOI: 10.1016/s0268-005x(03)00101-2.

(14) Antony, Allwyn. (2012). A Review on Pectin: Chemistry due to General Properties of Pectin and its Pharmaceutical Uses. Scientific Reports. 1. 1- 3. 10.4172/scientificreports.553.

(15) Begum, Rokeya & Yusof, Yus & Aziz, Mohammad & Uddin, M.. (2017). Structural and functional properties of pectin extracted from jackfruit (Artocarpus heterophyllus) waste: Effects of drying. International Journal of Food Properties. 20. 10.1080/10942912.2017.1295054.

(16) Tyagi, P., Lucia, L. A., Hubbe, M. A., & Pal, L. (2019). Nanocellulose-based multilayer barrier coatings for gas, oil, and grease resistance. Carbohydrate Polymers, 206, 281–288. https://doi.org/10.1016/j.carbpol.2018.10.114

(17) Sukyai P, Anongjanya P, Bunyahwuthakul N, Kongsin K, Harnkarnsujarit N, Sukatta U, Sothornvit R, & Chollakup R. (2018). Effect of cellulose nanocrystals from sugarcane bagasse on whey protein isolate-based films. https://doi.org/10.1016/j.foodres.2018.02.052

(18) Agustin, M. B., Ahmmad, B., De Leon, E. R. P., Buenaobra, J. L., Salazar, J. R., & Hirose, F. (2013). Starch-based biocomposite films reinforced with cellulose nanocrystals from garlic stalks. Polymer Composites, 34(8), 1325–1332. https://doi.org/10.1002/pc.22546

(19) Singh, G., Chandoha-Lee, C., Zhang, W., Renneckar, S., Vikesland, P. J., & Pruden, A. (2016). Biodegradation of nanocrystalline cellulose by two environmentally-relevant consortia. Water Research, 104, 137–146. https://doi.org/10.1016/j.watres.2016.07.073

(20) Tayeb, A. H., Tajvidi, M., & Bousfield, D. (2020). Paper-based oil barrier packaging using lignin-containing cellulose nanofibrils. Molecules, 25(6). https://doi.org/10.3390/molecules25061344

(21) Zhao, Y., Xiao, S., Yue, J., Zheng, D., & Cai, L. (2020). Effect of enzymatic hydrolysis lignin on the mechanical strength and hydrophobic properties of molded fiber materials, Holzforschung, 74(5), 469-475. doi: https://doi.org/10.1515/hf-2018-0295

(22) Lewis, A., Waters, J. C., Stanton, J., Hess, J., & la Cruz, D. (2016). Macromolecular Interactions Control Structural and Thermal Properties of Regenerated Tri-Component

Blended Films. International Journal of Molecular Sciences, 17(12). https://doi.org/10.3390/ijms17121989

(23) Richard, T. (1996). The Effect of Lignin on Biodegradability. Cornell Composting, Cornell Waste Management Institute.