

Biopolymer Films for Product Packaging

Partnered with Method Products, pbc.

Constancia Dominguez, Josue Ruiz,
Grayson Hamaker-Teals, Amanda Guan

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Product Packaging Team



(From left to right)

Constancia Dominguez

MS in Environmental Health Science & Industrial Hygiene Program

Josue Ruiz

MPH in Epidemiology & Biostatistics Program

Grayson Hamaker-Teals

BS in Chemical Biology

Amanda Guan

BS in Materials Science and Engineering



Kaj Johnson, Method

Senior Director of R&D

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Executive Summary

For this project, the Greener Solutions course challenged our team to work with Method to design a safer alternative to using PFAS (Per- and Polyfluoroalkyl Substances) as a moisture and grease barrier within the product packaging industry. Our presented challenge was not only to find alternatives suitable for replacing the current physical characteristics and properties of the barriers applied on paper packages, but also to utilize renewable resources that involved fewer human and environmental harms in the creation, use, and disposal of the products. Method Products offer a wide range of cleaning products; for our project we narrowed these down to the three most basic: laundry powder (an example of dry powders), laundry detergent (an example of high concentrated liquid solvent), and dish soap refill (an example of high water content solutions).

We developed our initial strategy, biopolymer films, after we considered different renewable resources for our product base. Biopolymers are derived from natural sources and can act as a moisture barrier; this led us to consider its purpose as a package which best works with dry powders, due to its lower threshold for moisture barrier. Building off of renewable biopolymers, our group considered additional properties to existing packages to enhance their uses. Chemical additives, in the form of cross-linking reagents, improve biopolymer based film properties for highly concentrated liquid solutions by increasing the water moisture barrier of the products. Our final strategy, physical additives, takes the form of nanofillers: natural clays and fibers. The threshold of this strategy falls in between highly concentrated liquids and high water content liquids due to its increased strength for moisture barriers. These three strategies collectively correspond directly to a specific product package. That being said, with more experimentation of the specific combination of biopolymers and additives incorporated within films for product packaging, future teams would be able to develop a package suitable for a combination of dry powders and high water content solutions.

Introduction

Background

In the last 50 years, synthetic, petroleum-based plastics have become an indispensable part of our everyday lives. First developed in 1907 as electrical insulation, synthetic plastics soon found their place in single-use applications, such as shopping bags, plastic cutlery, and product packaging. Synthetic plastic has become so ubiquitous that 8% of the world's oil consumption goes towards its raw material and production. However, unlike bio-based plastics that eventually break down, the EPA reports that “every bit of plastic ever made still exists.” In response to these hazard concerns that first arose in the 1960s, environmental groups and industry have pushed for recycling initiatives and infrastructure. Even so, most synthetic plastics go straight to landfills or the ocean, and recycling them requires even more energy than manufacturing them. Furthermore, research shows that the largest culprits of plastic waste are containers and packaging.⁷⁴

Therefore, paper, or cellulose-based, packaging, has been proposed as a promising replacement for synthetic plastic packaging. In addition to requiring less energy to recycle than to make it from scratch,⁷⁴ paper packaging's structural integrity, low cost, and biodegradability make it an especially attractive alternative. However, because of its fibrous and hydrophilic nature, cellulose-based packaging alone cannot adequately address moisture barrier needs, especially in formulated product packaging. As a result, paper packaging has traditionally relied on the barrier properties compensated by polyolefins, such as polyethylene and polypropylene, along with per- and polyfluoroalkyl substances, PFAS (**Figure 1**).

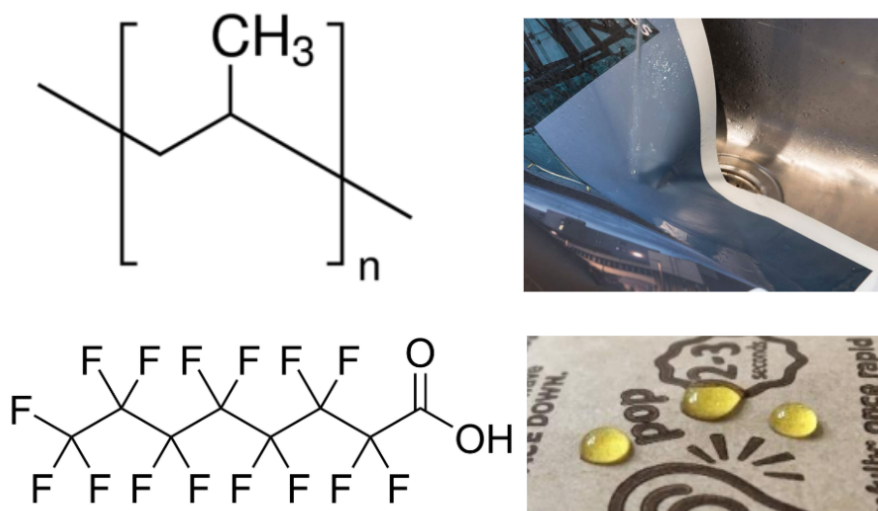


Figure 1: (Top) Polypropylene chemical structure and application as a coating for water resistant printer paper⁷⁵; (Bottom) Perfluorooctanoic acid (PFOA) chemical structure and application as grease barrier for food packaging.⁷⁶

However, while technically excellent, as exemplified by polypropylene's outstanding water resistance and PFOA's ability to cause beading of oil droplets, both polyolefins and PFAS present environmental and health concerns. Polyolefins, although recyclable on their own, are still synthetic and render the entire packaging system non-biodegradable, non-recyclable, and ultimately persistent in the environment when applied as a film. On the other hand, PFAS are known to be toxic, carcinogenic, and persistent. The negative externalities of these bad actors suggest a need for sustainable alternatives that not only eliminate the aforementioned hazards, but also perform as a sufficient moisture barrier for paper packaging.

Method Products, pbc.

Method Products, headquartered in San Francisco, California, produces planet-friendly and design-driven cleaning products, such as laundry powders, liquid detergents, and dish soaps (**Figure 2**).



Figure 2: Overview of Method Home's expansive array of cleaning products as advertised on their website, methodhome.com.⁷⁷




With brands such as Method, Ecover, Babyganics, and Mrs. Meyers Clean Day, Method Products promotes responsible sourcing and ingredients throughout its supply chain. Currently, recycled plastic bottles and pouches house their naturally-derived, biodegradable, and vegan formulations--some packaging even has a 70% lower carbon footprint compared to virgin plastics. In addition, Method designs their packaging with mostly plastics 1-PET and 2-HDPE for maximum recyclability, efficiency, and reliability. They also utilize mixed materials, plastic 7, for their current refill pouches that offer a 78-82% water, energy, and plastic savings compared to a standard plastic 1 or 2

bottle.⁷⁷ That being said, in an effort to continue pioneering greener solutions, Method has expressed interest in moving towards cellulose-based, paper packaging for its wide line of products. Since current moisture barriers for paper-packaging rely on persistent PFAS and petroleum-based films, our challenge is to find an alternative in coatings for cellulose-based packaging that improves moisture barrier properties, lowers environmental hazards, and reduces negative health impacts. In addition to these alternatives, the materials would need to be compatible with surfactant-based products that would not damage the primary packaging. Collectively, these strategies will allow Method Home to further champion sustainability in formulated products.

Approach and Inspiration

Product Needs and Success Criteria

Our first priority in determining the best solution for moisture barrier films in formulated product packaging was to categorize Method products by dilution and water content, and thus their moisture barrier requirement (**Figure 3**). Through discussions with Kaj Johnson, Senior Director of R&D at Method, we divided Method products into three types of formulations, as tabulated below.

Laundry Powders 	Detergents + Concentrates 	Soaps + Dilute Liquids 
<p>Laundry powders can cake and draw in moisture. This can make films brittle.</p> <p>Films should prevent moisture coming into the package.</p>	<p>Concentrated liquids can dissolve films, but barrier issues can be solved by the product composition.</p> <p>Films should keep liquid contained and not dissolve in solution.</p>	<p>Dilute liquids can dissolve moisture barrier films and need a very strong moisture barrier.</p> <p>Films should keep liquid contained and not dissolve in solution.</p>

Increasing dilution and moisture barrier requirements

Figure 3: Moisture barrier spectrum for three different types of Method products. Film for paper packaging should aim to contain the product without causing any damage to the primary packaging.

The first type of formulation is laundry powders and other solid formulations. While powders may not leak out of a package in the same way other formulated products would, they may draw in moisture and cake, in addition to making packaging films brittle. Thus, barrier films should prevent moisture from coming into the package. Next along the dilution spectrum are laundry detergents and other concentrated liquids. Because product composition may resolve concerns of concentrates dissolving moisture barrier films, the primary goal for this mid-class of formulated products is to keep liquid contained. Finally, because of their high water content, soaps and other dilute liquids require the strongest moisture barrier. In this case, films should, once again, keep liquid contained and ideally not dissolve in solution.

With these technical considerations, we outline our three success criteria for a moisture barrier material or treatment below in **Figure 4**.

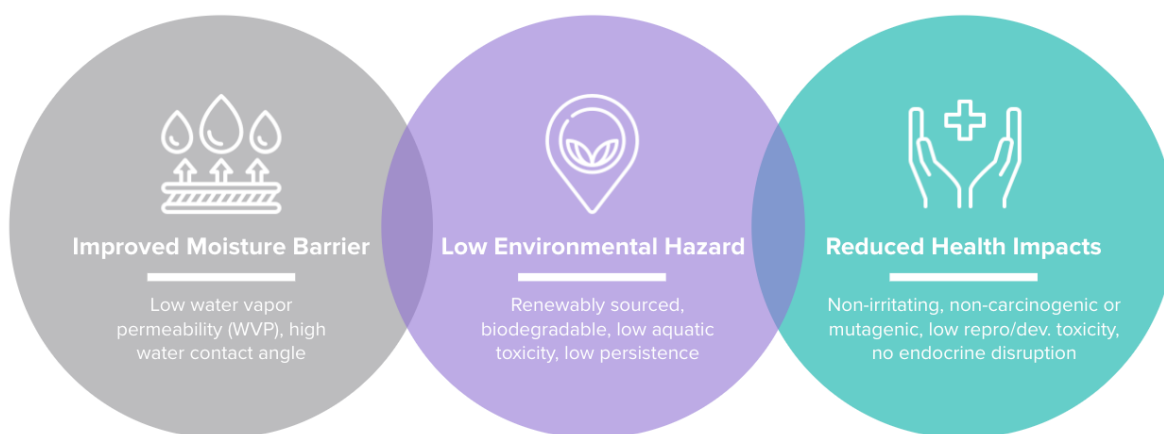


Figure 4: Outline of success criteria for proposed alternatives.

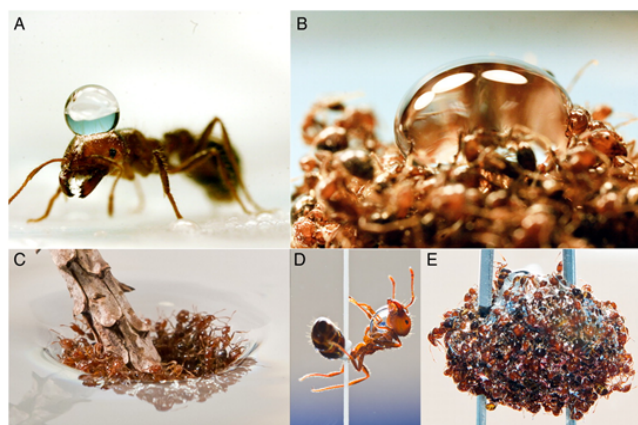
First, improved moisture barrier properties will be evaluated through water vapor permeability and water contact angle, as measures of product transmission and hydrophobicity, respectively. Second, the environmental hazards that we aim to lower are aquatic toxicity and persistence. The solution should also be biodegradable and not animal-based to uphold Method's vegan, cruelty-free product vision. Third, the solution should have low reproductive and developmental toxicity, in addition to being non-carcinogenic, non-mutagenic, non-irritating to the eyes and skin, and non-endocrine disruptive. We approached our evaluation, as detailed in the following strategy sections, by making recommendations based on how proposed solutions compared to bad actors in both technical and hazard assessments.

On top of the aforementioned success criteria, our group explored converting formulated liquids and powders into solid tablet products that consumers could add water to at home. This approach shows promise in completely eliminating the need for a moisture barrier, but we did not further investigate the strategy because we wanted to pursue a solution that would best adapt to Method's current eco-friendly product line.

Inspiration

Our group found initial inspiration in waterproof ant rafts--many ant species have a chitin polymer coating within their exoskeleton, and by lightly biting onto each other, they create a waterproof and breathable barrier (**Figure 5**). Furthermore, while ants bite onto each other in order to form a very large scale form of weaving together a moisture barrier, on a chemical scale, this became a metaphor and jumping point to look into chemical weaving, specifically in the form of crosslinking.⁵⁰

Water repellency of the ant rafts.



Nathan J. Miot et al. PNAS 2011;108:19:7669-7673

PNAS

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Figure 5: Water repellency of ant exoskeleton (composed of chitin) as an ant raft formation via “cross-linking” obtained from *Proceedings of the National Academy of Sciences*.⁵⁰

A large concern for biopolymers as a moisture barrier, as expanded on later in *Alternative Recommendation 1*, is that biopolymers often underperform in comparison to leading industry moisture barriers (PFAS and polyolefins) in terms of mechanical and moisture barrier properties. Additives can help compensate for these shortcomings. Vulcanization, as depicted in **Figure 6** below, uses sulfur to crosslink rubber, achieving increased tensile strength and elasticity among other properties.⁵¹ Thus, the metaphor of physically networked waterproof ant rafts and the actual strengthening of vulcanized rubber inspired us to investigate the potential of both chemical and physical crosslinking alternatives.

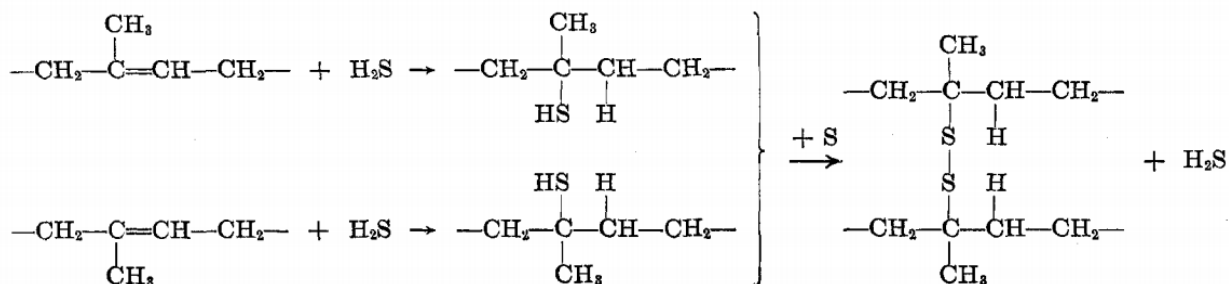


Figure 6: Vulcanization of rubber via sulfur.⁵¹

Alternative Recommendation 1: Biopolymer-based films

Background

Opposing common beliefs, biopolymers actually preceded the invention of plastics from petroleum-based sources. Biopolymers are obtained from natural sources, either biosynthesized or chemically synthesized from biological material. Inspired by the chitin in waterproof ant rafts, our team pursued biopolymer films as our first strategy. In addition to being biodegradable, biopolymers are safe for consumption; many biopolymers, such as chitin (converted to chitosan after deacetylation) and pectin, function as food-grade gelling agents. In addition, due to the large variety and blends of biopolymers, they offer the opportunity to design seemingly endless combinations catering to specific desired functionalities. “Smart packaging” technologies, such as biopolymer additives designed to behave differently after exposure to different substances and environments, will further enhance biopolymer combination designs.

Additionally, biopolymers are an attractive alternative because of their ability to be cross-linked via chemical additives (alternative 2) and can reinforce their barrier properties through physical additives (alternative 3). For this investigation, we analyzed the technical performance and hazard assessment of three biopolymers: chitin, pectin, and gelatin (**Figure 7**).

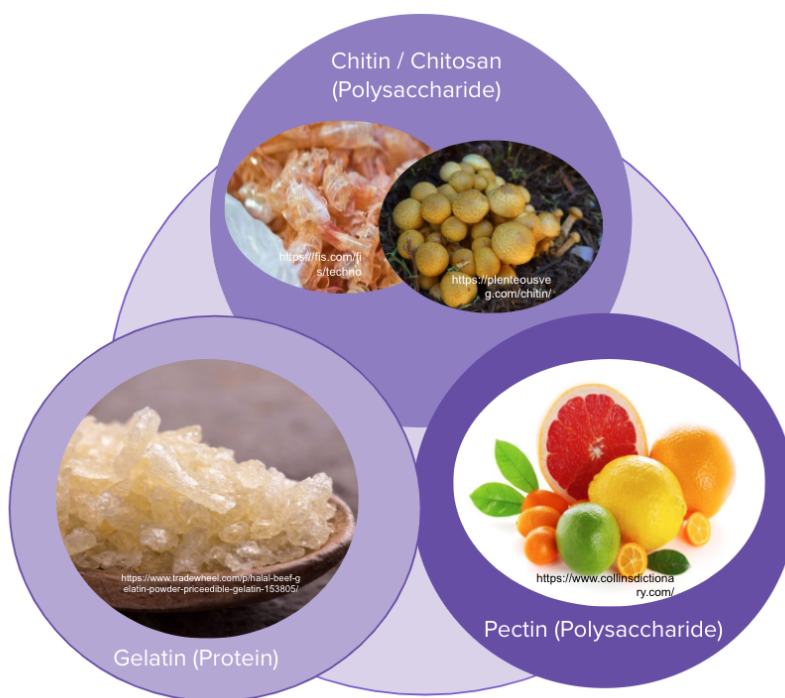


Figure 7: Biopolymers of interest for alternative recommendation 1.

These three biopolymers are attractive candidates for the application of biopolymer based films as they are all current waste products that can be utilized for another purpose, thus making a linear economy more circular. Additionally, their application in hydrogel films used for the pharmaceutical industry is readily available, and research has been recently extended to their application in the food packaging industry due to their high level of biodegradability.

Chitin, the second most abundant biopolymer in the world after cellulose, comes from a multitude of natural sources such as squids, crustacean shell waste, and fungi. Its deacetylated form, chitosan, has a positive charge on the amino group under acidic conditions and binds to negatively charged molecules such as fats and lipids. The ability of the free amine groups in chitosan that allows for the formation of covalent bonds with metal ions is of great interest.⁶ Furthermore, pectin is a linear and stiff polysaccharide extracted from citrus peels and apple pomace by hot dilute mineral acid. Specifically, the low-methoxyl pectins provide the ideal charge interactions for hydrogel films.⁶ Generally polysaccharides, including chitosan and pectin, display minimal toxicity and are widely available. They have the potential to form strong films, but because of their hydrophilic nature, they exhibit poor water vapor resistance properties. In addition, polysaccharides have been combined with proteins, such as gelatin, to form composite hydrogel films. Gelatin was the selected protein of interest due to the vast research available for its combination with pectin through electrostatic interactions in hydrogel films.^{6,17} Gelatin is most commonly derived from animal collagen; however, there are vegan alternatives available. Through the combination of either pair of polysaccharide-polysaccharide or polysaccharide-protein, they can create the foundation for a sustainable film, but also have the option for further mechanical and barrier property enhancements that will be discussed in alternative recommendations 2 and 3.

Technical Performance

As a preliminary strategy, biopolymers alone as a moisture barrier film were evaluated for their barrier and mechanical properties. We describe each specific performance metric in detail below.

- *Water vapor permeability (WVP)*: Measure of how much water vapor passes through a barrier in a given amount of time. Unlike water vapor transmission rate (WVTR), WVP is normalized by the thickness of the barrier. Ideally, a good moisture barrier would have a low WVP.
- *Water contact angle*: Angle between a barrier film and the outer edge of a water droplet on its surface. More hydrophobic, water-resistant surfaces cause significant beading and increased water contact angles. In general, a water contact angle over 90 degrees would signify hydrophobicity.

- *Tensile strength*: Material resistance to deformation. Ideally, we want our moisture barrier film solution to be stiff enough (high enough tensile strength) to hold the shape of packaging and the formulated contents inside.
- *Total elongation at break*: Percentage that describes the change in length when the material snaps, breaks, or fractures. Elastic materials have higher percent elongations. Although our alternative does not need to be particularly stretchy, very low elongations may present a brittleness concern.

We evaluated the potential success of leading biopolymer alternatives--chitin/chitosan, pectin, and gelatin--by comparing their technical properties against those of “gold standards” PFAS, polyethylene, and polypropylene obtained from material databases. As PFAS describes a large class of fluorinated substances, Teflon film was used as a baseline for performance criteria comparisons, as it is prevalent in non-stick coatings and has an abundant amount of data to compare.

From our ant exoskeleton inspiration, we first evaluated chitosan, the deacetylated form of chitin. Chitosan has a WVP several orders of magnitude higher than those of the leading industry coatings,³⁰ a comparable water contact angle,³⁸ and slightly lower tensile strength and elasticity.^{40,41} Because chitosan is created from the deacetylation of chitin, its properties may hinge upon the extent of deacetylation, which may affect overall properties. Next, pectin, a biopolymer found in fruit skins, was evaluated, and similar to chitin, demonstrated a WVP several orders of magnitude higher than those of the gold standard materials. In addition, pectin falls short of the 90 degree hydrophobicity benchmark in water contact angle. In terms of mechanical properties, pectin demonstrates some rigidity with a medium tensile strength and poor elasticity. Lastly, we investigated gelatin. Again, it should be noted that gelatin is derived from animal products, and thus may not be a fitting solution for Method but still reflects valuable information regarding the moisture barrier potential of biopolymer proteins as a whole. Gelatin lacked specific quantitative data for its moisture barrier properties, but was described by Shit and Shah in 2014 as non-ideal.³³ Tensile tests on gelatin demonstrate relatively high tensile strengths, definitely exceeding those of all of the gold standard solutions, but has very poor elasticity, which may become an obstacle in product packaging.⁴² These results, in addition to specific quantitative data, are summarized in **Table 2**. Biopolymers clearly have inferior barrier and mechanical properties to PFAS and polyolefins, indicating a need for potential additives to improve its performance.

Furthermore, some data gaps stem from product requirements--moisture barrier films may not need to be 400% elastic like polyethylene. More specific research and evaluation must be done with Method product formulations in these paper packaging-film encasements in order to best understand the necessary threshold of water resistance and mechanical strength.

		PFAS*	Polyethylene	Polypropylene	Chitin/Chitosan	Pectin	Gelatin
Barrier Properties	Water Vapor Permeability (WVP) (g/m ² day*atm)	0.00788 ⁽⁴³⁾	LDPE: 0.008 ⁽³³⁾ HDPE: 0.002 ⁽³³⁾	0.0575 ⁽⁴³⁾	.315 ⁽³⁰⁾	0.135 ⁽³⁴⁾	Non-ideal mechanical properties and water vapor barrier ⁽³³⁾
	Water Contact Angle	106.94° ⁽⁴⁷⁾	LDPE: 91° ⁽³⁸⁾ HDPE: 93° ⁽³⁸⁾	97° ⁽³⁸⁾	82-104° ⁽³⁸⁾	62.1° ⁽³⁴⁾	
Mechanical Properties	Tensile Strength (MPa)	10.0 - 45.0 ⁽⁴⁶⁾	LDPE: 13.2 ⁽³⁶⁾ HDPE: 13.9 ⁽³⁶⁾	18 - 22 ⁽⁴⁴⁾	Neat: 37.7 ⁽⁴⁰⁾ In 2% Solution: 6.99 ⁽⁴¹⁾	7.10 ⁽³⁴⁾	70 ⁽⁴²⁾
	Total Elongation at Break	40.0 - 650% ⁽⁴⁶⁾	LDPE: 456% ⁽³⁶⁾ HDPE: 334% ⁽³⁶⁾	50 - 145% ⁽⁴⁴⁾	Neat: 49.5% ⁽⁴⁰⁾ In 2% solution: 72.70% ⁽⁴¹⁾	7.17% ⁽³⁴⁾	1.5% ⁽⁴²⁾

*Teflon (Polytetrafluoroethylene-PTFE) was used as a baseline for PFAS performance criteria comparisons.

High Efficiency	Medium Efficiency	Low Efficiency	Data Gap
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Table 1: The technical performance comparison of the 3 alternative biopolymers for strategy 1 and the current baseline substances. High efficiency refers to properties similar or exceeding those of gold standards, medium efficiency refers to slightly worse, and low efficiency refers to much worse, often at least by one order of magnitude. LDPE = low density polyethylene; HDPE = high density polyethylene.

Hazard Assessment

PFAS are highly effective at repelling water and grease. The two types of PFAS that are most widely used are PFOS (perfluorooctane sulfonic acid) and PFOA (Perfluorooctanoic Acid). PFOA is one of the chemicals used as a baseline to evaluate the strategy's health and environmental performance for simplicity (**Table 2**). An evaluation of PFOA was conducted in 2008 by various authoritative agencies who concluded PFOA's high resistance against degradation in the environment and high incidence of bioaccumulation.²⁵ Additional studies have demonstrated that PFOAs have long-term toxic effects in aquatic organisms and have been linked to cancer in both humans and laboratory animals.^{23,26,27} Following PFOA, the next two chemicals that were classified as baselines within the product packaging industry were the polyolefins, polyethylene and polypropylene. Both are the most common form of synthetic polymers used for film coatings due to their benchmark abilities to seal paper by overcoming its porosity and hygroscopicity.¹ However, the use of polyolefin films to achieve such a moisture barrier causes the material to lose its biodegradation, thus displaying a high level of persistency.

The first alternative biopolymer is chitosan, the deacetylated form of chitin. Depending on the percentage of deacetylation of chitin, both forms may be present when added during the formulation process of a film. We assessed the potential hazards of chitosan because it is highly researched in biopolymer films for product packaging. Generally,

chitosan is biodegradable, presents minimal toxic effects in humans, and does not report any effects related to carcinogenicity or mutagenicity.^{4,9} Nevertheless, chitosan has been classified as hazardous to the aquatic environment by the Global Harmonized System of Classification and Labeling of Chemicals (GHS) due to toxicity studies that have been conducted in trout and zebrafish where oxygen interference and physiological disorders were noted.^{21,22} To mitigate this hazard during the manufacturing process of the biopolymer based films, chitosan should not be discarded into any bodies of water. Thus it should be immediately transferred to a separate designated container that will be taken to an approved waste disposal plant.

Leading into the next alternative, the team researched a type of biopolymer alternative that could recycle an existing waste product, while having substantial research in film applications available. A linear polysaccharide that can be extracted from citrus peels and apple pomace is pectin. Generally, it does not bioaccumulate in the environment and is not persistent. The European Food Safety Authority (EFSA) Panel on Food Additives and Nutrient Sources reported no chronic toxicity effects in its evaluation of pectin. Maintaining the same mindset of an alternative biopolymer that could be recyclable and have research readily available, gelatin was selected as the last alternative.

Similar to pectin, gelatin was not found to be persistent in the environment or bioaccumulative. Additionally, authoritative lists classified gelatin as low concern to human health. Compared to the baseline substances, these alternatives are easily sourced as they are either existing waste products or are naturally derived. Additionally, they are readily biodegradable compared to polyolefins and PFAS.

It is important to note that for most of the baseline substances and alternatives, authoritative documentation reports adverse effects to the respiratory system.^{2,7,8} If substances are manufactured in a powder form, precautions need to be in place when they are added during the formulation of the biopolymer films. Therefore, with the proper engineering controls, the hazards can be mitigated. This is crucial to consider from an occupational perspective during the formulation process and how they are added during the formulation process. The hazard assessment comparison between the baseline substances and the alternative biopolymers are summarized in **Table 2**.

<i>Bad Actors & Biopolymers</i>	PFAS	Polyethylene	Polypropylene	Chitin/Chitosan	Pectin	Gelatin
Persistence	Persistent in Environment ⁽²⁵⁾	CEPA classifies as a high level of persistence	CEPA classifies as a high level of persistence	Biodegradable ⁽⁴⁾	NICNAS - Tier I (No risk to the environment by natural decay)	NICNAS - Tier I (No risk to the environment by natural decay)
Bioaccumulation	Bioaccumulative ⁽²⁴⁾	OECD - Not classified as bioaccumulative	OECD - Not classified as bioaccumulative	NICNAS - Tier 1 (Substance that is derived from natural products or materials, not bioaccumulative)	NICNAS - Tier 1 (Substance that is derived from natural products or materials, not bioaccumulative)	NICNAS - Tier 1 (Substance that is derived from natural products or materials, not bioaccumulative)
Sensitivity / Irritation (Eye, Skin, Respiratory)	Eye irritants, adverse respiratory effects ⁽²⁷⁾	Adverse effects to respiratory health ⁽⁷⁾	Agent Causing Occupational Asthma ⁽⁸⁾	No adverse effects reported, Toxtree reported it an non-irritant for skin. ⁽⁹⁾	Agent Causing Occupational Asthma ⁽⁸⁾	Agent Causing Occupational Asthma ⁽⁸⁾
Toxicity (Dev & Repro, Systemic, Neuro.)	Reproductive, Developmental, Systemic, Neurological, Immunological ^(23, 26)			No adverse effects were reported for Humans ⁽⁹⁾	No adverse effects were reported in a chronic toxicity study	
Aquatic Toxicity	Aquatic Toxicity ⁽²⁷⁾	MSDS: Eco-toxicity is expected to be minimal	MSDS: Eco-toxicity is expected to be minimal	GHS Category 1- Hazardous to the aquatic environment, acute hazard. ^(21, 22)		OECD - Low ecotoxicological concern ⁽¹⁾
Carcinogenicity / Mutagenicity	Carcinogenic, ^(26, 27)	IARC Group 3 (Not classifiable as carcinogenic to humans)	IARC Group 3 (Not classifiable as carcinogenic to humans)	Literature reports no effects ⁽⁹⁾	NICNAS - Tier I (No risk to human health)	NICNAS - Tier I (No risk to human health)
Endocrine	Endocrine Disruptor ⁽²⁷⁾					

Low Hazard

Medium Hazard

High Hazard

Data Gap

Table 2 : The hazard assessment comparison of the 3 biopolymers for strategy 1 and the current baseline substances.

Feasibility

Although biopolymer based films pose minimal hazards in comparison to our baseline substances, they lack in both barrier and mechanical properties that are necessary to form a sufficient film for more dilute products but may be suitable to prevent drawing in moisture for products like laundry powders. This is why our first strategy with the incorporation of biopolymer films is placed on the lower end of the moisture barrier spectrum (**Figure 4**). As demonstrated in the technical performance, the biopolymers do offer less intensive barrier/mechanical properties, however this is not necessarily a lost case. For certain product needs, our biopolymer film is not required to be elongated for long periods of time; so while these alternatives may not hold to the same standard as PFAS, we have no practical need for that property in the desired product. Therefore, as chitosan has been heavily researched in terms of hazard effects across most endpoints, while efficiently performing with a high water contact angle, it is recommended that preliminary study efforts should be focused on chitosan as the primary alternative for biopolymer based films for product packaging.



Laundry Powders



Detergents



Soaps



Increasing dilution and moisture barrier requirements

Figure 8: The moisture barrier spectrum with the first alternative recommendation that is predicted to meet requirements for films that hold powder products.

Alternative Recommendation 2: Adding chemical cross-linking reagents to biopolymer based films

Background

A novel approach for biodegradable packaging materials has been studied that includes a dry polyion-complex hydrogel. When a normal dry hydrogel (e.g. a packaging film) begins to absorb water, hydration at the most polar hydrophilic groups will take place, thus leading to the swelling of the matrix.⁶ This novel approach builds on the idea of utilizing a dry hydrogel film for product packaging, but with the addition of chemical cross-linking reagents. It has been proposed that biopolymer interactions can be strengthened by covalently binding their different structures through the introduction of predominantly charge interactions from the chemical cross-linking reagents added in the dry hydrogels, thus creating a polyion-complex.⁶ This process of cross-linking in polymer chemistry leads to multidimensional extension of polymeric chains resulting in a stabilized network structure. The dry polyion-complex hydrogel concept can be applied to films used within product packaging to achieve a stronger moisture barrier. There are different types of cross-linking, but this report will solely focus on the chemical additives that can be added to biopolymer-based films to improve their desired mechanical properties and aqueous stability. In the industry, glutaraldehyde is a common cross-linking reagent due to its high performance and availability. However, toxicological concerns to human health remain for glutaraldehyde, therefore the team researched safer alternatives that could be naturally derived.

Technical Performance

The functional properties a film encompasses to achieve a moisture barrier is dependent on the combination of biopolymers selected. Each combination of biopolymers formulated within the films achieves limited mechanical and/or barrier properties. Therefore, chemical additives of crosslinking agents were considered as an alternative to address a property or properties the initial combination of biopolymers did not meet. To assess the technical performance of adding cross-linking reagents to different biopolymer based films, the team drew quantitative measures from the literature to obtain the following measures: water vapor permeability (WVP), water contact angle, tensile strength, and total elongation at break. Therefore, the values in **Table 3** are only relative values to the context of the studies the values were obtained from as the biopolymer based films were formulated in different ratios or concentrations, and may have had additional additives. Ultimately, the technical performance was assessed as high efficiency when there was an improvement of a metric, medium efficiency when there was little to no effect, and low efficiency when the metrics worsened.

Generally, glutaraldehyde is one of the most effective protein cross-linking reagents used in film formulations, therefore it was selected as a baseline for assessing the technical performance of the alternative chemical cross-linking reagents. We drew on examples in the literature to estimate how glutaraldehyde as a cross-linking reagent would change the technical performance of a biopolymer film. In a study by Farris et al., the mechanical properties of a composite film composed of both gelatin and pectin was investigated.⁵⁶ An increase in tensile strength and total elongation was noted, therefore improving the efficiency of the film's mechanical performance. Although glutaraldehyde does not address WVP or the exact water contact angle for liquid repellency in this example, this study provides insight that the combination of biopolymers into a single film with a cross-linking reagent could achieve the higher performance criteria necessary for a film. This is demonstrated in **Table 3** where the barrier properties of a film is addressed when looking into a single biopolymer based film composed of either gelatin or chitosan alone with the addition of glutaraldehyde.

For alternative cross-linking reagents, the team strove to research naturally derived alternatives to see how well they performed in comparison to glutaraldehyde. The first alternative, genipin, was successful in the medical field as a tissue fixative and was recently studied for its application in films. As its application in films is new, it was difficult to completely assess its barrier properties in pectin or gelatin based films separately as the literature available was limited. However, in the same study by Farris et al. that investigated the properties of a gelatin-pectin film, they also studied the film's performance with genipin. The investigators reported lower water sensibility of the film when cross-linked with genipin.⁶ It is assumed that this would improve WVP in the films. Fortunately, genipin's performance in chitosan based films was substantial. In a study that investigated a chitosan/polyethylene oxide film, an increase in tensile strength and elongation was reported when genipin was added.¹⁰ From the limited research that is available for genipin's application in films used for packaging, it has collectively been the reagent that has addressed most improvement in performance metrics. Ultimately, this demonstrates the need for further experimental research in different biopolymer based films, and the importance for developing a performance standard when reporting metrics in films as these values reported within the literature are often limited and vague.

During our research in plant phenolics as potential alternatives, ferulic acid became a great candidate as it is naturally derived and its ability to cross-link in gelatin based films has been studied.³² In a study by Cao et al., no WVP effects were noted when added to a gelatin film and had an increase in tensile strength.³² Alternatively in another study by Woranuch et al., ferulic acid was coupled with chitosan for packaging film. This study found a decrease in water WVP and no effect on tensile strength of the film.³⁷ Although the performance metrics for ferulic acid was readily available for its application in films, it did not become an ideal alternative as its efficiency was not as high as genipin.

However, the possibility of it being an alternative in other biopolymer based films remains.

		Glutaraldehyde			Genipin			Ferulic Acid		
Biopolymer		Pectin	Gelatin	Chitosan	Pectin	Gelatin	Chitosan	Pectin	Gelatin	Chitosan
Barrier Properties	Water Vapor Permeability (g*mm/kPa *m ² *hr)		Decrease from 1.8 to 0.8 ⁽⁵⁶⁾	Little effect on WVTR ⁽⁶⁸⁾	Lower water sensitivity in gelatin-pectin films ⁽⁶⁾		No effect on WVTR ⁽⁶⁸⁾		No effect (0.00208 to 0.00201) ⁽³²⁾	Increase from 2.05 to 2.67 in ⁽³⁷⁾
	Water contact Angle			Increase from 110 to 118 ⁶⁸			Increase from 110 to 115 ⁶⁸			
Mechanical Properties	Tensile Strength (MPa)	Increase from 11.1 to 21.6 with Gelatin ⁽⁵⁶⁾	Increase from 1.2 to 3.2 ⁽⁴⁹⁾	Increase appx. from 75 to 140 ⁽⁵⁷⁾		Increase from 1.0 to 6.8 ⁽⁴⁸⁾	Increase from 39 to 50 in dry film ⁽¹⁰⁾		Increase from 86 to 96 ⁽³²⁾	No effect (19 to 20) ⁽³⁷⁾
	Total Elongation at Break	Increase from 151 to 159 with Gelatin ⁽⁵⁶⁾	Increase appx. from 8 to 29% ⁽⁴⁹⁾			Decrease from 211 to 13% ⁽⁴⁸⁾	No effect in dry film (9 to 10%) ⁽¹⁰⁾		Decrease from appx. 4.5 to 3% ⁽³²⁾	Decrease from 10.4% to appx. 8.3- 9.3% ⁽³⁷⁾

High Efficiency

Medium Efficiency

Low Efficiency

Data Gap

Table 3: The technical performance comparison of the 2 alternative cross-linking reagents for strategy 2 and the current baseline substances.

Hazard Assessment

While glutaraldehyde has had great success because of its commercial availability, it has been classified as hazardous for both humans and aquatic organisms. Due to the extensive research available for glutaraldehyde, it was established as a baseline for the health and environmental performance of chemical cross-linking reagents demonstrated in **Table 4**. Specifically, glutaraldehyde has been identified as a neurotoxicant in humans, but also has reported chronic toxicity within aquatic organisms.^{6,14} As it is a hydrophilic substance that will mainly partition with water upon release its the environment, it has been classified by authoritative agencies as being highly persistent in the environment. However, the level of persistence in the environment should be limited depending on the dose that is released. Lastly, it is important to note that it is also listed as a potential endocrine disruptor by the Endocrine Disruption Exchange (TEDX). Due to its toxicity concerns and persistence in the environment, safer alternatives have been investigated to replace glutaraldehyde as a cross-linking reagent, but it has been difficult to do so because of its high technical performance.

An ideal alternative is genipin, as it is naturally derived from the extraction of gardenia fruit. Genipin reacts spontaneously with proteins, collagen, gelatin, and chitosan.

Through these spontaneous reactions, genipin has been used for cross-linking gelatin and as a tissue fixative.¹⁰ This is an aspect that should be taken with a precaution as it may have the ability to cross-link human proteins. However, this is a general precaution that should be taken into consideration when handling any type of cross-linking reagent. In a study by Jin et al. that was conducted in 2004, genipin was compared to glutaraldehyde as an alternative cross-linking reagent for chitosan based films.¹⁰ This study concluded that genipin was 10,000 times less cytotoxic than glutaraldehyde. Although this study did not provide more insight to how the toxicity of the alternative was assessed, it was a discovery that encouraged the team to investigate the use of this cross-linking reagent.

Moving forward with the inspiration to seek other natural cross-linking reagents, a study by Cao et al. in 2007 investigated plant phenolics, specifically ferulic acid, as cross-linkers for gelatin gels.³² No adverse effects from toxicity studies performed on aquatic organisms or humans have been reported by authoritative agencies. In addition, the European Union (EU) has reported no evidence of it being an endocrine disruptor, but data gaps remain if it demonstrates any levels of carcinogenicity or mutagenicity. Among the alternatives, ferulic acid has the most research readily available to assess its health and environmental impacts. With the data that is available, both of the alternatives demonstrate lower persistency in the environment and low to none levels of toxicity compared to glutaraldehyde. This is extremely important for when deciding which cross-linking reagent will be utilized for specific biopolymer(s) based films as the combination is dependent on the technical performance criteria that is prioritized to meet the moisture barrier requirement of a specific type of product packaging.

Crosslinking Reagents	Glutaraldehyde	Genipin	Ferulic Acid	
Persistence	NICNAS - As other aldehydes, the environmental persistence of glutaraldehyde is extremely limited	Biodegradable ⁽¹¹⁾	Biodegradable ⁽³⁷⁾	Low Hazard
Bioaccumulation	OECD - Not classified as bioaccumulative			Medium Hazard
Sensitivity / Irritation (Eye, Skin, Respiratory)	GHS - H335, H317, H318 - May cause respiratory, skin and eye irritation		GHS - H335, H317, H318 - May cause respiratory, skin and eye irritation	High Hazard
Toxicity (Dev & Repro, Systemic, Neuro.)	Neurotoxicant, Physical Toxicity Concerns ^(6, 13)	Low cytotoxicity reported ^(10,11)	ECHA - No adverse effects in Acute toxicity studies in humans	Data Gap
Aquatic Toxicity	GHS (H411) - Toxic to aquatic life with long lasting effects ⁽¹⁴⁾		ECHA - No adverse effects in Aquatic Toxicity studies	
Carcinogenicity / Mutagenicity			ECHA - No evidence of mutagenicity or genetic toxicity in the limited studies that are available	
Endocrine	Listed on TEDX as Potential Endocrine Disruptor		EU - No evidence of endocrine disrupting activity	

Table 4: The hazard assessment comparison of the 2 alternative cross-linking reagents for strategy 2 and the current baseline, glutaraldehyde.

Feasibility

Cross-linking reagents are often toxic compounds that can produce unwanted reactions with the bioactive substances present in dry films. Depending on the biopolymer or combination of biopolymers that are incorporated within films, genipin could potentially address the performance gaps biopolymers based films alone had in barrier properties, specifically water vapor permeability. The main challenge in this alternative recommendation is when comparing the hazard assessment for cross-linking reagents due to the remaining data gaps for a few critical endpoints. However, from the data that is available, it can be concluded that the presented alternatives are safer than glutaraldehyde. Additionally for the performance criteria, genipin scored higher in terms of efficiency compared to ferulic acid. Ferulic Acid, while considered more green than the current bad actors, underperforms in terms of tensile strength and WVP. Therefore, it is proposed that through the combination of the first two alternative recommendations of incorporating a biopolymer into a film with the addition of a chemical cross-linking reagent, a stronger moisture barrier for product packaging can be achieved. Thus, this second alternative recommendation is ranked higher on the moisture barrier spectrum for packaging that holds concentrated liquid products (**Figure 9**).



Figure 9: The moisture barrier spectrum with the second alternative recommendation that is predicted to meet requirements for films that hold concentrated liquid products.

Alternative Recommendation 3: Adding physical additives to biopolymer based films

Background

Nanotechnology brings additional water resistance to biopolymers and nanocomposite film. This added benefit further maintains the existing water vapor and gas permeability of composites and does not deteriorate them in the presence of high relative humidity or with direct water contact. Inorganic and organic nanoparticles can also be integrated with the biopolymers to contribute further in the barrier against water and oil. Specifically this alternative recommendation will focus on the incorporation of nanofillers into a biopolymer matrix to form nanocomposites found to enhance water barrier properties, while also maintaining the biodegradability component.⁶⁷ The category of nanofillers encompasses both natural clays and fibers. Within the natural clays, montmorillonite (MMT) best exemplifies a physical additive because it is the most widely used type of silicate clay in polymer nanocomposites. As demonstrated in **Figure 10**, different forms can take place with the addition of silicate layers with polymers.⁶⁰ The highest improvement in the barrier properties occurs in the exfoliated nanocomposite form, which maximizes the reactive relationship between the layered silicate and the polymers. Although this can provide great insight into the technical performance of films, its application to specific biopolymer based films needs further research before making final conclusions. Additionally, this performance metric is not consistently reported in the literature, therefore increasing its difficulty to make accurate recommendations of how it can address specific barrier properties.

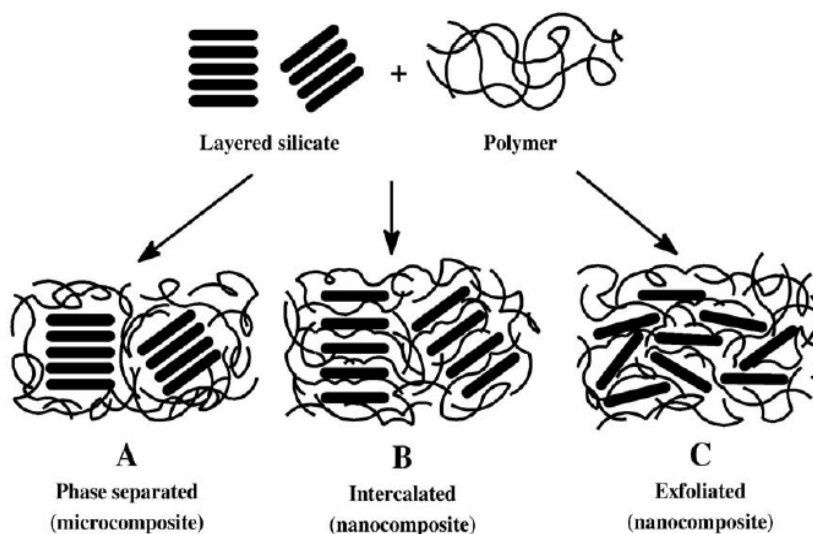


Figure 10: Scheme of three types of composite structures: (A) phase separated microcomposites, (B) intercalated nanocomposites, and (C) exfoliated nanocomposites.

The next category of nanofillers the team investigated were fibers, specifically Cellulose Nanocrystals (CNC). Among such nanomaterials, Cellulose Nanocrystals are primarily obtained from plant sources and improve the biopolymer properties: nanoscale dimensions, high surface area, unique morphology, low density renewability, biodegradability, and high mechanical strength.⁶¹ Crystalline nanocellulose fibers are known to be more efficient than their micro-sized counterparts for the reinforcement of polymers. Because the hydrogen bonding interactions between the nanosized particles lead to the formation of a percolated network, it provides a proper dispersion of the nanofibers in the matrix, thus leading to the reinforcement of the polymers.⁶⁹ The conversion of cellulose fibers into nanocrystals through acid hydrolysis results in the formation of whiskers with a large aspect ratio, mainly due to their nanoscale dimensions.⁶¹ As demonstrated in **Figure 11**, the acid treatment leads to the removal of the para-crystalline domains that are regularly distributed along the microfibrils, and leads to the formation of rod-like cellulose nanocrystals.⁷³ From there, the nanocrystals can be physically incorporated into various polymer matrices to form polymer nanocomposites.

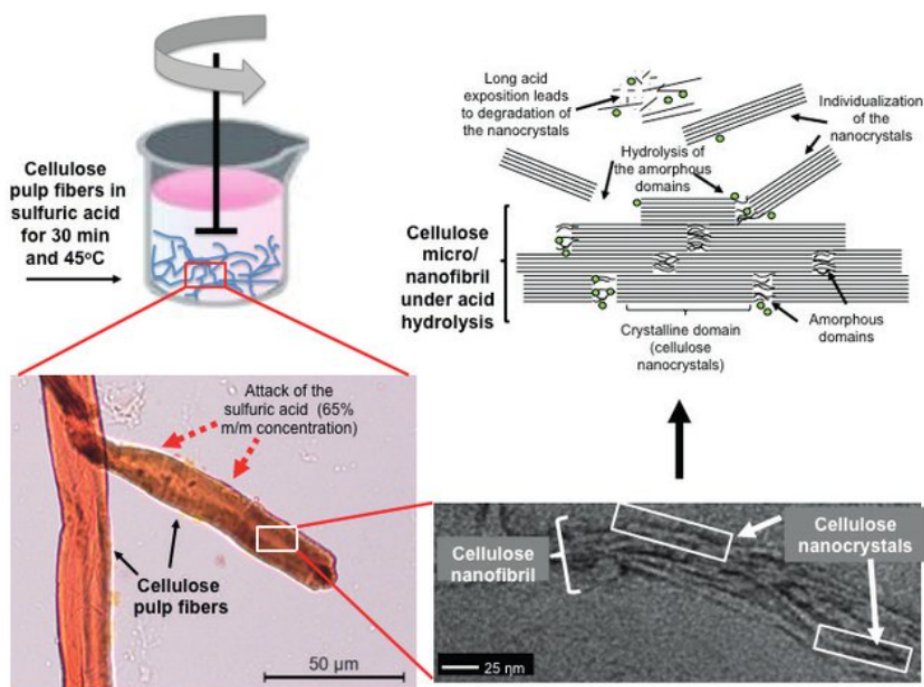


Figure 11: Scheme of the acid hydrolysis of the cellulose pulp fibers, with the individualization of the cellulose nanocrystals (Prado et al., 2017).

Technical Performance

Our first example of a natural clay, Montmorillonite, has extensive positive qualities due to its ability to strengthen biopolymer films and reinforces material in a naturally abundant, nontoxic, inexpensive, chemically and thermally stable manner.⁶⁶ Because of its hydrophilic character, montmorillonite can form stable suspensions in water, thus facilitating dispersion in water soluble polymers. In a study by Chaichi Maryam et al., an increase in the montmorillonite concentration within a pectin nanocomposite film caused a decrease in its water adsorption and water solubility. This suggests that at the nanoscale level, the swell component of montmorillonite will not concern the development of this barrier film.⁶⁰ As demonstrated in **Table 5**, the general trend notes a positive efficiency across the board for all of the other performance metrics obtained from the literature relating to biopolymer based films with the addition of montmorillonite. Additionally, all of the biopolymer based films had an increase in tensile strength, but a decrease in total elongation at break. There is a missing data gap for the water contact angle, which would need additional experimentation to properly fill and assess as a final moisture barrier film mixture.

Our other physical additive, nanocellulose components in the form of micro- and nanofibrillated cellulose (NFC/MFC) or cellulose nanocrystals (CNC) provide specific gas and oil barrier properties in addition to good mechanical properties when used in natural form. Neutralized CS (Chitosan) fibre mats are non-toxic and biocompatible, and therefore have great potential for its use as filtration membranes and tissue engineering scaffolds.^{17,18} We can also see from the information gathered in **Table 5** that all three of our biopolymer bases paired with cellulose nanocrystals showed a significant decrease in WVP (high efficiency compared to the biopolymer without the CNC) as well an increase in tensile strength (high efficiency compared to the biopolymer without the CNC). With a lack of data concerning the water contact angle measurements, more information is needed to see the effectiveness of cellulose nanocrystals on pectin and gelatin biopolymer based films; however the chitosan biopolymer based film appears to have moderate efficiency with this additive. The integrity of the total elongation at break for biopolymers with physical additives varies, with a highly efficient increase with pectin, a low efficiency decrease in gelatin and a lack of data concerning the effects of chitosan based biopolymers. In comparison with the biopolymer films with added montmorillonite, the cellulose nanocrystals infused biopolymers showed close similarities for both barrier and mechanical properties.

		Montmorillonite (MMT)			Cellulose Nanocrystals (CNC)		
Biopolymer		Pectin	Gelatin	Chitosan	Pectin	Gelatin	Chitosan
Barrier Properties	Water Vapor Permeability (g*mm/kPa *m2* hr)	Decrease from 2.52 to 1.51 ⁽⁵¹⁾	Decrease from 6.2×10^{-13} to 1.8×10^{-13} ⁽⁵²⁾	Decrease from 2.6×10^{-7} to 1.6×10^{-7} ⁽⁵⁴⁾	Decrease from 4.6×10^{-7} to 3.3×10^{-7} with 5 wt% addition of the CNC ⁽⁶⁰⁾	Dec. from 2.2×10^{-7} to 1.6×10^{-7} with 4 wt% addition of CNC ⁽⁶¹⁾	Decrease by 45% with 3% addition of CNC ⁽⁶³⁾
	Water contact Angle						Between 5° to 30° at a rate 22 of 2°/min ⁽⁶³⁾
Mechanical Properties	Tensile Strength (MPa)	Increase from 2.4 to 4.3 ⁽⁵¹⁾	Increase from 10 to 38 ⁽⁵⁵⁾	Increase from 61 to 69 in 5% MMT/Chitosan film ⁽⁵⁴⁾	Increase from 7.1 to 13.2 with 5 wt% addition of CNC ⁽⁶⁰⁾	Increase from 83 to 108 with 4 wt% addition of CNC ⁽⁶¹⁾	Increase from 79 (neat chitosan) to 86- 98 with the addition of 1- 10%, ⁽⁶⁹⁾
	Total Elongation at Break	Decrease from 6.6 to 5.4% ⁽⁵¹⁾	Decrease from 38 to 30% ⁽⁵⁵⁾	Decrease from 3.8 to 3.0 % in 5% MMT/Chitosan film ⁽⁵⁴⁾	Increase from 20 to 30% with 5 wt% addition of CNC ⁽⁶⁰⁾	Dec. from 38 to 23% with 4 wt% addition of CNC ⁽⁶¹⁾	

High Efficiency

Medium Efficiency

Low Efficiency

Data Gap

Table 5: The technical performance comparison of the 2 alternative physical additives for strategy 3.

Hazard Assessment

The physical additive montmorillonite unfortunately demonstrates its own human and environmental concerns, as displayed below in **Table 6**. According to the Canadian Environmental Protection Act Domestic Substances List, montmorillonite has high hazard (although a low confidence) for Persistence and Bioaccumulation, as well as an unspecified hazard level (again, low confidence) for concerns such as: Aquatic Toxicity Acute/chronic, Skin, Eye, Respiratory Irritation/ Sensitization, Systemic Toxicity, Endocrine Activity, Developmental and Reproductive Toxicity, Mutagenicity/Carcinogenicity. Unfortunately, there is not enough data to look into whether or not montmorillonite risks the endocrine disruptors of its users. It is important when assessing the health impacts of montmorillonite to consider in which states of matter the chemical will be utilized and in which demographics of people will be most impacted by the hazard. This being acknowledged, the Comparative Toxicogenomics Database cites montmorillonite as a possible therapeutic drug, used in medicine to assist in alleviating chemical and drug induced liver injuries. ^{48,49}

Our other physical additive, cellulose nanocrystals show less of a health and environmental concern. The **Table 6** below references a 2015 study by Celebi and Kurt discussing the various health properties of chitosan/cellulose nanocrystal films.⁶³ The same study discusses the various health impacts of cellulose nanocrystals, detailing the low level risks of: environmental persistence and bioaccumulation, toxicity (developmental, reproductive, systemic, nero), aquatic toxicity, and carcinogenicity/mutagenicity. Similar to montmorillonite, there is a data gap in the

endocrine disrupting capabilities of cellulose nanocrystals, something to look into before proceeding with its mass-manufacturing. The Association of Occupational and Environmental Clinics (AOEC) finds that cellulose nanocrystals pose a high respiratory sensitization hazard in its powdered form. This will not be of issue for consumers, who will mostly interact with cellulose nanocrystals in its final blended mixture packaging product rather than pure powdered substance. For factory workers handling large amounts of cellulose nanocrystals, facial protections would be a necessity to protect their lungs and respiratory systems. In summary, cellulose nanocrystals show a decrease in human and environmental health effects in comparison to the other physical additive, montmorillonite.⁶³

<i>Physical Additives</i>	Montmorillonite (MMT)	Cellulose Nanocrystal (CNC)	
Persistence	OECD - Classified as persistent	Biodegradable that provide environmental benefits ⁽⁶³⁾	Low Hazard
Bioaccumulation	OECD - Bioaccumulation is not determined		
Sensitivity / Irritation (Eye, Skin, Respiratory)	Study demonstrated that damage to the lungs can occur through repeated exposure if inhaled ⁽⁵¹⁾	AOEC - Respiratory sensitization	Medium Hazard
Toxicity (Dev & Repro, Systemic, Neuro.)		EU - Low oral acute toxicity and no Adverse effects on reproductive performance or developmental effects were observed from toxicity studies, Nontoxic ⁽⁶³⁾	
Aquatic Toxicity	AICIS - low toxicity and/or low bioavailability.	OECD - Low ecotoxicological concern	High Hazard
Carcinogenicity / Mutagenicity	NICNAS- Chemical identified as low concern to human health	NICNAS- Chemical identified as low concern to human health	
Endocrine			Data Gap

Table 6: The hazard assessment comparison of the 2 alternative physical additives for strategy 3.

Feasibility

Nanotechnology is able to maintain the existing water vapor and gas permeability of composites through its integration with the biopolymers to contribute further in the barrier against water, while ideally maintaining biodegradability of the film. There is substantial research available for both montmorillonite and cellulose nanocrystals in terms of its application to biopolymer based films and their health and environmental performance. Both alternatives can drastically improve the barrier properties of films, specifically in the reduction of water permeability for packaging that will contain concentrated or diluted products. Thus, this third alternative recommendation is ranked

higher on the moisture barrier spectrum in **Figure 12**. Although the water contact angle remained as a data gap for most of all the biopolymer based films, this once again demonstrates the need for a standardized procedure for reporting technical performance of films in the literature. A significant portion of the literature reports the X-ray diffraction (XRD) angles of the films, but this performance metric does not directly address its influence on barrier properties and only provides insight for the composition of the films. However with the combination of XRD and transmission electron microscopy, this can show the dispersion of clay particles within the films as discussed in the background component of this alternative recommendation (**Figure 10**).⁷² With what is known about these dispersion phases, it is predicted that the exfoliated phase exhibits the highest improvement in barrier properties, but more research into how it specifically improves these properties are necessary.⁶⁰ This would be a great experimental standard to be implemented when assessing the technical performance of films for packaging.

Lastly, among the two alternatives, Cellulose Nanocrystals maintain the ideal biodegradability component that is desired for a film, unlike montmorillonite since it demonstrates a high level of persistence in the environment. Additionally, both exhibit low concerns for human health. Cellulose Nanocrystals would be the safer alternative as it poses low concern to the environment while also displaying a high efficiency for barrier properties in films. Depending on the type of packaging required for a specific product, total elongation at break as a mechanical property may not necessarily be as highly prioritized for the film as water vapor permeability would be. Experimental research would need to identify the potential moisture barrier that could be achieved through the combination of natural clays and cross-linking reagents in biopolymer based films to see if the two alternatives can meet the performance criteria the other does not meet. It is important to note that the characteristics of both the polymers and clay particles can affect the interactions between the two components. Specifically within the polymer itself, its concentration, molecular weight, and functional groups it encompasses should be taken into consideration. Additionally for the clay particles, its size, shape, and surface charge should also be noted, especially during the suspension.⁶⁰ Ultimately, the components within the product (specifically pH, fragrance, enzymes, etc.) that the packaging will hold could also impact the film's formulations. However, this is a precaution to consider throughout all three alternative recommendations, especially if the recommendations are combined.



Laundry Powders



Detergents



Soaps



Increasing dilution and moisture barrier requirements

Figure 12: The moisture barrier spectrum with the third alternative recommendation that is predicted to meet requirements for films that hold diluted liquid products.

Recommendations

The shift from the status quo to greener solutions is an uphill battle, so the following recommendations acknowledge the complexity of such an endeavor. First, the expense of new technology is challenging to many companies switching to more sustainable resources, so the short term and long term costs are an important consideration. Recognizing that the renewable sources for the biopolymer films may at first pose an additional cost to manufacture, but can assist in reducing the long term cost—for example, if waste products can be collected for their high chitin content and used as the basis for the biopolymer films. Secondly, filling out any remaining data gaps, both for the health hazard assessment and the physical performances, must occur before the finalization of product packaging assessments. This will ensure that the performance of the alternatives properly matches the current methods in terms of stability as a package, as well as not incurring any damaging human or environmental health risks. For specifics to the data gaps, refer to the tables in the appendix.

Furthermore, this project revolves around literature-based research, so any analysis offered involves a caveat that our data was compiled from a variety of other research, and so would need verification by purposeful investigative experiments to finalize any designs in the product packaging. We would propose that more research would be needed in order to increase the confidence level of these assessments, specifically that involving the data gaps highlighted above, but also decrease the costs associated with a change in biopolymer film design.

In terms of the next immediate steps, we recommend identifying Method products with paper packaging that may “overperform” in terms of their hydrophobicity and oleophobicity. For instance, could these products integrate a biopolymer film that performs at a lower level compared to polyolefins without sacrificing their market viability? Would sustainability-inclined consumers agree to reduced barrier properties if they were informed of the environmental benefits of the packaging? Answering these questions would require some degree of market research and consumer feedback. Next, we recommend creating a systematic approach to testing different permutations of biopolymer films with different physical and chemical additives. In our report, we’ve highlighted chitosan, pectin, and gelatin as good candidates for biopolymer films, but there may be a treasure trove of biopolymers that have not been researched or made into films yet.

Based on our research, we recommend a biopolymer film composed of chitosan, pectin, or gelatin as a viable alternative for laundry powder products, as they have low water content and do not require high levels of hydrophobicity as seen in **Figure 8**. The role of cross-linkers cannot be overstated as the first method of reinforcing the properties of these biopolymer films such as glutaraldehyde, genipin, and ferulic acid. A biopolymer film cross-linked with genipin or ferulic acid could be a viable alternative for detergents as they have moderate levels of moisture barrier requirements. Experimenting with

different forms of cross-linking such as physical, chemical, and enzymatic methods may prove useful in identifying the ideal biopolymer combination and cross-linking reagent. This systematic approach must also consider the different chemical and physical additives that could be added to reinforce the properties of such a biodegradable film. Of special note, we recommend further research into montmorillonite and cellulose nanocrystals. With sufficient iteration, biopolymer films with cellulose nanocrystals may be able to hold Method products such as the dish soap refills, which have the highest level of moisture barrier requirements. The central question that remains to be answered is: which biopolymer film formulation creates the greatest marked improvements in performance and contends with polyolefins?

Finally, we also recommend strategies that circumvent the need for paper packaging altogether such as concentrated solutions that consumers can dilute at home. An estimated 20% of global plastic packaging by weight could be replaced by reusable packaging if we only shipped active ingredients, which translates roughly to 97% less water transported, 87% fewer trucks on the road.⁷¹ Furthermore, the reduction in carbon emissions would help create a more sustainable model for Method and for the planet. The major limitation with this approach is that it requires consumers to have access to clean water, which may not be the case in places such as Flint, Michigan. In conclusion, the search for greener solutions remains a worthy and necessary pursuit that not only requires robust research and experimentation, but also ingenuity and creativity.



Figure 13: The moisture barrier spectrum with the all three alternative recommendations that are predicted to meet requirements for films that hold powder, concentrated liquid, and diluted liquid products.

Appendices

Appendix A. Project Members

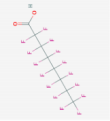
Constancia Dominguez is a first year M.S. student in Environmental Health Science program with a concentration in Industrial Hygiene at UC Berkeley. With a background in Microbiology and Bacterial Genetics, she applied her knowledge in assessing the health risks of alternatives for sustainable product packaging, while also learning about technical metrics that come into play for the development of a sustainable film for paper packaging. Her new research outside of Greener Solutions will analyze COVID-19 prevention and intervention for low-wage workers.

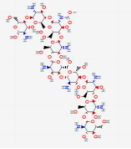
Grayson Hamaker-Teals studies Chemical Biology as a third year undergraduate student at UC Berkeley. He developed coursework for a class on Consumer Sustainability alongside the support of the Berkeley Center for Green Chemistry and will continue to instruct this course for the next semester. For future projects, Grayson will work alongside the BCGC to further develop PFAS alternatives and educate the community about consumer safety.

Josue David Ruiz is a second year M.P.H. student in the Epidemiology & Biostatistics program at the UC Berkeley School of Public Health. His research explores the relationship between gentrification and cardiovascular disease in California and the disproportionate impact of climate change on communities of color.

Amanda Guan is a fourth year undergraduate student majoring in Materials Science and Engineering and minoring in Public Policy. In addition to lobbying for more accessible waste management initiatives in low-income communities in California and New York, she currently researches polymer-induced nanocrystal crystallization mechanisms.

Appendix B. Chemical List

Existing Chemicals										
Monomer	Formulation/Source	Chemical Structure	Chemical Name	Formula	CAS Number	Other ID (SMILES, InChI etc.)	Boiling Point (Celsius)	Vapor Pressure	Chemical and Physical Properties Molecular Weight (g/mol)	Density
Perfluorooctanoic Acid	Derives from a perfluorooctane and an carboxylic acid		PFOA	C8HF16O2	335-67-1	SMILES: <chem>FC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(=O)O</chem> (10,12,14,16,18,20,22,24,26,28,30,32,34,36,38,40,42,44,46,48,50,52,54,56,58,60,62,64,66,68,70,72,74,76,78,80,82,84,86,88,90,92,94,96,98,100,102,104,106,108,110,112,114,116,118,120,122,124,126,128,130,132,134,136,138,140,142,144,146,148,150,152,154,156,158,160,162,164,166,168,170,172,174,176,178,180,182,184,186,188,190,192,194,196,198,200,202,204,206,208,210,212,214,216,218,220,222,224,226,228,230,232,234,236,238,240,242,244,246,248,250,252,254,256,258,260,262,264,266,268,270,272,274,276,278,280,282,284,286,288,290,292,294,296,298,300,302,304,306,308,310,312,314,316,318,320,322,324,326,328,330,332,334,336,338,340,342,344,346,348,350,352,354,356,358,360,362,364,366,368,370,372,374,376,378,380,382,384,386,388,390,392,394,396,398,400,402,404,406,408,410,412,414,416,418,420,422,424,426,428,430,432,434,436,438,440,442,444,446,448,450,452,454,456,458,460,462,464,466,468,470,472,474,476,478,480,482,484,486,488,490,492,494,496,498,500,502,504,506,508,510,512,514,516,518,520,522,524,526,528,530,532,534,536,538,540,542,544,546,548,550,552,554,556,558,560,562,564,566,568,570,572,574,576,578,580,582,584,586,588,590,592,594,596,598,600,602,604,606,608,610,612,614,616,618,620,622,624,626,628,630,632,634,636,638,640,642,644,646,648,650,652,654,656,658,660,662,664,666,668,670,672,674,676,678,680,682,684,686,688,690,692,694,696,698,700,702,704,706,708,710,712,714,716,718,720,722,724,726,728,730,732,734,736,738,740,742,744,746,748,750,752,754,756,758,760,762,764,766,768,770,772,774,776,778,780,782,784,786,788,790,792,794,796,798,800,802,804,806,808,810,812,814,816,818,820,822,824,826,828,830,832,834,836,838,840,842,844,846,848,850,852,854,856,858,860,862,864,866,868,870,872,874,876,878,880,882,884,886,888,890,892,894,896,898,900,902,904,906,908,910,912,914,916,918,920,922,924,926,928,930,932,934,936,938,940,942,944,946,948,950,952,954,956,958,960,962,964,966,968,970,972,974,976,978,980,982,984,986,988,990,992,994,996,998,1000,1002,1004,1006,1008,1010,1012,1014,1016,1018,1020,1022,1024,1026,1028,1030,1032,1034,1036,1038,1040,1042,1044,1046,1048,1050,1052,1054,1056,1058,1060,1062,1064,1066,1068,1070,1072,1074,1076,1078,1080,1082,1084,1086,1088,1090,1092,1094,1096,1098,1100,1102,1104,1106,1108,1110,1112,1114,1116,1118,1120,1122,1124,1126,1128,1130,1132,1134,1136,1138,1140,1142,1144,1146,1148,1150,1152,1154,1156,1158,1160,1162,1164,1166,1168,1170,1172,1174,1176,1178,1180,1182,1184,1186,1188,1190,1192,1194,1196,1198,1200,1202,1204,1206,1208,1210,1212,1214,1216,1218,1220,1222,1224,1226,1228,1230,1232,1234,1236,1238,1240,1242,1244,1246,1248,1250,1252,1254,1256,1258,1260,1262,1264,1266,1268,1270,1272,1274,1276,1278,1280,1282,1284,1286,1288,1290,1292,1294,1296,1298,1300,1302,1304,1306,1308,1310,1312,1314,1316,1318,1320,1322,1324,1326,1328,1330,1332,1334,1336,1338,1340,1342,1344,1346,1348,1350,1352,1354,1356,1358,1360,1362,1364,1366,1368,1370,1372,1374,1376,1378,1380,1382,1384,1386,1388,1390,1392,1394,1396,1398,1400,1402,1404,1406,1408,1410,1412,1414,1416,1418,1420,1422,1424,1426,1428,1430,1432,1434,1436,1438,1440,1442,1444,1446,1448,1450,1452,1454,1456,1458,1460,1462,1464,1466,1468,1470,1472,1474,1476,1478,1480,1482,1484,1486,1488,1490,1492,1494,1496,1498,1500,1502,1504,1506,1508,1510,1512,1514,1516,1518,1520,1522,1524,1526,1528,1530,1532,1534,1536,1538,1540,1542,1544,1546,1548,1550,1552,1554,1556,1558,1560,1562,1564,1566,1568,1570,1572,1574,1576,1578,1580,1582,1584,1586,1588,1590,1592,1594,1596,1598,1600,1602,1604,1606,1608,1610,1612,1614,1616,1618,1620,1622,1624,1626,1628,1630,1632,1634,1636,1638,1640,1642,1644,1646,1648,1650,1652,1654,1656,1658,1660,1662,1664,1666,1668,1670,1672,1674,1676,1678,1680,1682,1684,1686,1688,1690,1692,1694,1696,1698,1700,1702,1704,1706,1708,1710,1712,1714,1716,1718,1720,1722,1724,1726,1728,1730,1732,1734,1736,1738,1740,1742,1744,1746,1748,1750,1752,1754,1756,1758,1760,1762,1764,1766,1768,1770,1772,1774,1776,1778,1780,1782,1784,1786,1788,1790,1792,1794,1796,1798,1800,1802,1804,1806,1808,1810,1812,1814,1816,1818,1820,1822,1824,1826,1828,1830,1832,1834,1836,1838,1840,1842,1844,1846,1848,1850,1852,1854,1856,1858,1860,1862,1864,1866,1868,1870,1872,1874,1876,1878,1880,1882,1884,1886,1888,1890,1892,1894,1896,1898,1900,1902,1904,1906,1908,1910,1912,1914,1916,1918,1920,1922,1924,1926,1928,1930,1932,1934,1936,1938,1940,1942,1944,1946,1948,1950,1952,1954,1956,1958,1960,1962,1964,1966,1968,1970,1972,1974,1976,1978,1980,1982,1984,1986,1988,1990,1992,1994,1996,1998,2000,2002,2004,2006,2008,2010,2012,2014,2016,2018,2020,2022,2024,2026,2028,2030,2032,2034,2036,2038,2040,2042,2044,2046,2048,2050,2052,2054,2056,2058,2060,2062,2064,2066,2068,2070,2072,2074,2076,2078,2080,2082,2084,2086,2088,2090,2092,2094,2096,2098,2100,2102,2104,2106,2108,2110,2112,2114,2116,2118,2120,2122,2124,2126,2128,2130,2132,2134,2136,2138,2140,2142,2144,2146,2148,2150,2152,2154,2156,2158,2160,2162,2164,2166,2168,2170,2172,2174,2176,2178,2180,2182,2184,2186,2188,2190,2192,2194,2196,2198,2200,2202,2204,2206,2208,2210,2212,2214,2216,2218,2220,2222,2224,2226,2228,2230,2232,2234,2236,2238,2240,2242,2244,2246,2248,2250,2252,2254,2256,2258,2260,2262,2264,2266,2268,2270,2272,2274,2276,2278,2280,2282,2284,2286,2288,2290,2292,2294,2296,2298,2300,2302,2304,2306,2308,2310,2312,2314,2316,2318,2320,2322,2324,2326,2328,2330,2332,2334,2336,2338,2340,2342,2344,2346,2348,2350,2352,2354,2356,2358,2360,2362,2364,2366,2368,2370,2372,2374,2376,2378,2380,2382,2384,2386,2388,2390,2392,2394,2396,2398,2400,2402,2404,2406,2408,2410,2412,2414,2416,2418,2420,2422,2424,2426,2428,2430,2432,2434,2436,2438,2440,2442,2444,2446,2448,2450,2452,2454,2456,2458,2460,2462,2464,2466,2468,2470,2472,2474,2476,2478,2480,2482,2484,2486,2488,2490,2492,2494,2496,2498,2500,2502,2504,2506,2508,2510,2512,2514,2516,2518,2520,2522,2524,2526,2528,2530,2532,2534,2536,2538,2540,2542,2544,2546,2548,2550,2552,2554,2556,2558,2560,2562,2564,2566,2568,2570,2572,2574,2576,2578,2580,2582,2584,2586,2588,2590,2592,2594,2596,2598,2600,2602,2604,2606,2608,2610,2612,2614,2616,2618,2620,2622,2624,2626,2628,2630,2632,2634,2636,2638,2640,2642,2644,2646,2648,2650,2652,2654,2656,2658,2660,2662,2664,2666,2668,2670,2672,2674,2676,2678,2680,2682,2684,2686,2688,2690,2692,2694,2696,2698,2700,2702,2704,2706,2708,2710,2712,2714,2716,2718,2720,2722,2724,2726,2728,2730,2732,2734,2736,2738,2740,2742,2744,2746,2748,2750,2752,2754,2756,2758,2760,2762,2764,2766,2768,2770,2772,2774,2776,2778,2780,2782,2784,2786,2788,2790,2792,2794,2796,2798,2800,2802,2804,2806,2808,2810,2812,2814,2816,2818,2820,2822,2824,2826,2828,2830,2832,2834,2836,2838,2840,2842,2844,2846,2848,2850,2852,2854,2856,2858,2860,2862,2864,2866,2868,2870,2872,2874,2876,2878,2880,2882,2884,2886,2888,2890,2892,2894,2896,2898,2900,2902,2904,2906,2908,2910,2912,2914,2916,2918,2920,2922,2924,2926,2928,2930,2932,2934,2936,2938,2940,2942,2944,2946,2948,2950,2952,2954,2956,2958,2960,2962,2964,2966,2968,2970,2972,2974,2976,2978,2980,2982,2984,2986,2988,2990,2992,2994,2996,2998,3000,3002,3004,3006,3008,3010,3012,3014,3016,3018,3020,3022,3024,3026,3028,3030,3032,3034,3036,3038,3040,3042,3044,3046,3048,3050,3052,3054,3056,3058,3060,3062,3064,3066,3068,3070,3072,3074,3076,3078,3080,3082,3084,3086,3088,3090,3092,3094,3096,3098,3100,3102,3104,3106,3108,3110,3112,3114,3116,3118,3120,3122,3124,3126,3128,3130,3132,3134,3136,3138,3140,3142,3144,3146,3148,3150,3152,3154,3156,3158,3160,3162,3164,3166,3168,3170,3172,3174,3176,3178,3180,3182,3184,3186,3188,3190,3192,3194,3196,3198,3200,3202,3204,3206,3208,3210,3212,3214,3216,3218,3220,3222,3224,3226,3228,3230,3232,3234,3236,3238,3240,3242,3244,3246,3248,3250,3252,3254,3256,3258,3260,3262,3264,3266,3268,3270,3272,3274,3276,3278,3280,3282,3284,3286,3288,3290,3292,3294,3296,3298,3300,3302,3304,3306,3308,3310,3312,3314,3316,3318,3320,3322,3324,3326,3328,3330,3332,3334,3336,3338,3340,3342,3344,3346,3348,3350,3352,3354,3356,3358,3360,3362,3364,3366,3368,3370,3372,3374,3376,3378,3380,3382,3384,3386,3388,3390,3392,3394,3396,3398,3400,3402,3404,3406,3408,3410,3412,3414,3416,3418,3420,3422,3424,3426,3428,3430,3432,3434,3436,3438,3440,3442,3444,3446,3448,3450,3452,3454,3456,3458,3460,3462,3464,3466,3468,3470,3472,3474,3476,3478,3480,3482,3484,3486,3488,3490,3492,3494,3496,3498,3500,3502,3504,3506,3508,3510,3512,3514,3516,3518,3520,3522,3524,3526,3528,3530,3532,3534,3536,3538,3540,3542,3544,3546,3548,3550,3552,3554,3556,3558,3560,3562,3564,3566,3568,3570,3572,3574,3576,3578,3580,3582,3584,3586,3588,3590,3592,3594,3596,3598,3600,3602,3604,3606,3608,3610,3612,3614,3616,3618,3620,3622,3624,3626,3628,3630,3632,3634,3636,3638,3640,3642,3644,3646,3648,3650,3652,3654,3656,3658,3660,3662,3664,3666,3668,3670,3672,3674,3676,3678,3680,3682,3684,3686,3688,3690,3692,3694,3696,3698,3700,3702,3704,3706,3708,3710,3712,3714,3716,3718,3720,3722,3724,3726,3728,3730,3732,3734,3736,3738,3740,3742,3744,3746,3748,3750,3752,3754,3756,3758,3760,3762,3764,3766,3768,3770,3772,3774,3776,3778,3780,3782,3784,3786,3788,3790,3792,3794,3796,3798,3800,3802,3804,3806,3808,3810,3812,3814,3816,3818,3820,3822,3824,3826,3828,3830,3832,3834,3836,3838,3840,3842,3844,3846,3848,3850,3852,3854,3856,3858,3860,3862,3864,3866,3868,3870,3872,3874,3876,3878,3880,3882,3884,3886,3888,3890,3892,3894,3896,3898,3900,3902,3904,3906,3908,3910,3912,3914,3916,3918,3920,3922,3924,3926,3928,3930,3932,3934,3936,3938,3940,3942,3944,3946,3948,3950,3952,3954,3956,3958,3960,3962,3964,3966,3968,3970,3972,3974,3976,3978,3980,3982,3984,3986,3988,3990,3992,3994,3996,3998,4000,4002,4004,4006,4008,4010,4012,4014,4016,4018,4020,4022,4024,4026,4028,4030,4032,4034,4036,4038,4040,4042,4044,4046,4048,4050,4052,4054,4056,4058,4060,4062,4064,4066,4068,4070,4072,4074,4076,4078,4080,4082,4084,4086,4088,4090,4092,4094,4096,4098,4100,4102,4104,4106,4108,4110,4112,4114,4116,4118,4120,4122,4124,4126,4128,4130,4132,4134,4136,4138,4140,4142,4144,4146,4148,4150,4152,4154,4156,4158,4160,4162,4164,4166,4168,4170,4172,4174,4176,4178,4180,4182,4184,4186,4188,4190,4192,4194,4196,4198,4200,4202,4204,4206,4208,4210,4212,4214,4216,4218,4220,4222,4224,4226,4228,4230,4232,4234,4236,4238,4240,4242,4244,4246,4248,4250,4252,4254,4256,4258,4260,4262,4264,4266,4268,4270,4272,4274,4276,4278,4280,4282,4284,4286,4288,4290,4292,4294,4296,4298,4300,4302,4304,4306,4308,4310,4312,4314,4316,4318,4320,4322,4324,4326,4328,4330,4332,4334,4336,4338,4340,4342,4344,4346,4348,4350,4352,4354,4356,4358,4360,4362,4364,4366,4368,4370,4372,4374,4376,4378,4380,4382,4384,4386,4388,4390,4392,4394,4396,4398,4400,4402,4404,4406,4408,4410,4412,4414,4416,4418,4420,4422,4424,4426,4428,4430,4432,4434,4436,4438,4440,4442,4444,4446,4448,4450,4452,4454,4456,4458,4460,4462,4464,4466,4468,4470,4472,4474,4476,4478,4480,4482,4484,4486,4488,4490,4492,4494,4496,4498,4500,4502,4504,4506,4508,4510,4512,4514,4516,4518,4520,4522,4524,4526,4528,4530,4532,4534,4536,4538,4540,4542,4544,4546,4548,4550,4552,4554,4556,4558,4560,4562,4564,4566,4568,4570,4572,4574,4576,4578,4580,4582,4584,4586,4588,4590,4592,4594,4596,4598,4600,4602,4604,4606,4608,4610,4612,4614,4616,4618,4620,4622,4624,4626,4628,4630,4632,4634,4636,4638,4640,4642,4644,4646,4648,4650,4652,4654,4656,4658,4660,4662,4664,4666,4668,4670,4672,4674,4676,4678,4680,4682,4684,4686,4688,4690,4692,4694,4696,4698,4700,4702,4704,4706,4708,4710,4712,4714,4716,4718,4720,4722,4724,4726,4728,4730,4732,4734,4736,4738,4740,4742,4744,4746,4748,4750,4752,4754,4756,4758,4760,4762,4764,4766,4768,4770,4772,4774,4776,4778,4780,4782,4784,4786,4788,4790,4792,4794,4796,4798,4800,4802,4804,4806,4808,4810,4812,4814,4816,4818,4820,4822,4824,4826,4828,4830,4832,4834,4836,4838,4840,4842,4844,4846,4848,4850,4852,4854,4856,4858,4860,4862,4864,4866,4868,4870,4872,4874,4876,4878,4880,4882,4884,4886,4888,4890,4892,4894,4896,4898,4900,4902,4904,4906,4908,4910,4912,4914,4916,4918,4920,4922,4924,4926,4928,4930,4932,4934,4936,4938,4940,4942,4944,4946,4948,4950,4952,4954,4956,4958,4960,4962,4964,4966,4968,4970,4972,4974,4976,4978,4980,4982,4984,498				

Alternative Chemicals										
	Monomer	Strategy and Inspiration	Chemical Structure	Chemical Name	Formula	CAS Number	Other ID (SMILES, InChI etc.)	Chemical and physical properties		
								Boiling Point (Celsius)	Vapor Pressure	Molecular Weight (g/mol)
Chitin	Chitosan	Deacetylated form of Chitosan		Poliglucam, Chitosol	C58H103NO38	9012-76-4	InChI=1SC58H103NO38/c1-87-56(80)65-28-38(84)46(19)10-74(96-55)28(104-45-18)9-73(95-46)27(11)12(13)14(15)16(17)18(19)20(21)22(23)24(25)26(27)28(29)30(31)32(33)34(35)36(37)38(39)40(41)42(43)44(45)46(47)48(49)50(51)52(53)54(55)56(57)58(59)60(61)62(63)64(65)66(67)68(69)70(71)72(73)74(75)76(77)78(79)80(81)82(83)84(85)86(87)88(89)89(90)91(92)93(94)94(95)96(97)98(99)100(101)102(103)104(105)106(107)108(109)110(111)112(113)114(115)116(117)118(119)120(121)122(123)124(125)126(127)128(129)130(131)132(133)134(135)136(137)138(139)140(141)142(143)144(145)146(147)148(149)150(151)152(153)154(155)156(157)158(159)160(161)162(163)164(165)166(167)168(169)170(171)172(173)174(175)176(177)178(179)180(181)182(183)184(185)186(187)188(189)190(191)192(193)194(195)196(197)198(199)200(201)202(203)204(205)206(207)208(209)210(211)212(213)214(215)216(217)218(219)220(221)222(223)224(225)226(227)228(229)230(231)232(233)234(235)236(237)238(239)240(241)242(243)244(245)246(247)248(249)250(251)252(253)254(255)256(257)258(259)260(261)262(263)264(265)266(267)268(269)270(271)272(273)274(275)276(277)278(279)280(281)282(283)284(285)286(287)288(289)290(291)292(293)294(295)296(297)298(299)300(301)302(303)304(305)306(307)308(309)310(311)312(313)314(315)316(317)318(319)320(321)322(323)324(325)326(327)328(329)330(331)332(333)334(335)336(337)338(339)340(341)342(343)344(345)346(347)348(349)350(351)352(353)354(355)356(357)358(359)360(361)362(363)364(365)366(367)368(369)370(371)372(373)374(375)376(377)378(379)380(381)382(383)384(385)386(387)388(389)390(391)392(393)394(395)396(397)398(399)400(401)402(403)404(405)406(407)408(409)410(411)412(413)414(415)416(417)418(419)420(421)422(423)424(425)426(427)428(429)430(431)432(433)434(435)436(437)438(439)440(441)442(443)444(445)446(447)448(449)450(451)452(453)454(455)456(457)458(459)460(461)462(463)464(465)466(467)468(469)470(471)472(473)474(475)476(477)478(479)480(481)482(483)484(485)486(487)488(489)490(491)492(493)494(495)496(497)498(499)500(501)502(503)504(505)506(507)508(509)510(511)512(513)514(515)516(517)518(519)520(521)522(523)524(525)526(527)528(529)530(531)532(533)534(535)536(537)538(539)540(541)542(543)544(545)546(547)548(549)550(551)552(553)554(555)556(557)558(559)560(561)562(563)564(565)566(567)568(569)570(571)572(573)574(575)576(577)578(579)580(581)582(583)584(585)586(587)588(589)590(591)592(593)594(595)596(597)598(599)600(601)602(603)604(605)606(607)608(609)610(611)612(613)614(615)616(617)618(619)620(621)622(623)624(625)626(627)628(629)630(631)632(633)634(635)636(637)638(639)640(641)642(643)644(645)646(647)648(649)650(651)652(653)654(655)656(657)658(659)660(661)662(663)664(665)666(667)668(669)670(671)672(673)674(675)676(677)678(679)680(681)682(683)684(685)686(687)688(689)690(691)692(693)694(695)696(697)698(699)700(701)702(703)704(705)706(707)708(709)710(711)712(713)714(715)716(717)718(719)720(721)722(723)724(725)726(727)728(729)730(731)732(733)734(735)736(737)738(739)740(741)742(743)744(745)746(747)748(749)750(751)752(753)754(755)756(757)758(759)760(761)762(763)764(765)766(767)768(769)770(771)772(773)774(775)776(777)778(779)780(781)782(783)784(785)786(787)788(789)790(791)792(793)794(795)796(797)798(799)800(801)802(803)804(805)806(807)808(809)810(811)812(813)814(815)816(817)818(819)820(821)822(823)824(825)826(827)828(829)830(831)832(833)834(835)836(837)838(839)840(841)842(843)844(845)846(847)848(849)850(851)852(853)854(855)856(857)858(859)860(861)862(863)864(865)866(867)868(869)870(871)872(873)874(875)876(877)878(879)880(881)882(883)884(885)886(887)888(889)890(891)892(893)894(895)896(897)898(899)900(901)902(903)904(905)906(907)908(909)910(911)912(913)914(915)916(917)918(919)920(921)922(923)924(925)926(927)928(929)930(931)932(933)934(935)936(937)938(939)940(941)942(943)944(945)946(947)948(949)950(951)952(953)954(955)956(957)958(959)960(961)962(963)964(965)966(967)968(969)970(971)972(973)974(975)976(977)978(979)980(981)982(983)984(985)986(987)988(989)990(991)992(993)994(995)996(997)998(999)1000(1001)1002(1003)1004(1005)1006(1007)1008(1009)1010(1011)1012(1013)1014(1015)1016(1017)1018(1019)1020(1021)1022(1023)1024(1025)1026(1027)1028(1029)1030(1031)1032(1033)1034(1035)1036(1037)1038(1039)1040(1041)1042(1043)1044(1045)1046(1047)1048(1049)1050(1051)1052(1053)1054(1055)1056(1057)1058(1059)1060(1061)1062(1063)1064(1065)1066(1067)1068(1069)1070(1071)1072(1073)1074(1075)1076(1077)1078(1079)1080(1081)1082(1083)1084(1085)1086(1087)1088(1089)1090(1091)1092(1093)1094(1095)1096(1097)1098(1099)1100(1101)1102(1103)1104(1105)1106(1107)1108(1109)1110(1111)1112(1113)1114(1115)1116(1117)1118(1119)1120(1121)1122(1123)1124(1125)1126(1127)1128(1129)1130(1131)1132(1133)1134(1135)1136(1137)1138(1139)1140(1141)1142(1143)1144(1145)1146(1147)1148(1149)1150(1151)1152(1153)1154(1155)1156(1157)1158(1159)1160(1161)1162(1163)1164(1165)1166(1167)1168(1169)1170(1171)1172(1173)1174(1175)1176(1177)1178(1179)1180(1181)1182(1183)1184(1185)1186(1187)1188(1189)1190(1191)1192(1193)1194(1195)1196(1197)1198(1199)1200(12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Appendix C. Hazard Assessment Table

Alternative Recommendation	Common name or trade name	CAS Number	Group I Human Endpoints			Group II and Group III Endpoints			Ecotoxicity	Persistence	Fate	Physical Hazard		
			Carcinogenicity	Developmental and Reproductive Toxicity	Endocrine Activity	Systemic Toxicity	Neurotoxicity	Skin, Eye, Respiratory Irritation/Sensitization				Aquatic Toxicity/Acute/Chronic	Biodegradation	Other Potential
Baseline	Perfluorooctanoic Acid (PFOA)	335-67-1	Carcinogenic (26, 27)	GHS - Japan Toxic to reproduction Category 1A (H302)	ChemSec - SIN List Endocrine Disruption	EU - GHS (H-Statements) H372 - Causes damage to organs through prolonged or repeated exposure	Neurotoxicant (23, 26)	Eye irritants, adverse respiratory effects (27)	GHS - Japan Hazardous to the aquatic environment (acute) - Category 3 (H402)	Persistent in Environment (25)	Biocumulative (24)	Melting point/range: 55 - 56 °C (131 - 133 °F) - lit.		
	Polypropylene	9003-37-0	IARC Group 3 (Not classifiable as to its carcinogenicity to humans)			LD50, oral (rat) >5000 mg/kg		ChemE - Toxicant Database classifies it as a sensitizer to respiratory system. Also, there is literature in chemical literature that it is a respiratory irritant (Ais S et al., 2015). The respiratory effects of occupational polypropylene fume exposure	MSDS: Ecotoxicity is expected to be minimal based on the low water solubility of polymers	Canadian Environmental Protection Act (CEPA) classifies as a high level of persistence	OECD classifies it as not bioaccumulative	Melting Point: 130-170 °C (266-334 °F) > 300 °C		
	Polyethylene	9002-88-4	IARC Group 3 (Not classifiable as to its carcinogenicity to humans)			LD50, oral (Rat): 4.9 kg		Quebec CSST: Moderate Hazard; Agent Causing Occupational Asthma. Additionally, occupational case reports of ocular irritation and systemic adverse effects in workers (polyethylene dust) and high production of synthetic polyethylene and high pressure polyethylene	MSDS: Ecotoxicity is expected to be minimal based on the low water solubility of polymers	Canadian Environmental Protection Act (CEPA) classifies as a high level of persistence	OECD classifies it as not bioaccumulative	Melting Point: 260 - 275 °F, Flash Point: 341 °C (645.8 °F)		
	Glutaraldehyde	111-30-8	Chronic toxicity of glutaraldehyde to aquatic organisms (DOI: 10.1016/j.aquatox.2004.12.001)	TEEX - Potential Endocrine Disruptors			Alterations in Neurotransmitters and Their Metabolites in Discrete Brain Regions after Inhalation of Disinfectant (6, 13)	GHS - H335 - May cause respiratory irritation, GHS - H317 - May cause an allergic skin reaction, GHS - H318 - Eye irritation	GHS - H411 - Toxic to aquatic life with long lasting effects	ACCS - Glutaraldehyde is a hydrophilic substance that will mainly partition to water upon release to the environment. Like formaldehyde, the environmental persistence of glutaraldehyde is extremely limited	OECD - Not classified as bioaccumulative	Melting -10 °C (14 °F)		
	Chitin	1338-61-4	Posses no unreasonable risk to human health based on Tier 1 assessment under the NICNAS IMAP assessment framework			No adverse effects were reported for Humans (9)		No adverse effects reported (9) Toxites reported it an non-irritant for skin.	"Suspected hazardous to the environment" (Fish Acute Toxicity model (KONRAD-Across) in which the model predicts that the chemical has a 9th LC50 of 35.79 mg/L (moderate reliability)?	NICNAS - Tier 1 (Substance that is derived from natural products or materials, not bioaccumulative)				
Alternative Recommendation 1: Biopolymer based films	Chitosan	9612-78-4	Posses no unreasonable risk to human health based on Tier 1 assessment under the NICNAS IMAP assessment framework			No adverse effects were reported for Humans (9)		Toxites: NOT skin corrosion R34 or R35, Not Irritating or Corrosive to skin. National Toxicology Program (NTP) conducted a 90-day subchronic inhalation study in which chitosan were reported in eye or skin irritation tests in rabbits or pigs, respectively	GHS Category 1 (New Zealand 5.1.1.1.1) - Hazardous to the aquatic environment (acute hazard)	NICNAS - Tier 1 (Substance that is derived from natural products or materials, not bioaccumulative)		Melting point: 102.5 °C (216.5 °F)		
	Gelatin	9000-70-8	Posses no unreasonable risk to human health based on National Industrial Chemicals Notification and Assessment Scheme (NICNAS IMAP) assessment framework	NICNAS - Tier 1 (Substance that is derived from natural products or materials, not bioaccumulative)				Agent Causing Occupational Asthma (2)	OECD - Low ecotoxicological concern	NICNAS - Tier 1 (No risk to the environment by natural decay)		Posses no unreasonable risk to the environment based on the Tier 1 assessment under the framework NICNAS IMAP assessment (Substance that is derived from natural products or materials, not bioaccumulative)	Reactivity: Nonreactive under normal conditions, stable under normal conditions	
	Pectin	9000-68-6	Low concern to human health by application of expert validated rules under the NICNAS targeted tier 1 approach	NICNAS - Tier 1 (Substance that is derived from natural products or materials, not bioaccumulative)		No adverse effects were reported in a chronic toxicity study (12)		Agent Causing Occupational Asthma (2)		NICNAS - Tier 1 (No risk to the environment by natural decay)		Posses no unreasonable risk to the environment based on the Tier 1 assessment under the framework NICNAS - Tier 1 (Substance that is derived from natural products or materials, not bioaccumulative)		
	Genipin	6902-77-8				Low cytotoxicity reported (10, 11)			ECHA - According to the few useful data available for classification, it appears that the fenolic acid does not have adverse effect on the tested organisms at concentrations up to a 100 mg/L. Labeling Classification, Labelling and Packaging (CLP) classification		Biodegradable (11)			
Alternative Recommendation 2: Biopolymer based films with the addition of chemical cross-linking reagents	Ferulic acid (FA)	537-98-4	ECHA - No evidence of mutagenicity or genetic toxicity in the limited studies that are available		EU - No evidence of endocrine disrupting activity	ECHA - systemic toxicity studies (via oral route) reported no adverse effects		GHS - H335, H315, H319 - May cause respiratory, skin and eye irritation				ECHA: Ferulic acid appears to be rapidly biodegradable in water under aerobic conditions, and as in soil under aerobic conditions.	Melting point/range: 168 - 172 °C (334 - 342 °F) - lit.	
Alternative Recommendation 3: Biopolymer based films with the addition of physical additives	Montmorillonite (MMT)	1318-93-0	ACCS - Chemical identified as a low concern to human health by application of expert validated rules under the NICNAS targeted tier 1 approach					In study by Gibbs, A.R. and F.D. Pooley (1994) demonstrates that an inorganic clay mineral, through prolonged or repeated exposure (inhaled (51)	ACCS - An inorganic substance with low toxicity and low concern to the environment.	OECD - Classified as persistent, bioaccumulation is not determined				
	Cellulose Nanocrystal	9004-34-6	ACCS - Chemical identified as a low concern to human health by application of expert validated rules under the NICNAS targeted tier 1 approach	European Commission, the EFSA Panel on Food Additives and Nutrient Sources added to Food (ANS) reported no adverse effects on reproductive and developmental toxicity studies		According to a study conducted in 2015 by Celebi, Hacer, Kurt, Ayes, classified as low concern to the European Commission, the EFSA Panel on Food Additives and Nutrient Sources added to Food (ANS) reported low oral toxicity		AOEC - Respiratory sensitization	OECD - Low ecotoxicological concern	According to a study conducted in 2015 by Celebi, Hacer, Kurt, Ayes, classified as low concern to the European Commission, the EFSA Panel on Food Additives and Nutrient Sources added to Food (ANS) reported low oral toxicity				

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