Compostable Alternatives to Polyethylene Packaging for Frozen Kelp

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Introduction and Background

During Fall 2021, our team partnered with Noble Ocean Farms, a startup in Cordova, Alaska, to help create sustainable and biodegradable packaging. Noble Ocean Farms aims to strengthen food systems through harvesting and distributing kelp. Currently, the company uses conventional polyethylene (PE) vacuum-sealable bags to freeze kelp products for distribution. However, polyethylene has detrimental environmental and human health consequences. In its early stages, polyethylene can create hazardous environments for workers, and, at the end of its lifecycle, polyethylene persists in the environment for indefinite periods of time. Even after several decades, polyethylene can create hazards for animals, agriculture, and ecosystems.

Our planet is facing an immense plastic crisis. In 2018, over 35.69 million tons of plastics were produced worldwide and ppproximately 3 million tons were recycled and 5.6 tons combusted.[1] The remaining plastic ended up in landfills, oceans, or other facets of the earth. The majority of this plastic (14.8 million tons) came from packaging materials, such as those used at Noble Ocean Farms.[1] In an effort to change the packaging industry, we aim to create a packaging product that reduces or eliminates traditional hazardous plastics from the industry. Our team has investigated current bioplastics and alternative packaging methods to achieve the mission of eliminating as much plastic waste as possible during the food packaging process.

Approach

We established three different strategies to investigate the creation of environmentally friendly, biodegradable packaging. The first strategy completely replaces PE with a bioplastic, which is significantly less persistent in the environment. The second strategy uses a durable material (ie. paperboard) in combination with a bioplastic laminate/coating, eliminating traditional plastics completely. The third strategy involves the combination of a bioplastic packaging with a structural material separate from the bioplastic. Strategies two and three intend to mitigate the drawbacks of bioplastics by introducing a new medium while the first strategy largely relies on adding chemical additives to an existing bioplastic to develop a single material with comparable performance.

Criteria for Success

Initially, Noble Ocean Farms requested that we incorporate vacuum-sealability into our packaging product. However, this requirement limited our potential solutions. Vacuum-sealable packaging creates drawbacks because bioplastics must have the capacity to withstand high pressures involved in this process. The co-founder of Noble Ocean Farms, Skye Stertz, proposed flash freezing the kelp apart from considering packaging constraints because flash freezing prevents freezer burn, which serves the same function as vacuum sealing.

Aside from vacuum-sealability, we were required to meet several other criteria in order to determine the most appropriate packaging alternative. The material had to meet the technical criteria for transporting frozen kelp. For example, the plastic needed a moisture and oxygen barrier permittivity that was up to industry standards for frozen food packaging. Additionally, the packaging had to withstand shipping and handling which requires certain tensile strength and temperature stability to prevent degradation prior to consumption. Table 1 displays important values for the necessary technical performance required to have a viable alternative to existing packaging.

Technical Performance

Barrier properties cover oxygen permeability, water resistance, and oil resistance. Water resistance is measured by water vapor permeability and Cobb60. Oil resistance is indicated by the Kit value, where a Kit value of 6 is considered good and a kit value of 12 is excellent.[2]

For temperature considerations, we list the melting temperature, degradation temperature, and the glass transition temperature. The melting temperature is when the plastic has melted, which is not to be confused with the degradation temperature which is when the plastic breaks down into its monomers. The glass transition temperature is the point at which a plastic goes from rubbery to "glassy" and usually represents when the material becomes more brittle. A lower glass transition temperature means that the polymer stays rubbery at lower temperatures and thus stays flexible and less prone to breakage at low temperatures.

For mechanical properties, the materials chosen must be durable to last through handling and processing. To withstand external conditions, such as dropping/falling during transportation, the material must have decent tensile strength. Additionally, the package may undergo certain strain during handling which requires flexibility characterized by elongation at break. The higher the tensile strength and elongation at break, the more mechanically durable a material is.

Table 1: Technical criteria for frozen food packaging

	Barrier Properties				**Working Temperature Range**			**Mechanical Properties**	
Name of criteria	Oxygen Permeability	Water Permeability	Cobb60	Kit Value	Glass Transition Temperature	Melting Temperature	Degradation Temperature	Tensile Strength	Elongation at Break (%)
Definition	How much oxygen can penetrate over time	How much water can penetrate over time	How much water is absorbed by a material	How repellent a material is to liquid	Temperature at which a material transitions to brittle from ductile	Temperature in which a material changes phase from solid to liquid	Temperature in which a material loses fundamental properties	Strength a material can withstand before fracture	Elongation a material can endure before fracture
Good	Less than 20 g/m^2/24 hrs	Less than 1 g/m^2/24 hrs	Less than 10 g/m^2	≥7	Below 5 °C	40°C below Degradation	Above 140°C	Above 10 MPa	At least 100%
Okay	20 - 100 g/m^2/24 hrs	1 - 50 g/m^2/24 hrs	10 - 50 g/m^2	5 - 6	5 - 60 °C	20° - 40°C difference	100 - 140°C	5 - 10 MPa	7% to 100%
Bad	Greater than 100 g/m^2/24 hrs	Greater than 50 g/m^2/24 hrs	Greater than 50 g/m^2	Less than 5	Greater than 60 °C	Less than 20°C different	Less than 100°C	0 - 5 MPa	Less than 7%

Health and Environmental

Additionally, the ideal alternative packaging would also be home-compostable in the natural Alaskan environment within six months. Noble Ocean Farms was open to industrial compostable standards if home-compostable options were not available, however Alaska has limited industrial compost facilities. Home-compostability means that the packaging should break down into water, carbon dioxide (CO_2), and biomass in ambient conditions while also being beneficial to the soil and environment. Industrial compost is regulated under the ASTM D6400, which means >90% of the material must decompose in 6 months in a 58 ° C environment. Home composting does not have any standards in the U.S, but the EU and Australia follow similar standards in which the material must be >90% decomposed by 1 year in 20-30 ° C environments.[3,4]

The hazards of the materials chosen should also be minimized as much as possible to mitigate the negative health and environmental impacts of the kelp packaging. The bad actor, Polyethylene has moderate Group 1 and 2 human health endpoints and ecotoxicity, but the most concerning endpoint is persistence in the environment. Polyethene can take hundreds of years to decompose which leads to accumulation in landfills and the environment.[5] Polyethylene decomposes into microplastics, which produces secondary human and environmental health impacts. Hazard information for several bioplastics and materials was difficult to characterize due to limited information available online. Available health and environmental information came from material safety data sheets, online databases (e.g. Pharos), Globally Harmonized System (GHS), authoritative and screening lists alongside GreenScreen to assess chemical hazards.

The form in which bioplastics are tested varies in that some of the hazard information is applicable only when the polymer is generated as fine granules or considered in its monomer form. As a polymer, most plastics including those that are petroleum-based would be deemed non-hazardous given their large molecular size which prevents them from accessing sensitive human areas such as crossing the blood-brain barrier. However, the monomer form of petroleum-based plastics can pose severe health risks which merits consideration when thinking about the end of life for these products. It is also worth noting that many of the petroleum-based plastics are derived from natural gas and oil feedstocks which continues a dependency on fossil fuels and contributes to environmental pollution.[6]

Inspiration

Certain well-characterized bioplastics demonstrate excellent barrier properties. However, when considered on their own, they are not feasible packaging alternatives due to their lack of structural integrity. Using these fragile bioplastics on their own would not allow the packages to survive the shipping process. Thus, we tried to decrease the amount of bioplastic that our packaging alternative used since mineralization rates can often be linked to the surface area to volume ratio of plastics. Because of these concerns, we needed a strategy which would enable the use of a wider range of available bioplastics and would minimize the amount of bioplastics needed.

When searching for examples of other products that are frozen, packaged, and transported, we used ice cream as a model for our product because it uses a very small amount of plastics while also remaining at below freezing temperatures. Ice cream containers are made of a paperboard-based structural element coated on both sides with low-density polyethylene (LDPE). Using a paperboard layer increases the structural integrity of the packaging, largely preventing the plastic coating from warping, opening possibilities for the use of more fragile coating materials. Additionally, the paperboard layer also only needs a thin spray or laminate of LDPE to be used, instead of the thick layer of plastic needed for vacuum-sealable plastic. Finally, paperboard, a cellulose-based engineered paper product, is cheap, readily available, already in use on the industrial scale, well-characterized, and can be biodegradable depending on its additives. Cellulose itself is usually used as the standard for composting tests, for home and industrial composting.[7]

For Noble Ocean Farms purposes, the ice cream design still remained limiting; we used this structure as an inspiration for other creative solutions. Our designs consist of a stabilizing, cellulose-based structural component (such as paper, paperboard, chipboard, or molded pulp containers) as well as a double-sided biofilm barrier, which protects the structural component for the duration of frozen kelp storage. Ideally, the structural component would break apart quickly when exposed directly to water, while the biofilm would be home-compostable after a few months, i.e. decomposes without the need for high temperature and within 180 days.[7]

Strategies Overview

One of the simplest methods of eliminating polyethylene packaging would be a simple drop-in replacement of LDPE/HDPE for a biopolymer. Certain biopolymers such as PLA have already been brought into the food packaging industry as that direct substitution. As simple as this may be, there are some sacrifices in the compostability criteria to do so. For strategy 1, we are considering what materials may work in simply replacing a typical polyethylene packaging with a biopolymer.

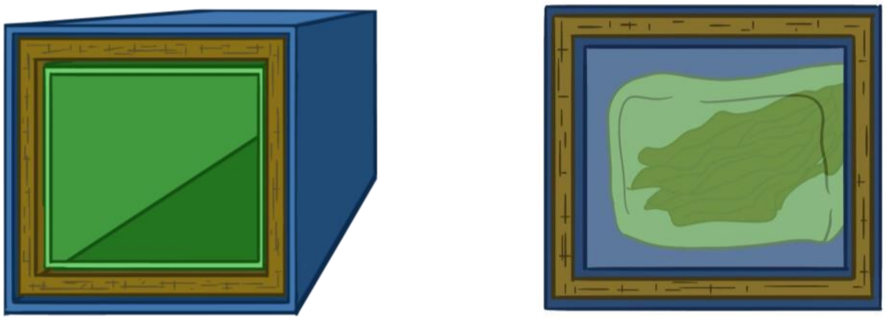

Figure 1: Visual for Strategy 2 (left). Cardboard base shown in brown. Blue represents the outer waterproof layer. Green is an inner waterproof layer. Visual for Strategy 3 (right). Blue represents the outer and inner waterproof layer. Green is an inner bioplastic bag.

For strategy 2, we are considering a structural material (such as chipboard) in conjunction with a bioplastic coating, similar to ice cream packaging. In strategy 1, the biggest shortcoming of the more compostable materials was the lack of durability; therefore, this strategy aims to take advantage of a structural material to overcome the barriers that biopolymers face when it comes to mechanical properties.

Strategy 1 sacrificed some compostability traits for technical performance while strategy 2 may require additional support to fully protect and hold the packaged kelp. Thus, strategy 3, we take the best of both strategy 1 and strategy 2 to make a fully compostable, environmentally friendly packaging by incorporating a bioplastic bag with an external structural material with a bioplastic coating.

Strategy 1

Materials

Several bioplastics exist that have the potential to completely replace petroleum based packaging with the correct plasticizers and additives. Some of the most relevant bioplastics to our mission are PLA, PHAs, PBS, PCL, PBAT and thermoplastic starch (TPS).

Polylactic acid (PLA) is a bioplastic that has been increasing in popularity due to having similar properties to traditional petroleum-based plastics and being easily manufactured from sources like corn. PLA is already in use today for many food packaging companies due to having established technical performance on par with industry standards.

Unlike PLA, polyhydroxyalkanoates (PHAs) are a category of bioplastics that are biobased and biodegradable in ambient conditions. PHAs are also very versatile due to the ability to manipulate their properties by changing the length of the polymer chain.[8,9] However, the need for plasticizers (such as citrate esters) is higher with this material due to weaker technical properties. PHAs fall into two categories based on the number of carbons in their monomeric form: 1) short-chain-length (SCL) PHAs, with three to five carbons, and 2) medium-chain-length (MCL) PHAs, with six to fourteen carbons. SCL-PHAs include poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxyvalerate) (PHV).

Polybutylene succinate (PBS) is a biodegradable plastic created from renewable feedstock (such as glucose and sucrose) that breaks down into water and carbon dioxide in soil due to microorganisms.[10] Polycaprolactone (PCL) is a plastic often added to plastics to increase mechanical properties such as tensile strength.[11] PCL is often used in starch-based plastics due to the readily available nature of the material. Polybutyrate adipate terephthalate (PBAT) is another plastic made from fossil sources but what sets it apart from traditional petroleum plastics is its ability to biodegrade.[12] Thermoplastic starch (TPS) is a completely biodegradable bioplastic made through inexpensive renewable plant feedstocks.[13] It is a common biopolymer but it can be difficult to standardize due to the vast range of properties it may have based on additives and source material.[13]

Technical Performance

Compared to the other biodegradable bioplastics our group considered, PLA is a promising candidate when it comes to barrier properties. Thanks to its low oxygen permeability (Table 2), PLA can maintain modified atmosphere packaging (MAP) conditions. Although it has higher water permeability compared to our bad actor, it has the second lowest water permeability of the bioplastics we considered (Table 2). PLA has a tensile strength of about 50 MPa compared to LDPE/HDPE which is about 60 MPa.[14] PLA also has a wide temperature range for traditional thermal processing methods.

Although PLA has good barrier properties and tensile strength, its application as a freezer bag material is significantly limited by its high glass transition temperature and low flexibility in its pure form. Based on these two properties, we predict that plastic bags made of pure PLA would likely crack or shatter if handled too roughly in the packaging or shipping processes.

SCL-PHAs like PHB are often strong with excellent barrier properties, but suffer from extreme brittleness and high glass transition temperatures. Many pure SCL-PHAs have extremely narrow working temperature ranges for traditional thermal processing techniques, and may begin to degrade in the process of creating packaging from them. Because of these shortcomings, pure SCL PHAs cannot be used as a drop-in replacement for LDPE. On the other hand, studies have shown MCL-PHAs like poly(3-hydroxyhexanoate) (PHH or PHHx) and poly(3-hydroxyoctanoate) (PHO) to have significantly lower melting points and limited elastomeric properties at best. At temperatures near or above their low melting points, MCL-PHAs become amorphous and sticky, and thus unsuitable for traditional thermal processing techniques.[15]

PBS has many comparable mechanical properties to polyethylene and is actually more flexible than PLA and does not require plasticizers. Its glass transition temperature is significantly lower than that of an industrial freezer (-20 °C). With a wide working temperature range comparable to that of LDPE, it could be easily used in existing plastic handling machinery. It outperformed LDPE in tensile strength (Table 2).[16] From a technical performance perspective, the largest drawback of PBS is its poor barrier properties. However, as an additive, it demonstrates remarkable compatibility with a wide range of bioplastics, and should be considered as a means to improve mechanical properties.

PBAT has much better mechanical properties compared to other bioplastics when it comes to flexibility (higher elongation at break (close to 700%) compared to PLA and PBS) and toughness. It is often used as an additive to bioplastics to increase the strength of the material.

TPS has poor mechanical properties; however, it is often used in conjunction with PCL and other additives to increase its ability to perform at industry standards.

Table 2: Technical performance properties for Strategy 1 materials

Properties		PLA[1,14,17–19]	PHB[20,21]	PBS [10,18,22,23]	PCL [24–26]	PBAT [12,16,27]	TPS [28,29]	LDPE [20,30]
Barrier	O2 permeability (g/m2/24 hrs)	Good	Good	Fair	775	Good	Fair	19.2
	H20 permeability (g/m2/24 hrs)	12.6	Fair	Fair	177	240	Good	0.037
Temperature	melting temp (°C)	175	180	115	60	120	150	110
	degradation temp (°C)	300	220	600	380	338	350	370-510

	glass transition temp (°C)	50 - 80	4	-29	-60	-30	-75	−30
Mechanical	tensile strength (MPa)	50	40	28 - 31	20 - 42	18 - 25	6	10-15
	strain at break (%)	3.3	4.3	14.6	1675	580 - 800	60	300 - 500
Compostability		Fair	Good	Fair	Good	Fair	Good	Poor

Note about technical data: It was difficult to find comparable values for certain criteria (ex: barrier performance) therefore, to deduce the rating, the classification that the paper/article source from which the number was found was used.

Key:	Bioplastics	Bad Actors	Good	Fair	Poor

None of the materials had the necessary technical performance to be a simple drop-in replacement for petroleum-based plastics. To develop a PHA-based polymer that has the barrier and mechanical properties we desire, it is necessary to blend SCL and MCL hydroxyalkanoates. The most promising candidate found in our research was PHB/PHO (85/15) which had a significantly higher degradation temperature (264°C) than pure PHB (220°C) and over twice the amount of elongation at break. No information was available on the barrier properties of such a blend, but with the gross part of the blend composed of PHB, it would be likely that the blend has excellent barrier properties as well.

PCL has high flexibility, and films of polycaprolactone have been reported to have an elongation at break more than 1000%, which is drastically better than the 2% seen in PLA and other bioplastics, as well as our bad actor, LDPE. It also outperforms LDPE in tests of tensile strength (Table 2). However, PCL has high oxygen and water permeability, making it unsuitable to package frozen food requiring modified atmosphere conditions and increasing the likelihood of freezer burn.

PCL is a promising additive to solve some limitations of previously mentioned bioplastics. A PLA/PCL (80/20) blend overcomes numerous technical performance shortcomings of PLA alone, increasing the elongation at break of PLA by over 47%, while maintaining a tensile strength three times that of LDPE. Unfortunately, PCL is not compatible with all biodegradable bioplastics. When blended with PHB, the resulting blend had inferior technical performance to both PHB and PCL.[7]

Health and Environmental Performance

Our team and partner organization is interested in improving the product's persistence endpoint. While all the proposed polymers listed in Table 3 are less persistent in the environment compared to polyethylene, there are still some limitations. The main issue with PLA is that it is only industrially compostable at relatively high temperatures (at least 45°C).[5] PBAT is not completely biobased because it is a plastic made from fossil sources, but what sets it apart from traditional petroleum plastics is its ability to biodegrade.[16] The fate of PBAT is much better than polyethylene because certain grades are home compostable however not all grades meet the one year requirement.[12,16] PBS is a relatively new biopolymer which has promising evidence of biodegradability and compostability at the industrial level.[10] There needs to be more research into the specific standards such as the compost conditions, polymer thickness, or the degradation time to provide clarity in the level of compostability for bothe PBAT and PBS. There are several biopolymers including PHB, PCL, and TBS that are home compostable, which is the gold standard.

Table 3: Health and environmental effects for Strategy 1 materials

Common name or trade name	Group I Human Endpoints			Group II and Group II* Endpoints			Ecotoxicity	Fate	Physical Hazard
	Carcinogenicity	Developmental/ Reproductive Toxicity	Endocrine Activity	Systemic Toxicity	Neurotoxicity	Skin, Eye, Respiratory Irritation/ Sensitization*	Aquatic Toxicity	Persistence Bioaccumulation	Reactivity, flammability
PHB[31–33]	4	3	DG	DG	DG	1	DG	4	DG
PLA[34]	4	4	4	3	3	1	4	3	4
PCL [24]	4	DG	DG	4	DG	2	DG	4	DG
PBAT [12]	DG	DG	DG	DG	DG	3	DG	3	DG
PBS [10,23]	3	DG	DG	DG	DG	2	DG	3	DG
TPS [1,13]	3	DG	3	3	DG	DG	DG	4	DG
Polyethylene, and monomers[35,36]	3	DG	DG	3	3	3	3	2	1

**Irritation is a lower degree of concern as it only arises upon contact and does not increase biological responses upon future exposure. Most of these materials are only irritants.*

Biopolymers	Bad Actors	DG = Data Gap	4 = Low Hazard	3 = Moderate Hazard	2 = High Hazard	1 = Very High Hazard

Table 4: Compostability of materials in Strategy 1 [5,10,16,18,24]

	Home Compostable	Industrially Compostable
PHA (PHB)	Y	Y
PLA	N	Y
PBS	Y**	Y
PCL	Y	Y
PBAT	Y**	Y
TPS	Y	Y
HDPE/LDPE	N	N

***Certain grades of PBAT polymer are home compostable but other grades might not meet the 1 yr requirements. PBS has been labeled home compostable by one source and not by another. This seems to depend on the specific standards set by the reviewing agency.*

All of the biopolymers, including polyethylene, are not hazardous to human health in their polymer forms. An exposure route of concern is during the manufacturing process when the biopolymers are in a fine powder form. Occupational exposure to these fine powders present a respiratory irritation hazard. This hazard should be preventable by providing appropriate engineering devices or personal protective equipment to workers. Irritation endpoints are far less concerning than sensitizers that can be acute and trigger an immune response.[37]

Unfortunately, biopolymer blends are less well characterized than pure polymers, making it difficult to gather health and safety information on specific ratios. However, the health and safety hazards will likely be very similar to those of the pure polymers, if blend preparation on the industrial scale mirrors the work done by Naranic et al.[21] According to this study, PLA/PCL (80/20) biodegrades more readily in home and industrial compost environments compared to PHB/PHO (85/15).

Most of our listed biopolymers have data gaps on either human or environmental health endpoints. These gaps need to be investigated in order to complete a comprehensive hazard assessment.

Recommended Materials

For Strategy 1, we recommend using a PLA/PCL (80/20) blend as a direct substitute for polyethylene due to its increased material strength, wide thermal processing window, and improved biodegradability relative to other bioplastic options. Since PLA is already widely in use as an eco-friendly alternative to other forms of plastic, there are industrial processing methods available. The PLA/PCL blend meets Noble Ocean Farms' six month compostability criteria in industrial conditions and will stand up to rough shipping conditions well. However, because the PLA/PCL blend performs differently than polyethylene, some reengineering of packaging may be necessary to fully take advantage of the PLA/PCL blend's characteristics and to mitigate the effect of a high glass transition temperature.

Strategy 2

Strategy 2 is a bioplastic laminate over a structural material. Moldable pulp is commonly used already in packaging and is constructed from recycled materials such as newspaper or byproducts from paper plants. Examples include egg cartons or cup carriers.[38] Chipboard is a type of cardboard made from reclaimed paper materials.[39] Bamboo has thicker and stronger fibres, making it a very durable fabric.[40] The structural material can be a number of materials, but we will use chipboard as our current material choice since it is already commonly used in frozen food packaging. We envision a future where naturally produced biomaterials, like kelp, could be used as the base material though more work is needed to determine what kind of materials can be laminated with biofilms.

Polysaccharides are one of the main groups of polymeric biomaterials and include starch, cellulose, chitin, and alginate. We will explore these as biofilm materials. Starch polymer is composed of a mix of amylose and amylopectin, both polysaccharides.[2] Chitosan polymers are made from Chitin, which is a shellfish (shrimp and crab) waste product and is the second most abundant polysaccharide found in nature (after cellulose).[2,41] Alginates are the main structural polysaccharides from marine algae (brown seaweed).[2] Zein is a plant-based protein that has primarily been used as an edible coating.[42]

Technical Performance

Technical performance of the materials can be separated into four main categories: barrier properties, effective temperature range, mechanical properties, and compostability. These properties have been researched for the materials we find of most interest for thin film application (Table 2). These materials would function as thin films over a paperboard material, as is the industry standard for frozen foods packaging. LDPE (table 2, red) is used for comparison purposes as this petroleum-based film is commonly used in frozen food packaging for coating structural components, like paperboard boxes.

All of the biomaterial replacements for thin films in packaging - zein, starch, chitosan, alginate, and polyhydroxybutyrate (PHB) - have low permeability to oxygen, some even better than our petroleum-derived industry reference (LDPE). However, all of the biomaterials have worse moisture barrier properties, though additives can improve these to a certain extent. For example, adding xanthan gum and oleic acid can improve the water barrier properties of zein films.[43]

Cobb60 values indicate how much water is absorbed by the material in 60 seconds using mass change, so a lower Cobb60 indicates a better material for packaging purposes. Starch, chitosan, and alginate films all have high Cobb60 values, with alginate having the worst with reported values ranging from 54 to 149 grams per square meter in 60 seconds.[2] Zein has a Cobb60 value of 3.1 which is significantly better than the other biomaterials but no value for LDPE is available for comparison.[2] Zein, starch, chitosan, and alginate all have good or great kit values, indicating good oil repellency.

Table 5: Technical performance properties for Strategy 2 materials

Properties		PHB[20,21]	Zein [43–45]	Starch [46,29,31,32]	Chitosan [2,49,50]	Alginate [2,42,51]	LDPE [20,30]
Barrier	O2 permeability (g/m2/24 hrs)	Good	Good	Good	Good	Good	19.2*
	H2O permeability (g/m2/24 hrs)	Fair	Fair*	Poor	Poor	Poor	0.037*
	Cobb60 (g/m2)	180	3.1	38	25 to 34	54 to 149	30
	Kit value	220	12	7.5	12	7 - 12	12
Temperature	melting temp (°C)	4	94	149-155	88	220	110
	degradation temp (°C)	40	270 to 415	250–350	>250	~250	370-510
	glass transition temp (°C)	4.3	139	36	140 - 150	81	−30
Mechanical	tensile strength (MPa)	Good	7.1 - 7.7	Poor	22.2–39.6	12.99 - 21.71	10-15

	strain at break (%)	🟧	7	2%	13–73.6	4.94 - 5.14	300 - 500
Compostability		🟩	Good	Good	Good	Good	Poor

Note about technical data: It was difficult to find comparable values for certain criteria (ex: barrier performance) therefore, to deduce the rating, the classification that the paper/article source from which the number was found was used.

Key:	Bioplastics	Bad Actors	Good	Fair	Poor

LDPE has a degradation temperature in the range of 370°C to 510°C which is very high, especially compared to its melting temperature of 110°C.[20] A large separation in the melting temperature and degradation temperature means the material is a thermoplastic (i.e. it can be melted and extruded into shape without the material breaking down). Because PHB has a very similar degradation temperature (180°C) and melting temperature (175°C), there is a very narrow window of temperature where PHB can be safely processed without degrading.[20] Due to PHB's potential degradation at higher temperatures, heat-sealing techniques cannot be used to make packaging without risking the integrity of the material. In comparison, zein, starch, chitosan, and alginate all have degradation temperatures between 250°C and 415°C, indicating a lower chance of the material degrading during processing at elevated temperatures. LDPE also has the best glass transition temperature (-30°C) compared to any of our materials which might be a concern depending on the temperatures of the packaging process and storage. Of the biomaterials, the glass transition temperatures are all above freezer temperatures (-18°C), which indicates that these materials would become brittle when stored in their intended conditions.

While many of these biopolymers have high tensile strength as compared to LDPE, they all have much worse elongation properties, indicating that they are hard but brittle materials. These materials would not be a flexible packaging material on their own, but they will have improved mechanical properties if the material they are laminated on is a strong material. Currently, the material of choice is paperboard, which is strong. However, paperboard will decompose upon exposure to water which means that any film needs to have good water barrier properties and the ability to remain attached to ensure continuation of protection.

Biopolymers are not necessarily biodegradable. It is important to ensure that these materials are compostable and to investigate multiple compostable conditions. The region of interest for this product is Alaska, which does not have robust industrial composting capabilities; thus, the materials need to be home-compostable. However, data on whether the materials are home compostable was not easy to acquire. Starch and PHB are compostable by home- and industrial-composting standards.[7] Cellulose (which is the main component of paperboard) is often used as a reference material or control in composting studies and so is also indicated as meeting home and industrial composting standards.[7] Chitosan is biodegradable, which implies it meets industrial composting standards, but more research is needed.[52]

In general, these biofilms have low oxygen permittivity, but have poor water barrier properties, especially when compared to LDPE which is two orders of magnitude better than PHB. While the films are strong and have high degradation temperatures, these are not the highest priority properties for our intended use. These materials also all have high glass transition temperatures which might not make them suitable for use in frozen packaging, especially with the lack of flexibility of the materials. It is important to note that the glass transition temperatures and brittleness of these materials can be addressed with the addition of green plasticizers or additives, like glycerin, which have been proven to improve technical performance of the materials without affecting the biodegradability.

Health and Environmental Performance

PHAs are able to use food waste as a feedstock since the bacteria used to generate them feed on organic matter. Looking at the proposed bioplastics listed in Table 6, it is concerning to see that PHB and some others have high adverse skin, eye, and respiratory effects. This issue stems from the biopolymers being tested in a fine granular form, which can affect eye and respiratory organs if exposed to a sufficient concentration in air. This concern is quickly diminished when thinking about these biopolymers as a macroscopic product, such as the various foodware options that PLA is currently used as. Cellulose, a packaging material we are investigating, also exhibits a similarly high respiratory hazard when generated as a fine powder yet it is still regularly used in commercial packaging because it is rarely generated in such form.

Allergic reactions also represent a point of concern. Chitosan is derived from shellfish and thus is considered a potential allergen though there is no data to indicate chitosan has caused allergic reactions.[42] However, chitosan can also be sourced from fungi; if allergies become a larger concern, there is an alternate source for the biopolymer. Zein is a corn protein and people with corn allergies have reported allergic reactions, though this is likely due to non-zein additives in the films and these instances are rare.[42]

Though these alternative bioplastic and packaging materials have hazards, it is clear that compared to current petroleum-based forms of packaging, these alternatives have the potential to be much safer. Some of these materials, like cellulose, have become commonplace products and now lack any pressure for additional safety testing to be done. Still, there is work to be done in investigating the data gaps in the endpoints that remain. It is unclear how safe these alternatives will be as they break down into smaller subcomponents which is why we are also assessing the biodegradability of these alternatives.

PLA is a common bioplastic marketed as being compostable, however biodegradability is only achieved in industrial facilities.[21,53] PHAs, on the other hand, are much better biodegradable materials that are home-compostable, so they eliminate the need for special processing facilities and degrade in a shorter period of time. For example, PHB has been tested to meet ASTM and ISO standards for biodegradation in home environments as well as the OK biodegradable SOIL label, meaning that PHB will achieve 90% biodegradation at 28°C with no harm to the soil environment.[42,53,54] From Table 7, starch has also been proven biodegradable across a wide range of environments in addition to home composting such as marine, freshwater, and landfill environments.[53]

Table 6: Health and environmental effects for Strategy 2 materials

Common name or trade name	Group I Human Endpoints			Group II and Group II* Endpoints			Ecotoxicity	Fate	Physical Hazard
	Carcinogenicity	Developmental/ Reproductive Toxicity	Endocrine Activity	Systemic Toxicity	Neurotoxicity	Skin, Eye, Respiratory Irritation/ Sensitization*	Aquatic Toxicity	Persistence Bioaccumulation	Reactivity, flammability
PHB [31–33]	4	3	DG	DG	DG	1	DG	4	DG
Starch [55–57]	4	DG	DG	3	DG	3	4	4	3
Chitosan [42,58]	DG	DG	DG	4	DG	3	2	4	DG
Alginate [51,59–61]	4	DG	DG	DG	DG	DG	DG	4	DG
Zein	DG	DG	DG	DG	DG	2	DG	4	DG
Polyethylene, and monomers [35,36]	3	DG	DG	3	3	3	3	2	1

***Irritation is a lower degree of concern as it only arises upon contact and does not increase biological responses upon future exposure. Most of these materials are only irritants.**

Biopolymers	Bad Actors	DG = Data Gap	4 = Low Hazard	3 = Moderate Hazard	2 = High Hazard	1 = Very High Hazard

Table 7: Compostability of materials is Strategy 2 [7,53]

	Home Compostable	Industrially Compostable
PHB	Y	Y
Alginate	Y	Y
Zein	Y	Y
Chitosan	Y	Y
Starch	Y	Y
HDPE/LDPE	N	N

Recommended Materials

Based on the primary criteria of home compostability, barrier properties, and hazard minimization, the combination of chitosan/zein and chipboard is recommended for the bioplastic coating and structural material in strategy 2. Compared to alginate and starch, the chitosan/zein combination chitosan/zein has been heavily researched as a promising candidate for laminating paper products as it has already shown heavily improved barrier properties.[45] While PHB is a versatile biopolymer as well, the thermal constraints that may be required in this processing stage may be too intense to effectively coat a paper material. Both chitosan and chipboard are both cyclical materials, meaning that they come from waste sources already existing in our environment which reduces the environmental strain of food packaging necessary for this task. One important thing to note however, is it is likely that there may still be necessary additives to include in a chitosan/zein coating to ensure that the barrier is up to standard and will withstand handling.

Strategy 3

When considering Strategies 1 and 2, we often had to sacrifice either biodegradability for technical performance or vice versa to engineer a feasible alternative to polyethylene packaging. However, in Strategy 3 we investigate the combination of the previous two strategies to produce a packaging alternative that took the best of both worlds. Strategy 3 consists of a plastic bag contained inside a structural material coated with another bioplastic to protect the integrity of the container. The presence of a structural material allows the plastic bag to have more biodegradability at the expense of worse mechanical properties as it will largely be protected from most mechanical stress from handling. A plastic bag with good barrier properties compensates for a coating on the structural material with worse barrier properties, allowing us to use chemically simpler plastics or films to coat. Therefore, when conducting a survey of the possible materials for Strategy 3, we prioritize the home compostability of each component involved.

Technical Performance

The internal plastic bag would require the best barrier properties and compostability based on the research conducted in Strategy 1. Both thermoplastic starch and PHAs, such as PHB, have shown the best barrier properties while also meeting home compostability standards. Additionally, both TPS and PHAs have a range of temperatures at which they can be processed without degradation. PHAs have been of particular interest due to their ability to be blended. These blends often have enhanced properties; for example, a blend of PHB/PHO has been shown to have excellent barrier properties as well as compostability.

Table 8: Technical performance properties for Strategy 3 materials

Properties		TPS [13,28,29]	PHB [20,21]	Zein [42,43]	Starch [42,47,48]	Chitosan [2,49,50]	Alginate [2,42,51]	LDPE [20,30]
Barrier	O2 permeability (g/m2/24 hrs)	Fair	Good	Good	Good	Good	Good	19.2
	H2O permeability (g/m2/24 hrs)	Good	Fair	Fair*	Poor	Poor	Poor	0.037
	Cobb60 (g/m2)	N/A	N/A	3.1	38	25 to 34	54 to 149	30

	Kit value	N/A	N/A	12	7.5	12	7 - 12	12
Temperature	melting temp (°C)	150	180	94	149-155	88	220	110
	degradation temp (°C)	350	300	270 to 415	250–350	>250	~250	370-510
	glass transition temp (°C)	-75	4	139	36	140 - 150	81	−30
Mechanical	tensile strength (MPa)	6	40	7.1-7.7	Poor	22.2–39.6	12.99 - 21.71	10-15
	strain at break (%)	60	3 - 6	7	2%	13–73.6	4.94 - 5.14	300 - 500
Compostability		Good	Good	Good	Good	Good	Good	Poor

**when mixed with xanthan gum and oleic acid*

Note about technical data: It was difficult to find comparable values for certain criteria (ex: barrier performance) therefore, to deduce the rating, the classification that the paper/article source from which the number was found was used.

Key:	Bioplastics	Bad Actors	Good	Fair	Poor

The bioplastic used to coat the structural material would need to have decent barrier properties as well as mechanical properties due to their relatively higher exposure to handling and transport. Despite this, due to the presence of an additional barrier from the inner bioplastic bag, the coating may not need as high of a barrier to moisture and oxygen. To increase the simplicity of the engineering, we propose the use of chitosan as the material to coat the structural chipboard.

Health and Environmental Performance

Because Strategy 3 combines materials from the first and second strategies, the health and environmental performance mirrors the information above, but can be seen in direct comparison below in Table 9.

Table 9: Health and environmental effects for Strategy 3 materials

Common name or trade name	Group I Human Endpoints			Group II and Group II* Endpoints			Ecotoxicity	Fate	Physical Hazard
	Carcinogenicity	Developmental / Reproductive Toxicity	Endocrine Activity	Systemic Toxicity	Neurotoxicity	Skin, Eye, Respiratory Irritation/ Sensitization*	Aquatic Toxicity	Persistence Bioaccumulation	Reactivity, flammability
PHB [31–33]	4	3	DG	DG	DG	1	DG	4	DG
TPS [1,13]	3	DG	3	3	DG	DG	3	4	4

Starch [55–57]	4	DG	DG	3	DG	3	4	4	3
Chitosan [42,58]	DG	DG	DG	4	DG	3	2	4	DG
Alginate	4	DG	DG	DG	DG	DG	DG	4	DG
Zein[42]	DG	DG	DG	DG	DG	2	DG	4	DG
Polyethylene, HDPE, LDPE, and monomers [35,36]	3	DG	DG	3	3	3	3	2	1

Irritation is a lower degree of concern as it only arises upon contact and does not increase biological responses upon future exposure. Most of these materials are only irritants.

Biopolymers	Bad Actors	DG = Data Gap	4 = Low Hazard	3 = Moderate Hazard	2 = High Hazard	1 = Very High Hazard

***Table 10: Biodegradability of materials is Strategy 3* [7,53]**

	Home Compostable	Industrially Compostable
PHB	Y	Y
TPS	Y	Y
Alginate	Y	Y
Zein	Y	Y
Chitosan	Y	Y
Starch	Y	Y
HDPE/LDPE	N	N

All three strategies can pose health concerns in their manufacturing stages, particularly respiratory issues. After these packaging materials have been created, there are very low health risks that are of concern. As previously mentioned, the bioplastics used in all strategies have strict environmental requirements that must be met to be composted. Thus, there is still an environmental health hazard. However, this concern is much less significant than the current polyethylene alternative. Compared to Strategy 2, Strategy 3 does not require a thick coating of bioplastics on the cardboard base, so its health and environmental concerns are simpler. As a result, the concerns for health and environmental performance in this strategy are more similar to those of Strategy 1 than Strategy 2. There are no new health or environmental concerns that arise in Strategy 3 outside of the ones listed in the previous strategies.

As previously stated, all strategies have significant data gaps, and more research is needed in order to confidently state that there will be no health or environmental risks; but, thus far the research seems promising and the production of this product seems as if it would pose significantly less of a health and environmental concern than the current product in use, polyethylene.

Recommended Materials

As stated in previous sections, strategy 3 takes into account only materials that have home compostability and minimal environmental strain to consider the best parts of both strategy 1 and 2. With that in mind, the recommended materials would be PHB/PHO (80/20) for the inner bag, with a chitosan coating on a chipboard outer layer. Chitosan, as previously stated, is a great renewable material with cyclical uses and the inclusion of an inner bag allows it to rely relatively less on additives compared to strategy 2. Additionally, PHB/PHO (80/20) lacks some mechanical strength that would be required for strategy 1, however, has improved predicted barrier properties (based on the base single polymer) that would be beneficial for strategy 3. Therefore, we believe a combination of these materials would best serve as a great option for strategy 3.

Recommendations and Next Steps

Recommended Strategy

Our team has identified three potential strategies for producing a biodegradable frozen kelp packaging that replaces conventional polyethylene-based products. For strategy one, we proposed storing frozen kelp in a simple freezer-compatible bag that substitutes polyethylene for a PLA/PCL polymer blend. For strategy two, we were inspired by commercially available ice cream products and designed a packaging that uses a chipboard base with a chitosan/zein polymer coating. Lastly, for strategy three we merged the previous two strategies and designed a packaging that uses a PHB/PHO biopolymer bag housed inside a chipboard base coated with chitosan. Each strategy has pros and cons that were considered before deciding on a recommended strategy.

The benefits of strategy one are its ease of implementation, design simplicity, and increased biodegradability. Replacing the material of current plastic bag packaging from fossil-based polymer to biopolymer may result in easier adoption since the overall design is kept intact. Since this packaging is not multilayered, we expect it to biodegrade faster compared to our other strategies given its simplicity and thinness. Unfortunately, this also implies that we are sacrificing durability for biodegradability since this type of packaging is likely to exhibit wear and tear sooner than other strategies. Additionally, while we aim to steer away from fossil-based materials in our strategies, strategy one relies on an additive that is traditionally fossil-based.[3]

For strategy two, we recommend chitosan/zein as a bioplastic composite coating onto chipboard due to their investigated compatibility and strengths in technical criteria and home compostability. Strategy two is beneficial in that it promotes a circular economy since both chitosan and chipboard can be derived from waste streams.[2,39,41] Chipboard has already been used in the food packaging industry and its lamination is a well established manufacturing process. This strategy would have chipboard laminated with a chitosan/zein polymer blend that has been researched to demonstrate great material properties.[45] Drawbacks for this strategy include potentially requiring a thicker coating of polymer to meet performance criteria and insulate the kelp inside the packaging well. Also, this strategy again relies on a biobased additive that although remains biodegradable may impact production feasibility.

Building off strategies one and two, strategy three retains many of the benefits mentioned already for strategy two. This strategy also promotes a circular economy and relies on an already established manufacturing process for creating the chipboard base. In addition, this strategy allows for greater flexibility of the biopolymer used to create the inner plastic bag since durability is no longer a priority when housed inside a supporting chipboard enclosure. The multiple layers of this strategy make an excellent case for meeting all performance criteria we were looking for in a product. Yet, as alluded to earlier, this strategy's multiple layers have increased the overall complexity of this packaging solution and rely on two manufacturing processes, creating the plastic bag and laminating the chipboard base. The materials recommended for strategy three are chipboard (structural material), chitosan (for the coating of structural material), and PHB/PHO in an 80/20 ratio (for the inner bag) due to the home compostability and expected technical performance.

After considering each strategy and assessing their pros and cons, our team ultimately decided on strategy three as our recommended solution. We acknowledge that cost may be an issue in implementing this strategy but it is best at meeting performance criteria. This strategy benefits from the durability of a chipboard exterior and barrier properties of an inner bag enclosure, both working together to ensure the frozen kelp is kept in ideal condition. Additionally, this strategy consists of materials that are home-compostable thus remaining in line with our compostability goal.

Remaining Questions

The environmental and health impacts of the bioplastics and additives need further investigation and research. We are still unsure about what the most suitable material is for the structure of the packaging. Bamboo, molded pump, and paperboard need to be further explored to investigate the cost-benefit, contribution to the circular economy, and other potential unintended drawbacks. The method of spray-on technique of the biofilms might pose occupational health hazards that we need to further investigate. There might also be other methods of lamination that would work better that we need to look into. We also have questions on what are some potential bio-additives we could use in our manufacturing process so we are improving all aspects of the product.

Timeline

The strategies presented in this document cover biopolymers that may not be commercially available yet but can still serve as a starting point for our partner Nobel Ocean Farms. We have outlined current and upcoming companies involved in the manufacture of biodegradable plastic packaging to give an idea of the state of bioplastics available.

Currently, there are established companies involved in making biopolymers and applying them to product packaging. Mango Materials is a company with experience in producing PHA-based bioplastics and has partnered with consumer packaged goods companies.[62] Full Cycle is another company that is similarly converting organic waste into PHA.[63] These companies are already working on eliminating fossil-based packaging and showcase current market solutions. Coming soon, the startup company Sway is looking to take seaweed and convert it into a bioplastic.[64] It would be appealing if their finished bioplastic met the packaging requirements of frozen kelp so that the packaging and product inside were derived from the same source. Lastly, the chitosan/zein bioplastic we discussed earlier is still in the research stage with no clear indication of how soon it may become commercialized.[45] Though research on chitosan/zein is promising, it is likely too far in the future for our partner to use in packaging.

Our Team

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