# From Dirty Laundry to a Cleaner Planet: Exploring Eco-friendly Alternatives to Polyvinyl Alcohol (PVA) in Detergent Products

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# 1. Abstract

Polyvinyl alcohol (PVA) is used as packaging for single-use laundry detergent packs and sheets. PVA is an attractive synthetic polymer due to its water-soluble nature, film-forming properties, and inclusion on the EPA Safer Chemicals Ingredient List. However, current research shows that PVA requires very specific conditions to biodegrade. Our current wastewater treatment plants can only biodegrade a fraction of the PVA that enters the plant, releasing the rest into the environment. Further, while there are no demonstrated negative human health impacts of PVA, the precursors are carcinogenic and the synthesis of PVA is hazardous, PVA has been found to bioaccumulate, and PVA does not biodegrade in seawater or soil. The status quo is not sustainable and both consumers and companies are exploring options to replace PVA.

In collaboration with ECOS, we identified nine biopolymer alternatives to PVA in detergent packs and sheets. Our proposed alternatives include polysaccharides such as alginate, carrageenan, chitosan, pullulan, and cellulose and protein-based polymers including brewer's spent grain, soy, pea, and mung bean protein. We also identified several plasticizers and hygroscopicity reducers that could be incorporated into an alternative formulation to enhance flexibility and increase shelf-life, respectively. In this report, we evaluate the alternatives based on technical performance, compatibility with the current manufacturing process, and impact on health and the environment. Biopolymer-based alternatives show promise due to their low toxicity and high biodegradability; however, they exhibit lower strength and stability, necessitating additives and formulation optimization. This exploration underscores the potential of eco-friendly alternatives to PVA in detergent packs and sheets, enabling a future in which we can minimize our dependence on this synthetic polymer.

# 2. Background

# Problem Landscape

ECOS laundry detergent sheets and packs currently use polyvinyl alcohol (PVA) to encapsulate their detergent ingredients. These pre-measured and single-use detergent sheets and packs provide a convenient, mess-free solution for consumers. However, consumers and industry players are increasingly skeptical of PVA's biodegradability. In response, ECOS is actively exploring the possibility of phasing out PVA and replacing it with a biopolymer in their products. Adopting biopolymers poses a notable challenge as the alternative solutions may not fully meet all of ECOS's functional requirements on their own, potentially requiring additional additives to optimize the manufacturing process and overall performance of their detergent sheets and packs.

# Polyvinyl Alcohol in Laundry Sheets and Packs

In the context of laundry packs (Figure 1) and sheets (Figure 2), PVA plays a pivotal role in encapsulating detergent ingredients and providing structural integrity. Its water solubility in hot and cold temperatures makes PVA a useful ingredient in detergent packs and sheets.<sup>1</sup> Due to its water-soluble nature and small size, PVA is not classified as a source of microplastic pollution and it is listed on the EPA Safer Choice List. Various cleaning product companies and other industries use PVA due to its affordability and commercial availability. Its compatibility with detergent ingredients, coupled with its tensile strength and flexibility for ECOS's manufacturing processes, makes PVA a convenient binder for their laundry sheets and packs.



Figure 1: PVA films encapsulate detergent packs.



Figure 2: PVA provides the structure of detergent sheets.

### Polyvinyl Alcohol Concerns

Regulations require some industries to perform biodegradability tests on their products to satisfy OECD 301B guidelines. To satisfy the guidelines, a product must show at least 60% biodegradation within 28 days, measured by the amount of carbon dioxide released, and at least 10% biodegradation within the first 10 days.<sup>2</sup> ECOS packs and sheets currently satisfy the OECD 301B guidelines (Figure 3). While PVA-containing products pass the OECD 301B biodegradability standard, other detergent ingredients in the product may account for a high proportion of the truly biodegradable ingredients. While the biodegradation pathway of PVA has been well-characterized, true degradation requires ideal conditions that are not present in most wastewater treatment plants.<sup>3,4</sup>



Figure 3: ECOS Sheet passes the OECD 301B biodegradability standard, but fails to meet the readily biodegradability standard due to not reaching the biodegradability threshold within 10 days of achieving 10% degradation.

PVA degrades under a range of conditions, influenced by the degree of hydrolysis, composition, environment, presence of microorganisms, and the ratio of microorganisms.<sup>4,5</sup> As PVA is dissolved during loads of laundry, an estimated 61% ends up in wastewater treatment plants (WWTPs), with the rest traveling to other environmental sources (Figure 4). However, conventional WWTPs are not capable of effectively degrading PVA.



Figure 4: Modeled PVA usage and emissions in metric tons per year (mtu/yr) in the US (Source: Rolsky & Kelkar, 2021)

Once in the environment, PVA shows little to no degradation in soil and water (Figure 5, Table 1).<sup>6,7</sup> Although PVA has been modeled to be toxic to aquatic life and is thus on the DK-EPA Danish Advisory list (Aquatic Acute 1), no similar studies or government advisory lists have indicated PVA poses high hazards to water.

Soil Degradation								
Weeks	0	1	2	3	4	5	6	7
Weight Loss Rate (%)	17	31	33	28	29	29	35	35

Table 1: PVA biodegradation in soil as measured by weight loss rate.(Adapted from Su et al, 2022)



Figure 5: PVA Fails UNE-EN ISO 14851:2019 Seawater Biodegradability Standard. Study shows the comparison of a biodegradable substance as a control (C + PHB) to PVA (Source: Alonso-López et al., 2021)

PVA is a relatively inert polymer that is not carcinogenic to humans and has been administered orally to rats at a rate of 5 g/kg body weight (bw) per day without any observed adverse effects in a two-generation reproduction study.<sup>8</sup> Furthermore, the  $LD_{50}$  is in the range of 15-20 g/kg<sup>8</sup> and it is not reactive or flammable. PVA has been found in breast milk, so there are concerns about bioaccumulation and microplastic-like behavior.<sup>9</sup>

PVA's precursor chemicals pose higher health hazards than PVA, and this disproportionately affects the workers exposed during chemical manufacturing. Several of the chemicals used in PVA synthesis exhibit carcinogenicity, systemic toxicity, neurotoxicity, skin, eye, respiratory irritation and/or sensitization, bioaccumulation, and toxicity to aquatic wildlife. Since PVA is a synthetic chemical, it is necessary to look at the inputs in producing PVA to get a holistic view of the hazards PVA poses to human and environmental health.

Despite the relatively benign nature of PVA, there are hazards associated with the reactants and side products of the polymerization process (Table 2). The monomer, vinyl acetate, is a human carcinogen with potential for reproductive toxicity and is a potential endocrine disruptor.<sup>10,11</sup> It is on the US EPA Extremely Hazardous Substances List and has acute oral and respiratory toxicity.<sup>12</sup> It causes serious skin, eye, and respiratory irritation, and may cause drowsiness or dizziness.<sup>10,11</sup> It may cause organ damage over prolonged or repeated exposure and is on the Boyes neurotoxicants list.<sup>13</sup> Lastly, it is a highly flammable liquid with acute toxicity to aquatic life.<sup>10,11</sup> These hazards must be taken into account for those synthesizing, transporting, and handling the monomer.

While the monomer is not present in the final polymerized product, there are several impurities from the polymerization and transesterification reactions. The major impurity, methanol, is used as the solvent for transesterification. Methanol is of low concern for carcinogenic or genotoxic

effects, though it is suspected to be a developmental toxicity risk.<sup>14</sup> It has high acute toxicity and eye irritation, and is a flammable liquid.<sup>15,16</sup> Despite this, the low boiling point of methanol (65 °C) makes it extremely likely that almost all methanol evaporates during the drying of the final product.<sup>15</sup>

Methyl acetate is a transesterification byproduct with a similarly low boiling point (57 °C).<sup>17</sup> Methyl acetate has a potential concern as a carcinogen and has moderate developmental toxicity.<sup>18</sup> It has high respiratory, skin, and eye irritation, but low oral toxicity and moderate to low neurotoxicity.<sup>17–19</sup> It is a highly flammable liquid and has a very high to high persistence hazard.<sup>17,18</sup> Acetic acid is also used in PVA synthesis. Acetic acid is in vinegar, so it is not a toxicant at low concentrations, but at high concentrations, there are acute toxic effects in humans.<sup>20</sup> At high concentrations, it is an eye irritant and is flammable.<sup>20</sup> In the processing of PVA, acetic acid is used in high concentrations. Additionally, trimethylolpropane (1,1,1-Tris(hydroxymethyl)propane) is another side product in the synthesis of PVA. It is on the EU REACH and EC-CEPA VSL lists for being inherently toxic to humans. It is also an irritant to the respiratory tract and skin.<sup>21</sup> A small percentage of trimethylolpropane is found in the PVA films used in ECOS packs. The final impurity of concern is sodium acetate. Sodium acetate is modeled to have low genotoxicity but to cause inhalation, systemic, and skin irritation.<sup>22,23</sup> It can cause serious eye damage.<sup>22</sup> It is also on the US EPA Safe Chemicals Ingredients list as a processing additive.

	Group I Human Endpoints		Group	Group II and Group II*		Ecotoxicity	Fate	Physical	
	Group I		upoints		Endpoin	ts	Ecotoxicity	Fatt	Hazard
Name	Carcinogenicity	Developmental and	Endocrine	Systemic	Nounotovisity	Skin, Eye, Respiratory	Aquatic Toxicity	Persistence	Reactivity, Flammability
	Mutagenicity	Reproductive Toxicity	Activity	Toxicity	Neurotoxicity	Irritation/ Sensitization	Acute/Chronic	Bioaccumulation	Other Pchem Traits
Polyvinyl Alcohol	L	L	DG	L	L	L	H*	M*	L
Vinyl Acetate	Н	М	М	М	M	Η	Н	DG	Н
Acetic Acid	L	L; DG	DG	М	L	M; vH	М	vL	М
Methanol	L	H; L	DG	L	vH	L; M	L	vL	L; H
Sodium Hydroxide	DG	DG	DG	М	M	vH	М	vH	L
Sodium Acetate	L	DG	DG	L	DG	Η	DG	DG	L
Methyl Acetate	L	L	DG	Η	М	Η	DG	vH	Н
Trimethylolpropane	M	Н	DG	М	М	М	L	L	L
<i>italicized</i> = low confidence L = reasonable assumption of safety += not a consumer hazard H = not a consumer hazard H = not a consumer hazard					H vH very high				

Table 2. Hazard Assessment of PVA and its Precursors.

# 3. Approach/Inspiration

We aimed to identify alternative materials that can replace PVA used in ECOS detergent sheets and packs. In comparison to liquid detergent and liquid detergent packs, detergent sheets and powder detergent packs have a compelling environmental advantage due to reduced water usage in production and their low weight. Additionally, detergent sheets' environmental footprint outperforms other detergent types because of their compact packaging and ability to be packaged with composable materials for distribution. Therefore, we will prioritize the search for biopolymer alternatives to make detergent sheets. However, if we find PVA alternatives for detergent packs as well in the process, that will still be beneficial. By doing so, we are committed to removing the petrochemical-based PVA and truly progressing towards a more sustainable detergent product.

We evaluated potential alternatives according to their (i) technical performance, (ii) manufacturing compatibility, and (iii) health and environmental impact. The general criteria are summarized in Table 3.

Category	Criteria	Specification	
	Dissolution Rate	< 40 seconds in water of any temperature	
Technical Performance	Stability	2-year shelf life under ambient temperature and humidity	
	Chemical Compatibility	Does not change and/or interfere with active detergent ingredients. pH between 5 and 9.	
	TSCA	Listed on the TSCA Chemical List	
	Availability	Commercially available and accessible	
	Thermal Stability	Compatible with drying temperatures	
Manufacturing	Flexibility	Pliable and not brittle	
Compatibility	Tensile Strength	$\geq$ 47 MPa	
	Elongation*	290% when heated to 150 °C	
	Viscosity of detergent solution**	80,000 cps at 50 °C	

Table 3. Categories of criteria for selecting alternatives used in detergent packs and sheets

Health and Environmental Impact	Sourcing	Alternative comes from renewable sources that are not animal derived
	Toxicity	Non-toxic to human and aquatic life
	Biodegradability	<ul> <li>Satisfy OECD 301B Guideline:</li> <li>At least 60% biodegradation within 28 days, measured by the amount of carbon dioxide released</li> <li>At least 10% biodegradation within the first 10 days</li> </ul>
	Bioaccumulation	Does not bioaccumulate

\* Criteria necessary for detergent pack only

\*\* Criteria necessary for detergent sheet only

Our technical performance criteria include: solubility, shelf life stability, and compatibility with the detergent ingredients. For solubility, the PVA alternative must dissolve in both cold and hot water to deliver the detergent. Evaluating shelf life stability and compatibility is difficult without laboratory facilities, as many of these alternatives have not been tested in sheets and packs before. Thus, we used pH ranges as a proxy for chemical compatibility and investigated additives that will increase the lifetime regardless of alternative.

For manufacturing compatibility, we looked for commercially available materials, with the thermal and physical properties necessary for large-scale manufacturing. Packs are made by stretching a PVA film and heat-sealing it over the detergent ingredients. Sheets are made by mixing PVA with active ingredients into a viscous sludge, which is then coated on a rotating drying drum, where it dries into a sheet. For commercial availability, we looked at market size, with a presence on the Toxic Substances Control Act (TSCA) Chemical Substance Inventory as an additional advantage. For thermal properties, current ECOS packs manufacturing uses temperatures up to 150 °C to cut and heat-seal PVA films, while current ECOS sheets manufacturing heats up to 100 °C to dry the PVA mixture. For physical properties, ECOS sheets and packs need to be flexible and have the tensile strength to hold together around and coming off of the manufacturing equipment. The PVA films for packs need tensile strength values  $\geq 47$  MPa and the PVA sheets need tensile strength 1-10 MPa. For packs only, the PVA films have an elongation of 290% and can be stretched over the powder ingredients. For sheets only, the PVA mixture has a viscosity of around 80,000 cps; alternative mixtures should be able to achieve similar viscosity, but this depends on the concentration and formulation.

In evaluating the health and environmental impact of potential alternatives, conducted hazard assessments of each alternative to determine that they were non-toxic to humans, aquatic life,

and the environment. We aimed for our alternatives to not pose a risk of bioaccumulation, be known as readily biodegradable, and be sourced from renewable sources.

We searched for biologically sourced water-soluble polymers to investigate alternatives to PVA. By drawing inspiration from biopolymers and additives utilized in the food, pharmaceutical, and cosmetics industries, such as sodium alginate films as Impossible<sup>TM</sup> sausage casings, we ensure that our exploration remains anchored in materials with established safety and suitability profiles. This approach aligns with ECOS's commitment to eco-friendly practices and emphasizes a holistic consideration of technical performance, manufacturing compatibility, and health and environmental impact.

# 4. Strategy 1: Polysaccharides

In the search for replacements for polyvinyl alcohol, a synthetic polymer, natural polymers are an obvious standout due to their ubiquity and biodegradability. Polysaccharides, one of two classes of natural polymers, are carbohydrates composed of monosaccharide units bound by glycosidic linkages. Polysaccharides are used by organisms to store energy (e.g., glycogen, starch) and provide structure (e.g., cellulose in plant cell walls, chitin in crustacean exoskeletons). Structural polysaccharides are ideal candidates for providing structural support in laundry detergent products and most organisms are incapable of metabolizing them, preventing unwanted preemptive degradation. However, due to the widespread abundance of polysaccharides on earth, many microorganisms will be able to degrade polysaccharide products relatively quickly. Five polysaccharides—sodium alginate, carrageenan, chitosan, pullulan, and cellulose—were selected for investigation due to their water-solubility properties and established use in food and cosmetics.

### Sodium Alginate

Alginate is an anionic linear polysaccharide biopolymer that is found in the cell walls of brown algae (Figure 6).<sup>24,25</sup> It contains two monomers,  $\beta$ -d-mannuronic acid (M) and  $\alpha$ -1-guluronic acid (G), which form irregular patterns of GG, MG, and MM blocks within the polymer, altering the specific properties of the polymer.<sup>24,25</sup> The carboxylate groups in the alginate monomers are coordinated to cations, which are easily exchanged to affect the properties and functionality of the material.



Figure 6: Brown algae (left), the source of sodium alginate, whose structure is composed of mannuronic acid and guluronic acid monomers (right).

The manufacturing process of alginate involves relatively mild conditions and is performed at ambient temperatures.<sup>26</sup> In short, alginate is extracted from dried seaweed by crushing, washing with divalent cations, and swelling in acidic water. Then, sodium hydroxide is added to remove sodium alginate from seaweed, the solution is diluted, and the seaweed/alginate mixture is

filtered to remove the fibrous material. Lastly, alginate is purified by acidifying to precipitate alginic acid, dried to remove excess water, and undergoes ion exchange to add the desired countercations. Alginate is used in a variety of industries, including food, cosmetics, pharmaceuticals, fertilizers, textile printing, and medical devices.<sup>26</sup> Alginate is even used as a vegetable casing for Impossible<sup>TM</sup> sausages (Figure 7).



Figure 7. Impossible<sup>TM</sup> sausages wrapped in a vegetal casing containing sodium alginate (left) and highlighted ingredients of the vegetal casing (right).

#### Technical Performance & Manufacturing Compatibility

Sodium alginate meets many of the technical and manufacturing criteria for an effective alternative to PVA (Table 4). However, the lack of research on sodium alginate films for application in single-use detergent products has resulted in data gaps for certain criteria. Regarding technical performance, the dissolution rate for sodium alginate varies depending on the exact formulation and thickness. Ma reported that sodium alginate dissolves within 90 seconds at room temperature; however, our own preliminary testing on  $\sim 50 \ \mu m$  films indicates that it can dissolve in as little as 60 seconds, making the solubility comparable to the PVA benchmark.<sup>27</sup> The shelf life of sodium alginate products is less studied, especially regarding its use in single-use detergent products. One concern regarding the stability of sodium alginate films is their high hygroscopicity; sodium alginate powder has a shelf-life of several months in dark, cool, and dry places. Kimica-a specialized manufacturer that produces and sells alginate-recommends storage in cool and dry places due to the natural polymer chains gradually shortening over time.<sup>26</sup> Ultimately, the concentration of sodium alginate and the mixture of ingredients, including hygroscopicity-reducing additives, will alter the shelf life of the final product. Alginate is a relatively inert material, though the countercation plays a significant role in the physical properties of the material. Monovalent cations like sodium, potassium, and ammonium result in readily-soluble films. However, divalent cations such as calcium and magnesium result in an insoluble material. Similarly, reducing the pH to about 3.5 results in the

precipitation of sodium alginate due to the protonation of mannuronic and guluronic residues (pKa of 3.38 and 3.65, respectively).<sup>28</sup> Overall, sodium alginate meets the criteria of being readily soluble in cold water and compatible with the chemicals in traditional laundry detergents.

The manufacturing compatibility of sodium alginate varies greatly on the composition of the sodium alginate film (for packs) and detergent mixture (for sheets), and most research is limited to alginate films for applications such as food, drug, and product packaging. However, sodium alginate is currently used in a variety of applications, including in food, cosmetics, textile printing, pharmaceuticals, and medical devices. It is listed on the TSCA Chemical List and has a robust market size of at least 30 kilotons, about a tenth the size of the PVA market, though it is estimated that 6.5 million tons of alginate is produced by brown seaweed annually.<sup>29</sup> Sodium alginate suppliers, including Kimica, provide various product grades, depending on the desired viscosity, gel strength (mannuronic/guluronic ratio), purity, quality control specifications, etc. The thermal stability of sodium alginate is lower than PVA due to being a biopolymer; however, it requires lower temperatures (80 °C vs. 150 °C) to reach its glass transition temperature (Tg). A lower glass transition temperature may be beneficial in manufacturing due to enabling lower mixing temperatures (for sheets) and lower sealing temperatures (for packs). The flexibility of sodium alginate is not widely reported, but in our preliminary testing, a 10 cm diameter film could easily be flexed to form a straw-like shape, likely meeting the flexibility requirements of a drop-in PVA replacement. Many literature studies on sodium alginate focus on enhancing the strength and elasticity of sodium alginate, as the innate material is generally cited as relatively weak compared to synthetic polymers. Literature reports of the tensile strength vary greatly depending on the specific formulation, from 0.6 MPa (Chun et al. 2021) to 59 MPa (Ma 2020), but generally fall within 25-30 MPa.<sup>27,30</sup> With the addition of the plasticizer glycerol-an ingredient already present in ECOS detergent sheets-Janik et al. achieved tensile strengths of 75 MPa, well above the PVA benchmark.<sup>31</sup> For the current manufacturing process for packs, PVA sheets are heated to 150 °C before being elongated by 290%. While elongation of sodium alginate at elevated temperatures has not been extensively studied, elongation at room temperature is guite limited, with reported values below 5%.<sup>27,31</sup> Júnior et al. reported sodium alginate/hydrolyzed collagen films with elongation values of ~20%, which could be increased up to 36% upon the addition of 10% w/w SiO<sub>2</sub> relative to sodium alginate.<sup>32</sup> Lastly, a viscous solution is currently required for manufacturing PVA detergent sheets. While PVA is not the most important factor for controlling viscosity, it is important to note that sodium alginate is commercially available in a variety of grades depending on the desired viscosity.

Category	Criteria	PVA Benchmark	Sodium Alginate
	Dissolution Rate	$\leq$ 40 sec	~ 90 sec
Technical Performance	Stability	> 2 yr shelf life	Unknown
	Chemical Compatibility	Compatible with existing detergent blend, pH 5-9	Soluble in $pH > 4$ . Insoluble with divalent cations.
	Listed on the TSCA Chemical List	Yes	Yes
	Availability	Market Size: > 410 ktons (2022); \$998.21 million (2022)	Market Size: > 30 ktons (2022)
	Thermal Stability	$T_g = 150 \text{ °C}$ $T_M = 200 \text{ °C}$	$T_g = 80 \text{ °C}$ $T_M = 220 \text{ °C}$
Manufacturing Compatibility	Flexibility	Pliable, very flexible	Moderately pliable and flexible
Compationity	Tensile Strength	≥ 47 MPa	25-75 MPa, depending on formulation
	Elongation*	290%	5%
	Viscosity of detergent solution**	80,000 cps at 50 °C	Sodium alginate only: 20–1,500 cps at 20 °C depending on concentration and grade

Table 4. Technical and manufacturing criteria comparison for PVA and sodium alginate.

\* Criteria necessary for detergent pack only

\*\* Criteria necessary for detergent sheet only

#### Health and Environmental Performance

Sodium alginate is an appealing alternative as toxicity studies show low levels of human and environmental health risks. Sodium alginate salts are non-toxic, as studies have shown no adverse effects when rats and humans ingested high doses for several days.<sup>33,34</sup> It is ideal that sodium alginate does not pose toxic consequences when ingested, but further investigation is required for skin irritation, sensitization, and cases of alginate allergies.

Sodium alginate is a seaweed-derived natural biopolymer that is readily degraded by microorganisms in the environment. Studies have shown over 80% degradation of sodium alginate films in the soil after 30 days and complete degradation after 45 days.<sup>35,36</sup> Despite strong evidence of biodegradability in soil, there remains a data gap concerning specific degradation rates in water treatment plants, for which further investigation is needed.

Low aquatic toxicity is important given the waste endpoint of the product is in water systems. The Danish EPA reported in a model study that sodium alginate has very toxic and long-lasting effects on aquatic life. However, no other literature reported a similar conclusion. Given that the natural habitat of brown algae is the ocean, alginate salt is likely non-toxic in water. Any toxicity depends on how much is released into the environment and if the biopolymer has been modified.

On the production side of the life cycle, our partner raised questions on the sustainability of harvesting sodium alginate to ensure that there are no consequences as a result of over-farming. A company that produces alginate, <u>Kimica</u>, points out that seaweed is abundant and fertile, able to grow up to 60 meters in length at over tens of centimeters per day. To avoid overexploitation, they collect drift seaweed rather than harvesting it from kelp forests in the ocean. Further, algae byproduct after the extraction of alginic acid is used as feed, fertilizer, and soil conditioner rather than going to waste. Should our partner work with a manufacturer that sources their sodium alginate with similar initiatives, this alternative will be a sustainable resource.

### Carrageenan

Carrageenan is a polysaccharide derived from red algae (Figure 8). Carrageenan has three commercially available variants,  $\kappa$ -,  $\iota$ -, and  $\lambda$ -, derived from *Eucheuma cottonii*, *Eucheuma spinosum*, and *Chondrus crispus*.<sup>37</sup> In all forms, carrageenan thickens solutions, for which it is widely used in the food industry in ice creams, puddings, syrups, and infant formula.<sup>37</sup> Both  $\kappa$ -carrageenan and  $\iota$ -carrageenan are gelling agents, with  $\kappa$ -carrageenan able to form films on its own.<sup>38</sup> However,  $\lambda$ -carrageenan is only a thickener and cannot form films on its own.



Figure 8: Carrageenan source and variants, adapted from Guo et al., 2022,<sup>39</sup> with brown Carraphane<sup>TM</sup> film manufactured from Brabender.<sup>40</sup>

#### Technical Performance & Manufacturing Compatibility

Table 5 shows the technical performance and manufacturing compatibility of carrageenan compared with PVA. In terms of technical performance, of all of the commercially available carrageenan variants, only  $\lambda$ -carrageenan is soluble in hot and cold water.<sup>38</sup> However,  $\lambda$ -carrageenan does not form films on its own like  $\kappa$ -carrageenan can.<sup>41</sup> By adding  $\lambda$ -carrageenan to a casein-protein film, the flexibility and water solubility increases.<sup>42</sup> We propose a  $\kappa/\lambda$ -carrageenan hybrid film for the added properties of  $\lambda$ -carrageenan with the film properties of  $\kappa$ -carrageenan.

For manufacturing compatibility, carrageenan films are not thermally compatible with current ECOS packs manufacturing because they cannot heat seal. This is a common issue with many of the alternatives, as carrageenan films have a glass transition temperature higher than the degradation temperature, which means they will degrade before they heat seal to stick to themselves.<sup>41</sup>

For commercial availability, carrageenan's market in the Carraphane<sup>TM</sup> is a patented water-soluble, biodegradable carrageenan film by German company, Brabender, who are actively looking to partner with companies for applications of this film.<sup>40</sup> They produce the film via an extrusion process, which does not greatly modify the algae, so when dissolved and returned to the ocean, it serves as a nutrient source for new algae. The color may be a marketability concern for cleaning products.

Category	Criteria	PVA Benchmark	Carrageenan
Technical	Dissolution Rate	≤40 sec	λ-carrageenan readily soluble in hot and cold water <sup>38</sup> $\kappa$ - and ι-carrageenan readily soluble in hot water only <sup>38</sup>
Performance	Stability	> 2 yr shelf life	Unknown
	Chemical Compatibility	Compatible with existing detergent blend, pH 5-9	pH 6-10 <sup>38</sup>
	Listed on the TSCA Chemical List	Yes	Yes
	Availability	Market Size: > 410 ktons (2022); \$998.21 million (2022)	\$872 million (2022) <sup>43</sup> Carrageenan film, Carraphane, available via Brabender <sup>40</sup>
	Thermal Stability	$T_g = 150 \text{ °C}$ $T_M = 200 \text{ °C}$	Films stable to 115 °C <sup>44</sup> but $T_g > T_M$
Manufacturing Compatibility	Flexibility	Pliable, very flexible	Film flexibility increases with addition of $\lambda$ -carrageenan <sup>42</sup>
	Tensile Strength	≥47 MPa	39 MPa <sup>45</sup> for κ-carrageenan films
	Elongation*	290%	19.5% <sup>45</sup> for $\kappa$ -carrageenan films
	Viscosity of detergent solution**	80,000 cps at 50 °C	16 cP of dilute $\kappa$ -carrageenan <sup>46</sup>

**Table 5.** Technical and manufacturing criteria comparison for PVA and carrageenan.

\* Criteria necessary for detergent pack only

\*\* Criteria necessary for detergent sheet only

#### Health and Environmental Performance

Sourcing of carrageenan from seaweed is one of the only farming industries that doesn't require pesticides. Since carrageenan is biocompatible, biodegradable, and consumable, it is used as artificial tissue and as a flexible plastic replacement.<sup>47,48</sup> Once dissolved, carrageenan's aquatic toxicity is not a concern, as it serves as a nutrient source for new algae, benefitting the waters.

Carrageenan is used in the food industry, so there are many toxicological studies based on consumption. Food-grade carrageenan that is not modified greatly from the source is non-toxic, from rat, rabbit, and guinea pig studies, with no adverse effects found up to 5000 mg/kg.<sup>49</sup> In long-term feeding studies, mutagenicity studies, reproductive toxicity, and immune system toxicity, there are no adverse impacts of carrageenan.<sup>49</sup> Though no specific neurotoxicity studies have been conducted, because of the wide consumption as well as the other long-term toxicity studies conducted, we assume a low hazard for neurotoxicity, especially in this application where it is not intended to be consumed.

One important note about carrageenan that causes confusion in toxicological studies is the terminology "degraded carrageenan" or poligeenan.<sup>50</sup> Poligeenan is classified by IARC as a 2B carcinogen because studies link its high-dose consumption to tumor growth in the gastrointestinal tract.<sup>51</sup> However, poligeenan is only formed synthetically with extremely acidic conditions (pH 0.5-1) and high temperatures (>60 °C), meaning "degraded carrageenan" is a misnomer, as it is not achieved by biodegradation of carrageenan under normal conditions.<sup>52</sup>

#### Chitosan

Chitosan is a natural polymer composed of  $\beta$ -(1–4) D-glucosamine (deacetylated units) and N-acetyl-D-glucosamine (acetylated units) (Figure 9).<sup>53</sup> Chitosan is produced from chitin, the second most abundant polysaccharide—only behind cellulose—and has a market of \$1.1 billion (2022).<sup>53,54</sup> Chitin can be obtained from renewable sources, including crustacean waste streams (6 – 8 Mtons/yr), mushrooms (50 ktons/yr), fungal mycelia (80 ktons/yr), yeast, and insects (Figure 10).<sup>53,55,56</sup> To produce chitosan, chitin—which is insoluble in water—undergoes an alkaline deacylation under mild conditions to obtain a degree of N-acetylation below 50%. Chitosan powder derived from various biological sources can be found in Figure 10. Chitosan is one of the most studied materials for bio-based films, and it is inexpensive and commercially available.<sup>57</sup> It has received attention for food, chemical, and biomedical applications for its non-antigenic, non-toxic, biodegradable, biocompatible, and film-forming capabilities (Figure 9).<sup>57</sup>



Figure 9. Unprotonated chitosan structure (left) and pure chitosan film prepared with 1 w/w % chitosan and 1 w/w % acetic acid by Cazón and Vázquez 2019.<sup>53</sup>



Figure 10. Chitosan extracted from (a) mushroom, (b) crab shells, and (c) prawn exoskeletons. Figure from Margret et al. 2017.<sup>58</sup>

#### Technical Performance & Manufacturing Compatibility

Chitosan meets or exceeds many of the criteria for a viable PVA alternative, as shown in Table 6. Despite this, the technical performance data is potentially concerning for the usage of chitosan in single-use laundry detergent products. Firstly, chitosan has not been studied in the context of laundry products, and thus, dissolution rate, stability, and chemical compatibility have not been reported widely or optimized by the scientific community. Most literature that cites solubility refers to the initial dissolution of 1-2 w/w % chitosan powder into 1 v/v % acid solutions under stirring at room temperature within 1 hour, which is more than enough time to completely dissolve the chitosan.<sup>59</sup> However, Kim et al. reported the total soluble matter of the resulting chitosan films after leaving 4 cm<sup>2</sup> pieces in 30 mL distilled water for 24 h.<sup>59</sup> Interestingly, the dissolution of the films depended heavily on the acid used to protonate the chitosan amines, the degree of deacetylation of the chitosan, and the pH of the chitosan mixture before drying. Films

made from lactic acid had the highest solubility, with all lactic acid films dissolving entirely. Additionally, films produced at a higher pH (5 vs. 3 or 4) were much more soluble.<sup>60</sup> The stability of chitosan films over time has not been extensively investigated, and it depends on many factors: the degree of deacetylation, moisture content, purity, and environmental factors (temperature, humidity).<sup>61</sup> Stability has been cited as a problem for its practical applicability, specifically for pharmaceutical and biomedical applications.<sup>61</sup> Chitosan films stored over several months—particularly at higher temperatures (80 °C) and high humidities (70% relative humidity)—exhibit yellow/brown discoloration, which can also be observed by heating films at 120 °C for 2 h.<sup>62,63</sup> The character of the acid used to prepare the film influences the coloration of the film heavily, with films prepared with acetic, lactic, citric, and hydrochloric acid not exhibiting coloration over 5 months of storage at 22 °C.<sup>63</sup> An increase in stability can be obtained through stabilization agents such as polyols (sorbitol, mannitol, glycerol), which can slow the processes of depolymerization, oxidation, crosslinking, and deacetylation which lead to polymer degradation.<sup>61</sup>

Perhaps the largest hurdle to chitosan replacing PVA is the chemical compatibility of chitosan. To be soluble in water, the amine functional groups (pKa = 6.5) need to be protonated. This typically requires a solution of pH < 6.2, but glycerophosphate, a dietary supplement, has been used to extend the solubility of chitosan to pH 7.0–7.4.<sup>53,64</sup> The acid protonates the chitosan during film preparation and the protonation remains once the water evaporates. As shown by Kim et al., the resulting films can fully dissolve in neutral pH distilled water, although the degree of solubility is still dependent on the identity of the acid used to prepare the film.<sup>59</sup> Another compatibility issue that has not been investigated is the effect of negative surfactant compounds on the properties of the positively charged chitosan sheets. Additional research on the combination of chitosan with surfactants is required to fully elucidate any undesired effects.

Regarding manufacturing compatibility, chitosan alone meets almost the relevant criteria, and additives can added to obtain the desired properties. Chitosan is listed on the TSCA Chemical List, removing any barriers to use in commercial products. When heating, chitosan films lose water mass until 110 °C, the glass transition temperature is 130 °C, and decomposition occurs between 125–190 °C.<sup>65,66</sup> Due to decomposition occurring before the melting temperature, chitosan is not a thermoplastic and will degrade before it can be extruded, molded, or heat-sealed.<sup>53</sup> The flexibility of the sheet depends greatly on the identity of the acid, with lactic acid films being much more flexible than citric acid films, though plasticizers can be employed to enhance flexibility.<sup>63</sup> Pure chitosan films can be quite strong, ranging from about 5 MPa to almost 200 MPa.<sup>55,65</sup> The large range in strength again depends on many factors, including the range of molecular weights, degree of deacetylation, chitin source, and particle size.<sup>53</sup> One comparative study by Kim et al. examined the effect of acid, pH, and degree of deacetylation on tensile strength. They found that lower pH results in stronger films and acetic and propionic acid produced stronger films than lactic and formic acid. Other studies have also found that acetic

acid results in some of the strongest films.<sup>53,67</sup> One report that studied the effect of the plasticizers glycerol and sorbitol on tensile strength found that adding 40 w/w % glycerol increased the strength from 197 to 245 MPa, while sorbitol only decreased tensile strength.<sup>65</sup> Similarly to tensile strength, the elongation varies greatly with formulation and additives. Generally, elongation remains low at around 5%; however, films made with citric acid demonstrate elongations up to 120%, and films with lactic acid show elongation up to 495%, exceeding the requirements for detergent packs manufacturing.<sup>59,67</sup> One comparative study showed that 40 w/w % glycerol increased elongation from 5% to 44%, while a similar amount of sorbitol only decreased elongation, demonstrating the importance of the identity of the additive.<sup>67</sup> Importantly, tensile strength and elongation are typically inversely related, so careful adjustments must be made to ensure criteria for both properties are met. Lastly, specific values of viscosity in the literature are lacking, though it is reported that higher molecular weight chitosan is more viscous, and solutions above 2 w/w % chitosan become very viscous, reducing their industrial relevance.<sup>53,68</sup>

Category	Criteria	PVA Benchmark	Chitosan
	Dissolution Rate	$\leq$ 40 sec	< 1 h
Technical Performance	Stability	> 2 yr shelf life	> 5 months
1 erformance	Chemical Compatibility	Compatible with existing detergent blend, pH 5-9	pH < 6.5; interactions with negatively charged surfactants
Manufacturing Compatibility	Listed on the TSCA Chemical List	Yes	Yes
	Availability	Market Size: > 410 ktons (2022); \$998.21 million (2022)	> 6 Mtons from crustacean waste-stream (2020), \$1,088 million (2022)
	Thermal Stability	$T_g = 150 \text{ °C}$ $T_M = 200 \text{ °C}$	$T_g = 130 \ ^{\circ}C$ $T_{decomp} = 125 - 190 \ ^{\circ}C$
	Flexibility	Pliable, very flexible	Brittle, enhanced with plasticizers
	Tensile Strength	$\geq$ 47 MPa	5 – 245 MPa
	Elongation*	290%	5 - 495%

Table 6. Technical and manufacturing criteria comparison for PVA and chitosan.

Viscosity of detergent	80,000 cps at 50 °C	Very viscous beyond 2 w/w %
solution**		

\* Criteria necessary for detergent pack only

\*\* Criteria necessary for detergent sheet only

#### Health and Environmental Performance

Chitosan is a non-toxic and biodegradable alternative to PVA. It has been labeled as a food additive in Korea and Japan since 1995 and 1983, respectively. Furthermore, the US Food and Drug Administration has considered chitosan as generally recognized as safe for use in foods since 2001.<sup>53</sup> It is non-toxic to humans and animals, with no reported effects on mice fed at 10 g/kg of body weight.<sup>69</sup> Bioaccumulation is expected to be of low concern for polymers with molecular weight > 1,000, and many microorganisms can break down chitosan. Regarding aquatic toxicity, most reports-including those with marine fish and rainbow trout-show no adverse toxic effects when fed up to 10% chitosan. However, some literature reports found that when exposed to chitosan in 1 v/v % acetic acid, fish exhibit lesions similar to those induced by mercury exposure and die quickly.<sup>69,70</sup> While startling, it is important to note that under standard conditions, neutral bodies of water would insolubilize chitosan into a gel, where it could not enter the gills of fish. Chitosan has also been described as the active ingredient of KML V2 and KML V54, both of which are quite toxic.<sup>71</sup> However, chitosan only makes up 2% and 5.4% of the products, respectively, and the other potentially more toxic ingredients were not listed, making this report unreliable. Overall, chitosan is both non-toxic and biodegradable, and while there is a concern for the aquatic toxicity of solubilized chitosan, the low presence of acid in large bodies of water would prohibit this possibility.

#### Pullulan

Pullulan is a polysaccharide produced by several strains of fungi (Figure 11). Pullulan is widely used across industries due to its inert and biocompatible nature.<sup>72</sup> Pullulan is currently used in the food, pharmaceutical, dental, and cosmetic industries.<sup>72</sup> In the food industry, pullulan forms edible films and coatings to prolong shelf life. In the pharmaceutical industry, pullulan creates vegan capsules and helps bind tablets.

Pullulan is produced by mesophilic fermentation by a strain of fungus, typically *Aureobasidium pullulans*. The process of preparing pullulan varies across different industry uses. After fermentation, fungal cells are removed by microfiltration.<sup>73</sup> The filtrate is heat-sterilized and treated with activated carbon, removing pigments and impurities The filtrate then undergoes a cooling and deionization process using cation and anion exchange resins.<sup>73</sup> Then it is concentrated, dried, and pulverized.<sup>73</sup> Pullulan-used pharmaceuticals undergo a few more steps, such as purification by alcohol fractionation or membrane filtration and desalination.<sup>73</sup> Pullulan is more expensive than petroleum-based chemicals, but its cost can be reduced based on

optimizing fermentation (stirring vs non-stirring methods) and using thermotolerant and non-melanin strains of fungus, which will reduce the steps and temperatures required for the extraction.<sup>74</sup>



Figure 11: Pullulan sources and chemical structure.

#### Technical Performance & Manufacturing Compatibility

Pullulan meets many of the technical and manufacturing criteria for an alternative to PVA, as shown in Table 7. However, the lack of research on pullulan films for application in single-use detergent products has resulted in data gaps for certain criteria. Regarding technical performance, pullulan readily dissolves in water to make a stable, viscous solution that does not form a gel.<sup>75(p1)</sup> Many literature reports on pullulan's dissolution surround pullulan's use in drug delivery for the pharmaceutical and biotechnology industries. In these studies, researchers demonstrated pullulan is a fast-dissolving film that leads to a fast release of the drug.<sup>76</sup> More research needs to be conducted on pure pullulan films to determine their dissolution rate. The shelf life of pullulan has been studied in various applications, but none regarding its use in single-use detergent products. Capsuline Pullulan Capsules manufacturers empty capsules of 100% pullulan that last up to 5 years if stored in a dry, cool place. The capsules' optimal temperature is between 15-30 °C with relative humidity between 35-70%. Additionally, pullulan has been used as an edible film to extend the shelf life of foods.<sup>77</sup> Pullulan can stabilize proteins due to its high glass transition temperature.<sup>78</sup> While there is no apparent concern about pullulan's stability over time, the concentration of pullulan and the mixture of ingredients, including hygroscopicity-reducing and plasticizer additives, will alter the shelf life of the final product. Concerning technical performance, pullulan is readily soluble in cold water, biocompatible, and is used to help extend the stability of products on the market, so likely would not pose a shelf stability concern.

Similar to other alternatives, the manufacturing compatibility of pullulan varies greatly on the composition of the pullulan film (for packs) and detergent mixture (for sheets), and most research is limited to pullulan films for applications such as food, drug, and product packaging. Pullulan is listed on the TSCA Chemical List, however is an expensive polymer compared to petrochemical-based polymers due to its high production charges.<sup>78</sup> Despite this, the pullulan

market is growing and expected to reach \$130 million this year from \$129 million in 2017.79 Pullulan in powder form is available to commercially purchase. Pullulan has a pH between 5-7, but remains largely unaffected over a wide pH range (2-11).<sup>78</sup> The thermal stability of pullulan meets the manufacturing criteria outlined for sheets and packs. Pullulan is also stable up to 250-280 °C until it begins to decompose.<sup>78</sup> The glass transition temperature (Tg) of anhydrous PVA is 154.5 °C.<sup>80</sup> When exposed to 33% relative humidity and 25 °C for 72 hours, its glass transition temperature was 50.6 °C.<sup>80</sup> Pullulan films are heat-sealable, transparent, and flexible.<sup>81</sup> Many literature studies on pullulan focus on enhancing its strength and elongation, as the innate material is generally cited as relatively weak compared to synthetic polymers. Pullulan produced by A. pullulans (strain ATCC 15233) exhibited a tensile strength of 1.7 MPa and an elongation at break of 11.89%.<sup>82</sup> Pullulan films also can be brittle and have poor water resistance.<sup>83</sup> Pullulan has been crosslinked with plasticizers (glycerol) and water-resistant additives (glutaraldehyde) that improved elongation and stability in high-moisture environments.<sup>83</sup> However, Zhou et al were able to improve the elongation at break, temperature stability, and minimize friability of pullulan soft film and capsule with a Sorbitol-Glycerol ratio of 15:15.<sup>84</sup> As an innate material, pullulan would not meet the manufacturing compatibility requirements, but its properties could be further modified using additives such as plasticizers and low hygroscopic materials.

Category	Criteria	PVA Benchmark	Pullulan
	Dissolution Rate	$\leq$ 40 sec	Unknown
Technical Performance	Stability	> 2 yr shelf life	Unknown
	Chemical Compatibility	Compatible with existing detergent blend, pH 5-9	Soluble in pH 2 - 11 <sup>78</sup> Insoluble in organic solvents
	Listed on the TSCA Chemical List	Yes	Yes
	Availability	Market Size: > 410 ktons (2022); \$998.21 million (2022)	Market Size: \$130 million (2023) <sup>79</sup>
Manufacturing Compatibility	Thermal Stability	$T_g = 150 \text{ °C}$ $T_M = 200 \text{ °C}$	$T_g = 154.5 \text{ °C (anhydrous)}$ $T_M = 250 \text{ °C}^{78}$
	Flexibility	Pliable, very flexible	Flexible <sup>81</sup>
	Tensile Strength*	≥ 47 MPa	1.7 MPa <sup>82</sup>

 Table 7. Technical and manufacturing criteria comparison for PVA and pullulan.

Elongation*	290%	11.89% <sup>82</sup>
Viscosity of detergent solution**	80,000 cps at 50 °C	Unknown quantitative data but pullulan forms a viscous solution when it is added <sup>75(p1)</sup>

\* Criteria necessary for detergent pack only

\*\* Criteria necessary for detergent sheet only

#### Health and Environmental Performance

Pullulan has recently become widely commercially available, therefore there are some data gaps studying long exposure to pullulan. However, recent studies have indicated that pullulan poses no risk for cancer and has low systemic toxicity, neurotoxicity, irritation, and sensitization.<sup>85(p30),86</sup> Several microorganisms can degrade pullulan, and since humans can metabolize and excrete pullulan from the body, it cannot bioaccumulate in humans.<sup>79,85,87</sup> Pullulan is also biodegradable.<sup>88</sup>

The production of pullulan is relatively resource-efficient, as it relies on fermentation, raw materials for substrates, fungi, and technology for purification and extraction.<sup>89</sup> Despite several fungi strains' capability of producing pullulan, *Aureobasidium pullulans* is preferred due to its quality and high production rate.<sup>78</sup> To improve the lifecycle of pullulan, waste substrates like starch, distilled by-products, bakery waste, or agro-industrial residues can be used during production.<sup>79</sup> Should our partner work with a manufacturer that sources their pullulan from fungi that use waste sources as a substrate, pullulan will be a sustainably sourced alternative.

# Cellulose

Cellulose is a polysaccharide from the cell walls of plants (Figure 12).<sup>90</sup> There are several forms of cellulose that are used for a variety of applications, and there is a robust market for cellulose fibers, valued at \$3,825.6 million in 2022.<sup>90,91</sup> While pure cellulose is insoluble in water due to strong intramolecular hydrogen bonding, it becomes soluble when converted to cellulose ester or ether derivatives.<sup>92</sup> Modified cellulose derivatives enhance water retention capacity, pseudoplastic behavior, film-forming properties, and complexation.<sup>92</sup> Further, they are biocompatible and thus frequently used in pharmaceuticals, cosmetics, and food.<sup>81,92</sup>

Extraction of water-insoluble cellulose is by controlled esterification of pure raw cellulose with acetic acid and acetic anhydride.<sup>93</sup> This substitutes acetyl groups for all or a portion of the hydroxyl units on the cellulose chain.<sup>93</sup> To create the water-soluble form, acetylation is carried to completion to form cellulose triacetate, followed by hydrolysis to lower acetyl content to the

desired level.<sup>93</sup> For water-soluble cellulose acetate, this is 0.8 degrees of substitution compared to 2.4 for insoluble cellulose.<sup>93</sup>



Figure 12: Cellulose sources and chemical structure.

#### Technical Performance & Manufacturing Compatibility

Table 8 outlines cellulose's technical performance and manufacturing compatibility. On a manufacturing standpoint, it is highly customizable due to the many alcohol groups in its structure, allowing chemical modifications to modulate solubility. Several forms of cellulose are listed on the TSCA Chemical List.

METHOCEL<sup>™</sup> is a form of cellulose ether commercially available through ChemPoint. All grades are soluble in water and their viscosity depends on the degree of substitution and molecular weight. For instance, METHOCEL<sup>™</sup> E4M has a viscosity of 4,000 cps whereas A4C has a viscosity of 400 cps when added to water at 2%.<sup>94</sup> This leads to varying dissolution rates as well. This compound is stable at pH 2.0 - 13.0, making it stable in a variety of manufacturing conditions, but does not have a glass transition or melting temperature as it decomposes at 260 -270 °C.<sup>95,96</sup> This makes the heat sealing process of packs not possible. METHOCEL<sup>™</sup> is most soluble in cold water, and some forms gel at high temperatures. For instance, METHOCEL<sup>™</sup> F50 Food Grade has a gelation temperature of 62-68 °C.<sup>97</sup> Most average washing machines have hot cycles at 55°C, so this should not pose a problem. However, this is a consideration for machines that run hotter or for those who hand wash with higher temperatures.

Cellulose films tend to be brittle, but this is improved by the addition of plasticizers such as glycerol and sorbitol.<sup>98</sup> At baseline, microcrystalline cellulose film exhibits a tensile strength of 4.5 MPa, but the addition of a plasticizer improves this metric.<sup>98</sup> For example, films with 5% glycerol had a tensile strength of 9.4 MPa, and films with 25% glycerol had a tensile strength of 22.4 MPa.<sup>98</sup> The addition of glycerol also aids in the elongation of cellulose films. With no additive, the elongation at break is 5.1% to 13.1%.<sup>98</sup>

In contrast, films made of water-soluble cellulose acetate were reported to have excellent film-forming properties where they were clear in color, flexible, strong, and durable depending

on the viscosity grade. Elongation results were also low for this film at about 2-5.6% elongation, but tensile strength was higher at about 33-58 MPa.<sup>93</sup>

Category	Criteria	PVA Benchmark	Cellulose
	Dissolution Rate	$\leq$ 40 sec	Varies
Technical Performance	Stability	> 2 yr shelf life	Unknown
	Chemical Compatibility	Compatible with existing detergent blend, pH 5-9	Stable at pH 2.0-13.0
	Listed on the TSCA Chemical List	Yes	Yes
	Availability	Market Size: > 410 ktons (2022); \$998.21 million (2022)	Market Size: \$3,825.6 million (2022)
Monufacturing	Thermal Stability	$T_g = 150 \text{ °C}$ $T_M = 200 \text{ °C}$	Decomposition 260 -270 °C
Compatibility	Flexibility	Pliable, very flexible	Flexible
	Tensile Strength*	$\geq$ 47 MPa	4.5 MPa - 22.4 MPa
	Elongation*	290%	13.1%
	Viscosity of detergent solution**	80,000 cps at 50 °C	Varies

Table 8. Technical and manufacturing criteria comparison for PVA and cellulose.

\* Criteria necessary for detergent pack only

\*\* Criteria necessary for detergent sheet only

Health and Environmental Performance

Cellulose is a renewable, abundant, and naturally occurring material, making it an ideal choice.<sup>90,99</sup> It can be sourced from a variety of sources, including agricultural, forest, or recycling industries.<sup>99</sup> On a sustainability standpoint sourcing cellulose from waste streams would be ideal. Cellulose is appealing as it is non-toxic to humans and the environment. Given that it is completely derived from plants, it will readily biodegrade, with research showing at least 80%

biodegradation within 30-60 days in soil.<sup>98,99</sup> More research is needed to determine whether the film appropriately degrades within 28 days as per OECD-301B standards and in water sources.

One area of concern is the risk manufacturing cellulose poses when workers inhale the powder, causing irritation.<sup>99,100</sup> However, this can be mitigated through proper personal protective equipment and standard operating procedures. Otherwise, current literature suggests that cellulose poses no harm to humans or the environment.<sup>99</sup>

# Summary of Polysaccharides

We identified five potential polysaccharide alternatives to PVA: sodium alginate, carrageenan, chitosan, pullulan, and cellulose. We conducted a hazard assessment through a comprehensive literature review to compare the health and environmental impacts of the polysaccharide alternatives. We also assessed the technical performance and manufacturing compatibility of each alternative.

Name	Group I Human Endpoints			Group	o II and Gro Endpoints	oup II*	Ecotox- icity	Fate	Physical Hazard
	Carcinogenicity	Developmental	Endocrine	6 / · <b>T</b> · V	Nounotorioity	Skin, Eye, Respiratory	Aquatic Toxicity	Persistence	Reactivity, Flammability
	Mutagenicity	Toxicity	Activity	Systemic Toxicity	Irritation Sensitizatio		Acute / Chronic	Bioaccumulation	Other Pchem Traits
Polyvinyl Alcohol	L	L	DG	L	L	L	H*	M*	L
Sodium Alginate	L	L	DG	L	L	L	L*	vL	vL
Carrageenan	L	L	DG	L	L	L	vL	L	L
Chitosan	L	L	L	L	L	L	L*	L	DG
Pullulan	L	L	DG	L	L	L	L	vL	vL
Cellulose	L	L	DG	L	L	$M^+$	L	L	L
italicized = 1 L = reasona	ow confiden able assumpt	ce ion of safety		* = mixed literature data + = not a consumer hazard gap			DG very low	vL L M	H vH very high

Table 9.	Hazard	Assessment	Com	parison	of PVA	and Po	lysaccharides
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Table 9 shows a hazard table comparison of PVA and polysaccharide alternatives. Our identified polysaccharides are low toxicity and biodegrade with no concern for bioaccumulation. The

toxicity of these alternatives is generally well-researched, aside from data gaps regarding endocrine disruption. Though there were no specific neurotoxicity studies from sodium alginate and carrageenan, we make a reasonable assumption of safety for this application of detergent sheets and packs, as they are widely consumed. For cellulose, though it is a respiratory irritant, again for the application in detergent sheets and packs, it is not of concern to the consumer. All of these polysaccharide alternatives can be considered less toxic than PVA by our health and environmental criteria. Further, all of these polysaccharide alternatives can be derived from renewable sources, removing the harmful precursors that arise in the production of PVA.

We compared technical performance and manufacturing compatibility of our identified polysaccharide alternatives in Table 10. All of our alternatives are soluble in cold and hot water, and all but chitosan are soluble and compatible with expected pH ranges. For manufacturability, the elongation of the alternative films falls short of PVA, but sodium alginate and chitosan films can achieve the tensile strength needed for ECOS packs manufacturing. These are all commercially available in powder form, and some companies readily manufacture films. We have included in the table our recommendations for whether the PVA alternatives would best be used for sheets, packs, or both.

Name	Solubility Temperature	pH Compatibility	Tensile Strength (MPa)	Elongation (%)	Commercial Availability	Sheets, Packs, or Both	
Polyvinyl Alcohol	Cold and hot	5-9	47	290	Yes (Powder, Film)	Both	
Sodium Alginate	Cold and hot	>4	25-75	5	Yes (Powder)	Both	
Carrageenan	Cold and hot	6-10	39.3	19.5	Yes (Powder, Film)	Both*	
Chitosan	Cold and hot	<6.5	5-245	5-495	Yes (Powder, Film)	Packs	
Pullulan	Cold and hot	3-8	1.7	10	Yes (Powder)	Sheets	
Cellulose	Cold and hot	2-13	4.5-22.4	13.4	Yes (Powder, Film)	Both	
<i>italicized:</i> potential company partner *marketing aesthetic considerations							

**Table 10.** Technical Performance and Manufacturing Compatibility Comparison of PVA and Polysaccharides

# 5. Strategy 2: Proteins

Proteins are macromolecules made of amino acids and can be sourced from plants, animals, and microorganisms. They are attractive biopolymers as alternatives to synthetic polymers due to their biodegradability, renewability, and low health and environmental hazards. Recent development has focused on making protein-based films for biodegradable packaging materials and edible films.<sup>101-104</sup> One advantage of proteins over polysaccharides is their rich chemical functionality. Proteins have about 20 amino acids with side chains that are hydrophobic, hydrophilic, or charged, rendering various types of intermolecular interactions (e.g., hydrogen bonding, ionic bonding, and covalent bonding) which are factors that can affect the mechanical properties of protein-based films. There are two types of proteins: (1) fibrous proteins and (2) globular proteins. Fibrous proteins are long extended polypeptide chains that provide strength and protection in cell membranes, and they are water-insoluble. Globular proteins fold into spherical shapes, and they are soluble in water, acid, base, and salt solutions. Protein-based films are most commonly prepared by solution casting and drying. The mixing and drying temperature will affect the unfolding of proteins. However, the effect of protein unfolding on the mechanical properties of protein-based films is an ongoing research. Here, we explored four different water-soluble proteins derived from plants as PVA alternatives.

# Brewer's Spent Grain (BSG) Protein

Brewer's spent grain (BSG) is a waste byproduct that makes up about 85% of solid waste from the brewing industry (Figure 13). In Europe alone, breweries are estimated to produce about 2.5 million tons of BSG, resulting in substantial agro-industrial waste.<sup>105,106</sup> While BSG is rich in protein and fiber, it is mainly used as livestock feed. Due to its high nutritional values, extracting and utilizing BSG protein as food additives and biodegradable film has become a growing effort to reduce and upcycle waste. Typical extraction methods of BSG protein are alkaline solution extraction, organic solvent extraction, and ultrasonication.<sup>105,107</sup> Depending on the methods and purity of protein, the amino acid composition may differ, leading to different physical appearance and molecular weight.



Figure 13. Images of brewer's spent grain (left) and the protein isolate<sup>108</sup> (right)

#### Technical Performance & Manufacturing Compatibility

In general, BSG protein-based film is prepared by mixing and drying a solution of BSG protein and a plasticizer. The various reported methods showed that BSG protein is soluble in both cold and hot water.<sup>109-111</sup> Solubility is maximized at and above pH 6, which is favorable for the slightly basic condition posed by the detergent ingredients. Further hydrolysis of BSG protein improves its water solubility. The common plasticizers used are glycerol, sorbitol, and polyethylene glycol (PEG), which reduce the intermolecular interactions between protein chains and increase the film flexibility. Proaño et al. investigated the effect of PEG concentration on the physicochemical properties of the film.<sup>110</sup> As the weight ratio of PEG to BSG increases from 0.05 to 0.25, both moisture content and water solubility increase. At a 0.05-0.10 ratio (PEG:BSG), the film achieved higher tensile strength (1.0-1.2 MPa), higher elastic modulus (0.4-0.5 MPa), and moderate elongation (25%). While a higher ratio of PEG:BSG increases the elongation to 40%, the film is very hygroscopic and hard to handle. Shroti reported similar tensile strength of 1.45 MPa but higher elongation (60%) when glycerol (30% w/w) is used as the plasticizer.<sup>109</sup> However, Lee et al. reported a tensile strength of 4.32 MPa and 36% elongation using 40% w/w glycerol.<sup>112</sup> Given the different film preparation methods, it is uncertain to attribute the difference in mechanical properties to the specific plasticizer used. Additionally, BSG protein is thermally stable at 140 °C for 300 minutes,<sup>111</sup> which will be compatible with the current drying process of the detergent sheet without further degradation. The reported mechanical properties of BSG film do not meet the criteria for detergent packs but may be suitable for detergent sheets. Mixing and drying conditions (e.g., temperature, pH, and time) can all affect the mechanical properties of the resultant film. One main drawback of BSG protein is the protein degradation during malting and extraction processes. A composition study of extracted BSG protein (typically 30-50 kDa) showed shorter peptides of lower molecular weight (< 3000 Da).<sup>108,110</sup> Although the shorter peptides can increase water solubility and have a plasticizer-like effect, shorter polymer chains have poorer mechanical strength due to reduced chain entanglement. The film has a brown color, which may be a marketability concern if used for detergent sheets. In addition, BSG protein is currently not listed on the TSCA Chemical List. The opacity and color saturation depends on the film thickness and protein concentration. A comparison of the technical performance and manufacturing compatibility of PVA and BSG protein is summarized in Table 11.

Currently, BSG protein is commercially available as a powder film. MiTerro has developed BSG protein film for water-soluble detergent packs (Figure 14) and is looking to partner with companies for the application and commercialization of their film.



Figure 14. Images of BSG protein film (left) and sample detergent pack made with BSG protein film (right)

Category	Criteria	PVA Benchmark	BSG Protein	
	Dissolution Rate	$\leq$ 40 sec	Unknown	
Technical Performance	Stability	> 2 yr shelf life	Unknown	
	Chemical Compatibility	Compatible with existing detergent blend, pH 5-9	Better water solubility at pH>6 <sup>111</sup>	
	Listed on the TSCA Chemical List	Yes	No	
	Availability	Market Size: > 410 ktons (2022); \$998.21 million (2022)	~2.5 million tons of BSG produced in Europe	
Monufacturing	Thermal Stability	$T_g = 150 \text{ °C}$ $T_M = 200 \text{ °C}$	Thermal stable at 140 °C for >300 min <sup>111</sup>	
Compatibility	Flexibility	Pliable, very flexible	Flexible	
	Tensile Strength*	≥ 47 MPa	4.32 MPa <sup>112</sup>	
	Elongation*	290%	60% <sup>109</sup>	
	Viscosity of detergent solution**	80,000 cps at 50 °C	Unknown	

#### Table 11. Technical and manufacturing criteria comparison for PVA and BSG protein.

\* Criteria necessary for detergent pack only

\*\* Criteria necessary for detergent sheet only

#### Health and Environmental Performance

As BSG has been predominantly used as livestock feed, there is a lack of data regarding its toxicity towards human endpoints. BSG protein does biodegrade and does not bioaccumulate. However, there is no reported data on its degradation rate to determine if it satisfies the OECD 301B guideline. Endocrine activity will need to be further investigated. However, due to its natural origin, it is reasonable to presume BSG protein poses low hazards in terms of carcinogenicity, mutagenicity, developmental and reproductive toxicity, neurotoxicity, systemic toxicity, and skin, eye, and respiratory irritation and sensitization.

### Soy Protein

Soy protein is a protein derived from soybeans and is consumed as a plant-based protein supplement and in soy-based infant formulas (Figure 15).<sup>113</sup> It is extracted from ground soybeans using acids and bases,<sup>114</sup> or ultrasonication.<sup>115</sup> It is widely commercially available and can form biodegradable films.<sup>116,117</sup>



Figure 15. Soybeans with soy meal, commercially available soy protein isolate,<sup>71</sup> and soy protein films on paper.<sup>118</sup>

#### Technical Performance & Manufacturing Compatibility

Table 12 highlights the performance and manufacturability of soy protein. The solubility of soy protein films depends on the chemical treatment of acrylic acid.<sup>118</sup> With no treatment, it takes 20 minutes to dissolve at 20 °C,<sup>118</sup> approximately the temperature of cold water for laundry. It shows similar solubility temperature compatibility to PVA. No information was found on the lifetime and stability of films, but the pH range of stability was 3-8.5, which overlaps significantly with the pH currently used with PVA (pH 5-9).<sup>118</sup>

For manufacturing compatibility, soy protein films have several drawbacks. Without plasticizers, soy protein films are very brittle, but with the addition of glycerol, soy proteins can become more

flexible.<sup>119</sup> On their own, soy protein films do not have the tensile strength needed for manufacturing, with values of 2.34 MPa, but by integrating a starch into the film, researchers were able to increase the tensile strength up to 25.09 MPa.<sup>120</sup> For thermal stability, soy protein may not work with current manufacturing procedures because soy protein coagulates around 80 °C.<sup>121</sup> Additionally, a potential marketing concern is soy protein films are a brown-yellow color, which may not be appealing to consumers.

Category	Criteria	PVA Benchmark	Soy Protein
	Dissolution Rate	$\leq$ 40 sec	7 min in cold water <sup>118</sup>
Technical Performance	Stability	> 2 yr shelf life	Unknown
	Chemical Compatibility	Compatible with existing detergent blend, pH 5-9	pH 3-8.5 <sup>118</sup>
	Listed on the TSCA Chemical List	Yes	Yes
	Availability	Market Size: > 410 ktons (2022); \$998.21 million (2022)	\$7.7 billion for soy protein ingredients (2022) <sup>122</sup>
Monufacturing	Thermal Stability	$T_g = 150 \text{ °C}$ $T_M = 200 \text{ °C}$	$T_{g} = 64 \ ^{\circ}C^{120}$ coagulation 80 $^{\circ}C^{121}$
Compatibility	Flexibility	Pliable, very flexible	Flexible
	Tensile Strength*	≥ 47 MPa	25.09 MPa <sup>120</sup>
	Elongation*	290%	379% <sup>120</sup>
	Viscosity of detergent solution**	80,000 cps at 50 °C	$4,000 \text{ cP}^{120}$

Table 12. Technical and manufacturing criteria comparison for PVA and soy protein.

\* Criteria necessary for detergent pack only

\*\* Criteria necessary for detergent sheet only

#### Health and Environmental Performance

Soy protein is widely studied toxicologically. Studies in rats show no adverse effects from soy consumption for reproductive toxicity.<sup>113</sup> Moreover, these studies suggest potential beneficial effects, indicating that soy consumption may even offer protection against cancer growth.<sup>123</sup> There is some concern regarding the endocrine disruption of soy protein, where a byproduct from soy—genistein—may impact the development of the mammary gland.<sup>124</sup> However, this is found with prolonged consumption of soy. In detergent packs and sheets, if the soy protein is isolated at the beginning, and if the sheets and packs are not consumed, it should not be a consumer hazard.

Soy protein's primary health and environmental drawback is that soy is a common allergen and will cause skin sensitizing reactions to those allergic.<sup>124</sup> ECOS currently markets packs and sheets as hypoallergenic, so the marketing would need to be adapted. This also would make the packs/sheets inaccessible to consumers with soy allergies.

### Pea Protein

Pea protein is extracted from peas (Figure 16), which has high nutritional value and applications in the food industry. In general, pea seeds are milled into flour, which contains soluble fibers, starches, and proteins. The pea protein is then extracted through various methods, which include (i) alkaline extraction and isoelectric precipitation, (ii) alkaline extraction and ultrafiltration, (iii) salt extraction and dialysis, (iv) salt extraction and ultrafiltration, and (v) micellar precipitation.<sup>125</sup> Depending on the extraction process, the quality and functional properties of pea proteins may differ among suppliers. The extracted pea protein powder has a yellow-beige color.



Figure 16. Images of peas (left) and the protein isolate<sup>108</sup> (right)

#### Technical Performance & Manufacturing Compatibility

Pea protein film is prepared by mixing and drying a solution of pea protein and a plasticizer. Similar to BSG protein, pea protein is soluble in both cold and hot water and the solubility

improves at and above pH 6. Kowalczyk et al. compared the mechanical properties of pea protein film made using glycerol and sorbitol as plasticizers.<sup>126</sup> Overall, as plasticizer concentration increases from 3% to 8% (w/w), both tensile strength and elastic modulus decrease. Plasticizer concentration does not significantly affect the elongation. However, films prepared from solutions adjusted to higher pH (9 and 11) showed improved elongation. Sorbitol was a better plasticizer in optimizing the mechanical properties, with the best-performing film having a tensile strength of 7.0 MPa, elastic modulus of 270 MPa, and elongation of 140%. Heating the solution to 90 °C before casting showed minimal improvement in mechanical properties. Furthermore, Cheng et al. also demonstrated altering the secondary structure of pea protein through high-pressure homogenization improves the film tensile strength and elongation (200%).<sup>127</sup> The high pressure enhances the protein-protein and protein-glycerol hydrogen bonding and prevents the protein from unfolding, leading to improved mechanical properties. Additionally, pea protein is thermally stable up to 190 °C before denaturation<sup>128</sup>, which will be compatible with the current drying process for detergent sheets. A comparison of the technical performance and manufacturing compatibility of PVA and pea protein is summarized in Table 13. The tensile strength of pea protein film does not meet the criteria for detergent packs but is suitable for detergent sheets.

Pea protein is commercially available in powder form. Xampla, a company based in the UK, has developed Morro<sup>TM</sup> materials made out of pea protein. Two examples of their material applications are dishwasher detergent film and edible stock cube packaging (Figure 17). They may be a potential partner company to implement pea protein film for detergent packs.



Figure 17. Dishwasher detergent<sup>129</sup> (left) and edible stock cube packaging<sup>130</sup> (right) developed by Xampla

Category	Criteria	PVA Benchmark	Pea Protein
	Dissolution Rate	$\leq$ 40 sec	Unknown
Technical Performance	Stability	> 2 yr shelf life	Unknown
	Chemical Compatibility	Compatible with existing detergent blend, pH 5-9	Better water solubility at pH>6 <sup>131</sup>
	Listed on the TSCA Chemical List	Yes	No
	Availability	Market Size: > 410 ktons (2022); \$998.21 million (2022)	Market size: \$94.6 million (2022)
Monufacturing	Thermal Stability	$T_g = 150 \text{ °C}$ $T_M = 200 \text{ °C}$	Protein denature at 190 °C <sup>128</sup>
Compatibility	Flexibility	Pliable, very flexible	Flexible
	Tensile Strength*	≥ 47 MPa	7 MPa <sup>126</sup>
	Elongation*	290%	200% <sup>127</sup>
	Viscosity of detergent solution**	80,000 cps at 50 °C	Unknown

Table 13. Technical and manufacturing criteria comparison for PVA and pea protein.

\* Criteria necessary for detergent pack only

**\*\*** Criteria necessary for detergent sheet only

#### Health and Environmental Performance

Similar to BSG protein, pea protein is biodegradable and does not bioaccumulate. However, there is no reported data on its degradation rate to determine if it satisfies the OECD 301B guideline. Endocrine activity will need to be further investigated. Given its natural origin, it is reasonable to presume BSG protein poses low hazards in terms of carcinogenicity, mutagenicity, developmental and reproductive toxicity, neurotoxicity, systemic toxicity, and skin, eye, and respiratory irritation and sensitization.

# Mung Bean Protein

Mung beans have high nutritional values and antioxidant properties, making them attractive ingredients for the food industry (Figure 18). Mung bean starch is more commonly used for other applications, while the protein isolate is mainly used as animal feedstock.<sup>132</sup> The extraction of mung bean protein is performed by alkaline solubilization of mung bean flour, followed by precipitation.<sup>132,133</sup> The protein isolate has an off-white color.



Figure 18. Images of mung beans (left) and the protein isolate (right)

#### Technical Performance & Manufacturing Compatibility

Mung bean protein film is prepared by mixing and drying a solution of pea protein and a plasticizer. Table 14 shows mung bean protein's technical performance and manufacturing compatibility. It is soluble in both cold and hot water, but the solubility is better at more acidic (pH=2) and basic conditions (pH 8-12).<sup>133</sup> Moghadam et al. reported a tensile strength of 3.3 MPa and elongation of 81-83% of mung bean protein film made with glycerol (50% w/w) as a plasticizer.<sup>132,134</sup> In addition, Mojoodi achieved increased tensile strength (6.0 MPa) by increasing the protein concentration.<sup>135</sup> Currently, mung bean protein is only commercially available as powder, so application for detergent packs will likely be limited. The high protein degradation temperature (270 °C) meets the criteria for the current drying process for detergent sheets.<sup>135</sup> In comparison to BSG protein, soy protein, and pea protein, there has not been as much research on making mung bean protein films, which means further experimental modification and optimization will be necessary to achieve the desired properties.

Category	Criteria	PVA Benchmark	Mung Bean Protein
	Dissolution Rate	$\leq$ 40 sec	Unknown
Technical	Stability	> 2 yr shelf life	Unknown
	Chemical Compatibility	Compatible with existing detergent blend, pH 5-9	Better water solubility at pH $< 2$ and $>8$ , minimal water solubility at pH 4-7 <sup>133</sup>
	Listed on the TSCA Chemical List	Yes	No
	Availability	Market Size: > 410 ktons (2022); \$998.21 million (2022)	Market size: \$250 million (2022)
Manufacturing	Thermal Stability	$T_g = 150 \ ^{\circ}C$ $T_M = 200 \ ^{\circ}C$	Protein degradation at 270 °C <sup>135</sup>
Compatibility	Flexibility	Pliable, very flexible	Flexible
	Tensile Strength*	≥ 47 MPa	6.0 MPa <sup>135</sup>
	Elongation*	290%	81% <sup>134</sup>
	Viscosity of detergent solution**	80,000 cps at 50 °C	Unknown

Table 14. Technical and manufacturing criteria comparison for PVA and mung bean protein.

\* Criteria necessary for detergent pack only

\*\* Criteria necessary for detergent sheet only

#### Health and Environmental Performance

Mung bean protein does biodegrade and does not bioaccumulate. However, there is no reported data on its degradation rate to determine if it satisfies the OECD 301B guideline. Endocrine activity will need to be further investigated. Given its natural origin, it is reasonable to presume mung bean protein poses low hazards in terms of carcinogenicity, mutagenicity, developmental and reproductive toxicity, neurotoxicity, and systemic toxicity. Since mung bean is also part of the legume family, it may trigger an allergic reaction similar to that of soy protein. However,

there is a lack of research to confirm if it causes any skin, eye, and respiratory irritation and sensitization.

# Summary of Proteins

We identified four potential protein alternatives to PVA: brewer's spent grain (BSG) protein, soy protein, pea protein, and mung bean protein. We conducted a hazard assessment through a comprehensive literature review to compare the health and environmental impacts of the protein alternatives. Table 15 shows a hazard table comparison of PVA and protein alternatives. Due to their natural origin, the proteins are more readily biodegradable than PVA in both soil and water and do not bioaccumulate. However, further testing is necessary to confirm the biodegradation rate satisfies the OECD 301B Guidelines. Although there is a lack of toxicity studies on BSG, pea, and mung bean proteins, we reasonably assume they pose low hazards since they are consumables. Soy protein causes skin sensitization, which will be a concern for those who are allergic.

Nama	Group I Human Endpoints			Group II ai	nd Group II*	<sup>-</sup> Endpoints	Ecotox- icity	Fate	Physical Hazard
Iname	Carcinogenicity	Developmental	Endoanino Astivity	Sustania Taviaita	Nouvetovicity	Skin, Eye, Respiratory	Aquatic Toxicity	Persistence	Reactivity, Flammability
	Mutagenicity	Toxicity	Endocrine Activity	Systemic Toxicity	Neurotoxicity	Irritation/ Sensitization	Acute/ Chronic	Bioaccumulation	Other Pchem Traits
Polyvinyl Alcohol	L	L	DG	L	L	L	H*	M*	L
Brewer's Spent Grain Protein	L	L	DG	L	L	L	L	vL	L
Soy Protein	L	L	M*+	L	L	Н	L	L	L
Pea Protein	L	L	DG	L	L	L	L	L	L
Mung Bean Protein	L	L	DG	L	L	L	L	L	L
<i>italicized</i> = low confidence L = reasonable assumption of safety			* = mixed literature data + = not a consumer hazard gap			i very vi low vi	L M H	very high	

Table	15.	Hazard	Assessme	nt Corr	parison	of PVA	and Proteins
Lanc	10.	IIuZuIu	1 10000001110	In Con	ipuiison		und i rotoniis

We also assessed the technical performance and manufacturing compatibility of each protein alternative (Table 16). The solubility temperature and pH compatibility of the proteins align with

those of PVA. The protein-based films have much lower tensile strength needed for detergent packs, but they may be suitable for detergent sheets (in which the tensile strength is estimated to be 1-10 MPa). Soy protein and pea protein films have comparable elongation, while BSG and mung bean protein films will need further optimization. Additionally, we included in the table our recommendations for whether the protein alternatives would be most suitable for sheets, packs, or both.

Name	Solubility Temperature	pH Compatibility	Tensile Strength (MPa)	Elongation (%)	Commercial Availability	Sheets, Packs, or Both	
Polyvinyl Alcohol	Cold and hot	5-9	47	290	Yes (Powder, Film)	Both	
BSG Protein	Cold and hot	6-12	4.32	60	Yes (Powder, Film)	Packs*	
Soy Protein	Cold and hot	3-8.5	25.1	379	Yes (Powder)	Packs	
Pea Protein	Cold and hot	>6	7	200	Yes (Powder, Film)	Both	
Mung Bean Protein	Cold and hot	8-12	3.3	81	Yes (Powder)	Sheets	
<i>italicized:</i> potential company partner *marketing aesthetic considerations							

**Table 16.** Technical Performance and Manufacturing Compatibility Comparison of PVA and Proteins

# 6. Formulation Considerations: Potential Additives

### Plasticizers

Polysaccharide and protein-based films often have lower elongation than is necessary for sheets and packs. In packs, adequate elongation is necessary to give the film flexibility and the ability to stretch for compatibility with the pack-forming process. In sheets, flexibility is needed to tear the piece into portions. In general, plasticizers reduce film stiffness by reducing friction between polymer chains.<sup>53</sup>

We investigated two plasticizers to improve the elongation: sorbitol and glycerol (Figure 19). These are both water-soluble, and glycerol is currently used in the manufacturing process of sheets, making it easy to integrate. To note, with the addition of a plasticizer, while the elongation increases, the tensile strength tends to decrease.



Figure 19. Chemical structures of plasticizers sorbitol and glycerol

# Hygroscopicity Reducers

Polysaccharide and protein-based films absorb moisture from the air more readily than PVA. In other words, the potential replacements are more hygroscopic. For the sheets and packs to have the desired shelf stability, we investigated additives to reduce the hygroscopicity. Many of the polysaccharide and protein-based films have not had extensive lifetime studies yet. The additions of lower-hygroscopicity materials will decrease the moisture absorption from the air, and increase the shelf life.

We investigated three hygroscopicity reducers: erythritol, mannitol, and isomalt (Figure 20). All of these are water-soluble and have low hygroscopicity. These are used as artificial sweeteners to prevent hard candy from sticking together, improving the shelf life. In the hard candy industry, these are sprayed over like a coating. In this application, these may be sprayed over the sheets and packs as they come off of the manufacturing equipment.



Figure 20. Chemical structures of hygroscopicity reducers, erythritol, mannitol, and isomalt

### Health and Environmental Performance

#### Sorbitol

Sorbitol is a sugar alcohol that is naturally found in some fruits. Studies show no genotoxicity, mutagenicity, or reproductive or developmental toxicity.<sup>136</sup> There is potential carcinogenicity where rats were given 20% sorbitol in their diet over 78 weeks had a significant increase of unilateral and bilateral hyperplasia of the adrenal medulla.<sup>136</sup> However, this dosage and exposure duration is highly unlikely, especially in application to laundry detergent products, thus posing no consumer threat. Acute toxicity studies show an oral LD<sub>50</sub> of 17.5 g/kg bw in male rats, 15.9 g/kg bw in female rats, 23.2 g/kg bw in male mice, and 25.7 g/kg bw in female mice, all of which are "practically non-toxic" according to the Hodge and Sterner scale.<sup>136</sup> Sorbitol was found to be a slight skin irritant and a more significant eye irritant, but this is mitigated by proper PPE for workers.<sup>137</sup> For consumers, the dose used would be low enough that this does not pose a risk. Regarding environmental implications, the German FEA has deemed sorbitol Class 1 Low Hazard to waters for both acute and chronic aquatic toxicity.<sup>138</sup> Currently, there is no data on persistence and bioaccumulation.

#### Glycerol

Glycerol, or glycerin, is widely used across the pharmaceutical, food, and cosmetics industries as a solvent, plasticizer, and humectant. Glycerol is metabolized through the kidneys and liver to then be excreted through urine.<sup>139</sup> Glycerol is naturally found in humans. In rat studies, researchers found an oral LD<sub>50</sub> of > 10,000 mg/kg and a dermal LD<sub>50</sub> of > 21,900 mg/kg.<sup>139</sup> Research found no genotoxic effects in rats when they were fed up to 50mg glycerol per plate and found no carcinogenic effects when consumed up to 20% of their diet.<sup>139</sup> In reproductive studies on rats, no adverse effects were observed in rats orally administered 20% glycerin in water throughout gestation and nursing. Modeled data indicates glycerol does not persist in the environment.<sup>140</sup>

#### Erythritol

Erythritol is a low-hygroscopicity artificial sweetener, found naturally in fruits, vegetables, and fermented beverages.<sup>141</sup> It is estimated that erythritol consumption from natural sources is 25-100

mg/person/day.<sup>141</sup> In rat studies, there were no adverse effects when erythritol was consumed up to 6.6g/kg for 3 weeks.<sup>142</sup> The German FEA classifies erythritol as a low hazard to waters. Erythritol is an FDA Generally Recognized as Safe substance, and as such, many assume safety and do not study erythritol further, so we investigated with computational models. According to EPA CompTox computational models, it is not carcinogenic or toxic. By the OPERA model, it is degradable and not persistent.

#### Mannitol

Mannitol is a sugar alcohol and diuretic. In mice and rat studies, there has been no evidence of carcinogenicity, mutagenicity, reproductive, developmental, or systemic toxicity.<sup>136,143</sup> Acute toxicity studies show an oral LD<sub>50</sub> of 22 g/kg bw in rats and 17.3 g/kg bw in mice, which according to the Hodge and Sterner scale is "practically non-toxic".<sup>136</sup> There are neurotoxic implications, where mannitol may cross the blood-brain barrier and interfere with the brain's ability to maintain the pH of cerebrospinal fluid or worsen cerebral edema.<sup>144,145</sup> However, this is only in medical applications where mannitol is injected at frequent or high concentrations and would not be a concern for use in detergent. Skin or eye irritation has not been observed, but there may be irritation and discoloration when in contact with sensitive skin areas.<sup>136,146</sup> Additionally, chronic exposure in animals did lead to minimal laryngeal ulceration and sinus histiocytosis in the mediastinal lymph node for the high-dose group (197 mg/kg/d).<sup>136</sup> Both of these symptoms would be mediated with appropriate PPE and would not be a concern for consumers. Regarding environmental implications, the German FEA has deemed mannitol Class 1 Low Hazard to waters for both acute and chronic aquatic toxicity.<sup>147</sup> Currently, there is no data on persistence and bioaccumulation.

#### Isomalt

Isomalt, or palatinit, is a sugar substitute, which is used to make strong edible structures. In rat studies, it showed no carcinogenic, mutagenic, neurological, or reproductive toxicity when consumed up to 10% of their diet,<sup>148</sup> and researchers found an  $LD_{50}$  of > 2,500 mg/kg.<sup>149</sup> For its ecotoxicity, ECHA's QSAR predicts that isomalt will degrade rapidly in the environment into mannitol and sorbitol, with no concern for persistence and bioaccumulation, and little concern for aquatic toxicity.<sup>150</sup> The primary concern for isomalt is that in its pure powder form, it is a respiratory irritant by GHS. This can be mitigated by proper PPE for workers, and it is not a hazard for consumers.

		Group I Human Endpoints			Group II and Group II* Endpoints			Ecotox- icity	Fate	Physical Hazard	
Additive Role	Name	Name	Carcinogenicity	Developmental and Reproductive	Endocrine Activity	Systemic Toxicity	Neurotoxicity	Skin, Eye, Respiratory Irritation/	Aquatic Toxicity Acute/	Persistence Bioaccumulation	Reactivity, Flammability
		Mutagenicity	Toxicity	liceling	Ioxidiy		Sensitization	Chronic		Other Pchem Traits	
Plasticizer	Sorbitol	L	vL	DG	vL	L	$\mathrm{M}^{\scriptscriptstyle +}$	L	L	vL; M	
Tasticizei	Glycerol	L	L	DG	L	L	L	vL	L	vL; H	
	Erythritol	L	L	DG	L	L	$\mathrm{M}^{\scriptscriptstyle +}$	L	vL	vL	
Hygroscopicity Reducer	Mannitol	vL	vL	DG	vL	$\mathrm{M}^{\scriptscriptstyle +}$	L	L	L	vL, M	
	Isomalt	L	L	DG	L	L	$\mathrm{M}^{\scriptscriptstyle +}$	L	L	L	
	ety	* = mixed + = not a c	literature onsumer ha	data zard <sup>gap</sup>	DG very low	vL L M	H vH very high				

Table 17. Hazard Assessment Comparison of Additives

Table 17 shows the comparative hazard assessment of additives. The use of these additives in the formulation can improve flexibility and lifetime. There are data gaps for endocrine disruption, which should be further studied. The widespread use of these additives in the food industry leads to the pale green distinction where we assume safety. The additives that we found to enhance the performance of PVA alternatives are not hazardous for consumers. Overall, these additives may play an important role in enhancing the properties of detergent sheets and packs, aligning with the strategy of identifying environmentally friendly alternatives to PVA.

# 7. Conclusion

### **Overall Comparison**

In this report, we identified and investigated a range of bio-based, biodegradable materials that could replace PVA in packs and sheets. Since most of our potential alternatives pose little hazard to consumers, we will focus on the technical performance and manufacturing compatibility to make broader comparisons. Table 18 summarizes the overall technical performance of polysaccharides and proteins in comparison to PVA. The shortfalls of tensile strength and elongation are primarily because of stringent requirements for compatibility with current packs manufacturing, but many of these could be drop-in replacements for sheets if compatible with the other ingredients in the formulation. While no one option is a perfect drop-in replacement for both packs and sheets on its own, additives could overcome particular shortcomings.

Additionally, combinations of proposed alternatives can be synergistic. For example, Brewer's spent grain protein mixed with chitosan increased the tensile strength and elongation.<sup>112</sup> Also, combining  $\lambda$ -carrageenan with a protein film increased the flexibility and cold water solubility.<sup>42</sup> The synergistic effects between polysaccharides and proteins can be explained by PVA's structure. PVA is a semicrystalline polymer, in which the crystalline domains offer rigidity and are less affected by solvent penetration. When semicrystalline polymers undergo applied stress (e.g. tensile stress), the polymer chains in the amorphous domain stretch out while the polymer chains in the crystalline domain remain intact. This characteristic feature allows semicrystalline polymers to be ductile and deform elastically. Polysaccharides are amorphous polymers and do not have any crystallinity, which may explain the lower tensile strength and elongation. Proteins are neither amorphous nor semicrystalline polymers. However, they resemble the structure of semicrystalline polymers, in which the folded region acts like the crystalline domain and the unfolded region is similar to the amorphous domain.

Name	Solubility Temperature	pH Compatibility	Tensile Strength (MPa)	Elongation (%)	Commercial Availability	Sheets, Packs, or Both
Polyvinyl Alcohol	Cold and hot	5-9	47	290	Yes (Powder, Film)	Both
Sodium Alginate	Cold and hot	>4	25-75	5	Yes (Powder)	Both
Carrageenan	Cold and hot	6-10	39.3	19.5	Yes (Powder, Film)	Both*
Chitosan	Cold and hot	<6.5	5-245	5-495	Yes	Packs

Table 18	Technical	Performance	Com	narison	of $PV\Delta$	Poly	vsaccharides	and F	Proteins
Table 10.	recinical	remonnance	Com	parison	OF VA,	, <b>P</b> 01	ysaccharides	, anu r	Totems

					(Powder, Film)	
Pullulan	Cold and hot	3-8	1.7	10	Yes (Powder)	Sheets
Cellulose	Cold and hot	2-13	4.5-22.4	13.4	Yes (Powder, Film)	Both
BSG Protein	Cold and hot	6-12	4.32	60	Yes (Powder, Film)	Packs*
Soy Protein	Cold and hot	3-8.5	25.1	379	Yes (Powder)	Packs
Pea Protein	Cold and hot	>6	7	200	Yes (Powder, Film)	Both
Mung Bean Protein	Cold and hot	8-12	6.0	81	Yes (Powder)	Sheets
<i>italicized:</i> potential company partner *marketing aesthetic considerations				compatible		needs modification

# **Experimental Considerations**

During our research, data gaps and the relative ease of synthesizing biopolymer films inspired us to experiment with sodium alginate. Films were prepared through a modified procedure based on work by Janik et al. 2023 (Figure 21).<sup>31</sup> Briefly, a 45 mL aqueous solution of 1 w/w % (0.45 g) sodium alginate with glycerol plasticizer (30 w/w % based on the weight of alginate; 110  $\mu$ L) was prepared by stirring and heating to 60 °C for 2 hr. The films were then obtained by pouring the mixture into a 10 cm diameter petri dish and heating at 40 °C for roughly 48 hours until the excess liquid was removed. We also prepared a 2 w/w % sodium alginate film with 2 w/w % generic detergent according to the same procedure.

The film we created was surprisingly strong, transparent, and flexible. The film was 50 µm thick and by comparison, had a higher tensile strength than an ECOS laundry sheet. A portion of the film dissolved completely in water in about 60 seconds. The film could flex easily without cracking or breaking. Adding laundry detergent to the film resulted in a slightly more inflexible film, though it could also be flexed without breaking or cracking. The film was slightly discolored on one portion, though this was likely due to uneven drying due to not being on a completely flat surface.



Figure 21. 1 w/w % sodium alginate film (left) and demonstration of its flexibility (center). 2 w/w % sodium alginate film with 2 w/w % detergent (right).

This exercise illustrates some of the important variables and considerations that go into developing a formulation for an alternative to PVA. It is clear that the current manufacturing process has been carefully optimized for PVA, and thus, the use of a novel alternative would require the same optimization of additives, ingredient composition, and drying conditions. Variables to consider when making a biopolymer film include the concentration of the initial aqueous solution, polymer molecular weight (average and standard deviation), ratio of various monosaccharides, choice of counterion, potential synthetic modification (e.g., degree of hydrolysis for PVA), and choice of additives. Furthermore, a formulation that produces a good film may not be ideal for making a good sheet, since the addition of detergents and other ingredients can affect the properties of the sheet. Other variables to consider when making the sheet are the composition of the ingredients and drying conditions, such as drying time and temperature. The combinatorial landscape must be sufficiently explored before concluding that a potential alternative does not satisfy the criteria to replace PVA.

### **Remaining Questions**

Many of the alternatives presented in this report have not been studied as alternatives to PVA in laundry detergent products. Thus, information on the shelf life of natural polymer films is generally lacking. Additionally, while many of the alternatives investigated are naturally sourced and break down readily in the environment, little is reported regarding their ability to pass specific biodegradability standards such as OECD 301B. Thus, before seriously considering an alternative, more rigorous lab testing should be performed on the polymer to confirm its biodegradability.

In the course of investigating alternatives to PVA, the compatibility of the alternatives with other active ingredients and the current manufacturing processes were important considerations, but cannot be satisfactorily confirmed without laboratory experimentation. For sheets, it is important to study whether the negatively charged surfactants influence the properties of chitosan, a polymer that must be positively charged to dissolve. In addition, certain components of the sheet,

such as silica, kaolin, glycerin, and citric acid, will need to be adjusted appropriately to achieve the desired properties. For packs, the compatibility of each film with elongation and heat sealing should be further investigated. If a promising alternative is not compatible with the current manufacturing process, it is important to note that modifications to the manufacturing process are possible. For example, if a material cannot be heat-sealed due to degradation before reaching the melting temperature, there are bio-based glues that could be employed, such as the work of Chi et al. 2023.<sup>41</sup> Additionally, if a material is not compatible with the current form-fill-seal type of machines that are used to make the packs, perhaps other types of machines, such as a premade pouch machine, could be explored to manufacture the next generation of packs. Lastly, the application of hygroscopicity reducers either within the material or as a coating after manufacturing merits further investigation.

Cost and consumer preferences were outside the scope of this report. Due to not being used in the laundry industry, many of the alternatives require substantial investment and scale before the prices become competitive with PVA. However, as demand for PVA alternatives increases, market competition and innovation will bring material costs down. Consumer preference for an alternative to PVA may also result in tolerance to slightly higher detergent product prices (e.g., Blueland laundry detergent tablets) and/or a replacement with non-ideal properties (e.g., a product with a slightly green/brown tinge).

Through our research, we believe that several of our potential alternatives can be used to make the next generation of soluble and biodegradable laundry detergent packs and sheets. However, resources need to be contributed on several fronts—research and development, process chemistry, industry partnerships, and marketing and consumer testing—for a true PVA replacement to be realized. As demonstrated by the examples presented of biodegradable biopolymers in research and industry, the technology is already available. The next phase in replacing PVA is for an industry leader to spearhead the research and development required to bring an alternative product to market.

# 8. About the Authors



**Tiffany Chen** is a fifth-year Ph.D. candidate in Chemistry. Her research focuses on the synthesis and characterization of polymer grafted nanoparticles and their assemblies. She provided knowledge of polymer chemistry and mechanical properties of polymeric materials.

**Crystal Cho** is a second-year Environmental Health Sciences MPH student. One of her focuses is considering sustainability and toxicity for a holistic evaluation of human and environmental impacts of potential alternatives. Alongside Farah, she evaluated proposed alternatives for their biodegradability and toxicity.





**Luke Elissiry** is a third-year Ph.D. candidate in Synthetic Chemistry. In the Chris Chang Group, he develops molecular electrocatalysts for small-molecule activation. He provided chemistry expertise, performed initial experimentation, and evaluated the technical feasibility of potential alternatives.

**Sophie Koh** is a second-year Ph.D. student in Electrical Engineering. Her research in finding eco-friendly solvent alternatives for organic solar cells gave her an understanding of technical performance tradeoffs when searching for greener solutions.





**Farah Sevareid** is a second-year Global Health and Environment MPH student. She is interested in the toxicity and sustainability of personal care products. With Crystal, Farah evaluated the proposed solutions against health and environment criteria, focusing on biodegradability, toxicity, and bioaccumulation.

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# 10. References

- 1. Julinová M, Vaňharová L, Jurča M. Water-soluble polymeric xenobiotics Polyvinyl alcohol and polyvinylpyrrolidon And potential solutions to environmental issues: A brief review. *J Environ Manage*. 2018;228:213-222. doi:10.1016/j.jenvman.2018.09.010
- 2. Guhl W, Steber J. The value of biodegradation screening test results for predicting the elimination of chemicals' organic carbon in waste water treatment plants. *Chemosphere*. 2006;63(1):9-16. doi:10.1016/j.chemosphere.2005.07.082
- 3. Chiellini E, Corti A, D'Antone S, Solaro R. Biodegradation of poly (vinyl alcohol) based materials. *Prog Polym Sci.* 2003;28(6):963-1014. doi:10.1016/S0079-6700(02)00149-1
- Amann M, Minge O. Biodegradability of Poly(vinyl acetate) and Related Polymers. In: Rieger B, Künkel A, Coates GW, Reichardt R, Dinjus E, Zevaco TA, eds. Synthetic Biodegradable Polymers. Advances in Polymer Science. Springer; 2012:137-172. doi:10.1007/12\_2011\_153
- 5. Rolsky C, Kelkar V. Degradation of Polyvinyl Alcohol in US Wastewater Treatment Plants and Subsequent Nationwide Emission Estimate. *Int J Environ Res Public Health*. 2021;18(11):6027. doi:10.3390/ijerph18116027
- 6. Alonso-López O, López-Ibáñez S, Beiras R. Assessment of Toxicity and Biodegradability of Poly(vinyl alcohol)-Based Materials in Marine Water. *Polymers*. 2021;13(21):3742. doi:10.3390/polym13213742
- 7. Su C, Zhang X, Ge X, et al. Structural, physical and degradation characteristics of polyvinyl alcohol/esterified mung bean starch/gliadin ternary composite plastic. *Ind Crops Prod.* 2022;176:114365. doi:10.1016/j.indcrop.2021.114365
- 8. DeMerlis CC, Schoneker DR. Review of the oral toxicity of polyvinyl alcohol (PVA). *Food Chem Toxicol Int J Publ Br Ind Biol Res Assoc.* 2003;41(3):319-326. doi:10.1016/s0278-6915(02)00258-2
- 9. Ragusa A, Notarstefano V, Svelato A, et al. Raman Microspectroscopy Detection and Characterisation of Microplastics in Human Breastmilk. *Polymers*. 2022;14(13):2700. doi:10.3390/polym14132700
- 10. PubChem. Vinyl acetate. Accessed December 9, 2023. https://pubchem.ncbi.nlm.nih.gov/compound/7904
- C&L Inventory. Accessed December 9, 2023. https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/8510 9
- 12. Vinyl acetate Chemical Details. Accessed December 9, 2023. https://comptox.epa.gov/dashboard/chemical/details/DTXSID3021431
- 13. Vinyl acetate. Pharos. Accessed December 12, 2023. https://pharosproject.net/chemicals/2010830
- 14. Methanol: Systemic Agent | NIOSH | CDC. Published May 22, 2023. Accessed December 9, 2023. https://www.cdc.gov/niosh/ershdb/emergencyresponsecard\_29750029.html
- 15. PubChem. Methanol. Accessed December 9, 2023. https://pubchem.ncbi.nlm.nih.gov/compound/887
- C&L Inventory. Accessed December 9, 2023. https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/3721
   2
- 17. PubChem. Methyl acetate. Accessed December 9, 2023.

https://pubchem.ncbi.nlm.nih.gov/compound/6584

- 18. Methyl acetate. Pharos. Accessed December 9, 2023. https://pharosproject.net/chemicals/2009104
- C&L Inventory. Accessed December 9, 2023. https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/2391
- Clean Production Action. Acetic Acid (CAS# 64-19-7) GreenScreen® Assessment. Published online October 22, 2013. Accessed December 9, 2023. https://www.bizngo.org/images/ee\_images/uploads/plastics/GreenScreen\_Acetic\_Acid..pdf
- 21. PubChem. Trimethylolpropane. Accessed December 9, 2023. https://pubchem.ncbi.nlm.nih.gov/compound/6510
- 22. PubChem. Sodium Acetate. Accessed December 9, 2023. https://pubchem.ncbi.nlm.nih.gov/compound/517045
- 23. Sodium acetate. Pharos. Accessed December 9, 2023. https://pharosproject.net/chemicals/2006076
- 24. Bhatia AK, Dewangan S, Vaidya N. Chapter 22 Carbohydrates and derivatives as green corrosion inhibitors. In: Verma DK, Verma C, Aslam J, eds. *Computational Modelling and Simulations for Designing of Corrosion Inhibitors*. Elsevier; 2023:435-460. doi:10.1016/B978-0-323-95161-6.00024-2
- 25. Loureiro dos Santos LA. Natural Polymeric Biomaterials: Processing and Properties☆. In: *Reference Module in Materials Science and Materials Engineering*. Elsevier; 2017. doi:10.1016/B978-0-12-803581-8.02253-0
- 26. KIMICA Corporation manufacturer and worldwide supplier of alginate. KIMICA Corporation. Accessed October 19, 2023. https://kimica-algin.com/alginate/usage/
- 27. Ma J. Alternative water soluble polymeric films to poly(vinyl alcohol) for single unit dose products. http://purl.org/dc/dcmitype/Text. Universitat Rovira i Virgili; 2020. Accessed November 7, 2023. https://dialnet.unirioja.es/servlet/tesis?codigo=292567
- Kulig D, Zimoch-Korzycka A, Jarmoluk A, Marycz K. Study on Alginate–Chitosan Complex Formed with Different Polymers Ratio. *Polymers*. 2016;8(5):167. doi:10.3390/polym8050167
- 29. Saji S, Hebden A, Goswami P, Du C. A Brief Review on the Development of Alginate Extraction Process and Its Sustainability. *Sustainability*. 2022;14(9):5181. doi:10.3390/su14095181
- Wai Chun CN, Tajarudin HA, Ismail N, Azahari B, Mohd Zaini Makhtar M. Elucidation of Mechanical, Physical, Chemical and Thermal Properties of Microbial Composite Films by Integrating Sodium Alginate with Bacillus subtilis sp. *Polymers*. 2021;13(13):2103. doi:10.3390/polym13132103
- 31. Janik W, Nowotarski M, Ledniowska K, et al. Modulation of physicochemical properties and antimicrobial activity of sodium alginate films through the use of chestnut extract and plasticizers. *Sci Rep.* 2023;13(1):11530. doi:10.1038/s41598-023-38794-3
- 32. Marangoni Júnior L, Jamróz E, Gonçalves S de Á, da Silva RG, Alves RMV, Vieira RP. Preparation and characterization of sodium alginate films with propolis extract and nano-SiO2. *Food Hydrocoll Health*. 2022;2:100094. doi:10.1016/j.fhfh.2022.100094
- Anderson DMW, Brydon WG, Eastwood MA, Sedgwick DM. Dietary effects of sodium alginate in humans. *Food Addit Contam.* 1991;8(3):237-248. doi:10.1080/02652039109373974

- 34. EFSA Panel on Additives and Products or Substances used in Animal Feed (FEEDAP), Rychen G, Aquilina G, et al. Safety and efficacy of sodium and potassium alginate for pets, other non food-producing animals and fish. *EFSA J.* 2017;15(7). doi:10.2903/j.efsa.2017.4945
- Deepa B, Abraham E, Pothan L, Cordeiro N, Faria M, Thomas S. Biodegradable Nanocomposite Films Based on Sodium Alginate and Cellulose Nanofibrils. *Materials*. 2016;9(1):50. doi:10.3390/ma9010050
- 36. Perera KY, Jaiswal AK, Jaiswal S. Extending cheese shelf-life using eco-friendly sodium alginate-gelatin films reinforced with nanoclay. *Food Biosci*. 2023;56:103304. doi:10.1016/j.fbio.2023.103304
- Williams PA, Phillips GO. 11 The use of hydrocolloids to improve food texture. In: McKenna BM, ed. *Texture in Food*. Woodhead Publishing Series in Food Science, Technology and Nutrition. Woodhead Publishing; 2003:251-274. doi:10.1533/9781855737082.2.251
- Kulkarni VS, Shaw C. Chapter 5 Use of Polymers and Thickeners in Semisolid and Liquid Formulations. In: Kulkarni VS, Shaw C, eds. *Essential Chemistry for Formulators* of Semisolid and Liquid Dosages. Academic Press; 2016:43-69. doi:10.1016/B978-0-12-801024-2.00005-4
- 39. Guo Z, Wei Y, Zhang Y, et al. Carrageenan oligosaccharides: A comprehensive review of preparation, isolation, purification, structure, biological activities and applications. *Algal Res*. 2022;61:102593. doi:10.1016/j.algal.2021.102593
- 40. Water soluble films made from Carraphane | Brabender. Published April 28, 2023. Accessed December 13, 2023. https://www.brabender.com/en/water-soluble-films-made-from-carraphane/
- Chi W, Liu W, Xu S, Zhan X, Li J, Wang L. A new strategy to glue-seal κ-carrageenan film for packaging grease. *J Food Eng*. 2023;337:111248. doi:10.1016/j.jfoodeng.2022.111248
- 42. Totosaus A, Gutierrez R, Pérez-Chabela ML. Interaction Between Caseinate and Carrageenans Results in Different Physical and Mechanical Properties of Edible Films. *Acta Univ Cibiniensis Ser E Food Technol*. 2018;22(1):13-24. doi:10.2478/aucft-2018-0002
- 43. Carrageenan Market Size & Share Analysis Report, 2030. Accessed December 13, 2023. https://www.grandviewresearch.com/industry-analysis/carrageenan-market
- 44. Eha K, Pehk T, Heinmaa I, Kaleda A, Laos K. Impact of short-term heat treatment on the structure and functional properties of commercial furcellaran compared to commercial carrageenans. *Heliyon*. 2021;7(4):e06640. doi:10.1016/j.heliyon.2021.e06640
- 45. Rhim JW. Physical-Mechanical Properties of Agar/κ-Carrageenan Blend Film and Derived Clay Nanocomposite Film. *J Food Sci*. 2012;77(12):N66-N73. doi:10.1111/j.1750-3841.2012.02988.x
- 46. Iglauer S, Wu Y, Shuler P, Tang Y, Goddard WA. Dilute iota- and kappa-Carrageenan solutions with high viscosities in high salinity brines. *J Pet Sci Eng.* 2011;75(3):304-311. doi:10.1016/j.petrol.2010.11.025
- Chang YC, Lin CH. Degradable Carrageenan as a Substrate and Resistive Material for Flexible Applications. ACS Omega. 2023;8(13):12387-12392. doi:10.1021/acsomega.3c00165
- 48. Mahendiran B, Muthusamy S, Sampath S, et al. Recent trends in natural polysaccharide based bioinks for multiscale 3D printing in tissue regeneration: A review. *Int J Biol Macromol.* 2021;183:564-588. doi:10.1016/j.ijbiomac.2021.04.179

- 49. Weiner ML. Toxicological properties of carrageenan. *Agents Actions*. 1991;32(1):46-51. doi:10.1007/BF01983307
- 50. Cohen SM, Ito N. A Critical Review of the Toxicological Effects of Carrageenan and Processed Eucheuma Seaweed on the Gastrointestinal Tract. *Crit Rev Toxicol*. 2002;32(5):413-444. doi:10.1080/20024091064282
- 51. EFSA Panel on Food Additives and Nutrient Sources added to Food (ANS), Younes M, Aggett P, et al. Re-evaluation of carrageenan (E 407) and processed Eucheuma seaweed (E 407a) as food additives. *EFSA J.* 2018;16(4):e05238. doi:10.2903/j.efsa.2018.5238
- 52. Cohen SM, Ito N. A Critical Review of the Toxicological Effects of Carrageenan and Processed Eucheuma Seaweed on the Gastrointestinal Tract. *Crit Rev Toxicol*. 2002;32(5):413-444. doi:10.1080/20024091064282
- Cazón P, Vázquez M. Applications of Chitosan as Food Packaging Materials. In: Crini G, Lichtfouse E, eds. Sustainable Agriculture Reviews 36: Chitin and Chitosan: Applications in Food, Agriculture, Pharmacy, Medicine and Wastewater Treatment. Sustainable Agriculture Reviews. Springer International Publishing; 2019:81-123. doi:10.1007/978-3-030-16581-9\_3
- 54. Chitosan Market by Grade, Application & Region. MarketsandMarkets. Accessed December 14, 2023.

https://www.marketsandmarkets.com/Market-Reports/chitosan-market-202177578.html

- 55. Cazón P, Vázquez M. Mechanical and barrier properties of chitosan combined with other components as food packaging film. *Environ Chem Lett.* 2020;18(2):257-267. doi:10.1007/s10311-019-00936-3
- 56. Kaisler M, van den Broek LAM, Boeriu CG. Chitin and Chitosan as Sources of Bio-Based Building Blocks and Chemicals. In: *Chitin and Chitosan*. John Wiley & Sons, Ltd; 2019:229-244. doi:10.1002/9781119450467.ch9
- 57. Aider M. Chitosan application for active bio-based films production and potential in the food industry: Review. *LWT Food Sci Technol*. 2010;43(6):837-842. doi:10.1016/j.lwt.2010.01.021
- 58. Margret AA, Begum TN, Kumar AG. Discerning the Potential of Chitosan Extracted from Bio Resources as a Competent Brain Drug Carrier to Cross the Blood Brain Barrier. *Indian J Pharm Sci.* 2017;79(2):186-196. doi:10.4172/pharmaceutical-sciences.1000216
- 59. Kim K, Son J, Kim SK, Weller C, Hanna M. Properties of Chitosan Films as a Function of pH and Solvent Type. *Biol Syst Eng Pap Publ*. Published online January 1, 2006. https://digitalcommons.unl.edu/biosysengfacpub/111
- 60. Kim JH, Nam DH, Park CB. Nanobiocatalytic assemblies for artificial photosynthesis. *Curr Opin Biotechnol.* 2014;28:1-9. doi:10.1016/j.copbio.2013.10.008
- 61. Szymańska E, Winnicka K. Stability of Chitosan—A Challenge for Pharmaceutical and Biomedical Applications. *Mar Drugs*. 2015;13(4):1819-1846. doi:10.3390/md13041819
- Kam HM, Khor E, Lim LY. Storage of partially deacetylated chitosan films. *J Biomed Mater Res.* 1999;48(6):881-888. doi:10.1002/(sici)1097-4636(1999)48:6<881::aid-jbm18>3.0.co;2-2
- 63. Rajpal G. Color and Mechanical Properties of Chitosan Films during Storage. In: ; 2007. Accessed December 14, 2023. https://www.semanticscholar.org/paper/Color-and-Mechanical-Properties-of-Chitosan-Film s-Rajpal/6fc7bab6ae094ff38995a6f8ca6ad0411dcfdd56
- 64. Chenite A, Buschmann M, Wang D, Chaput C, Kandani N. Rheological characterisation of

thermogelling chitosan/glycerol-phosphate solutions. *Carbohydr Polym*. 2001;46(1):39-47. doi:10.1016/S0144-8617(00)00281-2

- 65. Rodríguez-Núñez JR, Madera-Santana TJ, Sánchez-Machado DI, López-Cervantes J, Soto Valdez H. Chitosan/Hydrophilic Plasticizer-Based Films: Preparation, Physicochemical and Antimicrobial Properties. *J Polym Environ*. 2014;22(1):41-51. doi:10.1007/s10924-013-0621-z
- 66. Jakubowska E, Gierszewska M, Nowaczyk J, Olewnik-Kruszkowska E. Physicochemical and storage properties of chitosan-based films plasticized with deep eutectic solvent. *Food Hydrocoll*. 2020;108:106007. doi:10.1016/j.foodhyd.2020.106007
- 67. Park S y., Marsh K s., Rhim J w. Characteristics of Different Molecular Weight Chitosan Films Affected by the Type of Organic Solvents. *J Food Sci*. 2002;67(1):194-197. doi:10.1111/j.1365-2621.2002.tb11382.x
- 68. Yeul VS, Rayalu SS. Unprecedented Chitin and Chitosan: A Chemical Overview. *J Polym Environ*. 2013;21(2):606-614. doi:10.1007/s10924-012-0458-x
- 69. Bullock G, Blazer V, Tsukuda S, Summerfelt S. Toxicity of acidified chitosan for cultured rainbow trout (Oncorhynchus mykiss). *Aquaculture*. 2000;185(3):273-280. doi:10.1016/S0044-8486(99)00359-2
- 70. Chou CM, Mi FL, Horng JL, et al. Characterization and toxicology evaluation of low molecular weight chitosan on zebrafish. *Carbohydr Polym*. 2020;240:116164. doi:10.1016/j.carbpol.2020.116164
- Waller DL, Rach JJ, Cope WG, Marking LL, Fisher SW, Dabrowska H. Toxicity of Candidate Molluscicides to Zebra Mussels (Dreissena polymorpha) and Selected Nontarget Organisms. J Gt Lakes Res. 1993;19(4):695-702. doi:10.1016/S0380-1330(93)71257-5
- 72. Pullulan an overview | ScienceDirect Topics. Accessed December 10, 2023. https://www-sciencedirect-com.libproxy.berkeley.edu/topics/chemistry/pullulan
- Wu S, Jin Z, Kim JM, Tong Q, Chen H. Downstream processing of pullulan from fermentation broth. *Carbohydr Polym.* 2009;77(4):750-753. doi:10.1016/j.carbpol.2009.02.023
- 74. Singh R, Gaur R, Tiwari S, Gaur MK. Production of pullulan by a thermotolerant aureobasidium pullulans strain in non-stirred fed batch fermentation process. *Braz J Microbiol*. 2012;43(3):1042-1050. doi:10.1590/S1517-838220120003000030
- 75. Tsujisaka Y, Mitsuhashi M. CHAPTER 16 PULLULAN. In: Whistler RL, Bemiller JN, eds. *Industrial Gums (Third Edition)*. Academic Press; 1993:447-460. doi:10.1016/B978-0-08-092654-4.50020-6
- 76. Krull SM, Ma Z, Li M, Davé RN, Bilgili E. Preparation and characterization of fast dissolving pullulan films containing BCS class II drug nanoparticles for bioavailability enhancement. *Drug Dev Ind Pharm*. 2016;42(7):1073-1085. doi:10.3109/03639045.2015.1107094
- Kraśniewska K, Ścibisz I, Gniewosz M, Mitek M, Pobiega K, Cendrowski A. Effect of Pullulan Coating on Postharvest Quality and Shelf-Life of Highbush Blueberry (Vaccinium corymbosum L.). *Materials*. 2017;10(8):965. doi:10.3390/ma10080965
- Agrawal S, Budhwani D, Gurjar P, Telange D, Lambole V. Pullulan based derivatives: synthesis, enhanced physicochemical properties, and applications. *Drug Deliv*. 29(1):3328-3339. doi:10.1080/10717544.2022.2144544
- 79. Coltelli MB, Danti S, De Clerk K, Lazzeri A, Morganti P. Pullulan for Advanced Sustainable Body- and Skin-Contact Applications. *J Funct Biomater*. 2020;11(1):20.

doi:10.3390/jfb11010020

- 80. Tian Y, Visser JC, Klever JobS, Woerdenbag HJ, Frijlink HW, Hinrichs WLJ. Orodispersible films based on blends of trehalose and pullulan for protein delivery. *Eur J Pharm Biopharm*. 2018;133:104-111. doi:10.1016/j.ejpb.2018.09.016
- 81. Nasrollahzadeh M, ed. Front Matter. In: *Biopolymer-Based Metal Nanoparticle Chemistry* for Sustainable Applications. Elsevier; 2021:i-ii. doi:10.1016/B978-0-12-822108-2.09991-9
- 82. Hernandez-Tenorio F, Giraldo-Estrada C. Characterization and chemical modification of pullulan produced from a submerged culture of Aureobasidium pullulans ATCC 15233. *Polym Test.* 2022;114:107686. doi:10.1016/j.polymertesting.2022.107686
- Chen CT, Chen KI, Chiang HH, Chen YK, Cheng KC. Improvement on Physical Properties of Pullulan Films by Novel Cross-Linking Strategy. *J Food Sci.* 2017;82(1):108-117. doi:10.1111/1750-3841.13577
- Zhou K, Yang Y, Zheng B, et al. Enhancing Pullulan Soft Capsules with a Mixture of Glycerol and Sorbitol Plasticizers: A Multi-Dimensional Study. *Polymers*. 2023;15(10):2247. doi:10.3390/polym15102247
- 85. Trinetta V, Cutter CN. Chapter 30 Pullulan: A Suitable Biopolymer for Antimicrobial Food Packaging Applications. In: Barros-Velázquez J, ed. *Antimicrobial Food Packaging*. Academic Press; 2016:385-397. doi:10.1016/B978-0-12-800723-5.00030-9
- Fiume MM, Heldreth B, Bergfeld WF, et al. Safety Assessment of Microbial Polysaccharide Gums as Used in Cosmetics. *Int J Toxicol*. 2016;35(1\_suppl):5S-49S. doi:10.1177/1091581816651606
- 87. Wolf BW, Garleb KA, Choe YS, Humphrey PM, Maki KC. Pullulan is a slowly digested carbohydrate in humans. *J Nutr*. 2003;133(4):1051-1055. doi:10.1093/jn/133.4.1051
- Lacroix M, Le Tien C. 20 Edible films and coatings from nonstarch polysaccharides. In: Han JH, ed. *Innovations in Food Packaging*. Food Science and Technology. Academic Press; 2005:338-361. doi:10.1016/B978-012311632-1/50052-8
- 89. Haghighatpanah N, Khodaiyan F, Kennedy JF, Hosseini SS. Optimization and characterization of pullulan obtained from corn bran hydrolysates by Aerobasidiom pullulan KY767024. *Biocatal Agric Biotechnol*. 2021;33:101959. doi:10.1016/j.bcab.2021.101959
- Carolin C F, Kamalesh T, Kumar PS, Hemavathy RV, Rangasamy G. A critical review on sustainable cellulose materials and its multifaceted applications. *Ind Crops Prod.* 2023;203:117221. doi:10.1016/j.indcrop.2023.117221
- 91. Cellulose Fiber Market. Accessed December 14, 2023. https://www.futuremarketinsights.com/reports/cellulose-fiber-market
- 92. Kadajji VG, Betageri GV. Water Soluble Polymers for Pharmaceutical Applications. *Polymers*. 2011;3(4):1972-2009. doi:10.3390/polym3041972
- 93. Wheatley TA. Water Soluble Cellulose Acetate: A Versatile Polymer for Film Coating. *Drug Dev Ind Pharm*. 2007;33(3):281-290. doi:10.1080/03639040600683469
- 94. METHOCEL<sup>TM</sup> Cellulose Ethers, DuPont ChemPoint ChemPoint. Accessed December 12, 2023. https://www.chempoint.com/products/iff/methocel-water-soluble-cellulose-ethers
- 95. PubChem. Cellulose. Accessed December 12, 2023. https://pubchem.ncbi.nlm.nih.gov/compound/16211032
- 96. General Properties of METHOCEL<sup>™</sup>, Premium Cellulose Ethers. Published online July 2009.
- 97. METHOCEL<sup>TM</sup> F50 Food Grade Industrial Cellulosics by IFF. Accessed December 15,

2023. https://www.industrialcellulosics.com/products/methocel/methocel-f50-food-grade

- Paudel S, Regmi S, Janaswamy S. Effect of glycerol and sorbitol on cellulose-based biodegradable films. *Food Packag Shelf Life*. 2023;37:101090. doi:10.1016/j.fpsl.2023.101090
- 99. Shatkin JA, Kim B. Cellulose nanomaterials: life cycle risk assessment, and environmental health and safety roadmap. *Environ Sci Nano*. 2015;2(5):477-499. doi:10.1039/C5EN00059A
- 100. Ede JD, Ong KJ, Goergen M, Rudie A, Pomeroy-Carter CA, Shatkin JA. Risk Analysis of Cellulose Nanomaterials by Inhalation: Current State of Science. *Nanomaterials*. 2019;9(3):337. doi:10.3390/nano9030337
- 101. Chen H, Wang J, Cheng Y, et al. Application of Protein-Based Films and Coatings for Food Packaging: A Review. *Polymers*. 2019;11(12):2039. doi:10.3390/polym11122039
- 102. Wittaya T. Protein-Based Edible Films: Characteristics and Improvement of Properties. In: Amer Eissa A, ed. *Structure and Function of Food Engineering*. InTech; 2012. doi:10.5772/48167
- 103. Mihalca V, Kerezsi AD, Weber A, et al. Protein-Based Films and Coatings for Food Industry Applications. *Polymers*. 2021;13(5):769. doi:10.3390/polym13050769
- 104. Hadidi M, Jafarzadeh S, Forough M, et al. Plant protein-based food packaging films; recent advances in fabrication, characterization, and applications. *Trends Food Sci Technol.* 2022;120:154-173. doi:10.1016/j.tifs.2022.01.013
- 105. Wen C, Zhang J, Duan Y, Zhang H, Ma H. A Mini-Review on Brewer's Spent Grain Protein: Isolation, Physicochemical Properties, Application of Protein, and Functional Properties of Hydrolysates. *J Food Sci.* 2019;84(12):3330-3340. doi:10.1111/1750-3841.14906
- 106. Hejna A, Marć M, Kowalkowska-Zedler D, Pladzyk A, Barczewski M. Insights into the Thermo-Mechanical Treatment of Brewers' Spent Grain as a Potential Filler for Polymer Composites. *Polymers*. 2021;13(6):879. doi:10.3390/polym13060879
- 107. Arauzo PJ, Du L, Olszewski MP, Meza Zavala MF, Alhnidi MJ, Kruse A. Effect of protein during hydrothermal carbonization of brewer's spent grain. *Bioresour Technol*. 2019;293:122117. doi:10.1016/j.biortech.2019.122117
- 108. Jaeger A, Sahin AW, Nyhan L, Zannini E, Arendt EK. Functional Properties of Brewer's Spent Grain Protein Isolate: The Missing Piece in the Plant Protein Portfolio. *Foods*. 2023;12(4):798. doi:10.3390/foods12040798
- 109. Shroti GK, Saini CS. Development of edible films from protein of brewer's spent grain: Effect of pH and protein concentration on physical, mechanical and barrier properties of films. *Appl Food Res.* 2022;2(1):100043. doi:10.1016/j.afres.2022.100043
- 110. Proaño JL, Salgado PR, Cian RE, Mauri AN, Drago SR. Physical, structural and antioxidant properties of brewer's spent grain protein films. *J Sci Food Agric*. 2020;100(15):5458-5465. doi:10.1002/jsfa.10597
- 111. Connolly A, Piggott CO, FitzGerald RJ. Technofunctional properties of a brewers' spent grain protein-enriched isolate and its associated enzymatic hydrolysates. *LWT - Food Sci Technol.* 2014;59(2):1061-1067. doi:10.1016/j.lwt.2014.06.054
- 112. Lee JH, Lee JH, Yang HJ, Song KB. Preparation and characterization of brewer's spent grain protein-chitosan composite films. *J Food Sci Technol*. 2015;52(11):7549-7555. doi:10.1007/s13197-015-1941-x
- 113. Ronis MJ, Gomez-Acevedo H, Shankar K, et al. Soy protein isolate feeding does not result

in reproductive toxicity in the pre-pubertal rat testis. *Exp Biol Med*. 2018;243(8):695-707. doi:10.1177/1535370218771333

- 114. Kumar P, Sharma M, Abubakar AA, et al. 2.16 Soybean: Sustainability Issues. In: Ferranti P, ed. *Sustainable Food Science A Comprehensive Approach*. Elsevier; 2023:219-231. doi:10.1016/B978-0-12-823960-5.00021-4
- 115. Das D, Panesar PS, Saini CS. Ultrasonic extraction of soy protein isolate: Characterization and comparison with microwave and enzymatic extraction methods. *J Food Sci.* 2023;88(7):2758-2779. doi:10.1111/1750-3841.16654
- 116. Soy Protein Isolate non-GMO (11b.). truenutritionstore. Accessed December 13, 2023. https://truenutrition.com/products/soy-protein-isolate
- 117. NOW Foods, Sports, Soy Protein Isolate, Pure Unflavored, 2 lbs (907 g). Accessed December 13, 2023. https://www.iherb.com/pr/now-foods-sports-soy-protein-isolate-pure-unflavored-2-lbs-907g/786
- 118. Zhao Y, Xu H, Mu B, Xu L, Yang Y. Biodegradable soy protein films with controllable water solubility and enhanced mechanical properties via graft polymerization. *Polym Degrad Stab.* 2016;133:75-84. doi:10.1016/j.polymdegradstab.2016.08.003
- 119. Guerrero P, Retegi A, Gabilondo N, de la Caba K. Mechanical and thermal properties of soy protein films processed by casting and compression. *J Food Eng.* 2010;100(1):145-151. doi:10.1016/j.jfoodeng.2010.03.039
- 120. Zhang J, Li F, Liu T, Li Y, Li J, Gao Q. Tough and strong biomimetic soy protein films with excellent UV-shielding performance. *Compos Part B Eng.* 2021;226:109379. doi:10.1016/j.compositesb.2021.109379
- 121. Ryan M, McEvoy E, Duignan S, et al. Thermal stability of soy protein isolate and hydrolysate ingredients. *Food Chem.* 2008;108(2):503-510. doi:10.1016/j.foodchem.2007.11.001
- 122. Soy Protein Ingredients Market: Trends, Opportunities & Forecast [Latest]. MarketsandMarkets. Accessed December 13, 2023. https://www.marketsandmarkets.com/Market-Reports/soy-protein-ingredients-market-857.h tml
- 123. Messina MJ, Persky V, Setchell KDR, Barnes S. Soy intake and cancer risk: A review of the in vitro and in vivo data. *Nutr Cancer*. 1994;21(2):113-131. doi:10.1080/01635589409514310
- 124. Sukalingam K, Ganesan K, Das S, Thent ZC. An insight into the harmful effects of soy protein: A review. *Clin Ter*. 2015;166(3):131-139. doi:10.7417/CT.2015.1843
- 125. Yang J, Zamani S, Liang L, Chen L. Extraction methods significantly impact pea protein composition, structure and gelling properties. *Food Hydrocoll*. 2021;117:106678. doi:10.1016/j.foodhyd.2021.106678
- 126. Kowalczyk D, Gustaw W, Świeca M, Baraniak B. A Study on the Mechanical Properties of Pea Protein Isolate Films: Mechanical Properties of Pea Protein Films. *J Food Process Preserv*. 2014;38(4):1726-1736. doi:10.1111/jfpp.12135
- 127. Cheng J, Li Z, Wang J, et al. Structural characteristics of pea protein isolate (PPI) modified by high-pressure homogenization and its relation to the packaging properties of PPI edible film. *Food Chem.* 2022;388:132974. doi:10.1016/j.foodchem.2022.132974
- 128. Ricci L, Umiltà E, Righetti MC, et al. On the thermal behavior of protein isolated from different legumes investigated by DSC and TGA. *J Sci Food Agric*.

2018;98(14):5368-5377. doi:10.1002/jsfa.9078

- 129. Morro Soluble Film. Accessed December 13, 2023. https://morro.earth/material/morro-soluble-film/
- 130. "World's First" Edible, Dissolvable Packaging Made from Pea Protein. Packaging World. Published November 2, 2021. Accessed December 13, 2023. https://www.packworld.com/news/sustainability/article/21796972/worlds-first-edible-dissol vable-packaging-made-from-pea-protein
- 131. Asen ND, Aluko RE. Physicochemical and Functional Properties of Membrane-Fractionated Heat-Induced Pea Protein Aggregates. *Front Nutr.* 2022;9. Accessed December 14, 2023. https://www.frontiersin.org/articles/10.3389/fnut.2022.852225
- 132. Moghadam M, Salami M, Mohammadian M, Emam-Djomeh Z. Development and characterization of pH-sensitive and antioxidant edible films based on mung bean protein enriched with Echium amoenum anthocyanins. *J Food Meas Charact*. 2021;15(4):2984-2994. doi:10.1007/s11694-021-00872-3
- 133. Brishti FH, Chay SY, Muhammad K, Rashedi Ismail-Fitry M, Zarei M, Saari N. Texturized mung bean protein as a sustainable food source: techno-functionality, anti-nutrient properties, *in vivo* protein quality and toxicity. *Food Funct*. 2020;11(10):8918-8930. doi:10.1039/D0F001463J
- 134. Moghadam M, Salami M, Mohammadian M, Khodadadi M, Emam-Djomeh Z. Development of antioxidant edible films based on mung bean protein enriched with pomegranate peel. *Food Hydrocoll*. 2020;104:105735. doi:10.1016/j.foodhyd.2020.105735
- 135. Mojoodi M, Nourani M. Mung bean protein films incorporated with cumin essential oil: development and characterization. *Int Polym Process*. 2022;37(3):303-315. doi:10.1515/ipp-2021-4213
- 136. Safety Assessment of Mannitol, Sorbitol, and Xylitol as Used in Cosmetics. Published online November 15, 2019.
- 137. Material Safety Data Sheet Sorbitol. Published online June 9, 2012.
- 138. Sorbitol. Pharos. Accessed December 14, 2023. https://pharosproject.net/chemicals/2010340
- 139. Becker LC, Bergfeld WF, Belsito DV, et al. Safety Assessment of Glycerin as Used in Cosmetics. *Int J Toxicol.* 2019;38(3\_suppl):6S-22S. doi:10.1177/1091581819883820
- 140. Glycerol Env. Fate/Transport. Accessed December 14, 2023. https://comptox.epa.gov/dashboard/chemical/env-fate-transport/DTXSID9020663
- 141. Grembecka M. Sugar alcohols—their role in the modern world of sweeteners: a review. *Eur Food Res Technol*. 2015;241(1):1-14. doi:10.1007/s00217-015-2437-7
- 142. Prooije AES van, Waalkens-Berendsen DH, Bär A. Embryotoxicity and Teratogenicity Study with Erythritol in Rats. *Regul Toxicol Pharmacol*. 1996;24(2):S232-S236. doi:10.1006/rtph.1996.0103
- 143. Abdo KM, Huff JE, Haseman JK, Alden CJ. No evidence of carcinogenicity of d-mannitol and propyl gallate in F344 rats or B6C3F1 mice. *Food Chem Toxicol*. 1986;24(10):1091-1097. doi:10.1016/0278-6915(86)90293-0
- 144. mannitol injection, USP () Warnings and Precautions | Pfizer Medical Information US. Accessed December 14, 2023. https://www.pfizermedicalinformation.com/mannitol/warnings
- 145. Tenny S, Patel R, Thorell W. Mannitol. In: StatPearls. StatPearls Publishing; 2023.

Accessed October 11, 2023. http://www.ncbi.nlm.nih.gov/books/NBK470392/

- 146. Mallinckrodt Baker, Inc. MANNITOL. Published August 20, 2008. Accessed December 14, 2023. https://us.vwr.com/assetsvc/asset/en\_US/id/8269623/contents
- 147. Mannitol. Pharos. Accessed December 14, 2023. https://pharosproject.net/chemicals/2009012
- 148. Smits-Van Prooije AE, De Groot AP, Dreef-Van Der Meulen HC, Sinkeldam EJ. Chronic toxicity and carcinogenicity study of isomalt in rats and mice. *Food Chem Toxicol*. 1990;28(4):243-251. doi:10.1016/0278-6915(90)90036-M
- 149. Musch K, Siebert G, Schiweck H, Steinle G. [Nutritional physiology of isomaltitol in the rat]. *Z Ernahrungswiss Suppl.* 1973;15:3-16.
- 150. Registration Dossier ECHA. Accessed December 13, 2023. https://echa.europa.eu/registration-dossier/-/registered-dossier/25123/6/2/1