Compostable Alternatives for Adhesive and Additives in PLU Stickers

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Executive Summary

Adhesives in PLU stickers are made from non-biodegradable materials, leading to diversion of compost with PLU stickers to landfills, production of micro-plastics, and the contribution of persisting single-use packaging in the environment. France recently passed standards that ban the usage of non-home compostable produce packaging, threatening the U.S. produce export industry and further incentivizing the need to develop compostable adhesive alternatives. Of the safer alternatives considered in this report, overall, frog glue, PHAs, carrageenan, and epoxidized soybean oil display the best technical performance as a pressure sensitive adhesive; more so, they all have very little to no health and environmental hazards associated with them. Other strategies may need further modification for better technical performance, but further hazard assessments must be conducted to ensure safety and home compostability.

Introduction

Background

PLU stickers are ubiquitous in U.S. produce markets, proving useful to different stakeholders.[1, 2] Grocery stores use them for inventory and to track how many items have been sold. Agricultural producers can showcase unique produce categories, and consumers can tell which country the produce was grown in and whether it was organically grown. They also play an important role in food safety, making it easier to check which items have been contaminated if there is a food poisoning outbreak.[3]

As an item that is frequently discarded with fruit or vegetable peels, current PLUs have a major drawback: they are not biodegradable. Recent standards enacted by France that will go into effect on January 1st, 2022 require all material sold with produce to be home compostable. This has an immediate and large monetary impact on U.S. agricultural exports.[4] In addition, there are reports of industrial composting facilities diverting rotting produce with PLUs to the landfill rather than contaminating their compost with plastic.[5] This practice causes avoidable emissions of greenhouse gases and contributes to environmental degradation through increased use of landfills. Lastly, mechanical and photodegradation of plastics in general leads to the exposure of microplastics - the effects of this are not well understood and may be harmful, especially for chronic exposure[6], so plastic contamination should be avoided if possible. Overall, these are compelling economic and environmental reasons to develop biodegradable alternatives for labeling produce.

To consider biodegradable alternatives, we first examine the composition of current products. PLUs, like other stickers, are made of a backing material on which the label is printed as well as an adhesive gum.[7] Typically, the backing material is composed of polyethylene and

inks for the label. The adhesive is composed of an elastomeric polymer with significant weight fractions of small molecule inclusions that help promote adhesion, stability or mechanical properties. While the bulk of the non-degradable substance is currently in the backing, stickers can easily be made of waxed paper or degradable plastic films without sacrificing quality. Unfortunately, the adhesive has much more complex requirements - while some producers say they have a solution to this problem, currently no option has been utilized at scale.[8, 9] Thus our main focus in this report is to examine potential alternative biodegradable pressure sensitive adhesive materials.

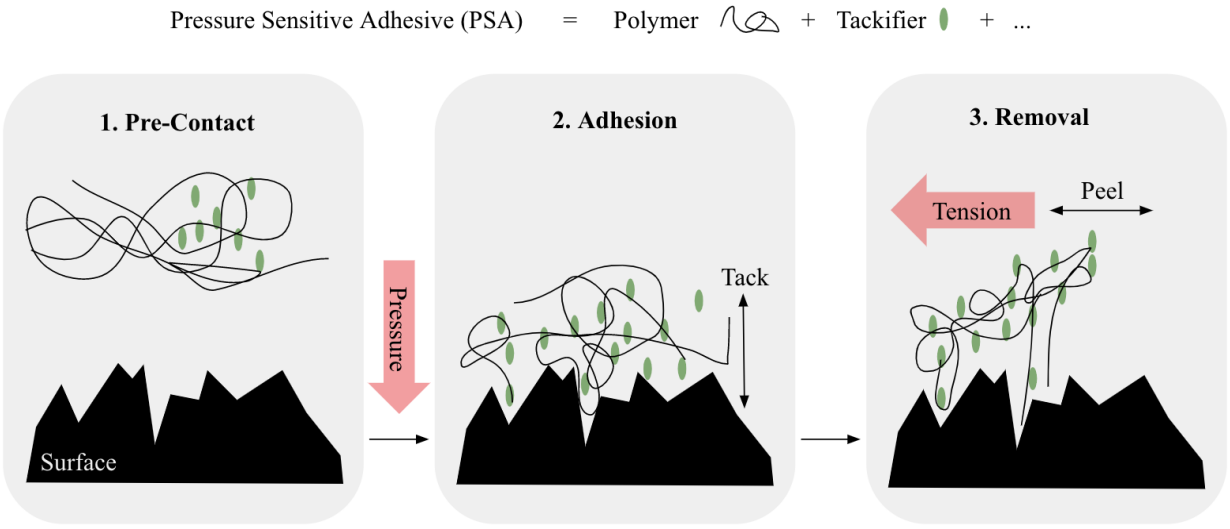

Figure 1. Composition and function of pressure sensitive adhesives.

To compare pressure sensitive adhesives (PSAs), we outline the mechanisms through which they function.[10] Fundamentally, a PSA is any substance (A) that will adhere to a surface (B) if it is pushed into that surface, can be (mostly) removed by pulling it away from the surface (C) and will do so reversibly (i.e. it can adhere to a surface more than once). This behavior requires certain material characteristics. First, the material must be soft enough to enter into microscopic surface cracks and allow for attractive intermolecular forces to develop between the surface and the adhesive. A physical measurement of this strength of adhesion is called tack. Second, it may not form a chemical bond with the surface - this would make it impossible to remove it cleanly. Third, the PSA must be somewhat elastic, allowing energy to be built up through pulling the adhesive away from the surface until the attractive intermolecular forces are overcome and the PSA snaps away from the surface. The tension required to pull the PSA away from the surface is called peel. Peel and tack are important adhesive properties which we will discuss in detail in our approach section on technical testing.[11]

Next, we examine the composition of PSAs and the role different components play in determining the overall properties. PSAs are composed of a polymer matrix and small molecules.[12] The polymer matrix is key to most of the adhesive properties, and as such must be

soft and elastic. Softness is usually an inherent property of a particular polymer, but it can be somewhat tuned by changing the length of polymer chains. Elasticity is a property that can be inherent in some polymers, but is often induced and enhanced through cross-linking different linear polymeric molecular chains with chemical bonds. The small molecules in the matrix change some of the underlying polymer properties, and are often referred to in functional groups. Plasticizers will make a PSA softer, while tackifiers will both soften the material and enhance the tack (chemical adhesion). Preservatives delay degradation of the formulation, and other small molecules may also be used to serve a variety of other functions.

Approach

It is crucial to consider the specific performance criteria to design a biodegradable alternative to existing produce labels..[13]

1) Produce labels must have adhesive properties…
    a) That are strong enough to adhere
        i) On a variety of different surfaces
        ii) Under different environmental conditions (i.e. humidity, temperature)
    b) That last at least one year
2) Labels must be safe…
    a) As a food-contact substance
    b) As a material that might be accidentally ingested
3) Labels must be degradable in home compost as specified by EN 13432 [14]:
    a) 90% material weight loss after 3 months
    b) 90% of material converted to CO_2 in 6 months.
    c) Beneficial for the composting process
    d) Composition within low limits set for heavy metals

In our approach to find potential solutions, we used functional substitution[14] to narrow our focus for a biodegradable pressure-sensitive adhesive. In the complexity hierarchy of functional substitution, our choice represents an end-use function substitution. Ultimately, designing a chemical drop-in replacement (i.e. a biodegradable polymer that is usable with existing formulations) would not fare well, because adhesive formulations are usually specifically designed to suit the polymer. In addition, most current formulations have hydrophobic polymers, whereas most biopolymers are hydrophilic, requiring the use of different tackifiers and additives to ensure the formation of stable mixtures. A systemic replacement (i.e. some other way to label produce) is difficult as well because produce has a variety of surfaces with a variety of colors and is stored under a variety of conditions. Laser tracing might not be readable on an eggplant, and rugged surfaces like a pineapple would be difficult to inscribe. Colored markings rub off easily and do not hold much information. Paper sleeves use a lot of

material and are easily ripped apart. A functional replacement, on the other hand, enables the general utility and ease of use of sticking with stickers, while allowing for flexibility in designing different chemical or chemo-mechanical systems that display reversible adhesive properties.

Technical Tests and Methodology

To assess technical performance, we chose a benchmark and key criteria for understanding how our alternatives perform as an adhesive. For an adhesive performance baseline, we selected Scotch Magic Tape because it is an effective PSA that is easily removable without leaving residue on or harming the substrate. For our key criteria, we focused on loop tack, peel adhesion, lap-joint shear, and dynamic shear. Loop tack is a measurement of the force needed to remove a loop of adhesive material from a surface at a constant speed [16], which measures how sticky the adhesive is at first contact under light pressure. Peel adhesion is the force needed to remove the adhesive material from the test surface at a constant speed, measuring the general adhesive strength. Shear is the force needed to remove an adhesive from a surface, pulling parallel to the surface. Lap-joint shear is an alternative method to peel adhesion, which assesses the adhesive strength of an adhesive; it describes the ability of an adhesive to resist force in-plane of the bonded surfaces (i.e. in plane of the adhesive film and substrate). On the other hand, dynamic shear is used to determine the cohesive strength of the adhesive, or how strong the bonds within the adhesive are. It is defined as the maximum force required to remove an adhesive from a certain area when pulled in a direction parallel to the surface.[16] The general adhesive strength does depend on the substrate, so it is important to test the adhesive on the particular substrate(s) of interest for their application. While PLU stickers must be able to adhere to a vast array of produce, it is impractical to test the adhesive performance on every fruit and vegetable. Instead, researchers can test with representative fruits to get a sense of how the PSA adheres to variable surface conditions. For example, apples and kiwis, for relatively smooth and textured surfaces, could be used as representative substrates. Literature has limited adhesive measurements on directly applicable substrates, so future investigation will require testing with produce for the most relevant adhesive values.

We also considered the force of adhesion in our technical performance discussion. The force of adhesion is poorly defined and non-standardized across literature, though it is often reported, sometimes even as the only adhesive value measured. Force of adhesion tests tend to be variations on peel adhesion and loop tack measurements, but can also include nanomechanical testing with tools like atomic force microscopy (AFM). Thus, force of adhesion values are fairly hard to compare, but were included when available for more metrics to report and to facilitate comparison between strategies when other measurements were scarce. Other technical properties that were used to assess and compare the performance of our strategies include tensile strength and elastic modulus. For similar reasons to the inclusion of the force of adhesion, these values were also discussed to have some parameter that could be compared across more alternatives with our benchmark. Tensile strength is a measure of the stress required to fracture a material

under uniaxial tension. Closely related is the elastic modulus, which assesses a material's resistance to recoverable deformation under uniaxial tension. Manufacturers could gain valuable insight and considerations regarding the physical behavior of alternatives, yet we do not believe tensile strength or elastic modulus to be significant factors in adhesive performance.

Hazard Assessment Methods

To assess environmental and human health impacts, we decided to look at three environmental hazard metrics and three human health hazard metrics related to our scope of compostable pressure sensitive adhesives. Our environmental hazard metrics include: persistence, bioaccumulation, and ecotoxicity (aquatic and terrestrial). Our human health hazard metrics include: carcinogenicity, single exposure toxicity, and skin/eye/respiratory irritation/sensitization. Our main method to assess hazard information was to first run the strategy through Pharos to get any available hazard information. Once we gain some hazard ratings, we look at the associated authoritative list and do further research on hazard information related to our strategy endpoints. This includes finding threshold levels or available safety data sheets, which we then use to convert their hazard rating score to a Globally Harmonized System of Classification and Labeling of Chemicals score.[17] Each metric of concern has a different Category rating. For our health hazards, acute toxicity ranges from Category 1-4, with 1 being the most dangerous. For carcinogenicity, it consists of Category 1A, 1B, and 2, each with different meanings and thresholds. For skin and eye sensitization, it ranges from 1A, 1B, 1C, 2, and 3, each with different meanings and thresholds. These metrics are based mainly from various LD_{50} and LC_{50}; however, if there are significant data gaps surrounding these values, a value of "DG" will be listed in the cell, indicating a data gap. For environmental endpoints, aquatic ecotoxicity consists of Category Acute 1-3 and Category Chronic 1-4, each with various thresholds based on specific aquatic species with varying exposure time at LC_{50} and EC_{40} values. Terrestrial ecotoxicity, persistence, and bioaccumulation endpoints are evaluated mainly based on available studies, in which we place their findings as close as we could based on similar scales mentioned in the GHS handbook. Low confidence in a score value will be indicated by an italicized cell value, particularly applicable to extrapolation of data or findings from various research studies. In order to further create a quick and understandable hazard level scale, we converted available GHS hazard category information into the GreenScreen Chemical Hazard Criteria labels, which consist of Very High (vH), High (H), Moderate (M), and Low (L).[18] However, if the strategy presents no apparent hazard for a specific endpoint, it will be listed as "None."

Possible Exposure Routes

In addition, we briefly consider possible exposure routes to different chemicals involved in this process throughout the product life cycle where appropriate. During production, there is

significant exposure hazard for individuals working at chemical plants producing small molecules for polymer production, especially for the methacrylates and isocyanates used to make polymethacrylates and polyurethanes most commonly used. Several of the potential solutions we investigated still require the use of hazardous chemicals during production. However, since production takes place in a restricted industrial environment with trained individuals overseeing the process, this exposure route poses a lower risk for the general public.

During labeling and sale of produce, individuals will come into incidental contact with PLU stickers, though not necessarily with the adhesive. More importantly, consumers will eat produce that may have residue of the adhesive used, or could accidentally ingest the entire label. Therefore, it is crucial that the adhesive used will not cause harm if ingested in amounts comparable to the adhesive present on the PLUs. Currently, PLUs must meet "food contact" standards by the FDA for these reasons.

After use, PLUs will ideally go through composting. In its current state, this practice will contribute to exposure of humans to microplastics from PLUs through use in agriculture, where runoff will eventually sweep microplastics into the water system. Placement in landfills, the natural environment, or the sewer system can also contribute to the same exposure route. Our ideal solution would eliminate this problem by degrading during the composting process.

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Strategies

Strategy 1: Proteins

Protein 1: Gluten

Inspiration

Vital wheat gluten is the protein isolate of wheat, produced as a by-product in the extraction of starch from wheat flour.[1,2] It is composed of two main proteins: gliadin and glutenin. Hydrogen bonding and hydrophobic interactions bind the polypeptide chains that make up gliadin, while disulfide bonds are what link the low- and high-molecular weight subunits glutenin is composed of.[2] Gliadin is responsible for the viscous properties of gluten, which allows for proper adhesion between gluten and surfaces. Glutenin is associated with gluten's elastic behavior, which contributes to its cohesive performance as an adhesive.[1] Together, they make gluten a standout bioprotein for use in PSA applications.

Technical Performance

Like many bio-derived solutions, inferior performance when compared to industry-standard synthetic polymers is an issue with gluten. Additives like plasticizers, which improve the overall flexibility, toughness, and processability of polymers, have been explored for gluten-based PSA systems.[3] Glycerol, a biodegradable plasticizer, has become a popular plasticizer of choice for its ability to improve the overall mechanical performance of gluten adhesives by promoting hydrogen bonding between gluten proteins, water content and the glycerol itself for better cohesion. The adhesive properties of the PSA can also be enhanced.[1, 4] One study tested the overall performance of several different gluten:glycerol ratios for PSAs and found the best adhesive properties were achieved with a 1:1 mixture. The tack and peel adhesion of the 1:1 formulation, while best of the combinations tried, are still weaker than desired, with about a magnitude worse performance compared to the benchmark (*Table 1*). The PSA's adhesion on a variety of food substrates, including mango, apple peel, pork skin, and flatbread, was also assessed. The force of adhesion on the pork skin and apple peel were the highest, which the authors contributed to their hydrophobicity. The mango and flatbread, with the lowest forces of adhesion, were more hydrophilic, although the gluten:glycerol formulation did successfully adhere to all substrates tested. There was also a noticeable drop in adhesive performance during the aging study the researchers performed. The adhesives were kept at 25 ℃ and 58% RH for 60 days, with their tack, peel strength and shear strength measured at several intervals during the aging period. It is important to note that the aging results were "sped up" by exposing the sticky side up to the air, rather than the label side.[1] Thus, the mechanical performance may not drop as significantly when the adhesive side is attached to produce in application as a PLU sticker.

Formulations of gluten and glycerol also effectively contain a third ingredient: water. This is because glycerol is hygroscopic and will readily absorb moisture in the air. Water content can be adjusted based on the relative humidity the adhesive is processed and stored in; a higher glycerol content will result in increased water uptake by the PSA.[1, 3, 4] As a plasticizer itself, water content has noticeable effects on the properties of the PSA. The performance of all the varying gluten:glycerol ratio formulations had the worst adhesion at the lowest relative humidity they were conditioned at (33% RH), and had the best mix of adhesive and cohesive properties at an intermediate humidity (58% RH).[1] Another study found that gluten:glycerol formulations with higher moisture content, especially when combined with higher temperatures and slower separation rates, are more likely to have cohesive failure upon removal from a surface. Cohesive failure, where the bonds within the PSA fail during removal, results in residue being left behind on the substrate, which is undesirable. This demonstrates that formulators can have some control over whether residue is left behind by formulating with a relative humidity that will more likely result in adhesive failure (between the PSA and the substrate) for a given temperature range.[3] It also indicates that the performance of a gluten:glycerol PLU sticker can vary based on the storage conditions, which is something that could be limiting for practical implementation.

A recent study found adding a mixture of salts to a gluten:glycerol PSA formulation can actually improve its adhesive performance. A combination of gluten, glycerol aqueous solution, and a mixture of KCl, Na2S2O3, NBr, and Na2CO3 salts were shaken at 25 ℃ for 24 hours and then exposed to air for 24 hours to fabricate the PSAs. The adhesive properties were measured using a lap shear test on a variety of substrates, and good adhesion strength for metallic, hydrophobic and hydrophilic surfaces was observed. Researchers noted a synergistic effect between glycerol and ions in the gluten-based formulation, with performance of the adhesive with only glycerol or only ions performing markedly worse. The glycerol promotes hydrogen bonding in the matrix while the anions from salts can facilitate protein folding and precipitation. This combination of hydrogen bonding and ionic interactions also allows for self-healing and recovery of the adhesive on a variety of substrates.[5] The importance of which salts were used was not discussed, so it seems possible to use only salts with appropriate food safety for a PLU application.

Health and Environmental Performance

The glycerol:gluten mixture is what is commonly used for PSA formulations; however, data assessing the health and environmental performance of this mixture is limited. Therefore, we assessed each component of this mixture separately for human health concerns. For the environmental component, we expect both glycerol and gluten to have low, if not no, persistence and bioaccumulation within the realm of home compostability. Because these are both naturally-derived compounds, we can expect that they will have little impact on the environment as a hazard. The German FEA does list glycerol as a low hazard with aquatic toxicity, yet they have low confidence in this statement.[6] Research has shown that some glycerol-biobased

solvents have low aquatic ecotoxicity, in which toxicity occurs in higher concentrations, much above than our desired level of use.[7]

Gluten

In terms of human health effects, gluten does not pose much harm to a majority of the population. Because it is found readily in many foods that humans are able to consume, many endpoints such as single exposure toxicity and carcinogenicity demonstrate no hazardous effects. However, in the case of gluten-sensitive individuals, exposure to gluten may cause serious health effects, particularly gastrointestinal pain and a change in quality of life.[8] This is particularly for individuals with Non-Celiac Gluten Sensitivity (NCGS), which contains a much more broad spectrum of how much gluten NCGS individuals can ingest before experiencing pain and human health concerns. It is important to note that gluten, in this scenario, must be ingested at a certain threshold in order to experience health concerns. However, the Roncoroni et al. study particularly looked at a low-gluten diet, which is an ingestion of 3.5 grams of gluten per day, which is theoretically much more than what an average consumer would interact with on a PLU sticker. For individuals with Celiac Disease (CD), several studies conducted clinical trials for a tolerable intake level for CD affected individuals, which range from 0.0015 to 2 grams of gluten ingested per day.[9, 10, 11] The U.S. FDA also conducted "a health hazard assessment for gluten exposure concluding that for individuals with CD, the tolerable intake level is 0.007 grams of gluten per day for adverse morphological effects and 1.5E-5 grams of gluten per day for adverse clinical effects".[11, 12] The Quebec CSST standards lists gluten as a moderate hazard for respiratory sensitization; however, it is specified that this is more of an occupational hazard for workers handling large amounts. This is mainly in relation to occupational asthma when workers are working with wheat and flour dusts, which contain gluten as a component.[13] With emerging food technology and research, scientists are in the midst of understanding how to modify gluten proteins in order to produce little to no allergenic properties.[14]

Glycerol

Glycerol also does not pose much harm to a majority of the population. Based on EU Standards, it lists glycerol as a potential concern for skin and eye irritation/sensitivity, yet it has not been fully classified as a concrete hazard for those endpoints. Safety Data Sheet values show that there are acute toxicity animal studies for glycerol. The oral LD50 for rats is 27,000 mg/kg, whereas the dermal LD50 for rabbits is greater than 10,000 mg/kg.[15] Thus, we would expect that at our levels of glycerol for PLU stickers, we would see very little toxicity effects for humans. Apart from skin and eye irritation/sensitivity, there are no other concerning human health-related endpoints for glycerol.

Remaining Questions

There are still remaining questions regarding the suitability of gluten as a pressure-sensitive adhesive alternative for PLU stickers. The gluten:glycerol formulation's sensitivity to water content brings into question its ability to handle washing cycles, and a large

range of relative humidities the PLU sticker will be exposed to over its life cycle. The observed degradation of its mechanical properties over time is also something to consider and study more, given the desired 1 year shelf life. While we have hope that the formulation can be improved to meet our benchmarked adhesive values, the recorded values for current formulations are not market ready and further R&D is required to assess the full potential of gluten as a suitable PSA. Additionally, individuals with CD would be exposed to potentially hazardous levels of gluten from these adhesives, which poses serious limitations and logistical challenges for any practical, scalable application for PLU stickers. Given the risk a gluten-based formulation poses to those with CD and the still-inferior adhesive performance compared to industry benchmarks, the viability of a gluten:glycerol PSA system for PLU stickers needs to be investigated further. Furthermore, if the development of a hypoallergenic gluten becomes well established, research on the adhesive properties of this hypoallergenic gluten will need to be reassessed.

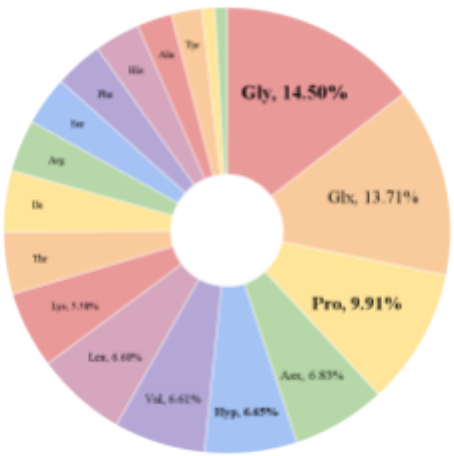
Protein 2: Nb-1R (derived from Notaden bennettii frog glue)

Inspiration

Notaden bennettii (Anura: Limnodynastidae) is a species of frog native to east Australia. When provoked, this small frog secretes a tacky and elastic adhesive material from its back. This glue-like secretion has many supposed survival purposes for the Notaden frog, but a notable concept for us is that according to multiple biomedical adhesive studies, the secretion is generally considered non-toxic to mammalian species.[16, 17, 18] This "frog glue" elastomeric adhesive consists mainly of proteins, with the most abundant being the Nb-1R glycoprotein. Nb-1R is a hefty 350 to 500 kDa structural protein that possesses a distinct proportion of glycine, proline, and 4-hydroxyproline amino acids (a common trend in bioadhesive proteins).[19] The recorded adhesive strength of Notaden frog glue is reliant on Nb-1R's unique chemical construction. Therefore, this protein is what makes frog glue a worthy PSA candidate, and it paves the way for potential bioinspired protein-based PSA solutions.

Technical Performance

Figure 2. The amino acid breakdown in mol % of type I frog glue (primarily Nb-1R) [19].



A look at the frog glue's composition can help uncover its technical aptitude. However, because researchers have developed multiple techniques to harvest Notaden frog glue, the exact glue constitution depends on the collection method. Out of the observed methods, one resulted in an Nb-1R majority glue with properties fit for an alternative PSA. This version of frog glue is known as "type I" frog glue. To collect type I glue, researchers stimulate a Notaden bennettii

frog's dermal musculature with an electrode to produce the exudate. They simultaneously irrigate the frog with a low pH buffer to collect the exudate. The low pH of the buffer causes the exudate to emulsify into two parts: a rising liquid and a settled, yellow hydrogel plug. This hydrogel plug consists mostly of the Nb-1R protein that drives the adhesion mechanism, and the amino acid breakdown of this type I product is found in *Figure 2*. Glycine (Gly), proline (Pro), and 4-hydroxyproline (Hyp) have been bolded due to their outstanding roles in the adhesive behavior of frog glue. Specifically, the balance and distribution of these amino acids in Nb-1R results in an amphiphatic protein with strong hydrophobic regions. As a result, Nb-1R is capable of establishing noncovalent protein-protein interactions, which allow the glue to solidify into a coherent substance upon drying. This scaffolding-behavior of Nb-1R is key to frog glue's adhesion mechanism, and not cross-linking. There is room for exploration with frog glue's adhesion chemistry, as the Nb-1R protein complex can form intermolecular disulfide bonds. One last biochemical consideration is the lack of 5-hydroxylysine and 3,4-dihydroxyphenylalanine (L-Dopa), which are compounds markedly found in the adhesive exudates of other organisms.

Type I frog glue has excellent ability to adhere to various substrates. This Nb-1R based hydrogel bonds to cardboard, wood, metal, glass, biological tissues, and a large variety of plastics (including nonstick PTFE) in both wet and dry conditions. This is especially important when considering that PLUs may be applied to dry or wet produce, depending on the washing cycle design. In addition, type I frog glue is able to de- and re-hydrate with no loss in performance, meaning that it can be kept as a solid before application, for ease of transportation and storage.

Lastly, the mechanical properties of frog glue are critical to PSA applications. Our primary source of technical data for Notaden frog glue is described by a series of tests conducted on type I frog glue at nano- and microscopic scales. Macroscopic lap-shear tests of type I glue were conducted by lap-jointing a pair of birchwood craft sticks with the hydrogel material. After a 1 week drying period, the pieces were tested to failure. With this method, the mean shear strength of type I frog glue was determined to be 1.7 ± 0.3 MPa. For comparison, the researchers performed this lap-shear test under the same conditions with various super glues and found that the dried type I frog glue displayed a shear bond strength comparable to that of cured cyanoacrylate glue (1.7 ± 0.7 MPa). While this may sound excessive for PLU PSA applications, it is important to note that a synthetic/bio-inspired frog glue may not be as well-tuned as nature's own design. Should a lab-replicated protein or bioinspired solution approach similar strengths, additives or fillers may be added to reduce bond performance. To consider the adhesive's performance in a humid environment, nanomechanical force-distance studies were performed on saturated type I frog glue using a scanning probe microscope equipped with a silicon nitride probe. Assuming that the glue behaved as a perfect rubber resulted in a mean elastic modulus of 171 ± 40 kPa, a mean resilience of $43 \pm 2\%$, and a mean adhesion value of 7.2 ± 2.3 nN.[19] These values suggest that Notaden frog glue may perform as an effective alternative to current PSA chemicals.

Health and Environmental Performance

The main component of the Notaden bennettii frog glue is a large glycoprotein called Nb-1R. Although this protein seems promising, there are several data gaps on the side of environmental degradation and human health safety concerns.

Although there are data gaps pertinent to our environmental endpoints (persistence, bioaccumulation, and ecotoxicity), we know that proteins are able to readily degrade in environments through various means, such as mineral degradation or photo degradation.[20,21] More so, environmental proteins associated with genetically engineered organisms have been found to have a rapid degradation rate.[22] Therefore, we hope to apply this knowledge towards the Nb-1R protein in both its naturally produced form and potential genetically engineered solution.

There are still several data gaps surrounding the human health endpoints; however, there is literature that exists suggesting no to low hazardous effects. Graham et al. notes the frog glue property as a potential in biomedical applications, in which small amounts of glue were implanted underneath mice's skin.[17] The study found no serious toxic effects, except for an initial necrosis of the skin due to the toxic metabolites present within the frog glue.[17] The removal of these metabolites have no effect on the tack and elasticity of the frog glue adhesive, impling that a safe PSA formulation could be engineered.[17] Furthermore, ex vivo studies in sheep demonstrated that the frog glue was able to bond meniscus tears and reattach tendons very well.[16] Although these are animal studies, the main component of this frog glue (Nb-1R glycoprotein) may have similar human biomedical applications and effects as scientists suggest. Thus, more research needs to be done to specifically test toxicity and possible carcinogenicity or sensitization in a human context.

Remaining Questions

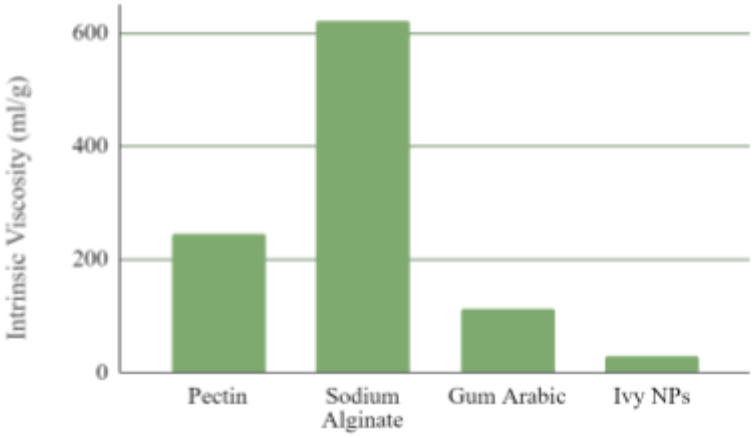
Despite the promise of Notaden frog glue, some questions stand between its theoretical prospects and realistic implementation. The scalability of a Notaden bennettii frog farm is comical to consider, but it is clear that to match the demand of the PLU PSA market, a bioinspired solution will need to be developed based on Nb-1R. Part of Nb-1R's strengths come from being a large, scaffolding protein with regions of varying polarity; the ability to recreate or draw inspiration from such a compound is a question well-suited to bioengineers in industry. Of course, the mechanical and health/environmental properties of this solution would likely differ, so further testing will be required to ensure satisfactory performance.

Protein 3: Arabinogalactan Proteins (AGPs)

Inspiration

English ivy travels and climbs up vertical surfaces by exuding a mucilage consisting of mostly nanoparticles. These nanoparticles are predominantly rich in arabinogalactan proteins (AGPs). The nanoparticles are spherical in shape, and adopt their structure from the spherical tertiary structure of the AGPs.[23] This nanoparticle structure makes the mucilage less viscous which is unique to English ivy nanoparticles. Furthermore, this low viscosity allows the exude to easily wet the surface the ivy is trying to climb, which is especially important in the attachment to rough substrates like tree bark. A comparison of the viscosity of the ivy nanoparticles to other biopolymers is shown in Figure 3.[23]

Figure 3. Viscosity of Ivy Nanoparticles compared to other bio-alternatives. Adapted from Huang et. al. [23]



While AGP is a main constituent of the ivy nanoparticle adhesive, extracting the mucilage from the plant is not realistically scalable. Therefore AGP nanoparticles can be considered as a bio-inspired strategy rather than a strategy reliant on bio-utilization. Understanding the role the nanoparticles play in the technical performance of this natural adhesive is critical in determining how it can be used to design safer adhesive alternatives.

Technical Performance

The ivy nanoparticles, in solution with water, calcium ions, and pectin wet the surface of the substrate, in order to initiate the adhesive process. Then the evaporation of the water in solution allows the particles to concentrate on the surface. Next, these concentrated particles form an adhesive film through interactions between the AGP-rich nanoparticles, calcium ions, and pectin. These interactions include electrostatic interactions with the positively charged calcium ions and van der Waals interactions with the pectin.[23] A schematic of the film formation is shown in *Figure 4*. This film creates a very strong adhesive, the metrics of which will now be investigated for applicatibality to PSAs.

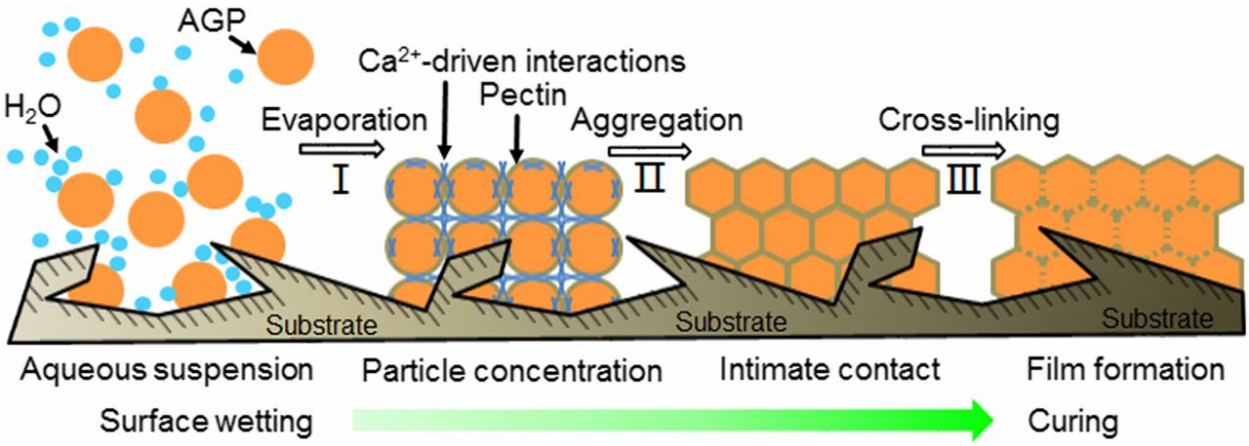


Figure 4. Schematic of the process ivy nanoparticles undertake to form an adhesive film on a rough substrate. (Taken from Huang et. al.[23])

In the previously mentioned paper that characterized English ivy's mucilage, they extracted the nanoparticles (109.6 nm diameter) to reconstruct a mimetic adhesive.[23] This adhesive consisted of a composite of the ivy nanoparticles, pectin, 2 millimolar calcium ions, and EGTA (a chelating agent). They tested the adhesive properties of lap joint shear and tensile strength for different compositions of the adhesive; with and without pectin, EGTA, or Ca^{2+} to identify the particles responsible for adhesion. Over a time period of 3 days, the composite consisting of ivy nanoparticles, pectin, and Ca^{2+} without EGTA had the strongest shear strength on a glass substrate of about 0.5 MPa. The adhesives consisting of EGTA or those without any Ca^{2+} had lower shear strengths (0.3 - 0.4 MPa) indicating that the calcium ions play an important role in the adhesion strength. The reconstructed adhesive was also tested for tensile strength using two clevis pins. The composite containing ivy nanoparticles, pectin, and calcium ions had the strongest tensile strength of about 0.3 MPa.[23]

Another article investigated the force of adhesion and Young's modulus (a measure of the elasticity of the adhesive) of English ivy nanoparticles grown in vitro using AFM (atomic force microscopy). AFM is able to accurately measure very small forces, down to piconewtons.[24] These nanoparticles were slightly smaller than those studied in the previously mentioned publication, having an average diameter of about 70 nm. The pull-off force, the force needed to retract the AFM tip from the adhesive, was measured, and averaged 298 nN. The article also notes that typically manufactured adhesives rely on additives to introduce tack, however, the nanoparticle composite of English ivy already exhibits a high elasticity of 1.035 - 1.297 GPa.[24]

Both of these articles make it clear that AGP-based nanoparticle adhesives are highly effective adhesives, as for their application for PLUs, synthetic design choices would need to be examined to produce a removable product that still maintains its biodegradability.

Health and Environmental Performance

Data assessing the health and environmental performance of arabinogalactan proteins (AGP) is limited. For the environmental component, we expect AGP to have little effect as it is a naturally occurring protein that should eventually biodegrade.

Nanoparticles can enter the body through the digestive tract, respiratory tract and dermal absorption. This may help create 'free radicals' which can cause cell damage and damage to the DNA. There is also concern that once nanoparticles are in the bloodstream they will be able to cross the blood-brain barrier.[25]

We can evaluate the concern for adsorption of the nanoparticles through the digestive, respiratory, dermal, and skin routes as outlined in Table 1. Since the reported AGP nanoparticles are between 70-110 nm, absorption into the blood is a potential concern, specifically for the English ivy nanoparticles grown in vitro (70 nm).[24]

Table 1. Values for which particles become hazardous relative to different exposure routes.[26]

Route of adsorption	Limitation
Digestive	Particle size > 100 nm
Respiratory	Particle size > 5 μm
Dermal	Particle is ionized or highly charged
Skin	Molecular weight > 400 Da

Remaining Questions

While we conclude from the information we do have on the health and environmental impacts of AGP that they are not likely to pose a threat to human health or the environment, a question remains with regards to evaluating the health and environmental impacts of bio-inspired designs based on AGP nanoparticles. In terms of environmental effects, current research in the field of microplastics is unveiling the harmful effects plastic nanoparticles can have on marine ecosystems.[27] Therefore, we suggest exploring bio-based polymer nanoparticles if this strategy is further developed.

Proteins Comparison

Technical Performance

We faced some difficulties trying to assess the technical performance of our protein strategies compared to our benchmark due to a lack of values available in literature for key performance metrics. In the following table, properties such as loop tack and peel adhesion are

listed for our control (Scotch Tape)[28] and the 1:1 Gluten: Glycerol composite at the highest performing relative humidity. The loop tack and peel adhesion are not listed for the other strategies because frog glue, AGP nanoparticles, and ionized gluten:glycerol have not yet been formulated as PSAs. Still, the data existing for lap-joint shear and force of adhesion provides us with an idea of how these strategies can perform as adhesives..From the adhesive data we do have, we can determine that the 1:1 Gluten:Glycerol solution is more easily removed from the surface of the substrate than Scotch Magic Tape.

Table 2: Technical performance values for each protein strategy versus Scotch Magic Tape

Property	**Scotch Magic Tape**	**Gluten:Glycerol** (1:1) at RH 58%	**Gluten:Glycerol** Ionized	**Frog Glue** Type I	**Reconstructed AGP Nanoparticles**
Loop Tack	**1.4 N/cm**[28]	**0.16 - 0.2 N/cm**[1]	—	—	—
Peel Adhesion	**1.7 - 2 N/cm**[28]	**0.16 - 0.2 N/cm**[1]	—	—	—
Lap-Joint Shear	—	—	**0.0248 MPa** (hog skin) **0.0168 MPa** (plastic) **0.0283 MPa** (glass) **0.0328 MPa** (paper) **0.0344 MPa** (stainless steel)[5]	**1.7 ± 0.3 MPa** (wood)[19]	**0.53 ± 0.033 MPa** (glass)[23]
Dynamic Shear	—	**11-15 MPa**[1]	—	—	—
Force of Adhesion	—	**3 N** (mango) **7 N** (porcine skin) **7 N** (apple peel) **5 N** (flatbread)[1]	—	**≥ 7.2 ± 2.3 nN, max. 18.9 nN** (nanomechanical)[19]	**298 ± 8.34 nN** (pull-off force, measured by AFM)[24]
Tensile Strength	**89.6 kPa**[28]	—	**150 kPa**[5]	**6.3 ± 0.3 kPa** (PP)[19]	**300 kPa** (clevis pins)[23]
Elastic Modulus	—	—	—	**171 ± 40 kPa**[19]	**$> 1 \times 10^6$ kPa**[24]

The shear strength of scotch tape was not reported, but we can note that between our proposed strategies, frog glue has the strongest shear strength. Further, the ionized gluten solution was tested on a variety of substrates, demonstrating its wide applicability. The force of adhesion was reported for the 1:1 Gluten:Glycerol solution, Nb-1R (frog glue), and the reconstructed ivy-mimetic. However, the test procedures and the reported numbers vary greatly, indicative of the lack of standardization of the use of the term “force of adhesion” in current literature.

The ionized gluten:glycerol PSA, as well as the reconstructed AGP nanoparticles, had significantly higher tensile strength than Scotch Magic Tape[28], while frog glue had a significantly lower tensile strength than any of the adhesives considered. The elastic moduli are available in literature only for type I frog glue and AGPs, and the stated values suggest that the reconstructed AGP nanoparticles are significantly stiffer than the hydrogel-like frog glue material.

Overall, significant data gaps exist for key performance metrics, which make it difficult to draw concrete conclusions. While, it does appear that a 1:1 Gluten:Glycerol formulation at 58% RH has worse adhesive performance than Scotch Magic Tape, modifications can be made to improve its ability as a PSA. Further testing is needed to truly compare the performance of the other protein-based alternatives to our benchmark.

Health and Environmental Performance

For our environmental endpoints (indicated as "Persistence", "Bioaccumulation", and "Ecotoxicity: Aquatic and Terrestrial"), we assume that they are home compostable and do not cause ecotoxicity because of their protein-like nature, as mentioned previously. More so, some of these proteins are large to the point that they will most likely not be able to cross the blood-brain barrier and cause neurological effects. Although we see research data gaps within the environmental performance endpoints, we also see this trend significantly more with human health performance endpoints. Although we cannot make definitive assumptions, it's important to note that there is a need for further research before implementing these potential strategies as a PSA.

We can see that all of our protein strategies tend to have no or very little environmental impact, which is desirable. However, we begin to tread into unsure territory, as several of our novel protein strategies contain several data gaps in the human health-related endpoints. Only glycerol is listed as a Category 5 hazard by GHS scoring guidelines, which translates to a low concern hazard. Although we assume that gluten will not pose any acute oral toxic effects to the average person, those with NCGS or CD are more susceptible to gluten. The U.S. FDA states a tolerable intake level of 1.5E-5 grams of gluten per day for adverse clinical effects, as previously stated. Further research studies are mentioned in the "Health and Environmental Performance" section for Gluten on previous pages.

Table 3: Health and Environmental Performance Evaluation for each Protein Strategy

Performance Endpoint		Gluten	Glycerol	Nb-1R	AGP
Persistence		*None*	*None*	*None*	*None*
Bioaccumulation		*None*	*None*	*None*	*None*
Ecotoxicity	**Aquatic**	*None*	*None*	*None*	*None*
	Terrestrial	*None*	*None*	*None*	*None*

Carcinogenicity	*None*	*None*	DG	DG
Single Exposure Toxicity	*None*	L	DG	DG
Skin, Eye, Respiratory Irritation/Sensitization	DG	DG	DG	DG

Hazard Rating: None (no hazardous effect), Low (L), Moderate (M), High (H), Very High (vH), data gap (DG)

Category Interpretation:[29]

- Glycerol: Single Exposure Toxicity
    - Listed as Low (L) or Category 5: Substances have relatively low acute toxicity hazard, but may pose as a hazard for vulnerable populations [Oral LD_{50} range of 2000-5000 mg/kg body weight]

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Strategy 2: Polysaccharides

Polysaccharide 1: Chitosan

Inspiration

Chitosan is a linear chain polysaccharide that is derived from chitin, which is sourced from crustaceans, insects, and fungi.[1] Chitin can be sourced from seafood waste, eliminating the concern that it would be taken away from a food source like many other polysaccharide based solutions. Chitin undergoes the process of deacetylation to swap its acetyl functional groups with hydrogens as in Figure 5. The nitrogens that the acetyl groups were attached to then become amines ($-NH_2$) which obtain a positive charge in acidic environments, when the pH < 5. These positive charges give rise to electrostatic interactions that increase the bonding ability of the adhesive.[2] Chitosan is unique in that it is one of the only cationic polysaccharides available.

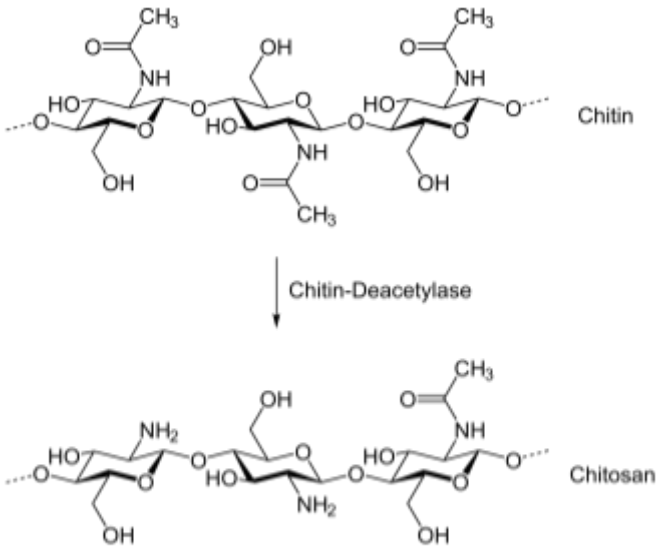

Figure 5. Formation of chitosan from chitin by deacetylation.[3]

Chitosan has been studied extensively in the biomedical field, specifically as a replacement for non-degradable sutures.[4] However, the main limitation for chitosan adhesives is their hydrophilic nature. Modifications to chitosan-based adhesives aim to improve their adhesive properties in wet environments (one example is outlined in the structural adhesives chapter).

Technical Performance

The adhesive performance and water resistance of chitosan are dependent on the molecular weight and degree of deacetylation (DD).[2] Most papers on chitosan adhesives report these parameters. In a paper by Abdelmoula et al. a chitosan formulation with high molecular weight and a lower DD was compared to one with a lower molecular weight and higher DD (Table 4). As expected, the formulation with a higher DD has stronger tensile strength because there are more positively-charged amine groups to contribute to the overall positive charge of the molecule. Similarly, higher molecular weight gives increased bonding strength. Furthermore,

chitosan formulations with similar molecular weights but higher DD are more water resistant, and therefore more appropriate formulations for PLU stickers.

Table 4: Comparison of Chitosan formulations from Abdelmoula et al.[2]

Property	**Scotch Magic Tape**	**Chitosan A** (>75% DD, high MW)	**Chitosan B** (90% DD, low MW)
Tensile Shear	—	**1.11 - 14.75 MPa**	**2.15 - 13.72 MPa**
Water Resistance	—	Weaker	Stronger
Tensile Strength	**89.6 kPa**	**0.61 - 2.84 MPa** (double lap bond strength)	**1.92 - 3.57 MPa** (double lap bond strength)

In addition to modifying the degree of deacetylation, researchers such as Mati-Baouche et al. have explored chemically modifying chitosan to improve its performance in wet environments.[5] In their paper, they suggest a chitosan adhesive alkylated with an octanol which conserves its bonding ability after exposure to water with a degree of substitution of 15%. Whereas the bond strength of a pure chitosan formulation decreases by a factor of nearly 10 upon immersion in water.[5] They also note an increase in viscosity of alkyl-chitosans as a function of the degree of substitution. However, in comparing the bond strength of the alkyl-chitosans to pure chitosan formulations, the pure chitosan formulations still offer better adhesive performance (Table 5). In order to obtain a balance between adhesion and water resistance, the authors suggest testing other alkyl-chitosan derivatives grafted with other aldehydes of various lengths and degrees of substitution.

Table 5: A comparison of pure chitosan and octanal substituted chitosan before and after being immersed in water. (Adapted from Mati-Baouche)[5]

	Before	**After**
Adhesive Formulation	**Bond Strength (MPa)**	**Bond Strength (MPa)**
Pure Chitosan	2.55 ± 0.02	0.28 ± 0.02
Chitosan DS 10%	1.30 ± 0.09	0.22 ± 0.01
Chitosan DS 15%	0.72 ± 0.53	0.73 ± 0.18

Health and Environmental Performance

Generally, chitosan is biodegradable, presents minimal toxic effects in humans, and does not report any effects related to carcinogenicity or mutagenicity.

Chitosan has been classified as hazardous to the aquatic environment by the Global Harmonized System of Classification and Labeling of Chemicals (GHS) due to toxicity studies that have been conducted in rainbow trout and zebrafish where oxygen interference and physiological disorders were noted.[6, 7] Rainbow trout in particular are quite sensitive to chitosan, even at low concentrations; their gills are affected by chitosan at concentrations ranging from 0.075 ppm to 0.75ppm.[7]

In all other human and environmental health endpoints, chitosan does not have any hazard level concerns. With chitosan being made from shellfish there is a possibility for allergy concerns. So far no studies have shown chitosan to cause allergic reactions in people allergic to shellfish. It has been tested as topic bandages in shellfish allergic patients, and no adverse reactions were reported.[8]

Chitosan is included in the EPA Safer Chemical Ingredient list as a "Green Circle."[9, 10]

Remaining Questions

The main question that remains for chitosan-based solutions is how best to improve adhesive performance in the presence of water. This is particularly important in the application of PLUs since the produce will be in contact with water throughout processing. A few recent experiments have suggested modifying the chitosan formulation either chemically (discussed above) or physically (micropatterning discussed in the structural chapter) which seem promising to start understanding how to make a generally applicable chitosan-based PSA for wet environments. Still, more work needs to be done to formulate the ideal solution and questions regarding how these modifications affect the biodegradation of the possible solutions remain.

Polysaccharide 2: Carrageenan

Inspiration

Carrageenan is a polysaccharide material extracted from a variety of red seaweeds.[11] It was traditionally used in Ireland as food and as a cure for respiratory ailments. Currently, it is used as a thickening and gelling agent, mainly for food, but also in pharmaceuticals and cosmetics. Worldwide carrageenan production reached 50,000 tons per year in 2009, so there is already considerable industrial capability built up. Chemically, carrageenan consists of repeated diglucoside units which may have one, two or three sulfate esters attached - these varieties are generally referred to as kappa, iota and lambda carrageenan, respectively. As a polyanionic polymer, it interacts well with water and is readily soluble in pure water, especially at elevated temperatures. Kappa and iota carrageenan form gels when exposed to alkali cations (particularly potassium), whereas lambda carrageenan does not solidify due to the higher negative charge of three sulfate esters per subunit.

Technical Performance

Iota carrageenan has demonstrated strong adhesion, especially under dynamic shear.[12] These measurements were conducted through pull-off tests, which are somewhat comparable to a tack test in that they measured adhesion after a short period of application. However, the surface was the parallel round steel plate geometry of a rheometer, with a diameter of 5 cm. While the authors of the study did not explicitly measure static shear, they calculated the expected value as 22-26 N, which can be increased to 33 N by mixing in casein, a protein widely used as a traditional wood glue. For a standard tack test, this would correspond to 4 N/cm. In another study, adhesive was evaluated as a paper adhesive and was found to have an adhesion strength of about 400 N/cm^2, though this might be a substantial overestimate.[13]

Due to the inherent polyanionic nature of carrageenan, it is very soluble in water. This limits the utility of carrageenan as an adhesive in humid environments or during washing - both of which are quite likely for PLU stickers.

Health and Environmental Performance

Carrageenan poses a high hazard to eye irritation, with a GHS score of category 2A which translates to a high hazard using the GreenScreen Criteria.[14] According to GHS guidelines, Carrageenan is a category 2 rating for carcinogenicity, meaning (Suspected) for any route of exposure or limited or marginal evidence of carcinogenicity in animals. According to the International Agency for Research on Cancer, World Health Organization (IARC) carrageenan has a Group 2B rating which is defined as possibly carcinogenic to humans and translates to a moderate hazard using the GreenScreen Criteria. After some research, the IARC rating for carrageenan was based off of degraded carrageenan in 1983.[15] Degraded carrageenan is not food and not the type of carrageenan we are proposing. With carrageenan's moderate hazard rating being due to degraded carrageenan, it is best to give the hazard rating a pass. Carrageenans environmental health endpoints (persistence, bioaccumulation, etc.) have no apparent hazards.

Although we cannot make definitive assumptions, it’s important to note that there is a need for further research before implementing this potential strategy.

Remaining Questions

From a technical standpoint, the main question that needs to be answered for use of carrageenan as an adhesive is how to control water solubility and increase binding to hydrophobic surfaces and study how humidity influences adhesion. In addition, no stability tests have been performed for adhesion, which would be necessary for any long-term use of carrageenan. From an environmental health and safety standpoint, questions surrounding the toxicity needed for Carrageenan to be carcinogenic. Further research of degraded carrageenan now known as Poligeenan is needed.

Polysaccharides Comparison

Technical Performance

Comparing our polysaccharide strategies, we can see that it is difficult to draw conclusions about their performance relative to our Scotch Tape benchmark.

Table 6. Comparison of polysaccharide solutions.

Property	Scotch Magic Tape	Chitosan Adhesive (Flat)	Carrageenan
Loop Tack	**1.4 N/cm**	—	—
Peel Adhesion	**1.7 - 2 N/cm**	—	—
Force of Adhesion	—	**2.4 ± 0.7 nN** (AFM)[16]	**4 N/cm**[13]

Comparing chitosan and carrageenan is also difficult, since the testing methods are not standardized and neither have been formulated as PSAs yet. However, both chitosan and carrageenan still seem promising as PSA adhesive alternatives as they are easily modifiable. While both have limitations in wet or humid environments, there is hope that they can be chemically or physically modified to overcome their hydrophilicity. Specifically, chitosan has been studied pretty extensively in the biomedical field, and we believe it may be easily adapted to a PSA formulation.

Health and Environmental Performance

It is important to know that both polysaccharides are on the EPA's safer choice Green circle list - so both of these chemicals have been verified to be of low concern based on experimental and modeled data. We can see that all of our polysaccharide strategies only have one area of concern. Chitosan has moderate aquatic ecotoxicity and carrageenan has high eye sensitization. Carrageenan tends to have no or very little environmental impact, which is desirable. These hazards may be more apparent in larger scale use in which people and/or aquatic wildlife are exposed to these substances at higher, more potent concentrations.

Table 7: Health and Environmental Performance Evaluation for each Polysaccharide Strategy

Performance Endpoint	Chitin/Chitosan	Carrageenan
Persistence	*None*	*None*

Bioaccumulation		*None*	*None*
Ecotoxicity	**Aquatic**	M	*None*
	Terrestrial	*None*	*None*
Carcinogenicity		*None*	*None*
Single Exposure Toxicity		*None*	*None*
Skin, Eye, Respiratory Irritation/Sensitization		*None*	H

Hazard Rating: None (no hazardous effect), Low (L), Moderate (M), High (H), Very High (vH), data gap (DG)

Category Interpretation:[17]

- Chitin/Chitosan: Aquatic Ecotoxicity
  - Listed as Moderate (M) or Category Acute 3: Substances are toxic to aquatic organisms with acute toxicity greater than 10 mg/L but less than or equal to 100 mg/L for 96 hour LC50 for fish, 48 hour EC50 for crustacea, and 72 or 96 hour ErC50 for algae or other aquatic plants.
- Carrageenan: Carcinogenicity
  - Listed as Moderate (M) or Category 2: Substances are suspected human carcinogens based on obtained human and/or animal studies. Evidence may be from either limited evidence of carcinogenicity in human or animal studies, yet it is not sufficiently convincing to place the substance in Category 1.
- Carrageenan: Skin, Eye, Respiratory Irritation/Sensitization
  - Listed as High (H) or Category 2A: Substances have the potential to induce reversible eye irritation, in which at least 2 of 3 tested animals had a positive response of listed metrics in the GHS Guidelines Revision 5.

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Strategy 3: Biolipids

Biolipid 1: Poly(hydroxyalkanoates) (PHAs)

Inspiration

Polyhydroxyalkanoates (PHAs) are a family of polyesters that are naturally produced by microbial fermentation of carbon-based feedstocks. There are over 150 different PHA monomers, and it is possible to blend different length monomers together to design materials with highly customized and unique properties. Medium chain length (mcl) PHAs have a backbone containing 6 to 14 carbon atoms.Polymer blends made from mcl-PHA monomers have been found to display adhesive properties.[1, 2] Because microbes can create and break down PHAs with ease, this compound is inherently biodegradable and compostable. In addition, since microbes simply require a carbon feedstock to generate PHAs, mcl-PHA adhesives can be made inexpensively from waste or low-value byproducts, such as glycerol or vegetable oils. Adhesives made this way are UV stable and have low gas and vapor permeability.[1] Mcl-PHAs are gaining traction in the biomedical research field due to their adhesive strength, biocompatibility, and lack of residual adhesive.[3, 4] For all these reasons, mcl-PHAs may offer a natural, safe, sustainable, and effective alternative to current PLU PSAs.

Technical Performance

As mentioned earlier, mcl-PHAs in particular have been found to display adhesive properties. In a study by Pereira et al. from 2019, an mcl-PHA biopolymer was produced by mesophilic bacterium from inexpensive crude glycerol. This biopolymer film exhibited strong adhesion with the intended biomedical applications.[1] Due to the film's good mechanical performance values, biocompatibility, and other desirable traits (with regards to PLU PSA applications), our biolipid report will primarily focus on this specific mcl-PHA adhesive.[1]

The biopolymer was produced by *Pseudomonas chlororaphis* subsp. *aurantiaca* (DSM 19603) bacterium with a volumetric productivity of 0.052 ± 0.002 g/L·h. The composition of monomers in the mcl-PHA adhesive is determined by the bacterial species. This particular bacterium assembled a product composed of 3-hydroxydodecanoate (43 ± 1.8 mol %), 3-hydroxydecanoate (29 ± 3.1 mol %), 3-hydroxytetradecanoate (12 ± 0.4 mol %), 3-hydroxyoctanoate (10 ± 1.5 mol %), and 3-hydroxyhexanoate (6 ± 0.3 mol %). An SEC chromatogram established that the polymer has an average molecular weight of 1.1×10^5 g/mol and a polydispersity index of 1.5, suggesting that it is well-homogenized. The film was characterized via X-ray diffraction analysis and found to be semi-crystalline, with a crystallinity value of 37% and a glass transition temperature of -44℃. Pure gas permeability measurements determined that the mcl-PHA film's permeabilities to O_2 (3.0×10^{-10} $cm^3 \cdot cm/cm^2 \cdot cm\ Hg \cdot s$) and CO_2 (8.9×10^{-9} $cm^3 \cdot cm/cm^2 \cdot cm\ Hg \cdot s$) are higher than those of polyethylene terephthalate, thus

preventing premature degradation of the adhesive. The variety of tests performed on the mcl-PHA biopolymer also revealed that it is not hygroscopic, and therefore does not exhibit swelling behavior. This is good news for a PLU candidate material, because it suggests the adhesive will perform well in wet and humid environments.

The mcl-PHA polymer is also impressive mechanically. The adhesive film elongated to 273% ± 27% of its original length before breaking, suggesting high cohesive strength. This is beneficial in PLU applications, as cohesive failure can cause the adhesive to break or leave behind residue. The film was also found to have a Young's modulus of 8.0 ± 0.17 MPa. Using about 200 mg of raw mcl-PHA polymer over a contact area of 6.25 cm^2 on porcine skin, the adhesive displayed a tension strength of 61.1 ± 20.6 kPa and a shear strength of 12.7 ± 2.1 kPa. An mcl-PHA peel test was administered on a human arm to determine the ability of the adhesive to adapt to skin textures and to gauge the degree of residue. To create the adhesive, the mcl-PHA was melted, spread as an even film onto a plastic sheet, and left to cool overnight. After solidification, the mcl-PHA adhesive film was placed onto human skin. The film displayed good adhesion to human skin, and was able to acclimate to hairs and wrinkles. Upon peeling, the adhesive lifted easily as a cohesive piece, left behind no residue, and did not cause any adverse reaction or external damage.

That being said, there is a prominent drawback to this particular mcl-PHA film when considering PLU PSA applications. According to differential scanning calorimetry tests, the film has a melting temperature near 43℃ and a degradation temperature of 285℃. While the high degradation temperature makes the adhesive easy to incorporate into hot-melt solutions, the relatively low melting point makes the raw polymer a weak choice in hot environments or storage conditions. However, as mentioned before, PHA products are highly customizable. Countless other polymers, enzymes, and more can be easily introduced during the formulation to change undesirable values and engineer an adhesive appropriate for reversible PLU PSA applications. A combination of chemistry, materials science, and genetic engineering knowledge may help develop a particular bacterial species that can form an idealized ratio of mcl-PHAs, or perhaps deduce an additive/filler that may be added to assist current PHA formulations.

Health and Environmental Performance

For the extent of this project, we mainly focus on medium chain length PHAs. However, it is important to note that depending on the type of PHA, there needs to be individual hazard and environmental assessment tests; this is because PHAs encompass such a large class and can be very customizable resulting in a variety of physical properties. Scientific literature points to various endpoint results based on short chain length PHAs, from which we can extrapolate information to generalize our PHA hazard assessments.

In terms of environmental concerns, we generally see very low to no hazard. Research shows that short chain length PHAs, such as P(3HB) tend to have low persistence in vitro and in vivo of living mammalian cells.[6] However, there are different studied environmental conditions

that may decrease or increase persistence time, in which ecological, physical, and chemical factors can have different effects on the biodegradation process.[7] More so, there seems to be no signs of bioaccumulation of PHAs in the environment. While short chain length PHAs made into bioplastics can degrade into microbeads, short-term toxic aquatic effects were not found in copepods.[8, 9] Nevertheless, we do recognize that more research on long term aquatic effects needs to be completed. Lastly, PHAs are generally considered non-toxic in terrestrial environments, yet downstream processes in mass generated PHAs need to utilize less toxic solvents in their formulation, since these solvents subsequently have hazardous environmental impacts.[10]

We also have reason to believe that PHAs pose little hazard to humans. There is literature available that suggests non-carcinogenic behavior seen via both in vitro and in vivo implantation.[6] We see PHAs utilized across the medical field in sutures, adhesion barriers, bone graft substitutes, and regeneration devices.[6] Furthermore, we see little to none acute toxicity effects, in which several studies note the non-toxic characteristics when using medium chain length PHAs as biomedical materials for things like heart valves or controlled drug delivery capsules.[3, 11] Still,, we do see a data gap in skin, eye, and respiratory sensitization and irritation. Prior to implementation, more research needs to be conducted to address this endpoint.

Remaining Questions

While mcl-PHAs as PSA alternatives seem highly promising due to their mechanical performance, biocompatibility, and relatively low cost, a question remains to the downstream health and environmental effects related to their production. More research needs to be conducted to discern what greener solvents can be used to mitigate negative downstream health and environmental effects. Research has shown that large scale extraction of PHAs using toxic solvents (i.e. chlorinated solvents, chloroform, diethyl ether, sodium hypochlorite, etc.), results in hazardous health outcomes and is highly inefficient, resulting in massive energy consumption, high greenhouse gas emissions rates, concentrated occupational exposure, toxic wastes and accidental release of these solvents into the environment.[10, 12] Additional research is needed to determine how to replace the use of these toxic solvents and eliminate this hazard bottleneck in downstream approaches to this strategy.

Biolipid 2: Epoxidized Soybean Oil

Inspiration

Plant oils are some of the most abundant renewable resources, attractive for their low cost, minimal toxicity, and biodegradability. As triglycerides composed of different ratios of saturated and unsaturated fatty acids, plant oils have useful reactive sites like double bonds and esters that allow for high tunability of their properties for various applications.[13] Plant oils have been especially popular for bio-based PSA development because their fatty acid make-up results

in low glass transition temperatures, high flexibility, and hydrophobicity. Previous studies have found that epoxidized soybean oil (ESO) has superb performance as a PSA. In the epoxidation process, soybean oil is reacted with peroxides or peroxy acids to oxidize the double bonds found in soybean oil.[14] This makes ESO capable of readily reacting with a number of chemical groups, offering many different synthesis pathways for PSA fabrication. Due to its accessibility, biodegradability, and processing flexibility, ESO is a promising potential alternative for PLU stickers.

Technical Performance

In the synthesis of ESO-based PSAs, ESO is typically cured with a curing agent. Any number of other renewable materials can be introduced as co-polymers or tackifiers for further modification of the formulation. Sometimes these additions double as curing agents themselves.[13, 14, 15, 16]

In one study, a PSA formulation made from copolymerized epoxidized soybean oil (ESO) and lactic acid oligomers (OLAs) was explored. Variable molar ratios of OLA/ESO were investigated, along with variable OLA chain lengths. The OLAs were synthesized in a melt-condensation reaction; different chain lengths were achieved by collecting the oligomers at different post-reaction times. Formulations with short chain OLA copolymers had the best overall adhesive performance. A PSA made from a 3:1 mixture of OLA collected 3 hours post-reaction and ESO had a peel strength of 3.8 N/cm and a tack of 8 N/cm with no residue left behind in the peel-off test (Table 8). These adhesive metrics easily outperform our chosen benchmark, making this alternative one of the best performing of those we surveyed. The glaring limitation with this formulation is its curing method. The copolymerization of OLA and ESO utilized a cationic UV polymerization process by coating a mixture of OLA, ESO, and a cationic photoinitiator onto a PET film and exposing the material to UV light. The UV curing process produces strong carbon-carbon bonds that will prevent the adhesive from biodegrading.[16]

Other means to cure ESO-based PSAs have been discussed in literature. One popular curing agent studied with ESO formulations is rosin acid (RA). Lei et al. utilized an oven-curable mixture of ESO, a RA-based copolyester, and the catalyst 4-dimethylaminopyridine (DMAP) for their PSA formulation. RA is a tackifier with resin curing capabilities that promotes cohesion within an adhesive through its rigid hydrogenated phenanthrene ring. To create their carboxyl-terminated copolyester, the investigators copolymerized acrylic rosin acid and acrylic acid, and then copolymerized acrylic rosin acid (ARA) with sebacic acid and 1,2 propanediol. A final mixture of the copolyester, DMAP, and ESO were mixed in a flask and stirred at 90 °C, coated onto a PET film, and cured in an oven at 160 °C for 30 minutes to 3 hours for a fully crosslinked PSA. The study found that increasing curing time decreased the tack of the PSA. The best performance was observed for adhesives cured for just 30 minutes, with the ESO-based PSA once again outperforming the benchmark metrics (Table 8). Additionally, the glass transition temperature of the adhesive is tunable through ARA concentration, as formulations with more

ARA had a higher T_g.[13] Due to the creation of fully crosslinked networks in this synthesis method, the approach taken by Lei et al. is also unlikely to biodegrade, so more work needs to be done to develop synthesis pathways for effective and compostable ESO-based pressure sensitive adhesives.

Health and Environmental Performance

For epoxidized soybean oil, we see similar trends in environmental and human health hazards as compared to PHAs. However, we do see more specific literature that details somewhat hazardous effects based on our chosen endpoints.

Although literature about bioaccumulation with epoxidized soybean oil is not widely available, ithas been noted that a 3 millimeter thick thermostat of epoxidized soybean oil can fully biodegrade in six to eight months.[17] Based on the New Zealand GHS guidelines, it is listed as a Category Chronic 2, indicating that epoxidized soybean oil is very ecotoxic in aquatic environments, particularly to algal species.[18] There is not much data pertaining to the terrestrial ecotoxicity endpoint, yet there is a lot of research on soybean biodiesel, which contains soybean oil mixed with various other components that may threaten terrestrial environments. A study showed that soybean oil biodiesel released 21.14% of hazardous substances, such as copper, sulfate, zinc, phosphate, and nitrate, that endanger the survival of terrestrial plants.[19] More so, we see a similar effect in aquatic environments, in which soybean oil biodiesel was found to release 65.63% of toxic substances, such as cadmium and chloride, into freshwater environments.[19]

In terms of human health hazards, research shows that thermally oxidized soybean oil is not carcinogenic in rats.[20] However, it is important to note that this is not the same as epoxidized soybean oil, so we make a low confidence assumption that this non-carcinogenic property exists in epoxidized soybean oil. Soy allergies are another possible concern for soy-sensitive individuals. Several scientific studies have demonstrated that soybean oil does not have allergenic effects on soy-sensitive individuals for the most part.[21] Nevertheless, this is mainly dependent on the purity of soybean oil, in which soybean oil that still contains the soy protein will cause allergic reactions.[22] In addition, a further study showed that soybean proteins can interact with oxidized soybean oil to then create products that may be an allergen to soy-sensitive individuals.[23] However, none of these studies or accessible information state the threshold levels for safe consumption of soy protein. Lastly, the New Zealand GHS guidelines further listed epoxidized soybean oil as a Category 3 skin irritant.[18]

Remaining Questions

Several questions remain for the practical implementation of ESO-based adhesives. Firstly, a synthesis pathway that will result in a biodegradable PSA needs to be determined, as current studies have not yet developed one. Additionally, data on how ESO-based PSAs perform on wet surfaces or in variable humidities has not been published to the best of our knowledge.

This data will be key for assessing their usage as PLU stickers. On the health and environmental side of things, more research needs to be done on epoxidized soybean oil's effect for certain endpoints, as some elements of our hazard assessment mainly relied on extrapolated values from soybean oil. Investigation into securing high-purity soybean oil for PSA synthesis is also important to eliminate any allergenic hazards for an ESO-based adhesive.

Biolipids Comparison

Technical Performance

Due to literature gaps, we had some difficulty comparing across the biolipid strategies and our benchmark. For the mcl-PHA adhesive, shear strength, tensile strength, and elastic modulus have been reported.[1] Of these three, 3M only reports tensile strength as a value for our comparison, which is slightly higher than that of given mcl-PHA formulation. For ESO-based adhesives, loop tack and peel adhesion values were available, allowing for direct comparison with Scotch Magic Tape. Both the OLA/ESO copolymer and ESO/RA-copolymer performed better than our benchmark, demonstrating the great adhesive properties of ESO-based PSAs. Unfortunately, no comparisons could be made between mid-chain length PHAs and ESO due to a lack of standardized literature data.

Table 8. Technical performance values for each biolipid strategy versus Scotch Magic Tape

Property	**Scotch Magic Tape**	**mcl-PHAs**	**OLA/ESO** 3:1 w/ short chain OLAs	**ESO/RA-copolyester** 87.7:12.3, 10% RA cured 0.5 hr
Loop Tack	**1.4 N/cm**	—	**8 N/cm**[S2]	—
Peel Adhesion	**1.7 - 2 N/cm**	—	**3.8 N/cm**[S2] (stainless steel)	**4.43 ± 1.25 N/cm**[S1] (printer paper)
Shear Strength	—	**12.7 ± 2.14 kPa** (porcine skin)	—	—
Tensile Strength	**89.6 kPa**	**61.1 ± 20.6 kPa** (porcine skin)	—	—
Elastic Modulus	—	**0.6 - 0.9 MPa**	—	—

Health and Environmental Performance

We can see more "no effect" labeling for endpoints under the PHA strategy, aside from the data gap with irritation and sensitization. Epoxidized soybean oil has more concerning hazard results, as it was flagged by two endpoints pertinent to the scope of a home compostable and safe adhesive. As mentioned previously, we expect to see little acute oral toxicity effects with epoxidized soybean oil with soy-sensitive individuals as long as the mixture is free from the soy protein. This must be researched more carefully to ensure that a pressure sensitive adhesive involving epoxidized soybean oil will not cause adverse allergies. The U.S. Consumer Product Safety Commission (CPSC) has done toxicological exams on epoxidized soybean oil and found low acute toxicity, with an oral LD_{50} value greater than 5000-40,000 mg/kg.[24] To reiterate, epoxidized soybean oil poses a moderate hazard for aquatic environments, with a GHS score of Category Chronic 2, which translates to a moderate hazard using the GreenScreen Criteria. We also see that epoxidized soybean oil is categorized as a Category 3 hazard under GHS for skin, eye, and respiratory irritation/sensitization, which translates to a low hazard under the GreenScreen criteria.

Table 9: Health and Environmental Performance Evaluation for each Biolipid Strategy

Performance Endpoint		PHAs	Epoxidized Soybean Oil
Persistence		*None*	*None*
Bioaccumulation		*None*	*None*
Ecotoxicity	**Aquatic**	*None*	M
	Terrestrial	*None*	*None*
Carcinogenicity		*None*	*None*
Single Exposure Toxicity		*None*	L
Skin, Eye, Respiratory Irritation/Sensitization		DG	L

Hazard Rating: None (no hazardous effect), Low (L), Moderate (M), High (H), Very High (vH), data gap (DG)

Category Interpretation:[25]

- Epoxidized Soybean Oil: Aquatic Ecotoxicity
    - Listed as Moderate (M) or Category Chronic 2: Substances are toxic to aquatic organisms with acute toxicity less than or equal to 1 mg/L with an LC50 of 10 mg/L. These substances may cause long-term adverse effects in aquatic environments based on available evidence concerning their environmental fate and behavior. These may present a long-term and/or delayed danger to structure and/or functioning of aquatic ecosystems.
- Epoxidized Soybean Oil: Single Exposure Toxicity

    - Listed as Low (L): Epoxidized soybean oil does not fall into the lowest category hazard rating for acute toxicity indicated by GHS (5) because it's LD_{50} range is much higher than the threshold of 5000 mg/kg bodyweight.
- Epoxidized Soybean Oil: Skin, Eye, Respiratory Irritation/Sensitization
    - Listed as Low (L) or Category 3: Substances have reversible adverse effects on dermal tissue and mildly skin irritation effects, based off of a mean Draize score greater than or equal to 1.5, but less than 2.3 for skin irritation effects.

Biolipids References

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Strategy 4: Structural Adhesives

Structural Adhesive: Gecko Feet

Inspiration

Another form of attachment present in nature are adhesives working through microscopic structure, which have developed through convergent evolution both in gecko feet and some insect limbs.[1] Geckos in particular can support their weight and walk, even upside down, on almost all types of surfaces. This requires strong universal and reversible adhesion, which are ideal characteristics for pressure sensitive adhesives. The materials used for these adhesives are usually not adhesive in and of themselves. What allows for the adhesion is the structure of the material, specifically the presence of microfibers. Gecko feet are covered with 3 million microfibers called setae, which are 30-130 μm long and 5 - 10 μm wide.[2] Each set is in turn covered with 100 - 1000 spatulae, a smaller layer of microfibers 2 - 5 μm long and 100 - 200 nm wide. This combination develops an adhesive force of 20 N over a surface of 2 cm^2 - an order of magnitude higher than what would be needed to attach a PLU sticker.

Technical Performance

Gecko-inspired adhesives function through interaction with surface inhomogeneities as well as through mechanical energy stored in the fibers and van der Waals interactions.[3] On a microscopic level, the microfibers are bent through applied pressure, which achieves adhesion under two main mechanisms. The first revolves around creating a higher interaction area with the surface, leading to more intermolecular interactions with the surface. The other centers around the creation of an elastic energy barrier when the microfibers are bent against the surface, resulting in an applied force needed for removal. This means that controlling the mechanical properties of the microfiber or micropillar arrays is crucial to the adhesive properties.

Scientists have discovered design rules for the interplay between fiber diameter, aspect ratio, material stiffness, covered area and surface energy that explain adhesion both for natural and synthetic microstructured adhesives.[4] Strength of adhesion generally increases with covered area and surface energy and is inversely proportional to the diameter of the fiber. Up to a point (dependent on the fiber diameter), making materials softer increases adhesion - however, the more crucial influence of stiffness is that the fibers need to be bendable. This limit on material stiffness can be increased by increasing the aspect ratio of the fibers. Two more limitations are the necessity of keeping fibers from collapsing and from sticking to each other. The first requires a tradeoff between stiffness and fiber diameter - fibers that are too small or too soft will collapse. Avoiding self-adhesion of the fibers necessitates limiting the flexibility of the fibers through control of Young's modulus, thickness and length. Together, these requirements define a small but multidimensional "Goldilocks area" in which effective adhesion is possible.

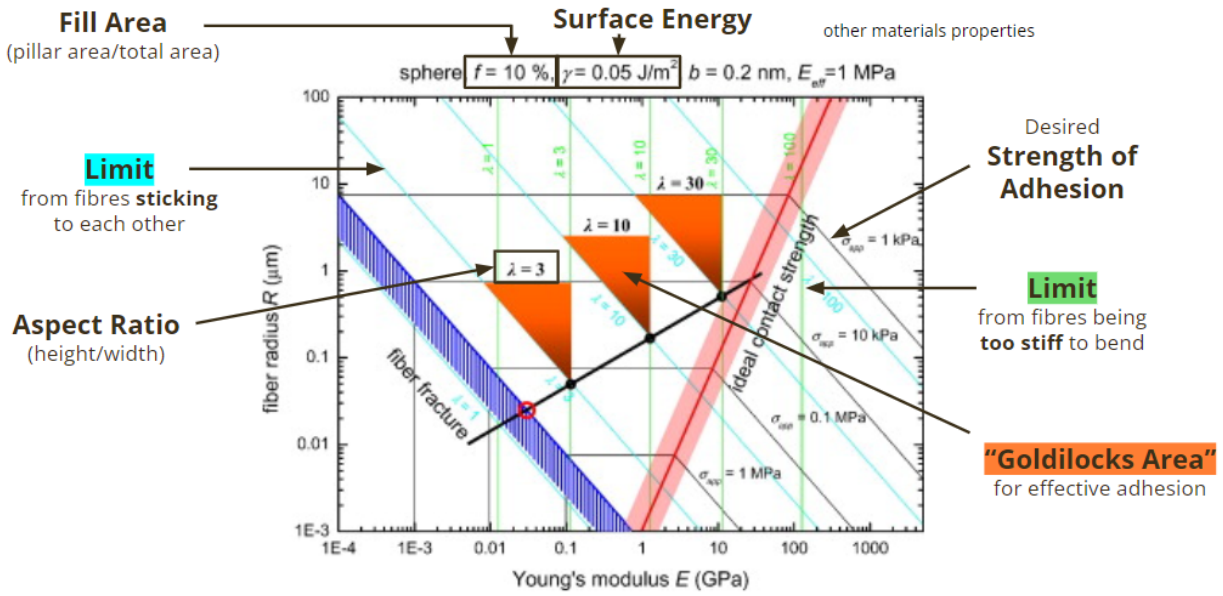

Figure 6. Design maps for adhesion of microfiber arrays[4]

While many successful synthetic microfiber/micropillar arrays have been developed with adhesive properties, the materials used to make them so far have not been biodegradable.[5, 2, 3] Mostly, this is because microstructures are often produced by in-situ polymerization with photolithography.[6] This process forms polymers with a carbon-carbon backbone which do not readily degrade. However, modern microfabrication methods may enable synthetic micropillar arrays made from biodegradable, bio-based materials that allow significant adhesion. Recently, researchers have created arrays of 10 μm diameter and 10 μm length micropillars by self-assembling soy-protein isolate in a micropatterned mold.[7] Based on the measured material stiffness of 300 MPa, decreasing the diameter of the pillars to below 1 μm and increasing the aspect ratio above 5-6 would allow effective adhesion of over 10 kPa. However, it is not clear that these changes are possible and this solution requires more basic research, a proof of concept, and technical development even before testing for effectiveness, stability, and scalability.

Micropatterning can also be used to increase the adhesion of existing adhesive formulations. As previously mentioned in our polysaccharide strategies, chitosan is a unique adhesive because of the inherent electrostatic properties introduced by the process of deacetylation from chitin. However, it does not perform well in wet and moist environments. To circumvent this limitation researchers introduced van der Waals interactions on top of the electrostatic ones by dry-casting the adhesive on a polycarbonate mold with arrays of nanosized holes ranging in diameter from 100 - 600 nm.[8] The resulting films had nanopillars with heights around 70 nm to mimic Gecko feet. An image of the micro-patterned adhesive is shown below. The force of adhesion of the gecko-inspired chitosan adhesive is double that of the non-structured thin film, measuring 5.5 nN by AFM.[8]

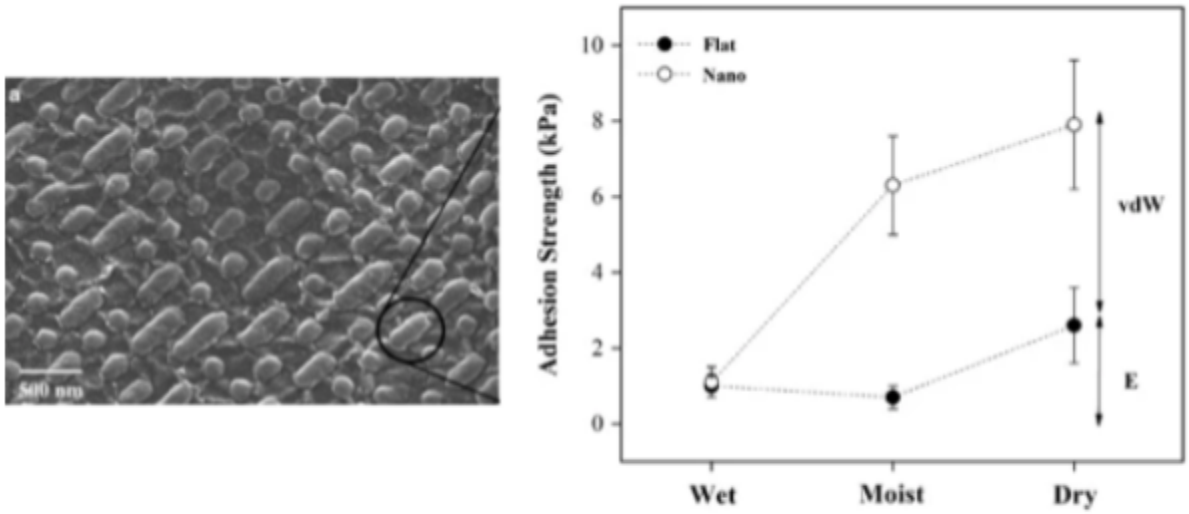

Figure 7: Micropatterning of chitosan adhesive and a comparison of the adhesion strength for flat vs. structured chitosan films.[8]

Health and Environmental Performance

While the hazard information for soy protein isolate has several data gaps, due to its organic nature, we presume no environmental hazard for bioaccumulation and ecotoxicity. However, more research needs to be done in order to fully assess all related endpoints should the soy protein isolate be considered for future adhesive development.

In terms of persistence, one study used urea-modified soy protein isolate to create a biodegradable plastic as an alternative for persisting petrochemical polymers. They found that with higher temperature levels, the urea-modified soy protein isolate-based plastic breaks down. Several samples had a first breakdown of the plastic around 103℃ with a weight loss of around 7-10%.[9] Another study found that soy protein isolate films not only have satisfactory functionality for industrial application, but also are blendable with other polymers. This polymer blend is still able to maintain its biodegradability in aquatic environments.[10] Data gaps in both the bioaccumulation and terrestrial ecotoxicity endpoints still persist.

For human health-related endpoints, we see interesting results regarding the carcinogenicity of the soy protein isolate. However, based on the study methods, this carcinogenic effect may be caused by other factors. One study found that after feeding rats 10% and 30% soy protein diets with varying amounts of trypsin inhibitor content (ranging from 3.2 mg to 35.8 mg per 1 g of soy protein isolate) and lactic casein, the rats showed growth of carcinogen-induced pancreatic foci.[11] It is important to note that this study was done in 1980 and could be outdated, with other factors contributing to the observed carcinogenic effect. This is supported by the results of another study, which discovered a 30% reduction in carcinogen-induced mammary tumor development in rats fed a 10% or 20% soy protein isolate diet compared to rats fed a casein diet.[12] In terms of acute toxicity, one study has shown that

ingesting soy protein above recommended levels can cause detrimental effects to the human body, such as developmental toxicity and hormonal disturbances.[13] A separate double-blind, placebo-controlled study determined that cumulative threshold doses for soybean allergic reactions range from 10 mg to 50 g for subjective symptoms, and 454 mg to 50 g for objective symptoms.[14] In addition, there seems to be severe oral allergic and anaphylactic reactions in individuals from proteins in soybeans.[15] Not much can be said about skin, eye, and respiratory irritation/sensitization as there does not appear to be data on these endpoints.

Overall, we largely see data gaps in our endpoints, with two confirmed as no to low hazards. For single exposure toxicity, the GHS scoring assigned soy protein isolate as a Category 5, which translates to a low grading based on the GreenScreen Criteria. More research is needed in order to fill in these data gaps to ensure environmental and human health safety. In terms of nanostructured chitosan specifically, based on our health and environmental assessment in the polysaccharide strategy, we see generally minimal hazard for chitosan adhesives. Since our nanostructured film is fabricated by molding the adhesive, we would predict that our health and environmental hazard assessments remain the same as the chitosan adhesive.

Table 10: Health and Environmental Performance Evaluation for Soy Protein Isolate (SPI)

Performance Endpoint		**Soy Protein Isolate (SPI)**
Persistence		*None*
Bioaccumulation		DG
Ecotoxicity	**Aquatic**	*None*
	Terrestrial	DG
Carcinogenicity		DG
Single Exposure Toxicity		L
Skin, Eye, Respiratory Irritation/Sensitization		DG

Hazard Rating: None (no hazardous effect), Low (L), Moderate (M), High (H), Very High (vH), data gap (DG)

Category Interpretation:[16]

- SPI: Single Exposure Toxicity
    - Listed as Low (L) or Category 5: Substances have relatively low acute toxicity hazard, but may pose as a hazard for vulnerable populations [Oral LD_{50} range of 2000-5000 mg/kg body weight]

Remaining Questions

While this solution is interesting and might transcend traditional limits on adhesives, it is also very far from application. It is far from clear whether the soy-protein isolate described here, or indeed any other commonly used biopolymer, would be suitable for forming gecko-inspired adhesives. Moreover, these adhesives evolved to adhere during short-term mechanical motion - it is possible that there are long-term relaxation processes of the polymers themselves or through humidity, sunlight or dust which would, over days and weeks, considerably reduce the adhesion force. Manufacturing these adhesives presents an additional barrier which may be cost-prohibitive. We discussed earlier the implications of the manufacturing process on the materials used - in addition, patterning at the micron and sub-micron scale is very expensive. How they fare in environments with variable humidities and temperatures is also unknown and requires further research. In addition to the health and environmental data gaps for soy protein isolate, questions arise in terms of the occupational hazards for mass handling of the soy protein isolate. It is unclear how the soy protein isolate may affect workers depending on routes of exposure. Much of the toxicity data covers acute oral toxicity; yet, because there are data gaps with respiratory irritation, it is unclear whether a powder form of soy protein isolate may cause occupational asthma (similar to gluten). In general, more concrete and recent research must be conducted in order to assess the validity of various outdated scientific research surrounding the health hazards of soy protein isolate.

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Preservatives

Technical Performance

As discussed earlier in the section on our approach, a drop-in replacement would be ineffective because formulations are tailored based on the individual adhesive. Since we pursued functional replacements, we also need to consider additives specific to the functional replacements we proposed. Preservatives are an essential additive for formulations based on biopolymers because they prevent the kind of unwanted premature degradation these materials are highly susceptible to.

There are three main classes of food-safe preservatives that can be applied to our solutions: organic acids, cationics, and phenols. Together, they offer enough coverage to provide an option for every formulation we have proposed. Organic acids are inexpensive preservatives used in the cosmetic and food industry and are effective in acidic environments. To work properly, the pK_a of the organic acid used must be at least as large as the formulation pH. This effectively limits this class of preservatives' use to systems with a pH of 5 or less.[1] Some possible food grade organic acids that could be used are benzoic acid and calcium sorbate.[2] Cationic quaternary salts are another class of preservatives that are traditionally used as disinfectants. While these cationic compounds are pH insensitive, because their antimicrobial properties originate from interactions driven by their positive charge, they will not work in anionic systems, like the ionized gluten:glycerol formulation, for example. Potential cationics include chitosan and polylysine, which are both considered food grade. A chitosan-based adhesive would also have antimicrobial properties, which would lower the potential number of additives for an optimized formulation. Phenols are antimicrobials that will work for most formulations as they are charge and pH insensitive. Food grade options include propyl gallate and thymol gallate.[1]

Health and Environmental Performance

We chose to look at a single representative preservative for each class to get a sense of their health and environmental performance. A more in-depth study of any preservative selected for addition to a formulation should be done to confirm any hazards they pose. In terms of preservative health and environmental performance, we do see some potential concerns, yet we expect these hazards to only be for high concentrations, which will be way above our expected preservative concentration for the PSA.

1. Organic acids (benzoic acid)

   The U.S. EPA conducted a literature review of several human health hazard studies, in which they found evidence of developmental toxicity, which includes developmental neurotoxicity, at levels around 30 mg/kg per day for pregnant golden

hamsters.[3] A study found that adverse reproductive effects do not occur up to 1000 mg/kg per day in Sprague Dawley rats, where the highest dose is double the existing NOAEL.[4] Based on GHS guidelines, benzoic acid is listed as a Category 1 hazard for eye irritation and a Category 2 hazard for skin irritation.[5] These categories indicate a high level of concern when exposed to high amounts of benzoic acid. The Canadian Environmental Protection Act (CEPA) lists benzoic acid as a high to very high hazard in regards to persistence with low confidence. However, searching benzoic acid with the Canadian Domestic Substances List yields no persistence hazard ratings, contributing to the low confidence in the previous statement.[6] Overall, the U.S. FDA has recognized benzoic acid as food safe with the World Health Organization claiming that an acceptable daily intake of benzoic acid is 5 mg/kg.[7] Much of the hazards that benzoic acid presents occurs at higher concentrations than what we would be using for PSA formulation.

2. Cationic (chitosan and polylysine)

   Unfortunately, very limited hazard data is available for polylysine or chitosan. Chitosan is recognized as a safer alternative by the EPA Design for Environment Green Circle program.[8] It also exhibits acute aquatic toxicity to rainbow trout at low levels (LC50 = 0.38 mg/L) according to data on the EPA CompTox dashboard. Polylysine is non-toxic in acute oral toxicity studies with rats, where mortality was observed at 5 g/kg and no mutagenicity was observed.[9] More data on these compounds would be required in order to find out whether they are safer alternatives to current-use preservatives.[1]

3. Phenols (propyl gallate)

   In terms of human health endpoints, propyl gallate does have some areas of concern, especially for skin sensitization and eye irritation. The EU GHS standards consider it a Category 1 skin sensitizer capable of causing allergic skin reactions, while GHS New Zealand lists it as irritating to the eye as a Category 2A compound. GHS Australia notes that it can be harmful if swallowed, for a Category 4 acute oral toxicity rating. Despite this rating, at the concentrations allowed by the FDA and other regulatory agencies in applications where ingestion is possible, this is not a concern. Unfortunately, propyl gallate could also pose a hazard for aquatic life. The EU Manufacturer REACH standards indicate it is very toxic to aquatic life and rank it as a Category 1.[10] However, this is an unverified submission, so additional information is needed to draw a conclusive statement. Overall, propyl gallate is generally recognized as safe for preservative usage as it is effective in preventing rancidity.[11]

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Conclusion

Overall Comparison

Technical Performance Comparison

Overall, we are hopeful that all of the proposed solutions are viable, albeit some with modifications. Frog glue, carrageenan, PHAs, and epoxidized soybean oil (ESO) have the most promising technical performance of the strategies we considered. Despite the lack of concrete numbers, the noted ability of frog glue in literature to adhere strongly to a nickel spatula while not being easily removed from the teflon tape it was attached to speaks to its adhesive and cohesive strength. We believe this could easily be controlled to make a removable PSA with some modifications. While chitosan needs modifications to perform well as a PSA, carrageenan offers a force of adhesion of 4.5 N/cm which is on par with what we would want for our PLU application. However, like chitosan, it does suffer from performing poorly in wet environments. Our third strategy category, biolipids, offers two promising alternatives, PHAs and ESO. Medium chain length PHAs have a similar tensile strength to that of Scotch Magic Tape and are easily modifiable. Further, the two reported ESO formulations have loop tack and peel adhesion values that are within the same order of magnitude as our benchmark.

Health and Environmental Performance Comparison

Overall, we hope to compare our hazard table with a current bad actor chemical used widely in pressure sensitive adhesive (PSA) formulation: acrylates. Using a variety of safety data sheets of common acrylic pressure sensitive polymers and their monomer units, scientific literature, and authoritative scientific lists/agencies, we compile hazard information for acrylates shown below. Some common acrylic monomer units used in PSA formulation that formed the basis of our hazard assessment are acrylic acid, methyl methacrylate, 2-ethylhexyl acrylate, and butyl acrylate.[1] In our table, we represent differing hazard assessments through ranges based on these four acrylates and their polymer forms.

Generally, acrylates tend to have higher rated GreenScreen hazard information and endpoint evaluations compared to our strategies. Our acrylates have generally low concern with their monomer units, yet much higher concern with their polymer units. Research suggests that acrylate monomer units tend to persist for less time in the environment and are readily biodegradable.[2,3] However, common PSAs utilize the polyacrylates because of their functionality, which still have high persistence levels. Thus, it's important to highlight that our strategies have far lower presumed persistence and bioaccumulation ratings than current polyacrylate persistence hazard ratings. We also see moderate to high levels of aquatic and terrestrial ecotoxicity in our acrylates, whereas our strategies have no found effect on marine or terrestrial toxicity unless noted. In terms of our human health concerns, we generally see significant hazards in acrylates

overall, especially for the skin, eye, and respiratory irritation/sensitization endpoints. However, much of our strategies have data gaps, making it difficult to compare them with current PSA formulations.. Further research is likely needed to get a better sense of how our strategies measure up.

Although many of these endpoints were taken from a consumer point of view of exposure, it is still important to acknowledge the occupational hazards that current PSA formulations and potential strategies may pose. Although we did not find serious occupational hazards among our strategies aside from gluten causing occupational asthma, we do know that long-term and acute exposure to acrylates pose a serious threat to occupational safety. Acrylates are known to cause occupational asthma and are well established as skin sensitizers, especially when working with large amounts of them for extended periods of time.[4] More so, occupational studies have shown neuropsychological symptoms associated with exposure to methacrylates among nail technicians.[5] Although a different industry, the chemical formulation used is the same as those used within the PSA industry, making it a cause for potential concern.

In conclusion, our strategies seem much less hazardous on our endpoints than an example of a current player in the PSA industry. However, there clearly needs to be more research and health assessments done in order to guarantee and ensure this safety. Our alternatives seem promising and we can hope to see their potential usage or as inspiration for a greener and more sustainable design for adhesives for PLU stickers.

Table 11: Overall Comparison between Common PSA Bad Actor and Our Four Strategies

		Monomer	**Polymer**	**Proteins**				**Polysaccharides**		**Biolipids**		**Structural**
Performance Endpoint		**Acrylates**		**Gluten**	**Glycerol**	**Nb-1R**	**AGP**	**Chitin/ Chitosan**	**Carrageenan**	**PHAs**	**Epoxidized Soybean Oil**	**SPI**
Persistence		*L*	*H-vH*	*None*	*None*	*None*	*None*	*None*	*None*	*None*	*None*	*None*
Bioaccumulation		*L*	*H-vH*	*None*	*None*	*None*	*None*	*None*	*None*	*None*	*None*	DG
Ecotoxicity	**Aquatic**	M-vH	*M-H*	*None*	*None*	*None*	*None*	M	*None*	*None*	M	*None*
	Terrestrial	M	M	*None*	*None*	*None*	*None*	*None*	*None*	*None*	*None*	DG
Carcinogenicity		L-M	*L-H*	*None*	*None*	DG	DG	*None*	M	*None*	*None*	DG

Single Exposure Toxicity	M-H	*M-H*	*None*	L	DG	DG	*None*	*None*	*None*	*None*	L
Skin, Eye, Respiratory Irritation/Sensitization	H	H	DG	DG	DG	DG	*None*	H	DG	L	DG

Hazard Rating: None (no hazardous effect), Low (L), Moderate (M), High (H), Very High (vH), data gap (DG)

Wrap-Up Comparison

For a final holistic comparison, we have put together a wrap-up table to estimate the overall performance of our alternatives compared to current PLU PSA compounds. In particular, we ask whether the adhesive is biodegradable, home compostable, safe, and high performing.

Table 12. Wrap-Up Comparison Table

Adhesive	Biodegradable	Home Compostable	Generally Safe	Good Technical Performance
Current PLU PSA	✘	✘	✔	✔
Gluten + Glycerol	✔	?	~	~
Frog Glue (Nb-1R)	✔	?	~	✔
AGP Nanoparticles	✔	?	~	~
Chitosan	✔	✔	✔	~
Carrageenan	✔	✔	✔	✔
PHAs	✔	✔	✔	✔
Epoxidized Soybean Oil	✔	?	~	✔
Structural Adhesives	✔	?	?	~

Legend	✔ Yes	~ Modifications Needed	✘ No	? Unsure

While all our solutions appear to be biodegradable, we cannot claim that some are home-compostable due to a lack of testing data. That being said, we do anticipate many of these alternatives being compostable due to their appearance in natural ecosystems. Our safety check is gauged by each alternative's performance on the health and environmental tables, particularly if the vast majority of endpoints are no to low hazard, and high hazards may be dismissed by an excessive LD50 value that would never be considered in PSA applications. Our technical ranking is determined by whether our solution hits the same order of magnitude or better performance

than the scotch tape benchmark for adhesive properties via numerical and verbal data in literature, and also if our solutions can do well in moist environments.

As can be seen by the quantity of green checks (and lack of red crosses), our alternatives across all four strategies have much potential. Some alternatives may simply need a few modifications to ensure that they can perform well without affecting the health and safety of the general public. For example, the protein-based adhesives including gluten, frog glue, AGPs, and structural soy protein may be modified to prevent adverse reactions in those with certain protein allergies or sensitivities. For technical performance, similar modifications may be applied to boost adhesion in certain environments. For example, the gluten and glycerol solution may be manufactured in specific humidity conditions and with particular salts such that it sticks better in wet environments. Or, the chitosan solution may be nanostructured to enhance performance on moist surfaces.

After crafting this report and table, we determined the highest potential PSA alternatives to be the bolded formulations: ionized gluten and glycerol, nanostructured chitosan, carrageenan, and medium chain length PHAs. Based on current literature, these solutions have very promising adhesive data to back them up across several fields of science and engineering, and they may require the least additional research to implement the soonest.

Final Statement

The breadth of strategies discussed in this report provide excellent context, inspiration, and potential alternatives for the future of greener pressure sensitive adhesives. With these strategies, we hope to provide a starting point for researchers to pursue safer and more sustainable solutions that will transform the adhesive industry for PLU stickers.

Conclusion References

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