## Access our presentation at the following link:

<u>https://docs.google.com/presentation</u> /d/1acjw-rxlfochUQWsByiQybu3G1RsN fdH72K9rxh\_YGY/edit?usp=sharing</u>

(The formatting changes if we convert to PPT)

## From Dirty Laundry to a Cleaner Planet:

Exploring Eco-friendly Alternatives to Polyvinyl Alcohol (PVA) in Detergent Products





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## **Overview**





Final assessment, future plans, questions



## Background

## Sheets and packs are promising single-use, low-carbon-footprint, detergent deliverers



# PVA is an industry standard material with unique properties



Background

Approac

**Strategies** 

## **PVA provides the structure of** detergent sheets



Images from ECOS manufacturing

**Polyvinyl Alcohol** 



~9:1 n/m

**Active Detergent** Ingredients

Background

## **PVA films encapsulate detergent packs**



- Heated to 150°C
- 47 MPa tensile strength
- 290% Elongation





#### Images from ECOS manufacturing

Background

#### Approac

#### Strategies



### **PVA poses health concerns**



#### **Bioaccumulation**

#### PVA in breastmilk





Ragusa et al. 2022

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# Does PVA pose environmental concerns?



## **PVA persists in the environment**

Metric tons (mtu/yr) of PVA used and degraded in US wastewater



Background		



## **Approach:** Replacing PVA

 $\mathbf{\mathbf{\mathcal{T}}}$ 



## PVA's replacement must follow ••• ECOS' priorities

Leaping Bunny Certified  $\mathcal{A}$ 

Hypoallergenic

100% Vegan

JJ

**Plant-Powered** 

**No Nasties** 

https://www.ecos.com/

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## **Criteria for selecting PVA alternative**

#### Technical Performance

- Soluble in all water temperatures
- Shelf stable for 2 years
- Compatible with existing detergent ingredients (5 < pH < 9)</li>
- Appearance
  - Consideration for marketability

#### Health and Environment

- Non-toxic to human and aquatic life
  - Biodegradable
    Must pass OECD
    301B Requirements
    - 60% converted to CO<sub>2</sub> over 28 days
- Does not bioaccumulate

#### Manufacturing Compatibility

- TSCA Chemical List
- Readily available and accessible material
- Physical properties for manufacturing processes
  - Heat stability
  - Flexibility
  - Tensile strength

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**Strategies 1) Polysaccharides** 2) Proteins Considerations

IL



## **Strategy 1: Polysaccharide-based**

#### **1** Sodium Alginate

2 Carrageenan

3 Chitosan

4 Pullulan



Background

Strategies



### **Sodium Alginate** Brown algae polymer used in food industry





**Na<sup>+</sup>**, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, ...



Ingredients: Water, Soy Protein Concentrate, Sunflower Oil, Coconut Oil, 2% Or Less Of: Methylcellulose, Salt, Yeast Extract, Vegetal Casing (Sodium Alginate, Konjac Gum, Guar Gum), Cultured Dextrose,

#### Pros

- Very soluble; dissolves fully within 90 seconds
- NaOH is only chemical used in manufacturing
- Strong (25 75 MPa), especially with glycerol

#### Cons

- Unknown shelf life
- Low max concentration; 2% w/w solutions
- Insoluble with divalent ions (very hard water)

#### Considerations

- Kimica, etc. already produce various kinds/ grades of alginates
- Can be sourced sustainably
- Drop-in sheet replacement; elongation is concern for packs

https://impossiblefoods.com/products/sausage

https://www.floridamuseum.ufl.edu/earth-systems/blog/sargassum-seaweed-or-brown-algae/

#### Background

Approad

#### **Strategies**



### Kappa- and Lambda- Carrageenan Red-algae polymers used in food industry



https://www.sciencedirect.com/science/article/pii/S2211926421004124

#### Kappa-Carrageenan Strong films (39 MPa) biodegrade in soil

- Stable up to 115°C
- Provides nutrient source for algae when degraded in ocean

Kappa-Carrageenan

- Insoluble in cold water
  - Cannot heat-seal

Lambda-Carrageenan

Improves flexibility

Lambda-Carrageenan

temperatures

Water soluble all water

• Does not form films on its own

#### Considerations

- Packs: Patented water-soluble Carrageenan film, Carraphane developed at German company, Brabender
- Sheets: potentially use a Kappa-Lambda hybrid

https://www.brabender.com/en/water-soluble-films-made-from-carraphane/

Background

Approac

Pros

Cons

#### Strategies

## Chitosan

#### Amine-containing polymer from crustaceans & fungi













Photos from Margret, et al. 2017

Background

#### Pros

- Strong (20 320 MPa)
- Manufacturing only requires acids/bases and mild conditions

Cazón1 & Vázquez, 2020

• Elongation up to 120%



- Only soluble in slightly acidic media (pH < 6.5)</li>
  - Acid controls film properties
- Soluble form is positively charged
- Not a thermoplastic; can be combined with one

#### Considerations

- Sourcing from fungi is expensive (5x) relative to crustacean waste-stream
- Cargill (US) & KitoZyme (EU) produce fungal-based chitosan for food, alcohol, and biomedical applications
- Adding glycerol leads to ↑ elongation & ↓ tensile strength

Approa

**Strategies** 

## Pullulan

#### Polymer produced from Aureobasidium pullulans







**Ingredients:** pullulan, menthol, sucralose, flavor, potassium ac 80, copper gluconate, glyceryl oleate, carrageenan, methyl sali thymol, menthyl succinate, ceratonia siliqua (carob) gum, gluco



Pros

- Readily dissolvable in hot and cold water
- Flexible
- Stable up to 250°C
- Biodegradable
- Consumable; non-toxic

#### Cons

- Low elongation at break (11%)
- Low tensile strength (1.7 MPa)

#### Considerations

- Expensive (high production charges compared to petrochemicals)
- Compatible with sheets if strengthened with a plasticizer

https://www.sciencephoto.com/media/799900/view/aureobasidium-pullulans-hyphae-and-spores-sem

https://www.listerine.com/on-the-go-oral-health/listerine-pocketpaks-cool-mint

https://doi.org/10.1111/1750-3841.12400

Background

#### Approac

Strategies

### **Cellulose** Polysaccharide from plants



#### Pros

- Renewable and abundant
- Highly customizable
- Non-toxic to humans and environment
- Biodegradable

https://en.wikipedia.org/wiki/Cellulose

Cons

- Brittle
- Low tensile strength (22.4 MPa) and elongation (13.4%)
- Gels at high temp

#### Considerations

- Vegan and can be derived from waste sources
- Widely available and affordable
- Compatible with sheets and packs

https://logosltd.ru/print/en/node/177/catalog/tovar/62

Background

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#### **Strategies**

## **Strategy 1: Polysaccharide Hazards**

	Group I Human Endpoints			Group	Group II and Group II* Endpoints			Fate	Physical Hazard
Common Name or Trade Name	Carcinogenicity	Developmental and Reproductive	Endocrine	Systemic Toxicity	Neurotoxicity	Skin, Eye, Respiratory	Aquatic Toxicity	Persistence	Reactivity, Flammability
	Mutagenicity	Toxicity	Activity			Irritation/ Sensitization	Acute/Chronic	Bioaccumulation	Other Pchem Traits
Polyvinyl Alcohol	L	L	DG	L	L	L	Н*	M*	L
Sodium Alginate	L	L	L	L	L	L	L*	vL	vL
Carrageenan	L	L	L	L	L	L	vL	L	L
Chitosan	L	L	L	L	L	L	L*	L	DG
Pullulan	L	L	L	L	L	L	L	vL	vL
Cellulose	L	L	L	L	L	M+	L	L	L
italicized: low conj	*mixed literatu	nixed literature <sup>+</sup> not a consumer ha			gradient: reason assumption of sa	able <sub>data</sub>	DG very vL	L M H vH high	
						Strategies			

## **Strategy 1: Polysaccharide Performance**

	Solubility (temp, pH)	Tensile Strength (MPa)	Flexibility Commercial Availability		Packs, Sheets, or Both
Polyvinyl Alcohol	Cold & hot, pH 5-9	47 (film)	$\checkmark$	Yes (powder, film)	Both
Sodium Alginate	Cold & hot, pH > 4	25 – 75		Yes (powder)	Both
Carrageenan	Cold & hot, pH 6-10	39.3		Yes (powder <i>, film</i> )	Both*
Chitosan	Cold & hot, pH < 6.5	20 – 320		Yes (powder, film)	Packs
Pullulan	Cold & hot, pH 3-8	1.7		Yes (powder)	Sheets
Cellulose	Cold & hot, pH 2-13	4.5 - 22.4	~	Yes (powder, film)	Both

italicized: potential company partner

\*marketing aesthetic considerations

Approach	Strategies	

## Strategies

IL

Polysaccharides
 Proteins
 Considerations

## **Strategy 2: Protein-based**



2 Soy Protein

**3** Pea Protein

Background

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Strategies

### Brewer's Spent Grain (BSG) Protein Byproduct of brewing industry



https://www.miterro.com/products/beer-waste-wat er-soluble-film-sample

#### Background

#### Pros

- Upcycling
- Can be hydrolyzed to adjust water solubility
- Stable for >300 min at 140° C and pH 6-12
- Biodegradable in soil and water
- Can form into a film with plasticizer

#### Cons

- Protein degradation during malting and extraction
- Brown color
- Low tensile strength (1.6 MPa) and elongation (60%)
- Not listed on TSCA Chemical List

#### Considerations

- Available from EverPro (powder) and MiTerro (film)
- Suitable for both sheets and packs

Approac

#### **Strategies**



https://truenutrition.com/products/soy-protein-isolate https://www.iherb.com/pr/now-foods-sports-soy-pro tein-isolate-pure-unflavored-2-lbs-907-g

### **Soy Protein** <sup>50</sup> Derived from soybeans

soyprotein soyprotein soyprotein soyprotein

Soy protein films on paper. Image from Zhao et al. (2016)

#### Pros

- Comparable water solubility to PVA at 20C
- Consumable, non-toxic for amounts in this application
- Flexible films biodegradable in wastewater treatment sludge

#### Cons

- Common allergen, may cause skin sensitization or asthma
- Needs chemical treatment for cold-water solubility
- Only stable up to 80C before onset of coagulation

#### Considerations

- Readily available commercially
- Could be used for both sheets and packs

Hypoallergenic

Background

Approa

**Strategies** 

## Pea Protein





- Consumable; non-toxic
- High thermal stability (190-200 °C)
- Moderate tensile strength and good elongation (200%)
- Biodegradable in soil and water



https://www.packworld.com/news/sustainability/article/21796972/world s-first-edible-dissolvable-packaging-made-from-pea-protein https://morro.earth/material/morro-soluble-film/

#### Not on TSCA Chemical List

#### Considerations

- Available from Xampla's Morro materials (soluble film)
- Could be used for both packs and sheets

Background

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Pros

Cons

#### **Strategies**

## **Strategy 2: Protein Hazards**

	Grou	Group I Human Endpoints			Group II and Group II* Endpoints			Fate	Physical Hazard	
Common Name or Trade Name	Carcinogenicity	Developmental and	Endocrine	Systemic Toxicity	Neurotoxicity	Skin, Eye, Respiratory	Aquatic Toxicity	Persistence	Reactivity, Flammability	
	Mutagenicity	Reproductive Toxicity	Activity			Irritation/ Sensitization	Acute/Chronic	Bioaccumulation	Other Pchem Traits	
Polyvinyl Alcohol	L	L	DG	L	L	L	H*	M*	L	
Brewer's Spent Grain Protein	L	L	L	L	L	L	L	vL	L	
Soy Protein	L	L	$M^+$	L	L	н	L	L	L	
Pea Protein	L	L	L	L	L	L	L	L	L	
italicized: low confidence *		*mixed literatu	d literature <sup>+</sup> not a consumer ha		azard gradient: reasona assumption of sa		able <sup>da</sup> Ifety	ata DG very ap low vL	L M H vH very high	
Background					Strategies					

## **Strategy 2: Protein Performance**

	Solubility (temp, pH)	Tensile Strength (MPa)	Flexibility	Commercial Availability	Packs, Sheets, or Both
Polyvinyl Alcohol	Cold & hot, pH 5-9	47 (film)	$\checkmark$	Yes (powder, film)	Both
BSG Protein	Cold & hot, pH 6-12	1.6	~	Yes (powder, film)	Both*
Soy Protein	Cold & hot, pH 3-8.5	2.3		Yes (powder)	Both
Pea Protein	Cold & hot, pH 6-12	7.0		Yes (powder <i>, film</i> )	Both

italicized: potential company partner

\*marketing aesthetic considerations

	Strategies	

## Strategies

IL

Polysaccharides
 Proteins
 Considerations



Additives can be used with polysaccharides or proteins Incorporated to improve functionality of the detergent sheets and/or packs with respect to:



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**Strategies** 

## Plasticizers increase flexibility of polymer films

#### Plasticizers to consider:





Benefits of these additives:



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**Strategies** 

## **Reducing hygroscopicity improves stability**

Sugar-free sweeteners that improve hard-candy lifetime:





**Strategies** 

## **Additive Hazards**

	Gro		roup I Human Endpo	ints	Group	II and Group II* En	dpoints	Ecotoxicity	Fate	Physical Hazard	
	Common Name or Trade Name	Carcinogenicity	, Developmental and	Endocrine	Systemic Toxicity	Neurotoxicity	Skin, Eye, Respiratory	Aquatic Toxicity	Persistence Bioaccumulation	Reactivity, Flammability	
		Mutagenicity	Toxicity	Activity			Sensitization	, leater en onie	bloaccumulation	Other Pchem Traits	
	Sorbitol	L	vL	L	vL	L	M+	L	L	vL; M	
	Glycerol	L	L	L	L	L	L	vL	L	vL; H	
S	Erythritol	L	L	L	L	L	M+	L	vL	vL	
aducer	Mannitol	vL	vL	L	vL	$M^{+}$	L	L	L	vL, M	
Re	Isomalt	L	L	L	L	L	$M^+$	DG	L	L	
	italicized: low confidence		*mixed literat	ure <sup>+</sup> n	ot a consumer l	nazard	gradient: reaso assumption of	onable safety <sub>gap</sub>	DG very low vL	L M H vH very	
				pproach		Strategies			Conclusion		

Plasticizers

Hygroscopicity



## Conclusion

7.

## **PVA Alternative Comparison**

	Solubility (temp, pH)	Tensile Strength (MPa)	gth Flexibility		ercial bility	Packs, Sheets, or Both
Polyvinyl Alcohol	Cold & hot, pH 5-9	47 (film)		Yes (powd	ler, film)	Both
Sodium Alginate	Cold & hot, pH > 4	25 – 75		Yes (po	wder)	Both
Carrageenan	Cold & hot, pH 6-10	39.3		Yes (powo	ler, film)	Both*
Chitosan	Cold & hot, pH < 6.5	20 - 320		Yes (powd	ler, film)	Packs
Pullulan	Cold & hot, pH 3-8	1.7		Yes (po	wder)	Sheets
Cellulose	Cold & hot, pH 2-13	4.5 - 22.4		Yes (powd	ler, film)	Both
BSG Protein	Cold & hot, pH 6-12	1.6		Yes (powd	ler, film)	Both*
Soy Protein	Cold & hot, pH 3-8.5	2.3		Yes (po	wder)	Both
Pea Protein	Cold & hot, pH 6-12	7.0		Yes (powo	Yes (powder, <i>film</i> )	
			italicized: potential com	pany partner	*marketi	ng aesthetic consideratior
			Strategies			Conclusion



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Strategies

# Only experimentation can answer remaining questions







**Film Variables**: concentration, polymer molecular weight, counterion, synthetic modification, additives

#### Packs:



Low Temp Heat Sealing Chi et al. 2023





**Sheet Variables**: composition of ingredients, drying time and temperature

Conclusion



Form-Fill-Seal vs. Premade Pouch Machine

vikingmasek.com/packaging-machines/

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trategies

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# Thanks!

Do you have a laundry list of questions?





Any stains of curiosity about PVA replacements?



Let's launder the details!



I'm ready for a sudsy discussion.

#### Feel free to fabricate your queries!



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