Strategies for Improving Moisture Barrier Properties of Seaweed-Based Poly Mailer Films

Sway Poly Mailer Team

Meet the Seaweed Squad!

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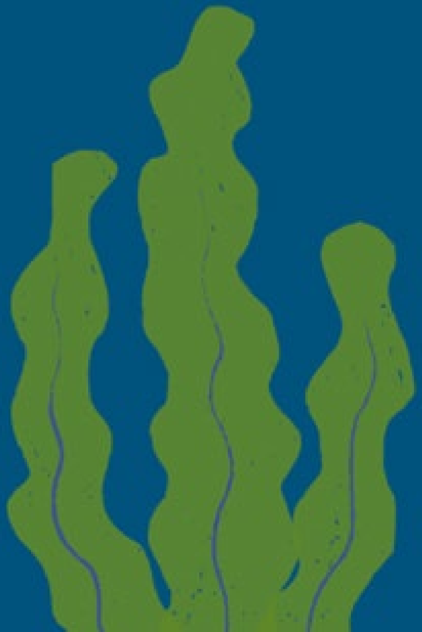
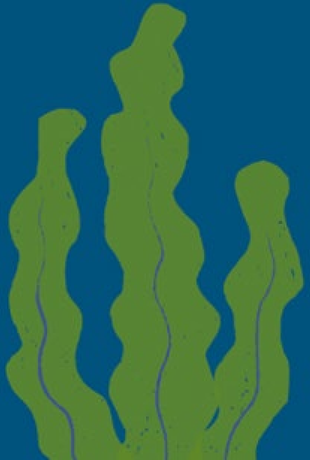
Presentation Roadmap

- Background
- Approach
- Inspiration
- Technical Performance
- Health Performance
- Conclusion
- Next Steps



Background

- **Goal:** improve the moisture barrier properties of bio-based poly mailers
- Sway: Bay Area Startup
  - Manufacturing seaweed-based thin films as an alternative to LDPE-based packaging (e.g. **poly mailers**)
- Formula and process for poly mailers:
  - Powdered seaweed, hot water, plant-based additives
  - Blended and molded
- Sway's poly mailers:
  - Sustainable
  - Compostable
  - Currently, ***highly hydrophilic***



Low-Density Polyethylene

- Traditional poly mailers are manufactured with **LDPE**

Figure 1: Structure of HDPE and LDPE

LDPE Pros:

- Durable
- Moisture resistant
- Low weight
- Flexible

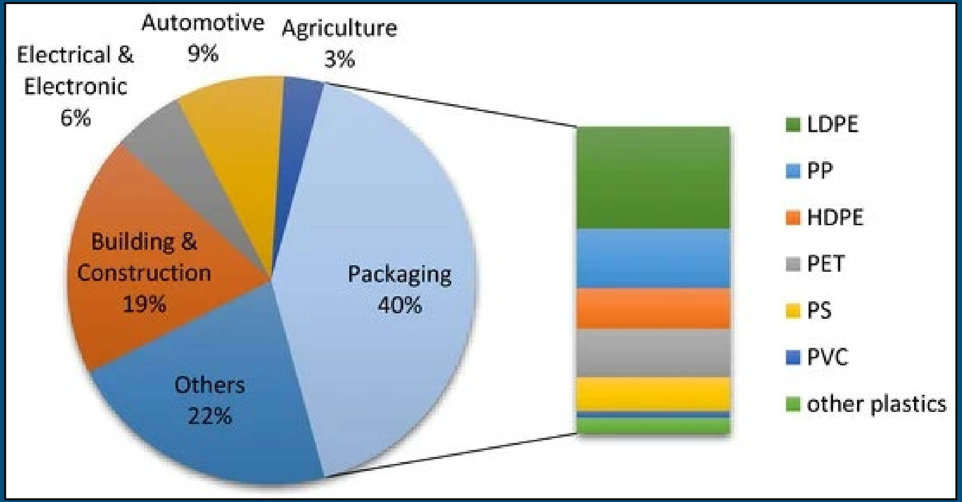
LDPE Cons:

- Persistent
- Microplastics
- Environmentally harmful manufacturing process

Difference Between HDPE and LDPE | Compare the Difference Between Similar Terms. https://www.differencebetween.com/difference-between-hdpe-and-vs-ldpe/

LDPE & Recyclability

- LDPE *is* recyclable
  - Unlikely to be recycled
- **~92%** of plastic turns up in landfills or environment
- Recycled LDPE + new LDPE → new LDPE products



Kedzierski, Frère, Le Maguer, Bruzaud; *Science of The Total Environment* **2020**, *740*, 139985.
Hopewell, Dvorak, & Kosior; *Philosophical Transactions of the Royal Society B: Biological Sciences* **2009**, *364*(1526), 2115–2126.

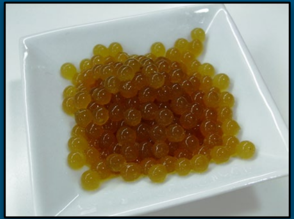
Project Requirements

1. 100% bio-based, compostable product
   - Home compost: 6 months (CO_2 conversion >90% in 12 months)
   - Industrial compost: ASTM D6400 (CO_2 conversion >90% in 6 months)
2. Non-petroleum based
3. Responsibly sourced
4. Must meet minimum mechanical requirements to function as a poly mailer, and optimize water barrier properties
   - LDPE poly mailers may be over-engineered, set alternate benchmarks

Our Approach

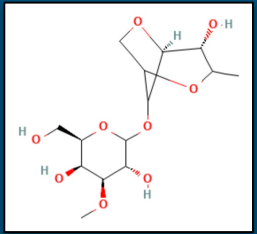
We used agar, sodium alginate, and/or κ-carrageenan as proxies for Sway's blend.

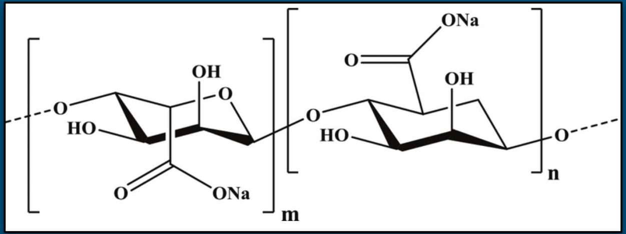
Agar
$(C_{14}H_{24}O_9)_n$

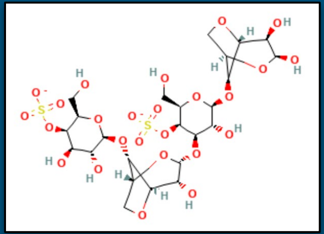


Sodium Alginate
$(C_6H_7NaO_6)_n$

K-carrageenan
$(C_{24}H_{36}O_{25}S_2)^{-2}_n$





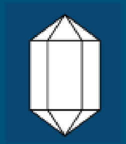


Narrowing Down Strategies

- Split up strategies into four categories and pairs of team members performed literature reviews for each group
- Selected 1-2 most promising options based on available literature

Category	Strategy	
Minerals	Silica nanoparticles additive	Montmorillonite (MMT) clay additive
Waxes/Lipids	Beeswax additive	
Polyesters	Polylactic acid (PLA) coating	
Crosslinkers	Chitosan + ferulic acid additive	

Inspiration: Minerals

	Montmorillonite (MMT) clay		**Silica nanoparticles**
	Major component of bentonite, which is a natural clay formed by volcanic ash.		Commonly found in nature as quartz, but also in plants - particularly abundant in rice husks.
	Bentonite has been used to line landfills and seal water wells.		Used in railroad track and floor coatings, paints and glazes, and as a binding agent.
	One of the most commonly used particles in biopolymer-based nanocomposites.		Silica nanoparticles used to enhance hydrophobicity of cassava starch film.

Flörke, O. W. et al; *Ullmann's Encyclopedia of Industrial Chemistry* **2000**. 1.
Currie, H. A., & Perry, C.; Annals of Botany; **2007**, 7, 1383.
Arayaphan, J., et al; *Iranian Polymer Journal* **2020**. 29, 749.
Ramesh, P. et al; *Silicon;* **2021**, 13, 109.
Park, J.-H., et al; Journal of Pharmaceutical Investigation, **2016**. 46, 363.

Inspiration: Waxes/Lipids

	Beeswax
	Bees secrete wax to form the structure of honeycomb, which is where bees store honey. It has high plasticity, and protects against moisture loss, corrosion, and abrasion.
	Human use of beeswax dates back to 1550 B.C., and is used in a variety of products today, including varnishes, polishes, and coatings for fruits and vegetables.
	Reusable and compostable beeswax food wraps are currently commercially available.
	Bees are important crop pollinators, so raising bees accounts for $15 billion in added crop value (worth 10-20x the value of beeswax and honey!)

Coppock, R. *Elsevier Enhanced Reader*; 2021.
Bogdanov, S. *Medicine, C. for V*; 2009.
FDA; 2021.

Inspiration: Polyesters

Polylactic acid (PLA)

Synthetic, synthesized by fermenting simple sugars from biomass (i.e. corn, cassava) to lactic acid.

Used for food packaging, bottles, cold drink cups, overwrap, films, trays and lids, and blister packaging.

Processed at industrial level with same technology as traditional petroleum-based thermoplastics, and economically competitive

Significant research going into copolymerization and blending approaches to improve performance.

Arrieta, M. P., et al. *Materials;* 2017. 9, 1008.

Inspiration: Cross -Linkers

	Ferulic acid		Chitosan
	Found in plants – cross-links to reinforce cell walls and block infection.		Chitin is the second most abundant natural compound after cellulose, found in exoskeletons and cell walls.
	Can be extracted from agricultural waste (maize, rice, and wheat bran).		Produced by deacetylating chitin, which can be obtained from feedstock (i.e. side products of crab/insect production)
	Applications in food preservation due to cross-linking activity.		Already used in food packaging and films

Priyadarshi, R.; *Innovative Food Science & Emerging Technologies*, **2020**, 62, 102346.
Raj, N. D., *Health Sciences Review*, **2022**. *5*, 100063.

Mechanical Requirements

	Performance Criteria	Sway's target	LDPE
Mechanical	Elastic Modulus (MPa)	500	150–340
	Strain at break (%)	>20	300-900
	Tensile strength (MPa)	>25	7-25
Water Barrier	Water Vapor Transmission Rate (g/100in^2/d)	<30	0.88
	Water Contact Angle (°)	>90°	~90
	Swelling	minimize (<100%)	-
	Solubility	minimize	insoluble

Bastarrachea, Dhawan, Sablani; Food Engineering Reviews; 2011, 3, 79
Hee, Ha, Ko, Yoon, Rhee, Kim, Lee, Khang; Journal of Biomaterial Science Polymer Edition 2007, 18 (5), 609

Technical Performance: Minerals

	Performance Criteria	Sway's target	Montmorillonite (Alboofetileh et al 2013)	% Change	Silica Nanoparticles (Hou et al 2019)	% Change
Mechanical	Elastic Modulus (MPa)	500	Sodium Alginate = 120 3% MMT addition = 210	+75%	N/A	–
	Strain at break (%)	>20	Sodium Alginate = 19 3% MMT addition = 14	-26%	Agar/Sodium Alginate = 33 2.5% silica addition = 37	+12%
	Tensile strength (MPa)	>25	Sodium Alginate = 18 3% MMT addition = 18	0%	Agar/Sodium Alginate = 45.2 2.5% silica addition = 56.8	+26%
Water Barrier	Water Vapor Transmission Rate (g/100in2/d)	<30	Sodium Alginate = 103 3% MMT addition = 62.5	-39%	Agar/Sodium Alginate = 22.31 2.5% silica addition = 18	-19.4%
	Water Contact Angle (°)	>90	Sodium Alginate = 75 3% MMT addition = 67	-11%	Agar/Sodium Alginate = 60 2.5% silica addition = 92	+53.3%
	Swelling (% increase from original weight)	<<100	Sodium Alginate = 2500 3% MMT addition = 1500	-40%	Agar/Sodium Alginate = 2000 2.5% silica addition = 1700	-15%
	Water Solubility (% reduction from original weight)	< extremely soluble	Sodium Alginate = 99.5 3% MMT addition = 67.7	-32%	Agar/Sodium Alginate = 59 2.5% silica addition = 56	-5.1%

Best

Worst

Alboofetileh, Rezaei, Hosseini, Abdollahi, *M. Journal of Food Processing and Preservation*, 2014, *38*, 1622
Hou, Xue, Xia Qin,, Zhang, Liu, Li, K.; *International Journal of Biological Macromolecules*; 2019, *125*, 1289

Technical Performance: Waxes/Lipids

	Performance Criteria	Sway's target	Agar/maltodextrin + (% wt.) Beeswax (Zhang et al. 2019)	% Change upon enhancement
Mechanical	Elastic Modulus (MPa)	500	Ref (0%) : 300 10%: 650 20%: 850	10%: +116.7% 20%: +183.3%
	Strain at break (%)	>20	Ref (0%): 12 10%: 12 20%: 20	10%: 0.0% 20%: +66.7%
	Tensile strength (MPa)	>25	Ref (0%): 12.5 10%: 22 20%: 28	10%: +76.0% 20%: +124.0%
Water Barrier	Water Vapor Permeability*** (g/m2/s/Pa)	–	Ref (0%): 9.59e-13 10%: 6.86e-13 20%: 7.87e-13	10%: -28.5% 20%: -17.9%
	Water Contact Angle (°)	>90	Ref (0%): 43.14 10%: 56.51 20%: 75.96	10%: +31.0% 20%: +76.1%
	Swelling (% increase from original weight)	<<100	Ref (0%): 80.20 10%: 67.05 20%: 65.56	10%: -16.4% 20%: -18.3%
	Water Solubility (% reduction from original weight)	< extremely soluble	Ref (0%): 57.81 10%: 54.64 20%: 48.87	10%: -5.5% 20%: -15.5%

Best

Worst

****Study did not provide measurements necessary to convert WVP to WVTR*

Zhang et al; *Food Hydrocolloids;* **2019**, *88*, 283.

Technical Performance: Polyesters

	Performance Criteria	Sway's target	PLA lamination - agar / κ-carrageenan / 5% clay (Rhim 2013)	% Change upon enhancement
Mechanical	Strain at break (%)	>20	Ref (Nanocomposite): 11.3 Double layer: 9.4 Triple layer: 17.9	Double layer: -16.8% Triple layer: +58.4%
	Tensile strength (MPa)	>25	Ref (Nanocomposite): 67.8 Double layer: 59.9 Triple layer: 50.7	Double layer: -11.7% Triple layer: -25.2%
Water Barrier	Water Vapor Transmission Rate (g/100in2/d)	<30	Ref (Nanocomposite): 152.95 Double layer: 7.22 Triple layer: 6.71	Double layer: -95.3% Triple layer: -95.6%
	Water Contact Angle (°)	>90	Ref (Nanocomposite): 54.5 PLA: 60.0	PLA: +10.1%
	Swelling (% increase from original weight)	<<100	Ref (Nanocomposite): 1615.3 Double layer: 958.2 Triple layer: 106.4	Double layer: -40.7% Triple layer: -93.4%
	Water Solubility (% reduction from original weight)	< extremely soluble	Ref (Nanocomposite): 56.3 Double layer: 29.4 Triple layer: 28.6	Double layer: -47.8% Triple layer: -49.2%

Best

Worst

Rhim; *Food Research International* **2013**, *51(2)*, 714.

Technical Performance: Cross -Linkers

	Performance Criteria	Sway's target	Chitosan and sodium alginate with ferulic acid crosslinker (Li 2019)	% change from reference (* denotes no significant difference)
Mechanical	Strain at break (%)	>20	CTS-SA ref: 27.97% CTS-FA-SA: 12.21% LBL CTS-FA-SA: 25.62%	CTS-FA-SA: -56.35% LBL CTS-FA-SA: -8.40%*
	Tensile strength (MPa)	>25	CTS-SA ref: 37.41 CTS-FA-SA: 39.78 LBL CTS-FA-SA: 51.70	CTS-FA-SA: 6.30%* LBL CTS-FA-SA: 31.20%
Water Barrier	Water Vapor Transmission Rate (g 100in^2 d^{-1})	<30	CTS-SA ref: 10.06 CTS-FA-SA 7.74 LBL CTS-FA-SA 2.94	CTS-FA-SA: -23.1% LBL CTS-FA-SA: -70.74%
	Water Contact Angle (°)	>90	CTS-SA ref: 70° CTS-FA-SA: 72° LBL CTS-FA-SA: 82°	CTS-FA-SA: 2.9%* LBL CTS-FA-SA: 17.14%
	Swelling (% increase from original weight)	<<100	CTS-SA ref: 272.08% CTS-FA-SA: 233.65% LBL CTS-FA-SA: 175.58%	CTS-FA-SA: -14.12% LBL CTS-FA-SA: -35.5%
	Water Solubility (% reduction from original weight)	< extremely soluble	CTS-SA ref: 46.13% CTS-FA-SA: 21.48% LBL CTS-FA-SA: 14.38%	CTS-FA-SA: -23.1% LBL CTS-FA-SA: -68.83%

Best

Worst

Li, Zhu, Guan, Wu; *Int. J. Bio. Macro*; **2019**, *122*, 485

Technical Performance: Summary

Performance Criteria % Change	PLA lamination agar / κ-carrageenan / clay (Rhim 2013)	Montmorillonite (3% wt. in SA) (Alboofetileh et al. 2013)	Silica Nanoparticles (2.5% wt. in agar/SA) (Hou et al. 2019)	Agar/maltodextrin + (20% wt.) Beeswax (Zhang et al. 2019)	CTS-FA crosslinked (Li 2019)
Strain at break	+58.4%	-26%	+12%	+66.7%	-8.40%
Tensile strength	-25.2%	0%	+26%	+124.0%	+31.20%
Water Vapor Transmission Rate	-95.6%	-39%	-19.4%	–	-70.74%
Water Contact Angle	+10.1%	-11%	+53.3%	+76.1%	+17.14%
Swelling	-93.4%	-40%	-15%	-18.3%	-35.5%
Water Solubility	-49.2%	-32%	-5.1%	-15.5%	-68.83%

Best

Worst

Health & Environmental Performance: Plastics

Low Density Polyethylene

- Environment
  - Not readily biodegradable/compostable
  - Persistent
  - Microplastics
    - Contamination
    - Ingestion & bioaccumulation
- Human
  - Microplastic consumption
    - Plasticizers = endocrine disruptors
    - Highly permeable
    - Disease vectors

Tang et al.; *Environ. Sci. Technol.* **2022**, *12*, 8507
Enyoh et al.; *Environ. Analysis* Health and Tox.; *2020*, **1**, 4

Health/Environmental Performance: Minerals

Silica Nanoparticles

- Environment
  - Natural source → quartz, rice husks
  - No change in CO_2 conversion rate of starch-based bioplastic film with addition of 0.2% silica nanoparticles (Ashok & Rejeesh, 2019)
  - No evidence of toxicity to soil microbes or aquatic environments
- Human
  - Acute immunotoxicity upon ingestion
  - Occupational exposure
    - Eye irritation
    - Silicosis (fibrotic lung disease) from inhaling nanoparticles
      - 25 - 35 nm
  - No evidence of contact irritation (consumers)

Montmorillonite (MMT) Clay

- Environment
  - Natural source → volcanic ash, bentonite
  - 30% decrease in CO_2 conversion rate of methyl cellulose film when cross-linked with 3% MMT (Rimdusit et al., 2008)
  - No evidence of toxicity to soil microbes or aquatic environments
- Human
  - Gastrointestinal irritation upon ingestion
  - Occupational exposure
    - Small concentration of crystalline silica
    - Working with nanoparticles
      - 2,000 - 13,000 nm
  - No evidence of contact irritation (consumers)

Martin; *J. Nutrition, Health, & Aging* **2007**, *2*, 94
Alboofetileh, Rezaei, Hosseini, Abdollahi, *M. Journal of Food Processing and Preservation* **2014**, *38*, 1622
Hou, Xue, Xia Qin,, Zhang, Liu, Li, K.; *International Journal of Biological Macromolecules*; **2019**, *125*, 1289

Health/Environmental Performance: Waxes/Lipids

Beeswax

- Environment
  - Naturally produced & sustainable
  - Ethical/safe harvesting
  - Readily biodegradable & home compostable
    - CO_2 conversion: 67% in 28 days and 79% in 84 days (Hanstveit, 1992)
- Human
  - Allergies (rare)
  - Intestinal blockages upon consumption
  - Pollutant concentration
  - Occupational hazards
    - Apiary safety

Calatayud-Vernich et al.; *Environmental Pollution*, **2018**, *241*, 106
El Agrebi et al.; *Science of the Total Environ.*, **2020**, *704*, 135312

Health/Environmental Performance: Polyesters

PLA

- Environment
  - Natural source → fermented sugars form lactic acid
  - 90% CO_2 conversion in 100 days (Pradhan et al., 2010)
  - NOT home compostable
  - Potential toxicity from accumulation of degradation products (microplastics)
- Human
  - Eye/skin/respiratory irritation possible during manufacturing
    - Inhalation (vapor)
    - Contact (vapor or liquid)
  - No evidence of contact irritation in solid form (consumers)

Ainali et al.; *Science of the Total Environ.* **2022**, *832*, 155014
Rezvani Ghomi et al.; *Polymers*, **2021**, *11*, 1854

Health/Environmental Performance: Cross-Linkers

Chitosan

- Environment
  - Natural source → cell walls, exoskeletons, shells
  - Evidence of biodegradability
  - Potential aquatic toxicity when dissolved
- Human
  - Occupational exposures
    - Possible respiratory irritation if inhaled
    - Potential for minor skin and eye irritation when working with dust

Ferulic Acid

- Environment
  - Natural source → commelinid plants
  - No change in CO2 conversion rate of PLA/PHB blend film with addition of 2% ferulic acid (Hernández-García et al., 2021)
- Human
  - Eye/respiratory irritation possible during manufacturing
    - Vapor or liquid form
  - Evidence for minor skin irritation upon contact (consumers)
  - Used in cosmetics (anti-inflammatory; topical)

Jiménez-Gómez & Cecilia; *Molecules*, **2020**, *17*, 3981
Woranuch et al.; *Carbohydrate Polymers*, **2015**, *115*, 744
Antonopoulou et al.; *Frontiers in Nutrition*, **2022**, *8*

Health/Environmental Performance: Summary

Common/trade name	CAS number	Human			Environment		
		Carcinogenicity	Toxicity	Sensitization & Irritation	Aquatic Toxicity	Persistence	Biodegradability & Compostability
Polyethylene (monomer: ethylene)	**9002-88-4**	Evidence of carcinogenic effects but not sufficient for classification	Reproductive/developmental/endocrine toxicity from **addition** of phthalate plasticizers; systemic toxicity (single exposure)	Moderate asthmagen (respiratory)	Harmful to aquatic life with long lasting effects; hazardous to the aquatic environment (acute)	Very persistent (polymer); bioaccumulation of **microplastic** particles	Non-biodegradable; non-compostable
Montmorillonite clay (MMT)	**1318-93-0**	Contains silica (carcinogenic via respiration)	No evidence of toxic effects	Potential gastrointestinal distress upon **consumption**; respiratory irritation (**nanoparticles**)	No evidence of aquatic toxicity	Unknown persistence or bioaccumulation	**30% decrease** in the rate of carbon conversion in 12 months with 3% MMT
Silica nanoparticles	**1344-09-08**	Respirable silica is a known human carcinogen	Acute immunotoxicity upon **ingestion** (proinflammatory response, oxidative stress)	Potential eye/respiratory irritation; **silicosis** (fibrotic lung disease)	No evidence of aquatic toxicity	Persistent (inorganic)	**No effect** on biodegradation with 0.2% addition of silica nanoparticles
Beeswax	**8012-89-3**	No evidence of carcinogenic effects	No evidence of toxic effects	Potential gastrointestinal distress upon **consumption**; **allergies** may cause contact-sensitization	No evidence of aquatic toxicity	No evidence of persistence or bioaccumulation	67% carbon conversion in 28 days and 79% in 84 days; home-compostable (observed in food packaging)
Polylactic acid (PLA)	**26100-51-6**	No evidence of carcinogenic effects	No evidence of toxic effects	Potential skin/eyes/respiratory irritation if **inhaled** and/or **absorbed** as a vapor or liquid	Microplastics may pose similar (albeit limited) threats to aquatic environments as LDPE microplastics	Unknown environmental persistence of microplastic particles	90% carbon conversion in 100 days; **not** home compostable
Chitosan	**9012-76-4**	No evidence of carcinogenic effects	Potential acute mammalian toxicity (FIFRA registered **pesticide**)	May cause respiratory irritation if **inhaled**; potential (minor) skin and eye irritation	Harmful to aquatic life with long lasting effects; hazardous to the aquatic environment (acute/chronic)	**High hazard:** acute/chronic bioaccumulation and persistence	Likely biodegradable (laboratory studies only; unknown carbon conversion rate in nature)
Ferulic acid	**1135-24-6**	No evidence of carcinogenic effects	Potential endocrine disruptor; specific target organ toxicity (single exposure)	Minor skin/eyes/respiratory irritation	No evidence of aquatic toxicity	Considered a persistent environmental pollutant in the event of **incomplete** degradation	92% carbon conversion in 35 days; ferulic acid/PHB/PLA film

Best ▮▮▮▮▮ Worst

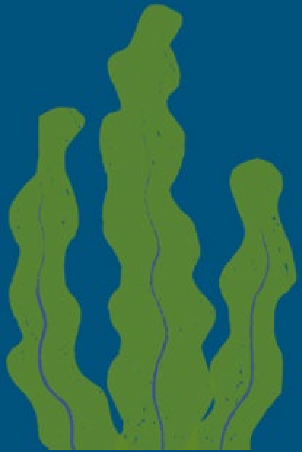
Conclusion

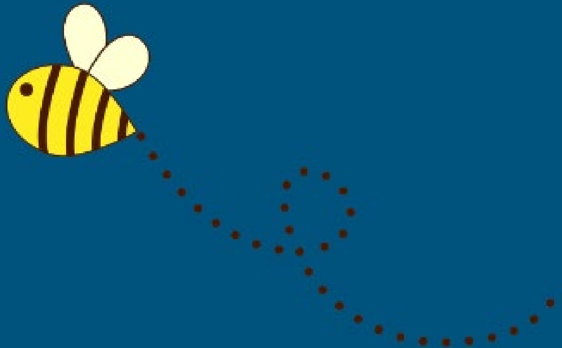
- Based on overall technical performance, biodegradability metrics, sourcing, and ecological co-benefits, **beeswax is our most promising strategy.**
- This is a novel approach to improving moisture barrier properties, and we are excited about its potential.

Recommendations & Next Steps

- Further research into combining strategies and testing different percentages of each component
- Testing different mixing strategies for additives
- Look into into occupational/engineering safety measures for working with nanoparticles and dust
- Further research into biodegradation by-products (particularly from minerals) and home compostability measures

Thank you!





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