Biopolymer Films for Product Packaging

Final Presentation
Fall 2020

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Meet The Team

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Overview

1. **Introduction**
   Background, approach, and inspirations
2. **Strategy 1: Biopolymer Films**
   Polymers from natural sources as a moisture barrier
3. **Strategy 2: Chemical Additives**
   Crosslinkers to improve biopolymer properties
4. **Strategy 3: Physical Additives**
   Nanoclays and nanofibers to reinforce biopolymers
5. **Recommendations**
   Final assessment, limitations, and future trends
6. **Questions and Discussion**

Method Products

Laundry Powders

Detergents

Soaps

Increasing dilution and moisture barrier requirements

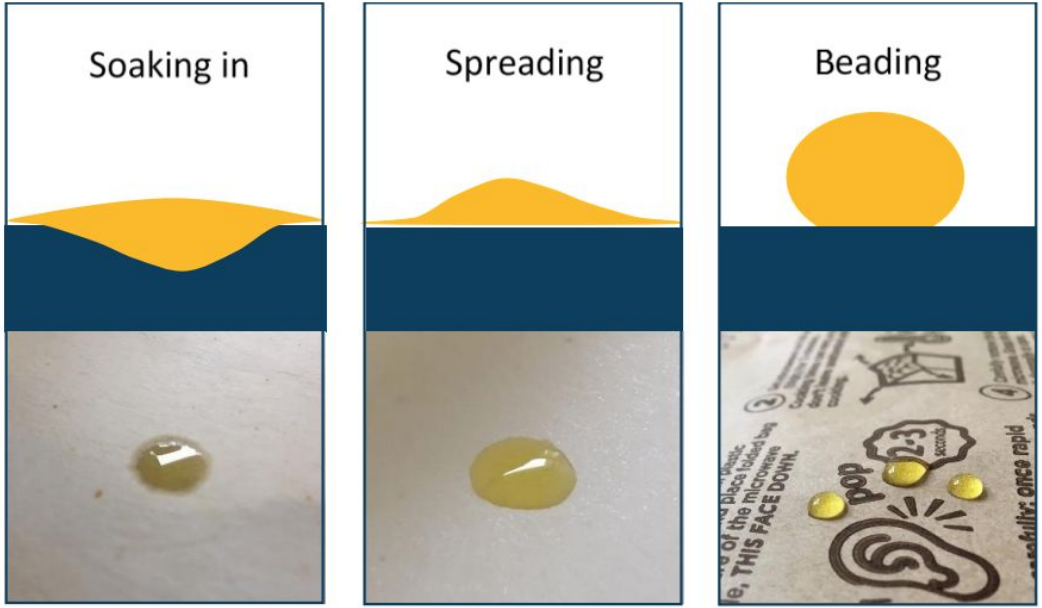
Paper-based Packaging

Properties
✓ Structural integrity
✓ Low cost
✓ Recyclability, biodegradability
✗ Poor moisture barrier

Barrier properties compensated by polyolefins

The Bad Actors: PFAS and Polyolefins

PFAS as a oil barrier:



Soaking in indicates lack of moisture or grease barrier.

Spreading indicates the presence of a barrier, but possibly not fluorinated.

Beading indicates the presence of a very oleophobic barrier, such as PFAS.

Image from
https://www.researchgate.net/publication/339230341_Forever_chemicals_in_the_food_aisle_PFAS_content_of_UK_supermarket_and_takeaway_food_packaging

The Bad Actors: PFAS and Polyolefins

Polypropylene Printer Paper:



Low cost, accessible, good moisture barrier, good sealant, printability

Not biodegradable or recyclable when applied on paper, persistent in the environment

Product Considerations

Laundry Powders 	Detergents + Concentrates 	Soaps + Dilute Liquids 
Laundry powders can **cake** and **draw in moisture**. This can make films **brittle**. Films should **prevent moisture coming into the package.**	Concentrated liquids can **dissolve** films, but barrier issues can be solved by the **product composition**. Films should **keep liquid contained** and **not dissolve** in solution.	Dilute liquids can **dissolve** moisture barrier films and need a **very strong moisture barrier.** Films should **keep liquid contained** and **not dissolve** in solution.

Increasing dilution and moisture barrier requirements →

Criteria

Improved Moisture Barrier

Low water vapor permeability (WVP), high water contact angle

Low Environmental Hazard

Renewably sourced, biodegradable, low aquatic toxicity, low persistence

Reduced Health Impacts

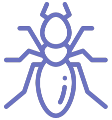
Non-irritating, non-carcinogenic or mutagenic, low repro/dev. toxicity, no endocrine disruption

Inspiration for Biopolymer Cross-linking Strategy

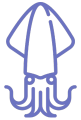
Inspired by interwoven waterproof ant rants and their innovative use of *chitin*

Image from https://www.pnas.org/content/pnas/108/19/7669.full.pdf

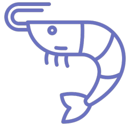
Sources of Chitin



Insects
cuticle, ovipositors, beetle cocoon



Squids
ommastrephes pen, logilo stomach wall



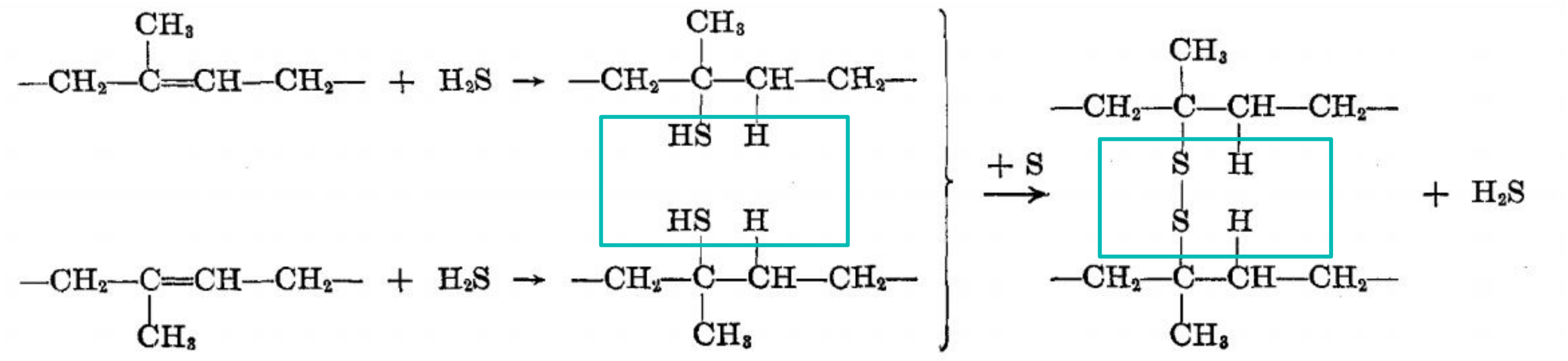
Crustaceans
crab shell, shrimp shell

Fungi
muco rouxi, aspergillis nidulans

Chitosan is the second most abundant biopolymer in the world!

Note: This is not analogous to biopolymer crosslinking, it is only a metaphor

Vulcanized Rubber Crosslinking



Vulcanization uses sulfur to crosslink rubber, achieving increased tensile strength and elasticity among other properties.

Proposed Strategies

1: Biopolymer Films

- Polymers derived from natural sources
    - Chitosan
    - Pectin
    - Gelatin

2: Chemical Additives: “Cross-linkers”

- Crosslinking film to improve barrier & mechanical properties with:
    - Genipin
    - Ferulic Acid

3: Physical Additives: “Nanofillers”

- Reinforcing film’s barrier & mechanical properties with:
    - Nanoclays
        - Montmorillonite (MMT)
    - Fibers
        - Cellulose Nanocrystals

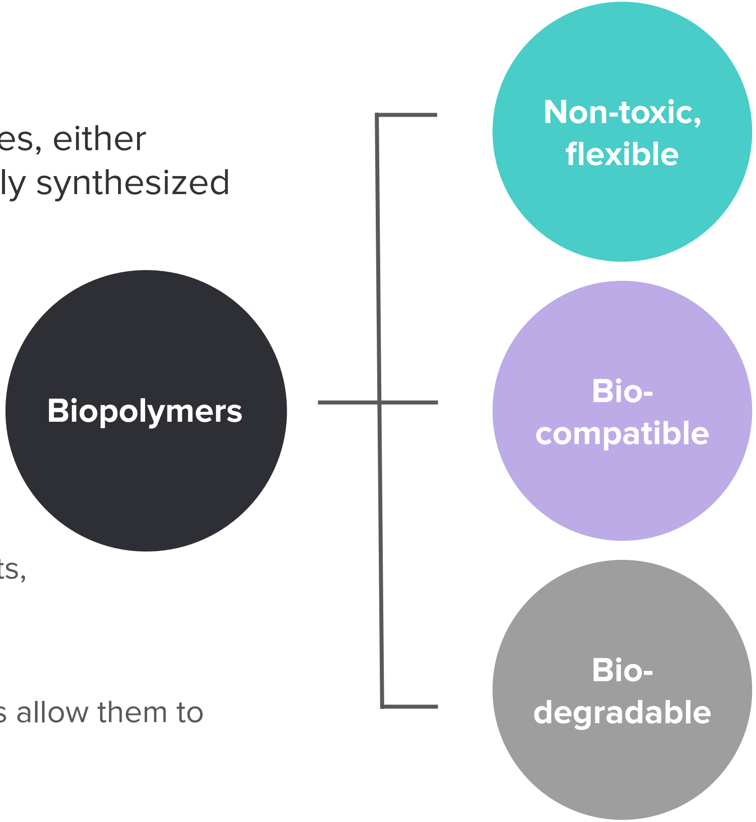
Biopolymers

Biopolymers are polymers obtained from natural sources, either entirely biosynthesized by living organisms or chemically synthesized from biological material.

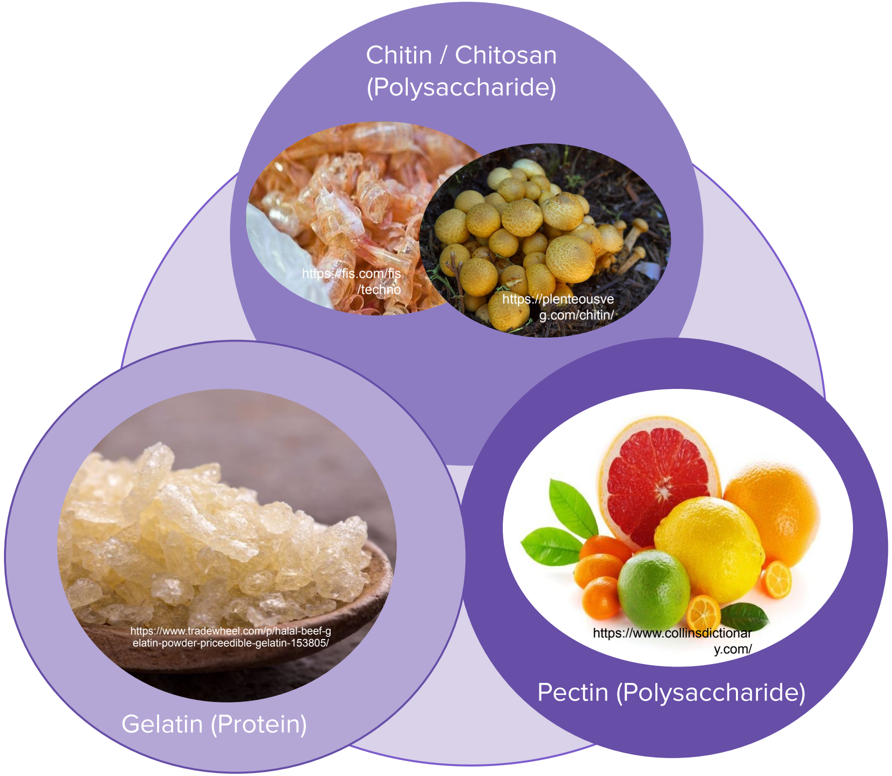
Endless Combinations
Because of the large variety and ability to mix biopolymers, there are many physical behaviors to design for certain functionalities.

Safe for Consumption
Chitosan, alginate, and pectin are natural polysaccharides that have been used for years as food-grade gelling agents, thickening agents, and stabilizers.

Crosslinking Opportunities
Biopolymers being able to crosslink with other composites allow them to be used as a matrix for a film or coating.



Selected biopolymers for film formulation



Performance Criteria for Bad Actors & Biopolymers

		PFAS*	Polyethylene	Polypropylene
Barrier Properties	Water Vapor Permeability (WVP) (g/m*day*atm)	0.00788	LDPE: 0.008 HDPE: 0.002	0.0575
	Water Contact Angle	106.94°	LDPE: 91° HDPE: 93°	97°
Mechanical Properties	Tensile Strength (MPa)	10.0 - 45.0	LDPE: 13.2 HDPE: 13.9	18 - 22
	Total Elongation at Break	40.0 - 650%	LDPE: 456% HDPE: 334%	50 - 145%

*Teflon (Polytetrafluoroethylene-PTFE) was used as a baseline for PFAS performance criteria comparisons.

High Efficiency | Medium Efficiency | Low Efficiency | Data Gap

Performance Criteria for Bad Actors & Biopolymers

		PFAS*	Polyethylene	Polypropylene	Chitin/Chitosan
Barrier Properties	Water Vapor Permeability (WVP) (g/m*day*atm)	0.00788	LDPE: 0.008 HDPE: 0.002	0.0575	.315
	Water Contact Angle	106.94°	LDPE: 91° HDPE: 93°	97°	82-104°
Mechanical Properties	Tensile Strength (MPa)	10.0 - 45.0	LDPE: 13.2 HDPE: 13.9	18 - 22	Neat: 37.7 In 2% Solution: 6.99
	Total Elongation at Break	40.0 - 650%	LDPE: 456% HDPE: 334%	50 - 145%	Neat: 49.5% In 2% solution: 72.70%

*Teflon (Polytetrafluoroethylene-PTFE) was used as a baseline for PFAS performance criteria comparisons.

High Efficiency | Medium Efficiency | Low Efficiency | Data Gap

Performance Criteria for Bad Actors & Biopolymers

		PFAS*	Polyethylene	Polypropylene	Chitin/Chitosan	Pectin
Barrier Properties	Water Vapor Permeability (WVP) (g/m*day*atm)	0.00788	LDPE: 0.008 HDPE: 0.002	0.0575	.315	0.135
	Water Contact Angle	106.94°	LDPE: 91° HDPE: 93°	97°	82-104°	62.1°
Mechanical Properties	Tensile Strength (MPa)	10.0 - 45.0	LDPE: 13.2 HDPE: 13.9	18 - 22	Neat: 37.7 In 2% Solution: 6.99	7.10
	Total Elongation at Break	40.0 - 650%	LDPE: 456% HDPE: 334%	50 - 145%	Neat: 49.5% In 2% solution: 72.70%	7.17%

*Teflon (Polytetrafluoroethylene-PTFE) was used as a baseline for PFAS performance criteria comparisons.

High Efficiency | Medium Efficiency | Low Efficiency | Data Gap

Performance Criteria for Bad Actors & Biopolymers

		PFAS*	Polyethylene	Polypropylene	Chitin/Chitosan	Pectin	Gelatin
Barrier Properties	Water Vapor Permeability (WVP) (g/m*day*atm)	0.00788	LDPE: 0.008 HDPE: 0.002	0.0575	.315	0.135	Non- ideal mechanical properties and water vapor barrier
	Water Contact Angle	106.94°	LDPE: 91° HDPE: 93°	97°	82-104°	62.1°	
Mechanical Properties	Tensile Strength (MPa)	10.0 - 45.0	LDPE: 13.2 HDPE: 13.9	18 - 22	Neat: 37.7 In 2% Solution: 6.99	7.10	70
	Total Elongation at Break	40.0 - 650%	LDPE: 456% HDPE: 334%	50 - 145%	Neat: 49.5% In 2% solution: 72.70%	7.17%	1.5%

*Teflon (Polytetrafluoroethylene-PTFE) was used as a baseline for PFAS performance criteria comparisons.

High Efficiency | Medium Efficiency | Low Efficiency | Data Gap

Hazard Assessment for Bad Actors & Biopolymers

Bad Actors & Biopolymers	PFAS	Polyethylene	Polypropylene
Persistence	H	H	H
Bioaccumulation	H	L	L
Sensitivity / Irritation *(Eye, Skin, Respiratory)*	M	M	M
Toxicity (Dev & Repro, Systemic, Neuro.)	H	D	D
Aquatic Toxicity	H	L	L
Carcinogenicity / Mutagenicity	H	L	L
Endocrine	H	D	D

Low Hazard | Medium Hazard | High Hazard | Data Gap

Hazard Assessment for Bad Actors & Biopolymers

Bad Actors & Biopolymers	PFAS	Polyethylene	Polypropylene	Chitin/Chitosan
Persistence	H	H	H	L
Bioaccumulation	H	L	L	L
Sensitivity / Irritation *(Eye, Skin, Respiratory)*	M	M	M	L
Toxicity (Dev & Repro, Systemic, Neuro.)	H	D	D	L
Aquatic Toxicity	H	L	L	M
Carcinogenicity / Mutagenicity	H	L	L	L
Endocrine	H	D	D	D

Low Hazard | Medium Hazard | High Hazard | Data Gap

Hazard Assessment for Bad Actors & Biopolymers

Bad Actors & Biopolymers	PFAS	Polyethylene	Polypropylene	Chitin/Chitosan	Pectin
Persistence	H	H	H	L	L
Bioaccumulation	H	L	L	L	L
Sensitivity / Irritation *(Eye, Skin, Respiratory)*	M	M	M	L	M
Toxicity (Dev & Repro, Systemic, Neuro.)	H	D	D	L	L
Aquatic Toxicity	H	L	L	M	D
Carcinogenicity / Mutagenicity	H	L	L	L	L
Endocrine	H	D	D	D	D

Low Hazard | Medium Hazard | High Hazard | Data Gap

Hazard Assessment for Bad Actors & Biopolymers

Bad Actors & Biopolymers	PFAS	Polyethylene	Polypropylene	Chitin/Chitosan	Pectin	Gelatin
Persistence	H	H	H	L	L	L
Bioaccumulation	H	L	L	L	L	L
Sensitivity / Irritation *(Eye, Skin, Respiratory)*	M	M	M	L	M	M
Toxicity (Dev & Repro, Systemic, Neuro.)	H	D	D	L	L	D
Aquatic Toxicity	H	L	L	M	D	L
Carcinogenicity / Mutagenicity	H	L	L	L	L	L
Endocrine	H	D	D	D	D	D

Low Hazard | Medium Hazard | High Hazard | Data Gap

Summary: films composed of biopolymers

Laundry Powders

Detergents

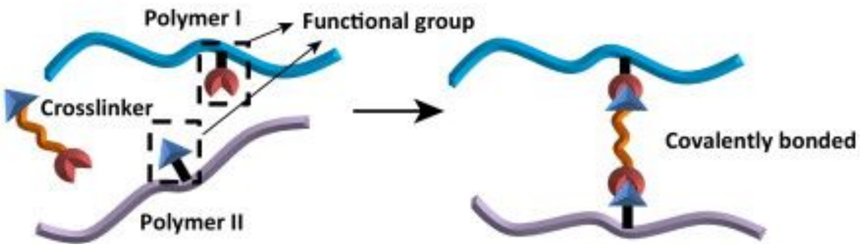
Soaps

Increasing dilution and moisture barrier requirements

Cross-linking

- **Cross-linking** is a "stabilization process in polymer chemistry which leads to multidimensional extension of polymeric chain resulting in network structure."

- Not only does technical performance depend on the **biopolymer combination**, it also depends on the **crosslinker** and the nature of its **crosslinking mechanism**.



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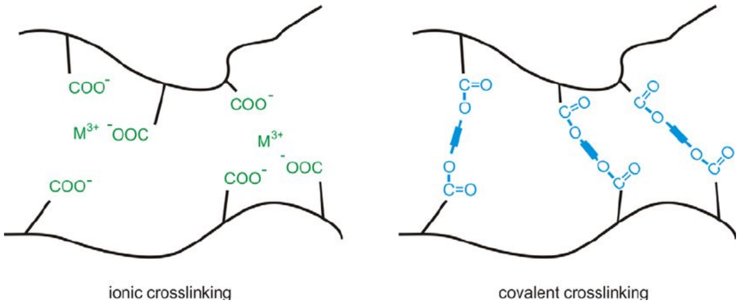


Image from https://www.researchgate.net/publication/263355077_Investigation_of_Cross-Linked_and_Additive_Containing_Polymer_Materials_for_Membranes_with_Improved_Performance_in_Pervaporation_and_Gas_Separation

Performance Criteria for Cross-linking Reagents

		Glutaraldehyde		
Biopolymer		Pectin	Gelatin	Chitosan
Barrier Properties	Water Vapor Permeability (g*mm/kPa *m2* hr)		Decrease from 1.8 to 0.8	Little effect on WVTR
	Water contact Angle			Increase from 110 to 118
Mechanical Properties	Tensile Strength (MPa)	Increase from 11.1 to 21.6 with Gelatin	Inc. from 1.2 to 3.2	Inc. appx. from 75 to 140
	Total Elongation at Break	Increase from 151 to 159 with Gelatin	Increase appx . from 8 to 29%	

High Efficiency

Medium Efficiency

Low Efficiency

Data Gap

Performance Criteria for Cross-linking Reagents

		Glutaraldehyde			Genipin		
Biopolymer		**Pectin**	**Gelatin**	**Chitosan**	**Pectin**	**Gelatin**	**Chitosan**
Barrier Properties	**Water Vapor Permeability** **(g*mm/kPa *m2* hr)**		Decrease from 1.8 to 0.8	Little effect on WVTR	Lower water sensitivity in gelatin-pectin films		No effect on WVTR
	Water contact Angle			Increase from 110 to 118			Increase from 110 to 115
Mechanical Properties	**Tensile Strength (MPa)**	Increase from 11.1 to 21.6 with Gelatin	Inc. from 1.2 to 3.2	Inc. appx. from 75 to 140		Increase from 1.0 to 6.8	Increase from 39 to 50 in dry film
	Total Elongation at Break	Increase from 151 to 159 with Gelatin	Increase appx . from 8 to 29%			Decrease from 211 to 13%	No effect in dry film (9 to 10%)

- High Efficiency
- Medium Efficiency
- Low Efficiency
- Data Gap

Performance Criteria for Cross-linking Reagents

		Glutaraldehyde			Genipin			Ferulic Acid		
Biopolymer		**Pectin**	**Gelatin**	**Chitosan**	**Pectin**	**Gelatin**	**Chitosan**	**Pectin**	**Gelatin**	**Chitosan**
Barrier Properties	**Water Vapor Permeability** **(g*mm/kPa *m2* hr)**		Decrease from 1.8 to 0.8	Little effect on WVTR	Lower water sensitivity in gelatin-pectin films		No effect on WVTR		No effect (0.00208 to 0.00201)	Increase from 2.05 to 2.67 in
	Water contact Angle			Increase from 110 to 118			Increase from 110 to 115			
Mechanical Properties	**Tensile Strength (MPa)**	Increase from 11.1 to 21.6 with Gelatin	Inc. from 1.2 to 3.2	Inc. appx. from 75 to 140		Increase from 1.0 to 6.8	Increase from 39 to 50 in dry film		Increase from 86 to 96	No effect (19 to 20)
	Total Elongation at Break	Increase from 151 to 159 with Gelatin	Increase appx . from 8 to 29%			Decrease from 211 to 13%	No effect in dry film (9 to 10%)		Dec. from appx. 4.5 to 3%	Decrease from 10.4% to appx. 8.3- 9.3%

Hazard Assessment for Cross-linking Reagents

Chemical Additives	**Glutaraldehyde**
Persistence	M
Bioaccumulation	L
Sensitivity / Irritation *(Eye, Skin, Respiratory)*	M
Toxicity (Dev & Repro, Systemic, Neuro.)	H
Aquatic Toxicity	H
Carcinogenicity / Mutagenicity	D
Endocrine	H

Low Hazard

Medium Hazard

High Hazard

Data Gap

Hazard Assessment for Cross-linking Reagents

Chemical Additives	Glutaraldehyde	Genipin
Persistence	M	L
Bioaccumulation	L	D
Sensitivity / Irritation *(Eye, Skin, Respiratory)*	M	D
Toxicity (Dev & Repro, Systemic, Neuro.)	H	L
Aquatic Toxicity	H	D
Carcinogenicity / Mutagenicity	D	D
Endocrine	H	D

Low Hazard

Medium Hazard

High Hazard

Data Gap

Hazard Assessment for Cross-linking Reagents

Chemical Additives	Glutaraldehyde	Genipin	Ferulic Acid
Persistence	M	L	L
Bioaccumulation	L	D	D
Sensitivity / Irritation *(Eye, Skin, Respiratory)*	M	D	M
Toxicity (Dev & Repro, Systemic, Neuro.)	H	L	L
Aquatic Toxicity	H	D	L
Carcinogenicity / Mutagenicity	D	D	L
Endocrine	H	D	L

Low Hazard

Medium Hazard

High Hazard

Data Gap

Summary: chemical additives for crosslinking

Laundry Powders

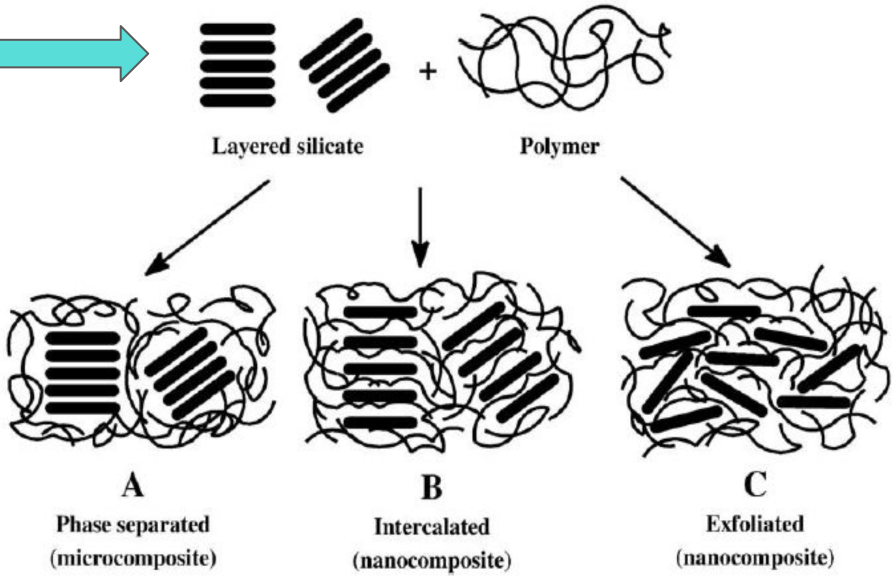
Detergents

Soaps

2

Increasing dilution and moisture barrier requirements

Nanofillers: Clays



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Nanofillers: Fibers

Cellulose nanocrystals and **cellulose nanocrystals-based composites** with their unique features, such as abundance, renewability, high strength and stiffness, eco-friendliness, and relatively low density received unprecedented interest from both academia and industries as replacement of conventional petroleum-based materials, which create ecological threats such as global warming and pollution [65]

Natural Fibers

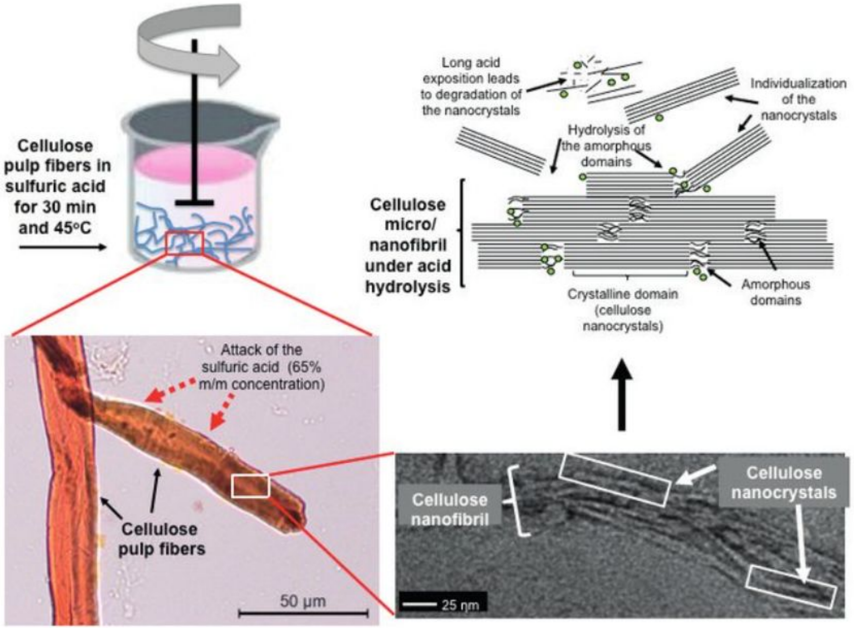


Figure 1: Scheme of the acid hydrolysis of the cellulose pulp fibers, with the individualization of the cellulose nanocrystals

Performance Criteria for Nanofillers

		Montmorillonite (MMT)		
Biopolymer		**Pectin**	**Gelatin**	**Chitosan**
Barrier Properties	**Water Vapor Permeability** (g*mm/kPa *m2* hr)	Decrease from 2.52 to 1.51	Decrease from 6.2×10^{-13} to 1.8×10^{-13}	Decrease from 2.6×10^{-7} to 1.6×10^{-7}
	Water contact Angle			
Mechanical Properties	**Tensile Strength (MPa)**	Increase from 2.4 to 4.3	Increase from 10 to 38	Increase from 61 to 69 in 5% MMT/Chitosan film
	Total Elongation at Break	Decrease from 6.6 to 5.4%	Decrease from 38 to 30%	Decrease from 3.8 to 3.0 % in 5% MMT/Chitosan film

High Efficiency

Medium Efficiency

Low Efficiency

Data Gap

Performance Criteria for Nanofillers

		Montmorillonite (MMT)			Cellulose Nanocrystals (CNC)		
Biopolymer		Pectin	Gelatin	Chitosan	Pectin	Gelatin	Chitosan
Barrier Properties	Water Vapor Permeability (g*mm/kPa *m2* hr)	Decrease from 2.52 to 1.51	Decrease from 6.2×10^{-13} to 1.8×10^{-13}	Decrease from 2.6×10^{-7} to 1.6×10^{-7}	Decrease from 4.6×10^{-7} to 3.3×10^{-7} with 5 wt% addition of the CNC	Dec. from 2.2×10^{-7} to $1.6 \times \times 10^{-7}$ with 4 wt% addition of CNC	Decrease by 45% with 3% addition of CNC
	Water contact Angle						Between 5° to 30° at a rate 22 of 2°/min
Mechanical Properties	Tensile Strength (MPa)	Increase from 2.4 to 4.3	Increase from 10 to 38	Increase from 61 to 69 in 5% MMT/Chitosan film	Increase from 7.1 to 13.2 with 5 wt% addition of CNC	Increase from 83 to 108 with 4 wt% addition of CNC	Increase from 79 (neat chitosan) to 86- 98 with the addition of 1- 10%
	Total Elongation at Break	Decrease from 6.6 to 5.4%	Decrease from 38 to 30%	Decrease from 3.8 to 3.0 % in 5% MMT/Chitosan film	Increase from 20 to 30% with 5 wt% addition of CNC	Dec. from 38 to 23% with 4 wt% addition of CNC	

Hazard Assessment for Nanofillers

Physical Additives	Montmorillonite
Persistence	H
Bioaccumulation	H
Sensitivity / Irritation *(Eye, Skin, Respiratory)*	M
Toxicity (Dev & Repro, Systemic, Neuro.)	D
Aquatic Toxicity	L
Carcinogenicity / Mutagenicity	L
Endocrine	D

Low Hazard

Medium Hazard

High Hazard

Data Gap

Hazard Assessment for Nanofillers

Physical Additives	Montmorillonite	Cellulose Nanocrystal
Persistence	H	L
Bioaccumulation	H	D
Sensitivity / Irritation *(Eye, Skin, Respiratory)*	M	H
Toxicity (Dev & Repro, Systemic, Neuro.)	D	L
Aquatic Toxicity	L	L
Carcinogenicity / Mutagenicity	L	L
Endocrine	D	D

Low Hazard

Medium Hazard

High Hazard

Data Gap

Summary: physical additives for nanofillers

Laundry Powders

Detergents

Soaps

3

Increasing dilution and moisture barrier requirements

Final Assessment

Laundry Powders

Detergents

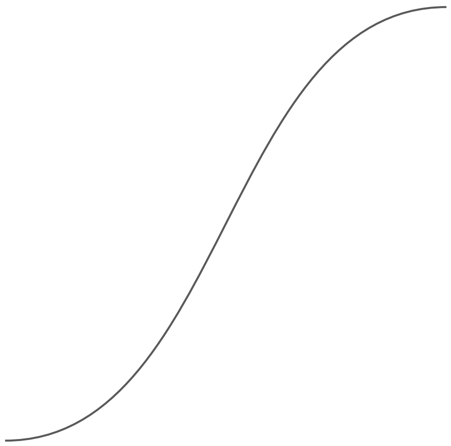
Soaps

1 2 3

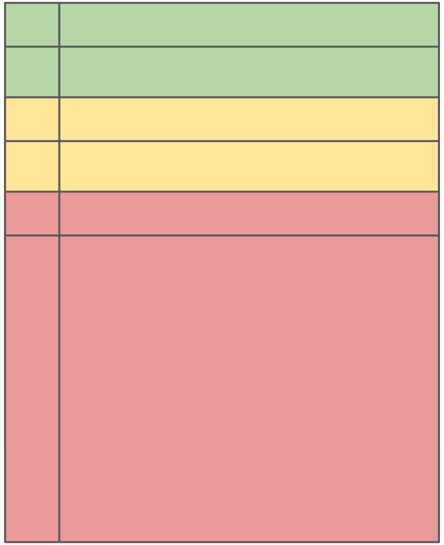
Increasing dilution and moisture barrier requirements

Limitations

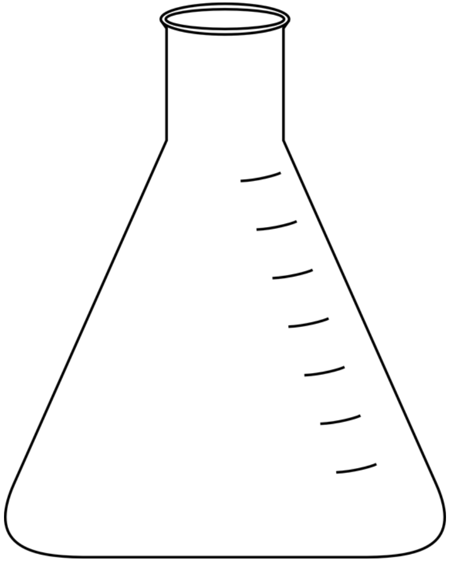
Cost & Scalability



Data Gaps



Iteration & Experimentation



Questions?

And Discussions

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