Development of Industrial Applications of Biodegradable Polymer Nanocomposites

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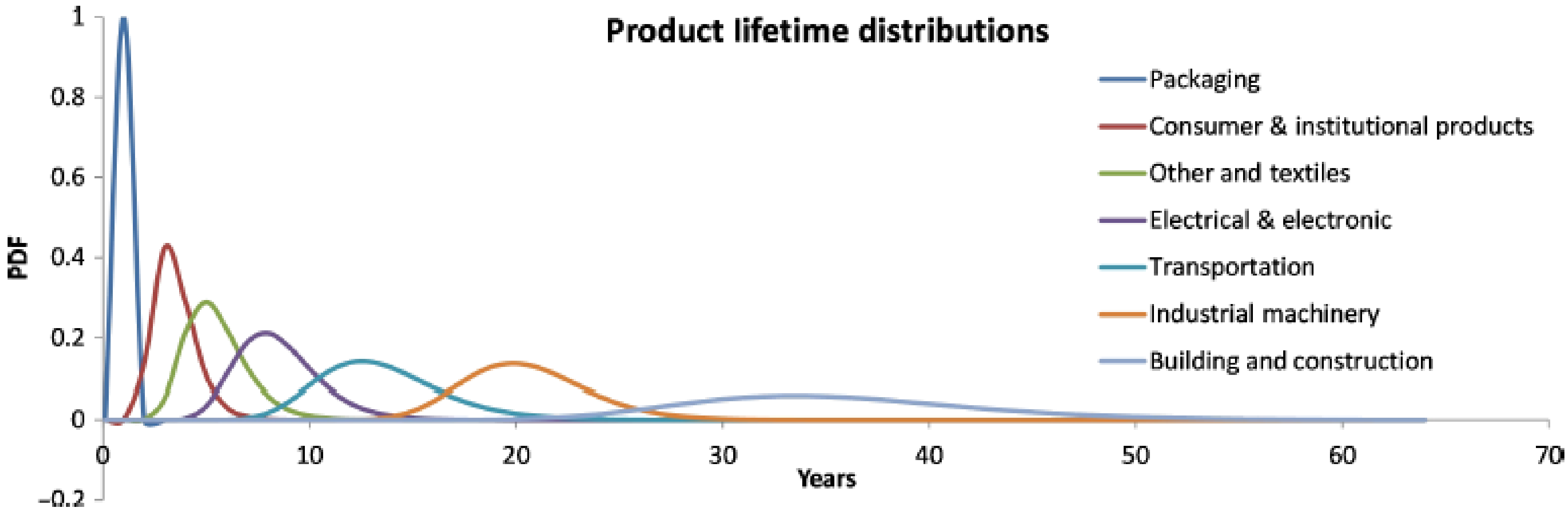
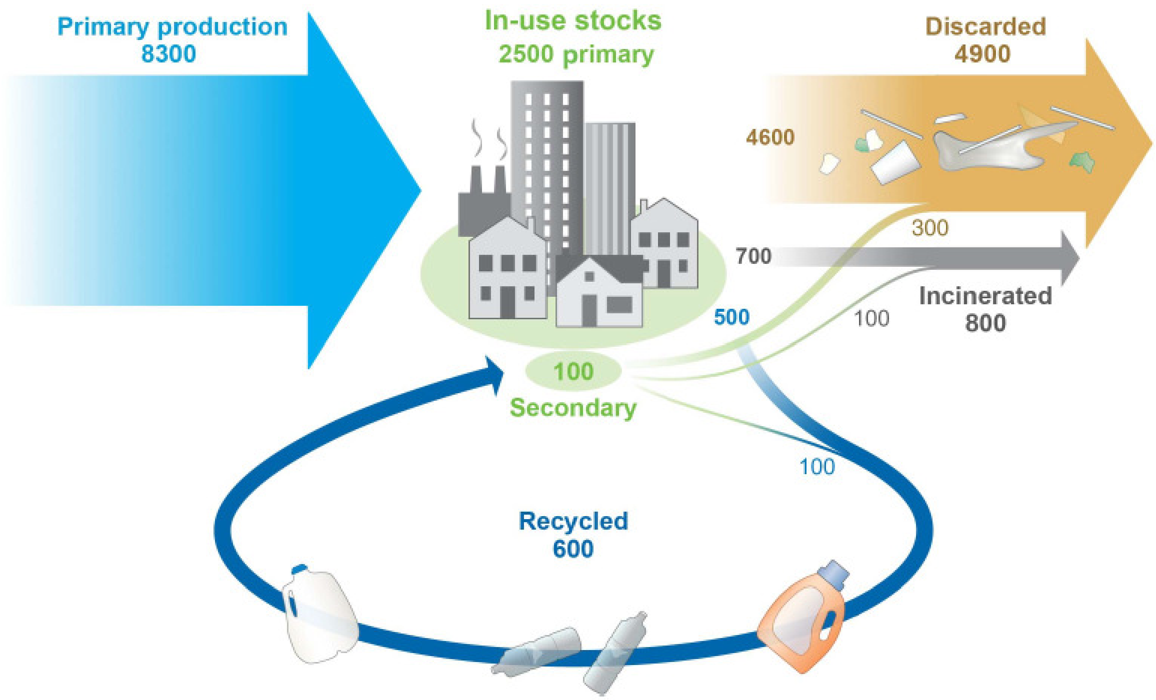
Plastic Production

- Packaging
- Transportation
- Textiles and fabrics
- Industrial machinery
- Electrical and electronics
- Building and construction
- Consumer & industrial products

Geyer, R, J R Jambeck, and K L Law. "Production, use, and fate of all plastics ever made." Science Advances, 2017.





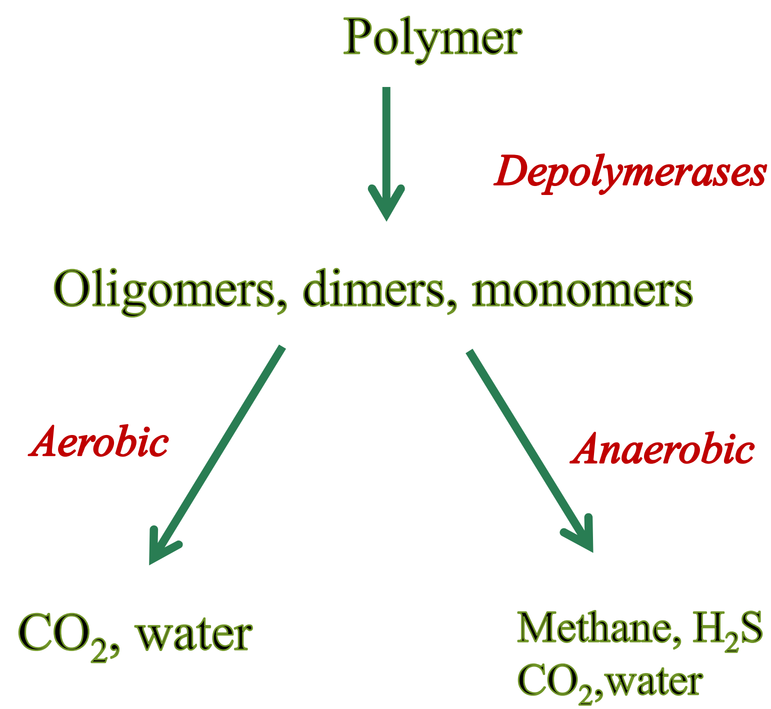
Geyer, R, J R Jambeck, and K L Law. "Production, use, and fate of all plastics ever made." Science Advances, 2017.

3 Different Fates of Plastic Waste

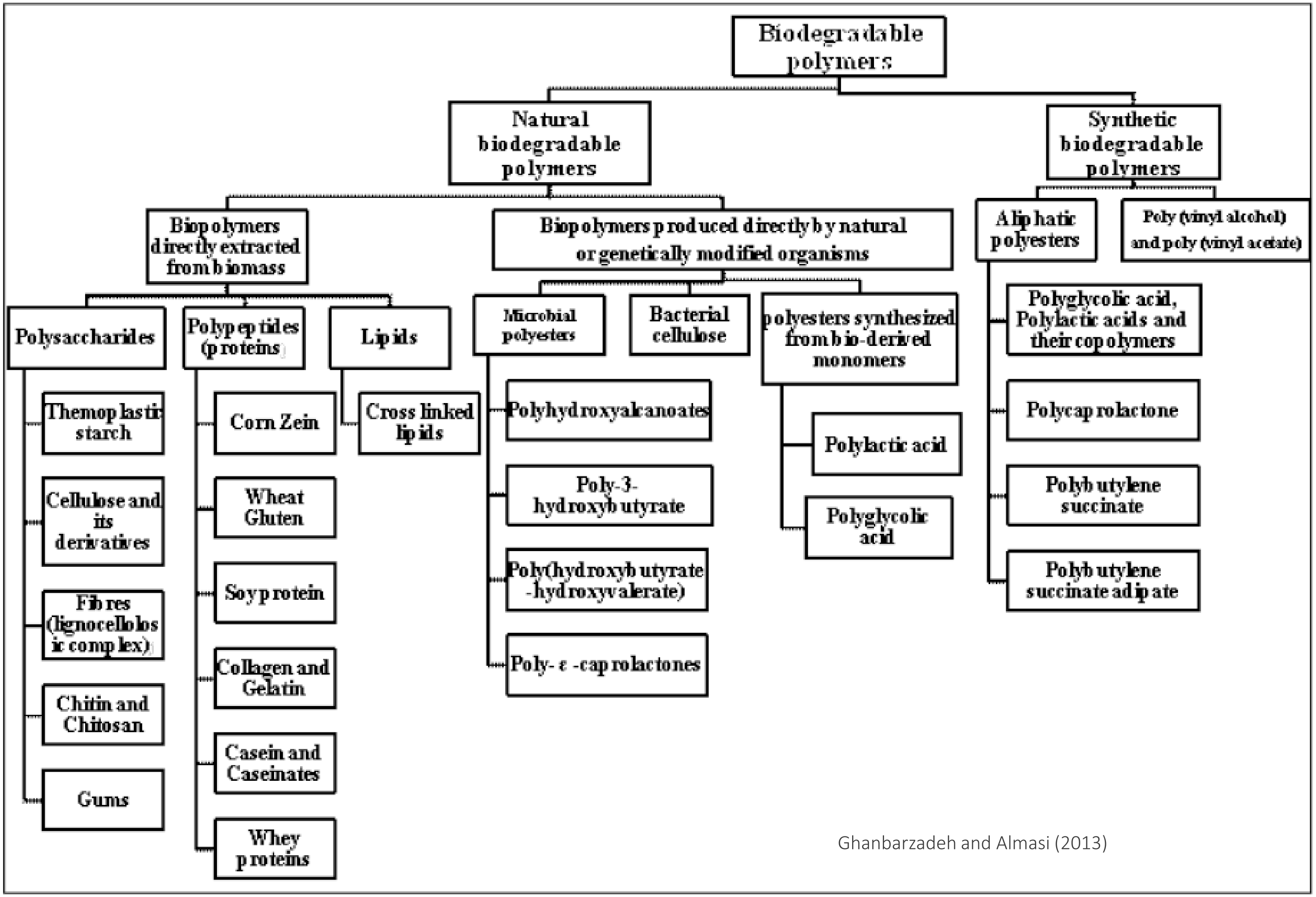
- *Containment*
- *Incineration*
- *Recycling*

What should we do?

Biodegradable plastics



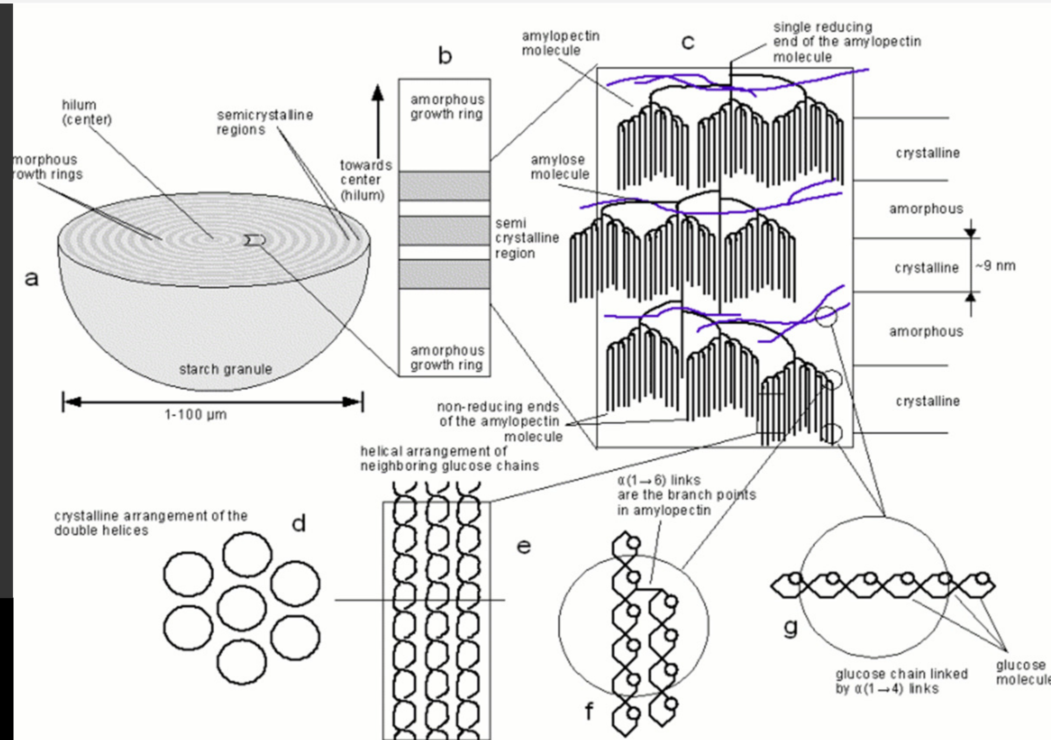
Wroblewska-Krepsztul, J, T Rydzkowski, G Borowski, M Szczpinski, T Klepka, and V K Thakur. "Recent progress in biodegradable polymers and nanocomposite-based packaging materials for sustainable environment." International Journal of Polymer Analysis and Characterization, 2018.



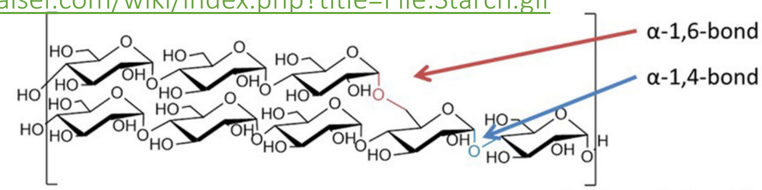
Ghanbarzadeh and Almasi (2013)

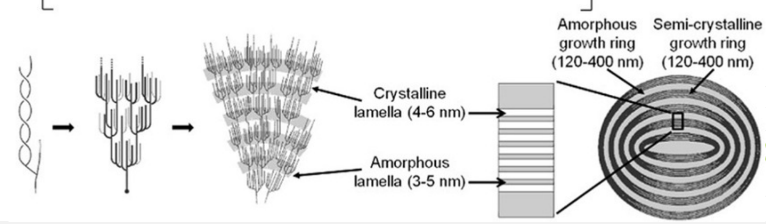
www.starch.eu/starch/#

Starch



www.braukaiser.com/wiki/index.php?title=File:Starch.gif

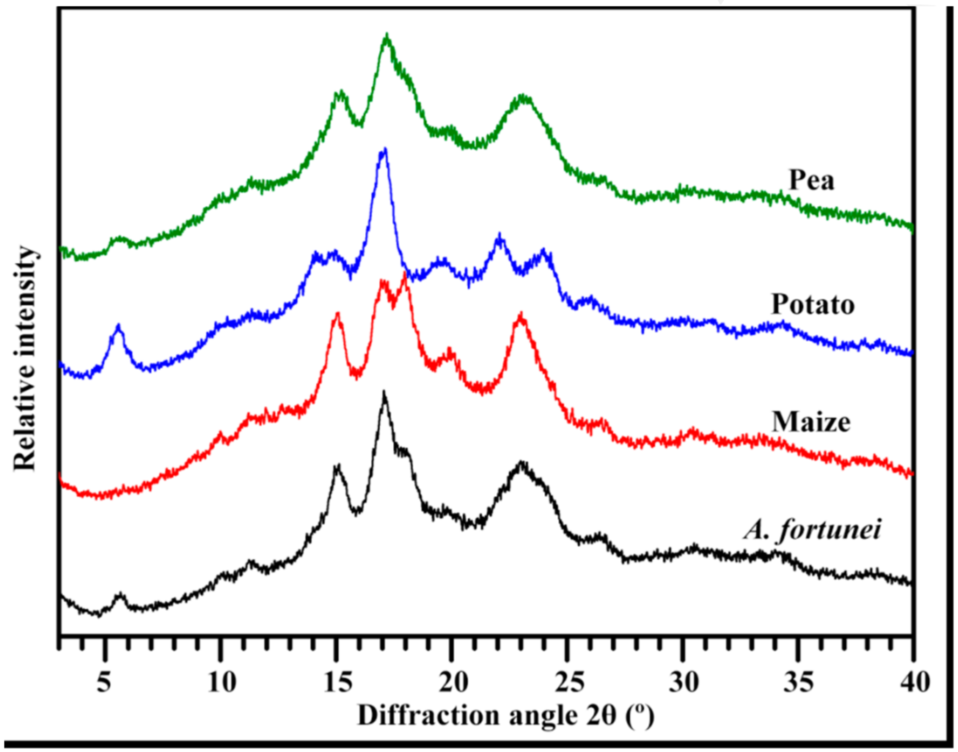




Crystallinity of Starch

Wang J, Guo K, Fan X, Feng G, and Wei C. Physicochemical properties of C-Type Starch from Root Tuber of Apios fortune in Comparison with Maize, Potato, and Pea Starches." Molecules 2018, 23, 2132; doi: 10.3390/molecules23092132.

1. Type A
   - Cereal starches such as maize, wheat, and rice;
   - Strong peaks at 15° and 23° 2θ and an unresolved doublet at 17° and 18° 2θ



Crystallinity of Starch

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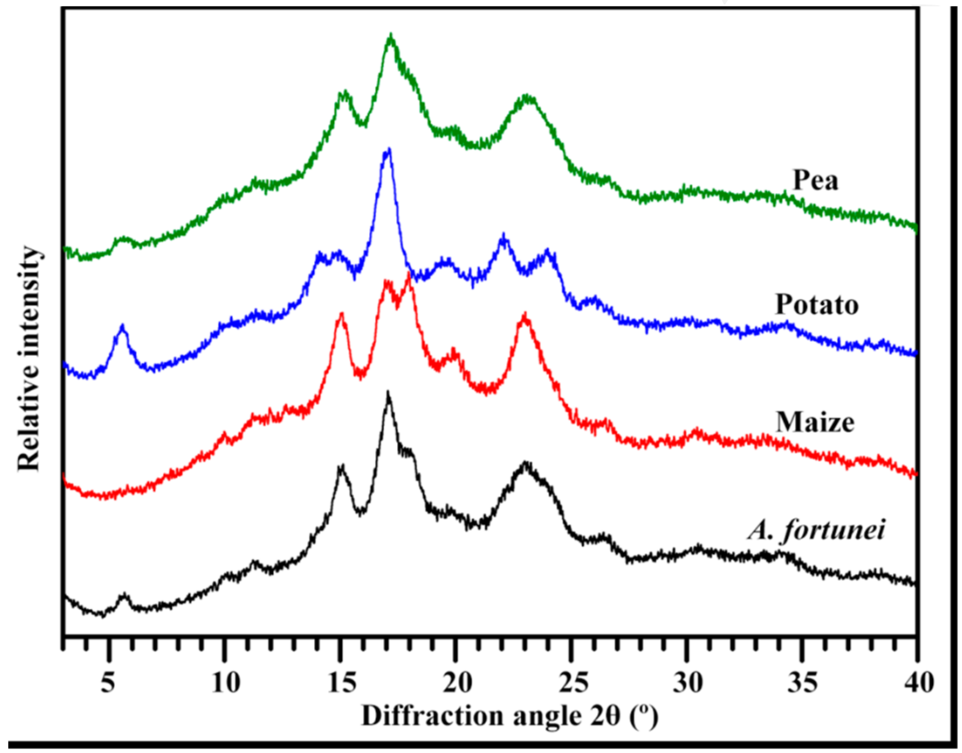
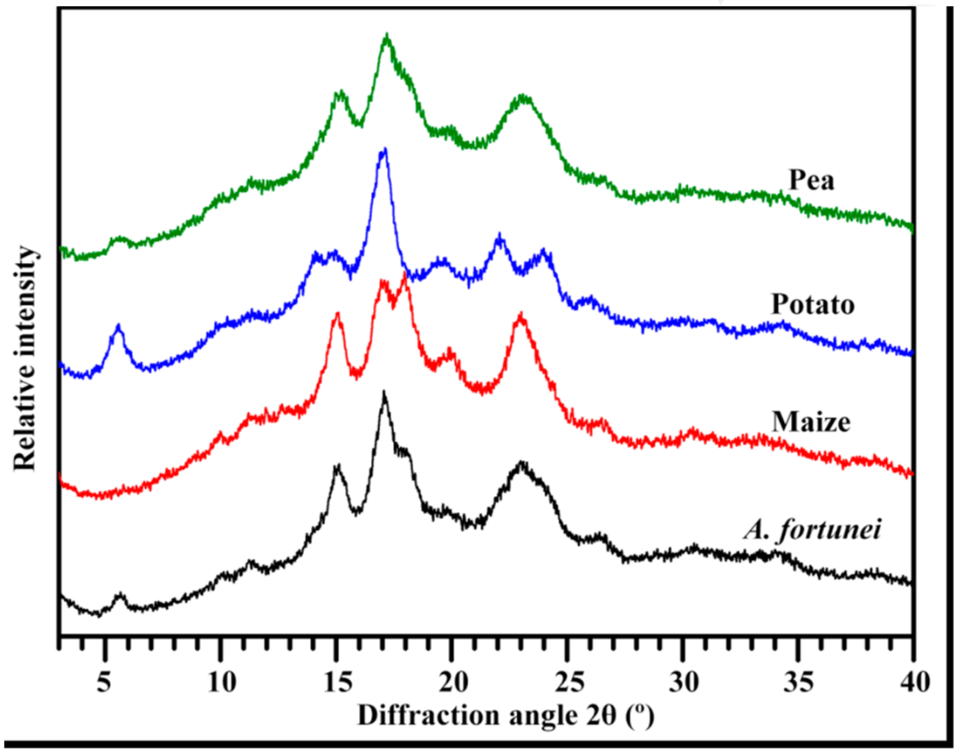
1. Type A
   - Cereal starches such as maize, wheat, and rice;
2. Type B
   - Tuber starches such as potato and sago;
   - Peaks at 5.6°, 15°, 17°, 22°, and 23° 2θ

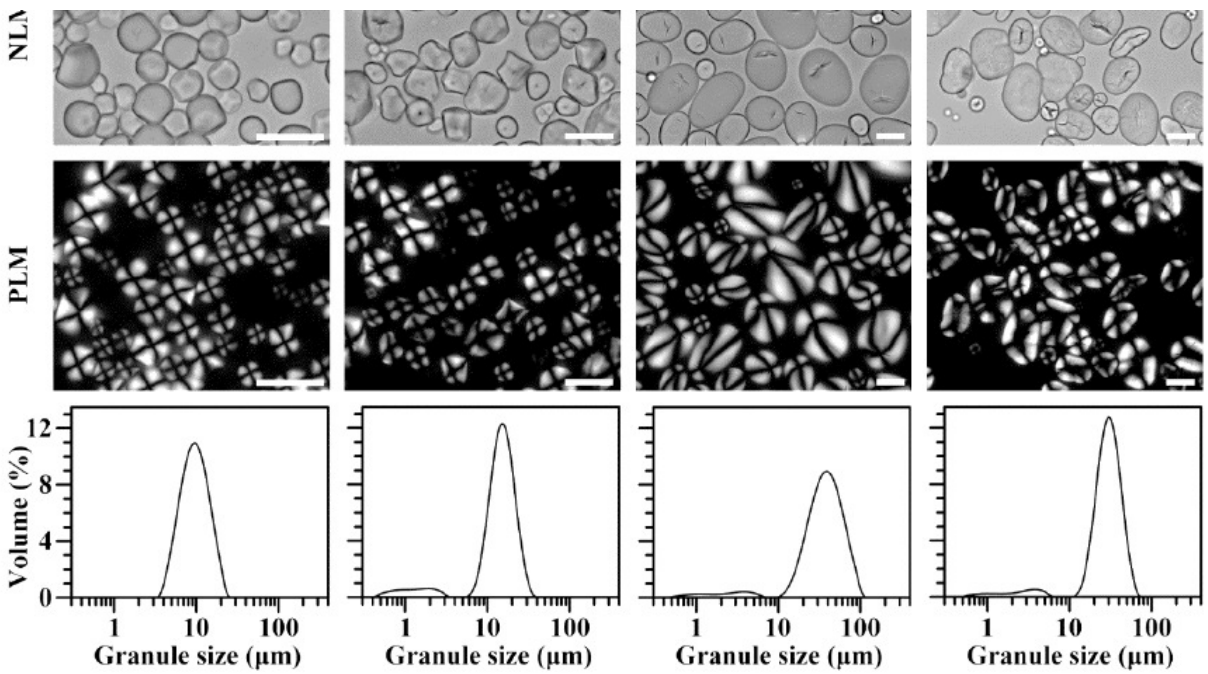


Crystallinity of Starch

1. Type A
   - Cereal starches such as maize, wheat, and rice;
2. Type B
   - Tuber starches such as potato and sago;
3. Type C
   - Bean and other root starches;
   - Peak at about 5.6° and 23° 2θ

Wang J, Guo K, Fan X, Feng G, and Wei C. Physicochemical properties of C-Type Starch from Root Tuber of Apios fortune in Comparison with Maize, Potato, and Pea Starches." Molecules 2018, 23, 2132; doi: 10.3390/molecules23092132.

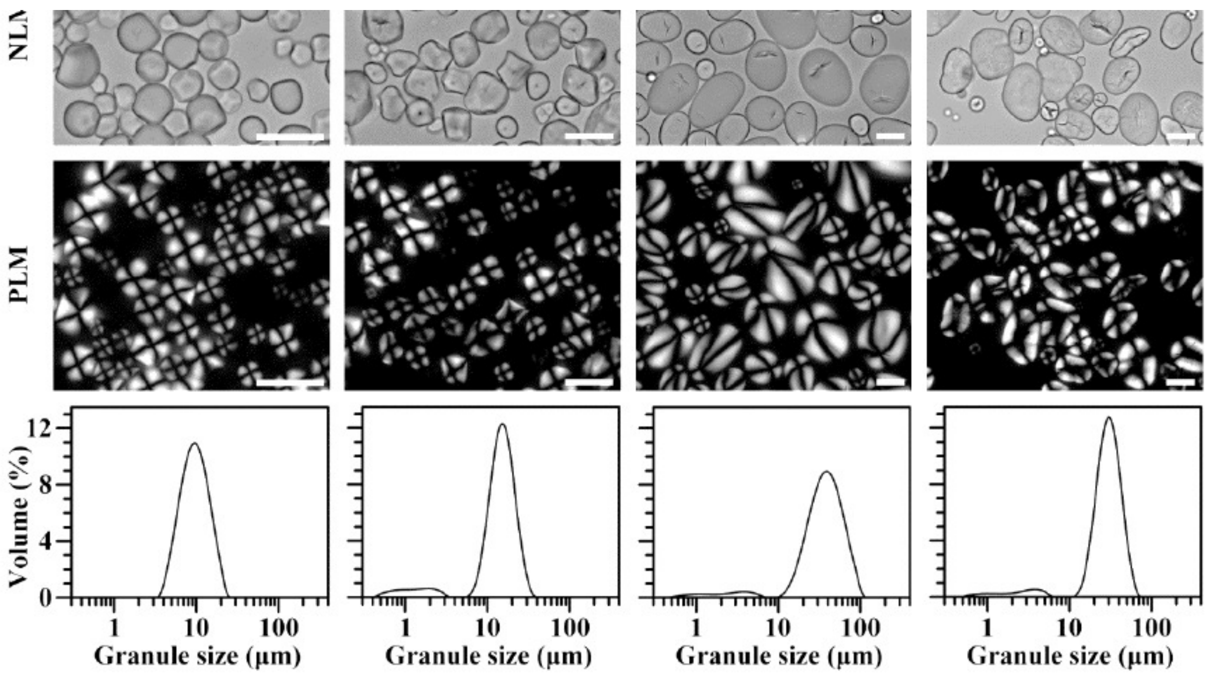




Starch granule morphology and size distribution

Wang J, Guo K, Fan X, Feng G, and Wei C. Physicochemical properties of C-Type Starch from Root Tuber of Apios fortune in Comparison with Maize, Potato, and Pea Starches." Molecules 2018, 23, 2132; doi: 10.3390/molecules23092132.

- GRANULE MORPHOLOGY
  - Maize: polygonal with central hila
  - Potato: small spherical granules with central hila and large ellipsoidal granules with eccentric hila
  - Pea: elliptical with central hila



Starch granule morphology and size distribution

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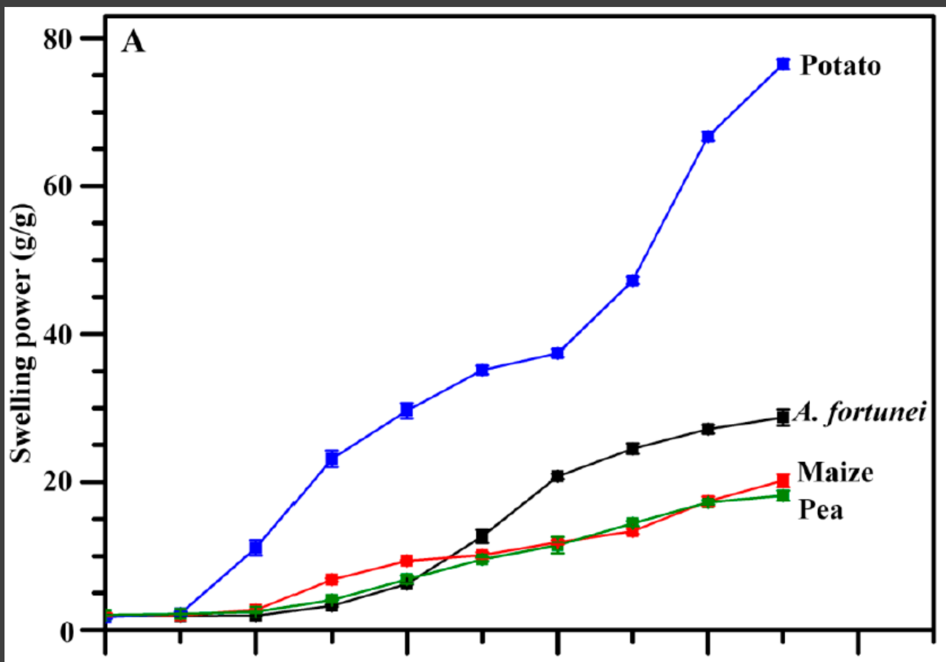
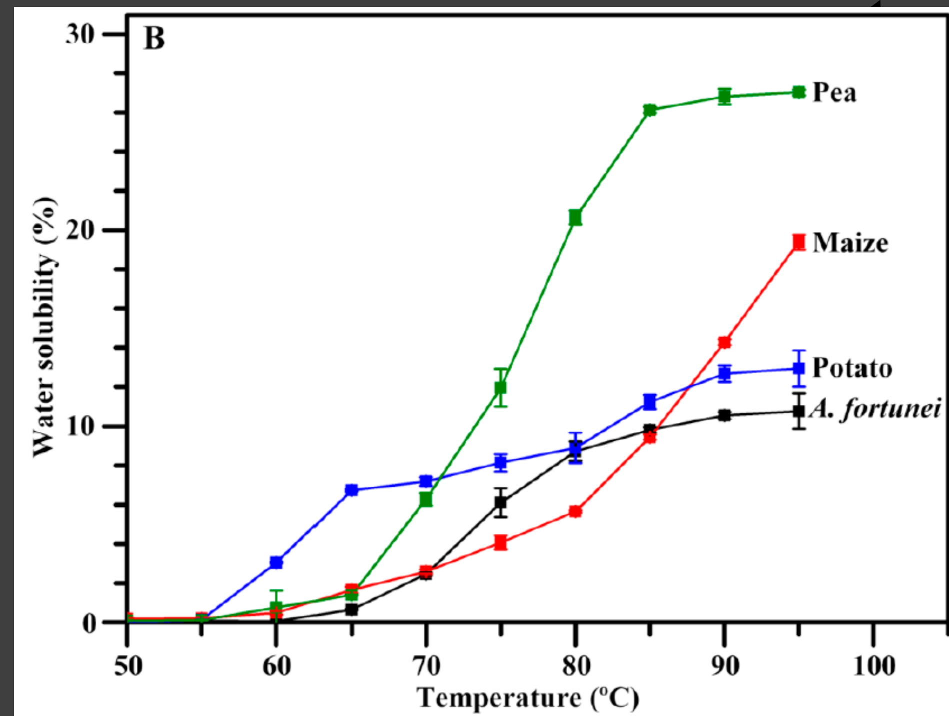
- GRANULE SIZE DISTRIBUTION
  - maize, potato, and pea have bimodal size distribution
  - Maize: 0.4 to 40 μm
  - Potato: 0.6 to 100 μm
  - Pea: 0.6 to 70 μm





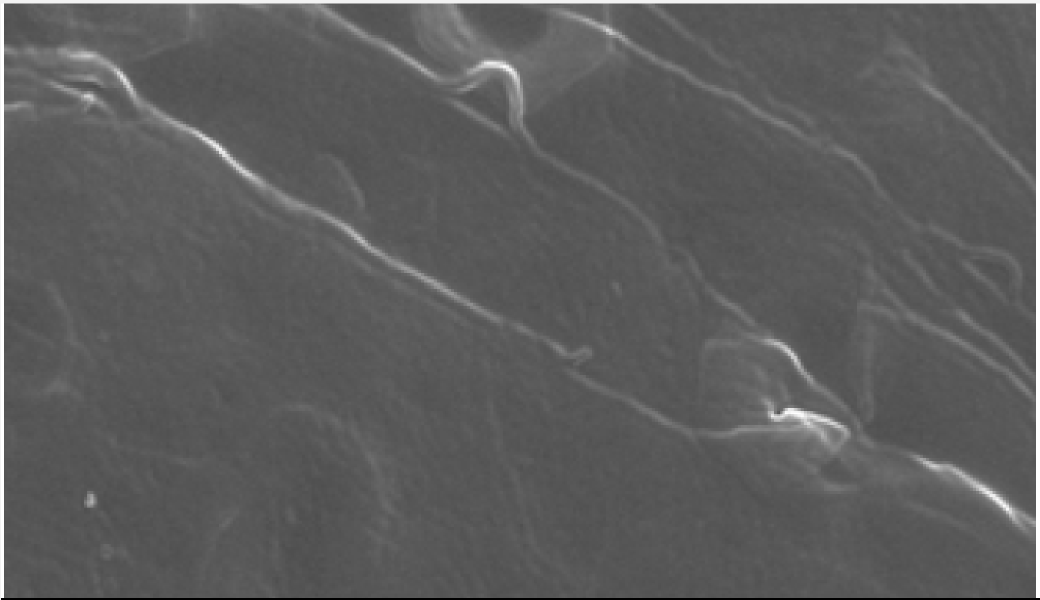
Wang J, Guo K, Fan X, Feng G, and Wei C. Physicochemical properties of C-Type Starch from Root Tuber of Apios fortune in Comparison with Maize, Potato, and Pea Starches." Molecules 2018, 23, 2132; doi: 10.3390/molecules23092132.

Swelling power & Water solubility of Starch

Applications of Starch

- Used in paper for wet end addition, size-press and surface coating;
- Internal strength and surface “feel” depend on starch
- Improves the printability and writing properties
  - Printing paper → 4.1%
  - Paper board → 2.0%
  - Industrial paper →1.9%
- Use of recycled paper increases need for additional starch

- Serves as binder to sugarless sweetener



Thermoplastic Starch

Processed typically using heat and pressure to completely destroy the crystalline structure, i.e. irreversible order-disorder transition termed gelatinization

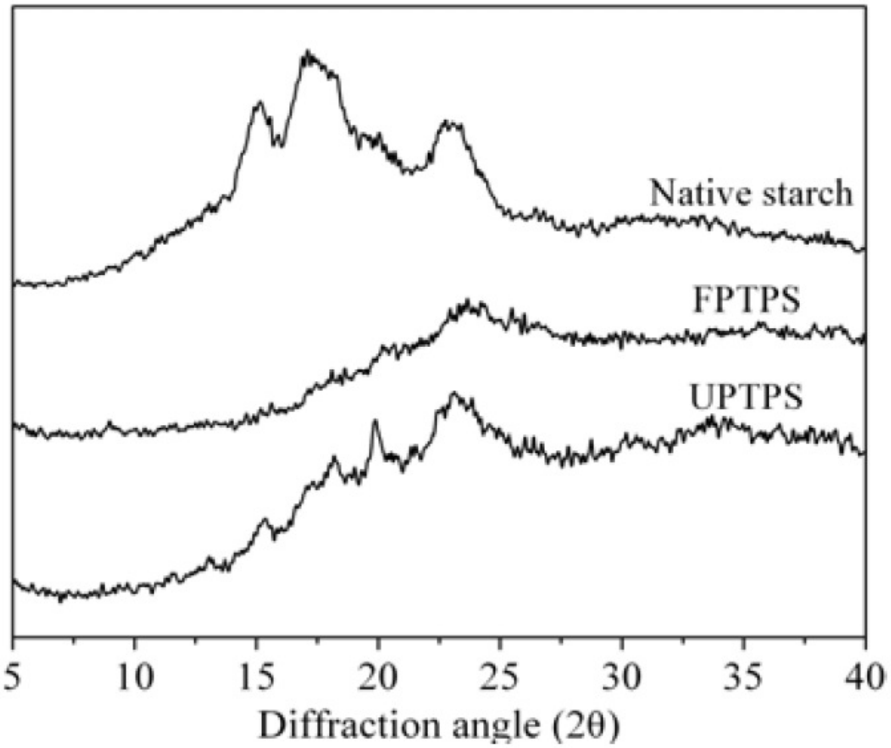


Figure 2. XRD spectra of native starch granules and TPS

Yingfeng, et al. (2012). Comparative Study of Plasticizing Effect of Corn Starch Using Formamide and Urea. International Conference of Biobase Material Science and Engineering (BMSE). Changsha, China. DOI: 10.1109/bmse.2012.6466167.

- Increase mechanical strength, frictional wear, and moisture resistance; as well as stabilizer and filler for colored inks in yarns for textiles
- Production of biodegradable, non-toxic and skin friendly detergents, hygiene and cosmetics
- Admixtures in plasters and insulation in construction industry, oil drilling, mineral and metal processing
- Production of biodegradable plastic films for disposable food serviceware, food packaging, purchase bags, composting bags, and loose filler products
- useful for making agricultural mulch films
- Used in medical applications, e.g. thermoplastic hydrogels for use as bone cements or drug-delivery carriers when blend with cellulose acetate

- Highly compostable
- High water vapor permeability
- Good oxygen barrier
- Not electrostatically chargeable
- Low thermal stability

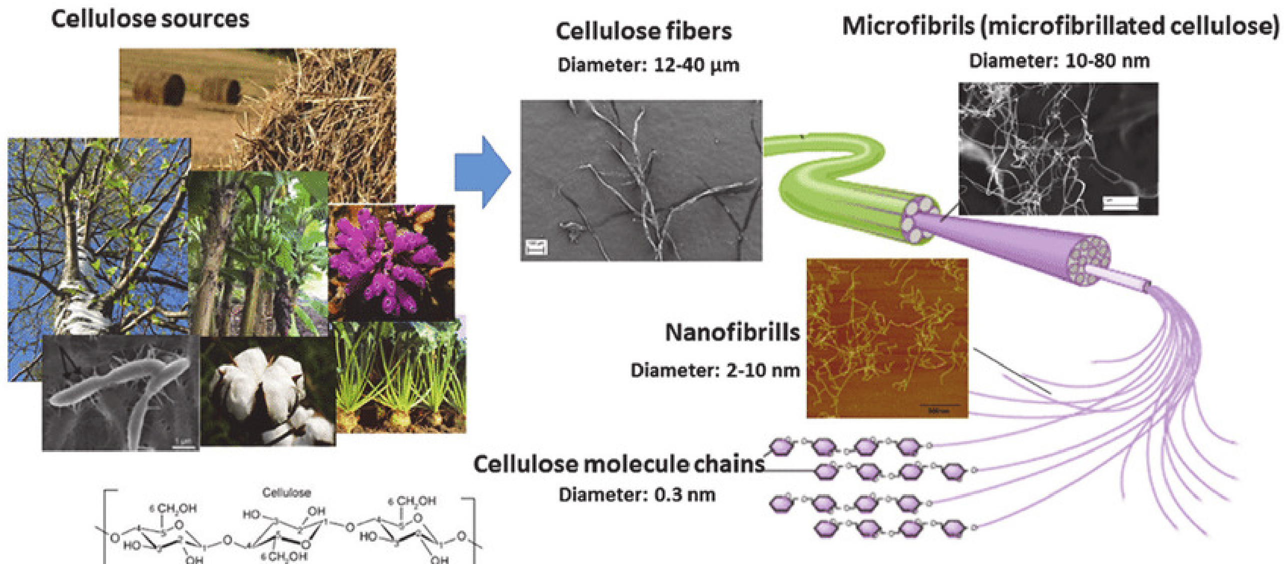
Why is Thermoplastic Starch still not widely used as biodegradable packaging material?

"Low resistance to water and the variations in mechanical properties under humid condition." - Ghanbarzadeh & Almasi (2013)

Ghanbarzadeh B. & Almasi H. "Biodegradable Polymers." Biodegradation – Life of Science. Chapter 6. InTech 2013. DOI 10.5772/56230.

Cellulose and Lignocellulosic Complex

www.hmicronpowder.com/industries/food/cellulose-powder



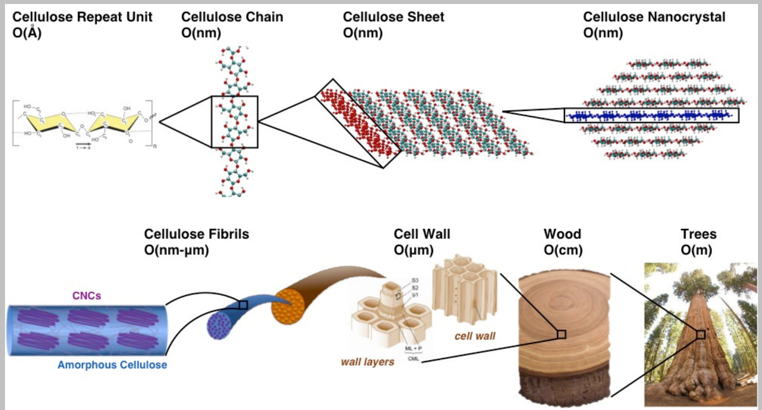
Terhi Suopajarvl (2015). Functionalized nanocelluloses in wastewater treatment. Thesis, University of Oulu.

www.storaenso.com/en/products/lignin

www.indiamart.com/proddetail/pectin-mrs-danisco-8083341797.html

Cellulose

- 100% linear polymer
- Highly crystalline with degree of crystallinity >70%
- Capable of intra- and intermolecular hydrogen bonding
- Creates a tight fiber structure
- High tensile strength



Katherine Wyatt (2016). Biodegradable and Bulletproof: Modelling cellulose nanocrystals for success in the real world. Yale Scientific, Feb 3, 2016.

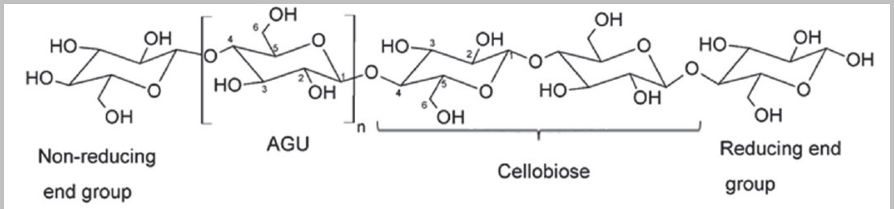


Fig. 5. Structure of cellulose with carbon atoms numbered in AGU and showing the repeating cellobiose unit in cellulose.

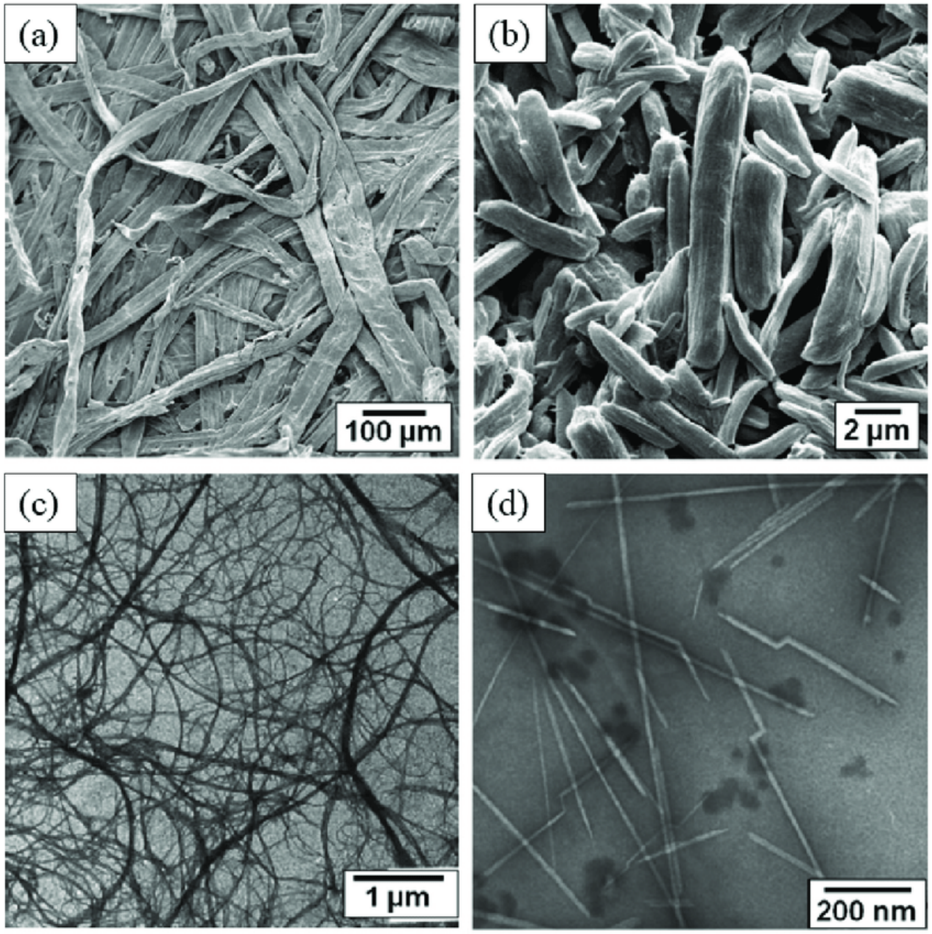
Terhi Suopajarvl (2015). Functionalized nanocelluloses in wastewater treatment. Thesis, University of Oulu.

Cellulose

- Resistant to oxidizing agents
- Insoluble in most solvents
- Easily hydrolyzed by acid to water-soluble sugars
- Modified into various forms: ethers, esters, and acetals

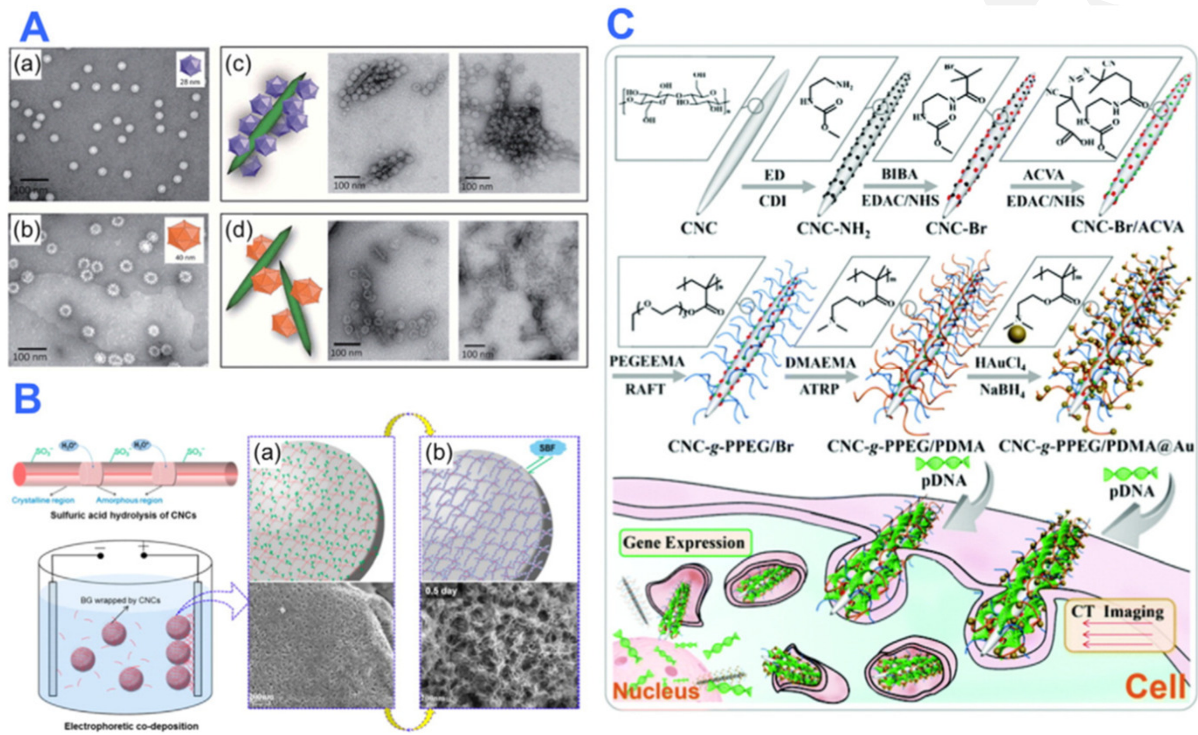
a) Wood fiber
b) Microcrystalline cellulose
c) Microfibrillated cellulose
d) Cellulose nanocrystals

Choi K, et al. (2017). Cellulose-based smart fluids under applied currents. Materials, 10, 1060. doi: 10.3390/ma10091060.



Cellulose Applications

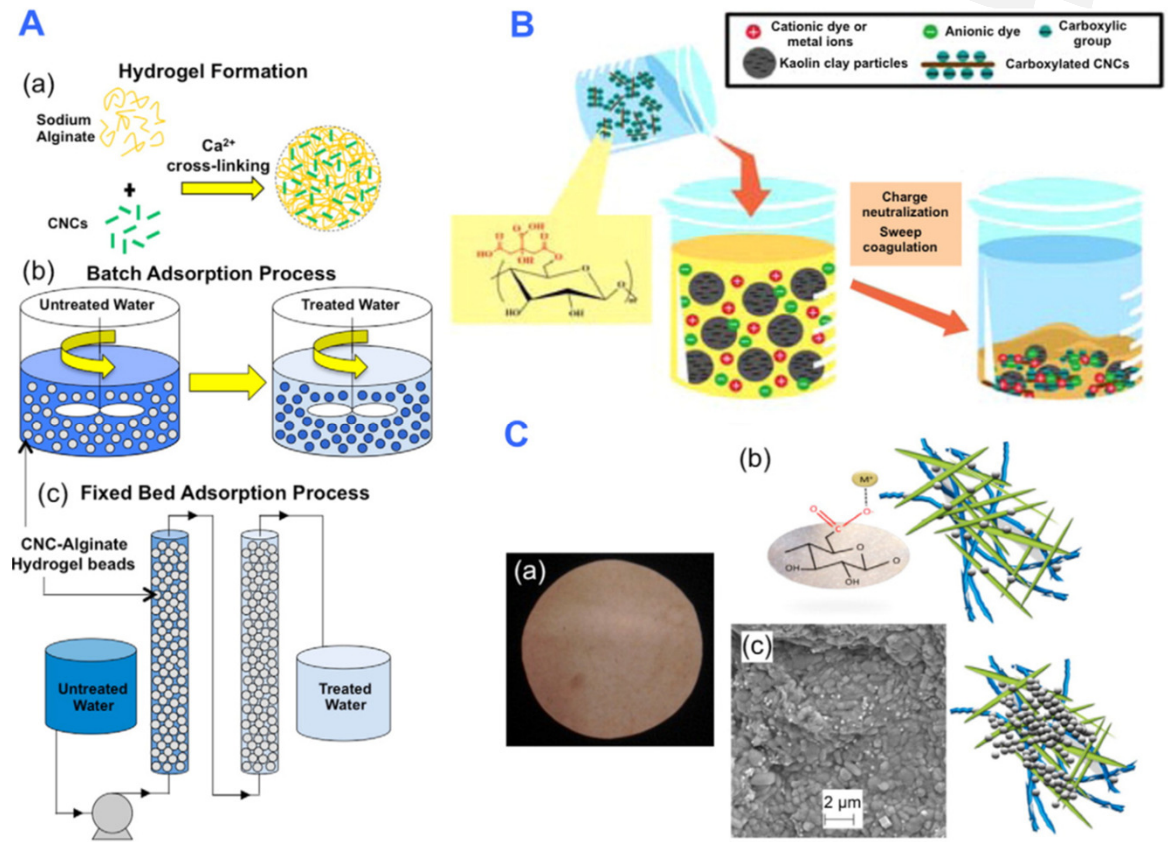
- Biomedical Engineering
  - Antimicrobial / antiviral systems
  - Tissue engineering
  - Drug / gene delivery
  - Biosensors
  - Protein scaffold / biocatalyst



Grishkewich N. et al. (2017). Recent advances in the application of cellulose nanocrystals. Current Opinion in Colloid and Interface Science 29 (2017) 34-45.

Cellulose Applications

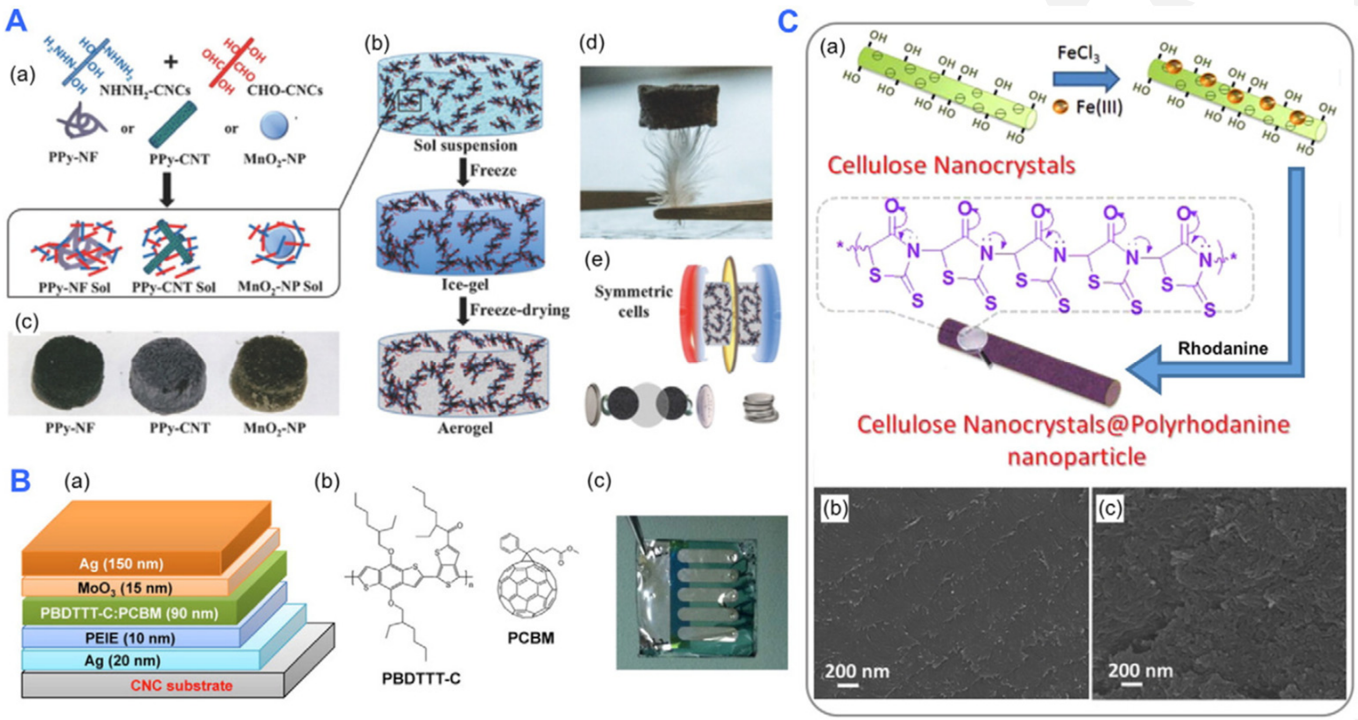
- Wastewater treatment
  - Adsorbents
  - Additional water treatment techniques



Grishkewich N. et al. (2017). Recent advances in the application of cellulose nanocrystals. Current Opinion in Colloid and Interface Science 29 (2017) 34-45.

Cellulose Applications

- Energy and electronics sector
  - Supercapacitors
  - Conductive films
  - Substrates
  - Sensors
  - Templating material / separator for energy storage



Grishkewich N. et al. (2017). Recent advances in the application of cellulose nanocrystals. Current Opinion in Colloid and Interface Science 29 (2017) 34-45.

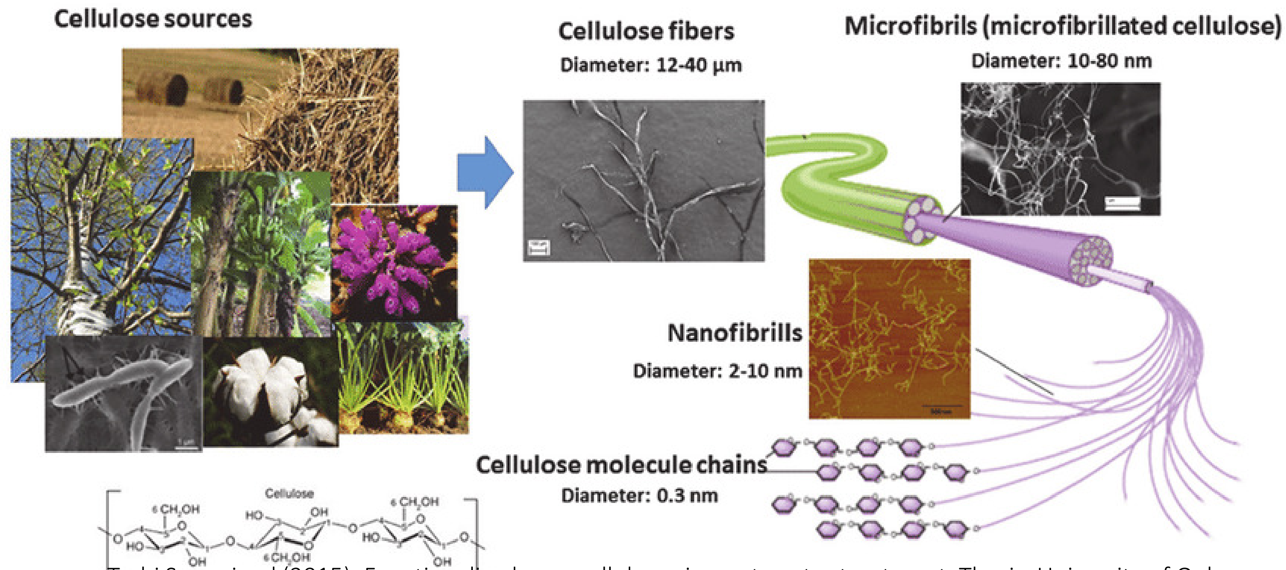
Cellulose Applications

- Other emerging applications

- Enhanced oil recovery – pickering emulsifier
- Drilling fluid
- Personal care – antioxidants
- Food sector – food additive / packaging films

Grishkewich N. et al. (2017). Recent advances in the application of cellulose nanocrystals. Current Opinion in Colloid and Interface Science 29 (2017) 34-45.

www.hmicronpowder.com/industries/food/cellulose-powder



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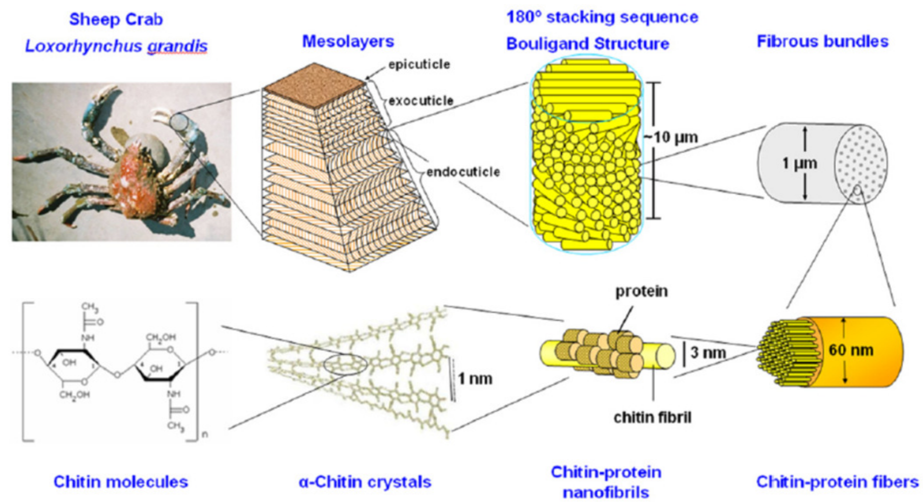
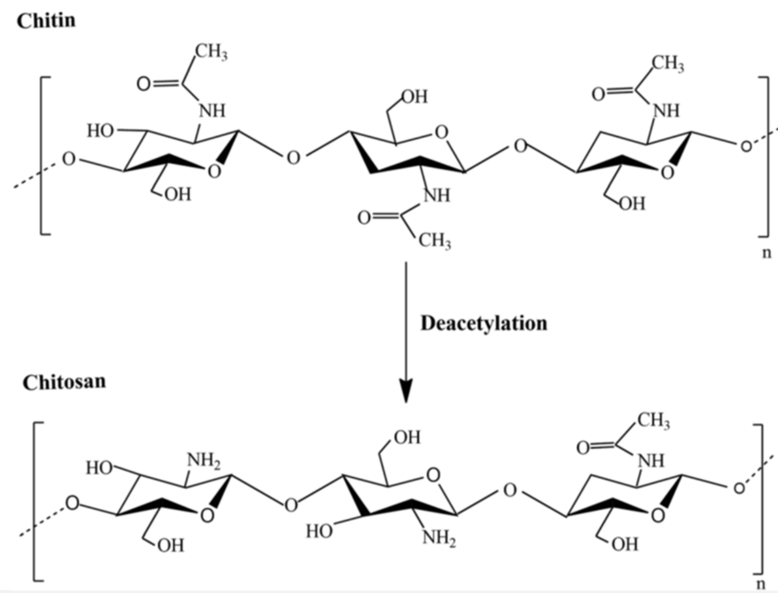
www.storaenso.com/en/products/lignin

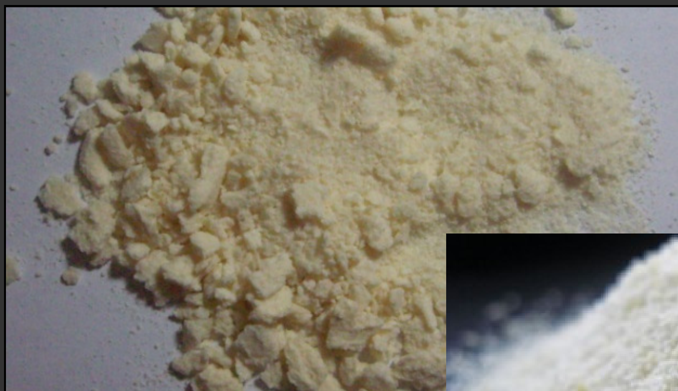
www.indiamart.com/proddetail/pectin-mrs-danisco-8083341797.html

Cellulose and Lignocellulosic Complex

Chitin and Chitosan







Biological Properties

Dictated by its degree of deactylation, distribution of acetyl groups, molecular weight, and viscosity

Islam S, et al. (2016). Chtin and Chitosan: Structure, Properties, and Applications in Biomedical Engineering. J. Polymer Environ. DOI 10.1007/s10924-016-0865-5.

Song et al. (2018). Application of Chitin / Chitosan and Their derivatives in the Packaging Industry. Polymers 2018, 10, 389, doi:10.3390/polym10040389.

- Analgesic
- Hemostatic
- Anti oxidant
- Antimicrobian
- Mucoadhesion
- Biodegradability
- Biocompatibility
- Anti cholesterolemic
- Adsorption enhancer
- Low to absent toxicity

Applications

- Cosmetics
- Food additives
- Drug carriers
- Pharmaceuticals
- Semi-permeable membranes
- Tissue engineering
- Artificial kidney membrane
- Wound healing / wound dressing

- Artificial skin
- Bone damage
- Artificial cartilage
- Liver
- Nerve
- Artificial tendon
- Burn treatment
- Blood anticoagulation / hemostatic effect

- Blood vessels
- Application for hernia
- Absorbable sutures
- Antimicrobial applications
- Drug delivery systems
- Cancer treatment
- Catheter
- Opthalmology

Islam S, et al. (2016). Chtin and Chitosan: Structure, Properties, and Applications in Biomedical Engineering. J. Polymer Environ. DOI 10.1007/s10924-016-0865-5.
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Potential Raw Materials for Bioplastic Fabrication

Raw Material	Origin	Advantages	Disadvantages
Zein	Maize protein	Good film forming property	Brittle
		Good tensile and moisture properties	
		Antimicrobial and antifungal activity	
		Good mechanical properties	
		Low oxygen and CO2 permeability	
Chitosan	Chitin derivative	Antimicrobial and antifungal activity	High-water sensitivity
		Good mechanical properties	
		Low oxygen and CO2 permeability	

Nayik, G A, N Jabeen, and I Majid. "Bioplastics and food packaging: a review." Cogent Food & Agriculture, 2015.

Focus on Potential Raw Materials for Biodegradable plastic Fabrication

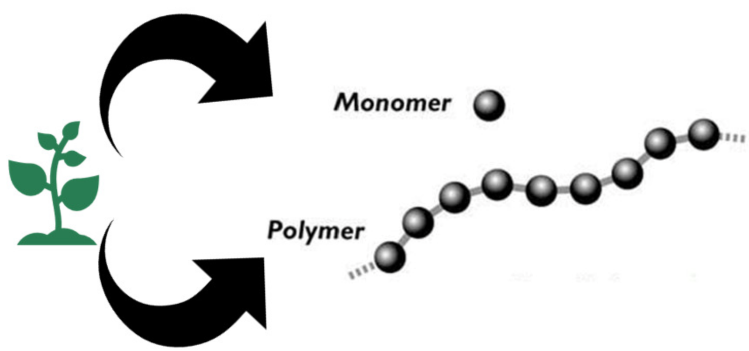
Raw Material	Origin	Advantages	Disadvantages
Thermoplastic Starch	Cassava, Potato, etc.	Good thermal insulation	Hight sensitivity to moisture
Chitin	Exoskeleton of crustaceans	Low sensitivity to moisture Good film forming property Good mechanical strength	
Cellulose	Plants		
Chitosan	Chitin derivative	Antimicrobial and antifungal activity	High-water sensitivity
		Good mechanical properties	
		Low oxygen and CO2 permeability	

Nayik, G A, N Jabeen, and I Majid. "Bioplastics and food packaging: a review." Cogent Food & Agriculture, 2015.

Challenges to Overcome

Diverse chemical functionality → Difficult control of molar mass, microstructure, and architecture → Inadequate thermal, mechanical, optical, etc. properties as food packaging material

Hillmayer, M A. "The promise of plastics from plants." Science, 2017: 868-70.



- To establish an efficient, environmental, and commercially viable techniques for chemical extraction from bio-based resources; and,
- To establish techniques for modification, customization, and processing into a set of useful and functional polymers

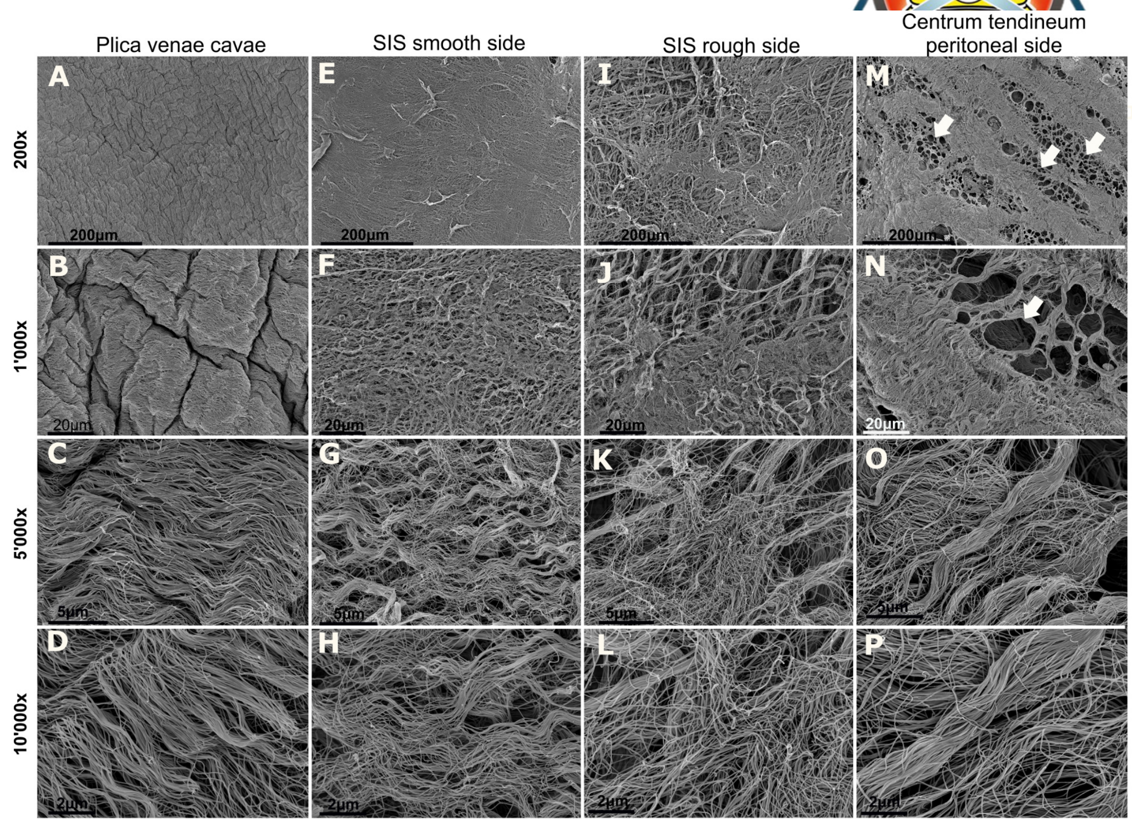
Biodegradable plastic is the future, for as long as:

- An efficient conversion process is done
- Bioplastic will have comparable properties to that of petroleum-based plastic.

[illegible]ayer, M A. "Th[illegible]romise of plastics from plants." Science, 2017: 868-70.

UP DMMME Composite Materials Laboratory
Local Research & Innovation

GOAL: To make a 100% **biodegradable plastic** materials from **bio-based** non-food resources for the **packaging & biomedical** industries

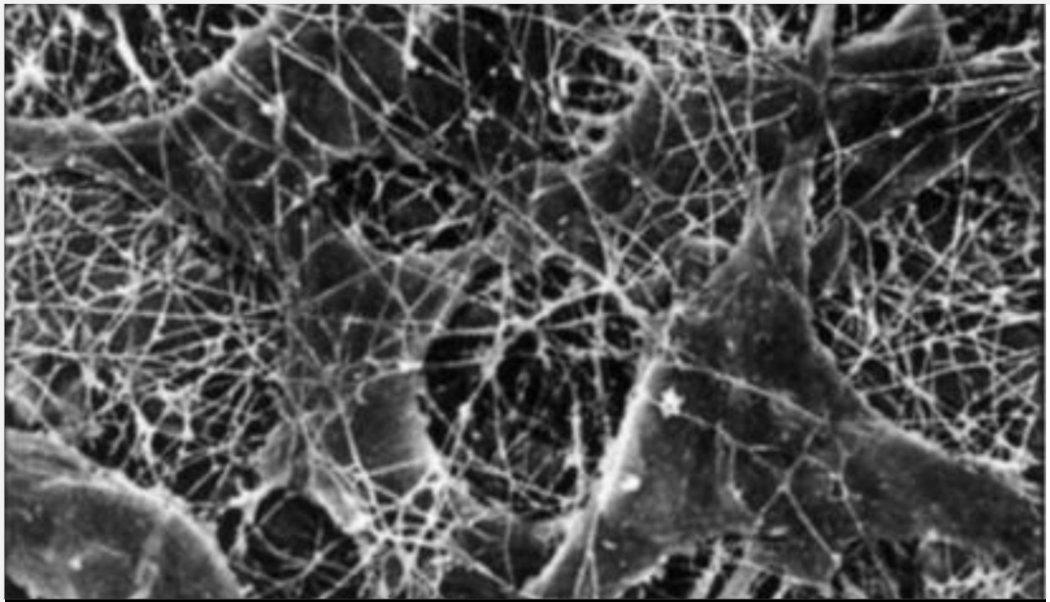


Maurer T, et al. (2018). Structural characterization of four different naturally occurring porcine collagen membranes suitable for medical applications. Plos One. DOE:10.137/journal pone.0205027. October 3, 2018.

UP DMMME Composite Materials Laboratory Local Research & Innovation

GOAL: To make a 100% biodegradable plastic materials from bio-based non-food resources for the packaging & biomedical industries

- To extract bio-based plastics from locally available non-food resources;
- To establish applicability of the bio-based materials for packaging and biomedical industries
- To investigate effect of modification on the biodegradability of bio-based plastics and its derivatives



Development of a biomedical device

Wound dressing & drug delivery

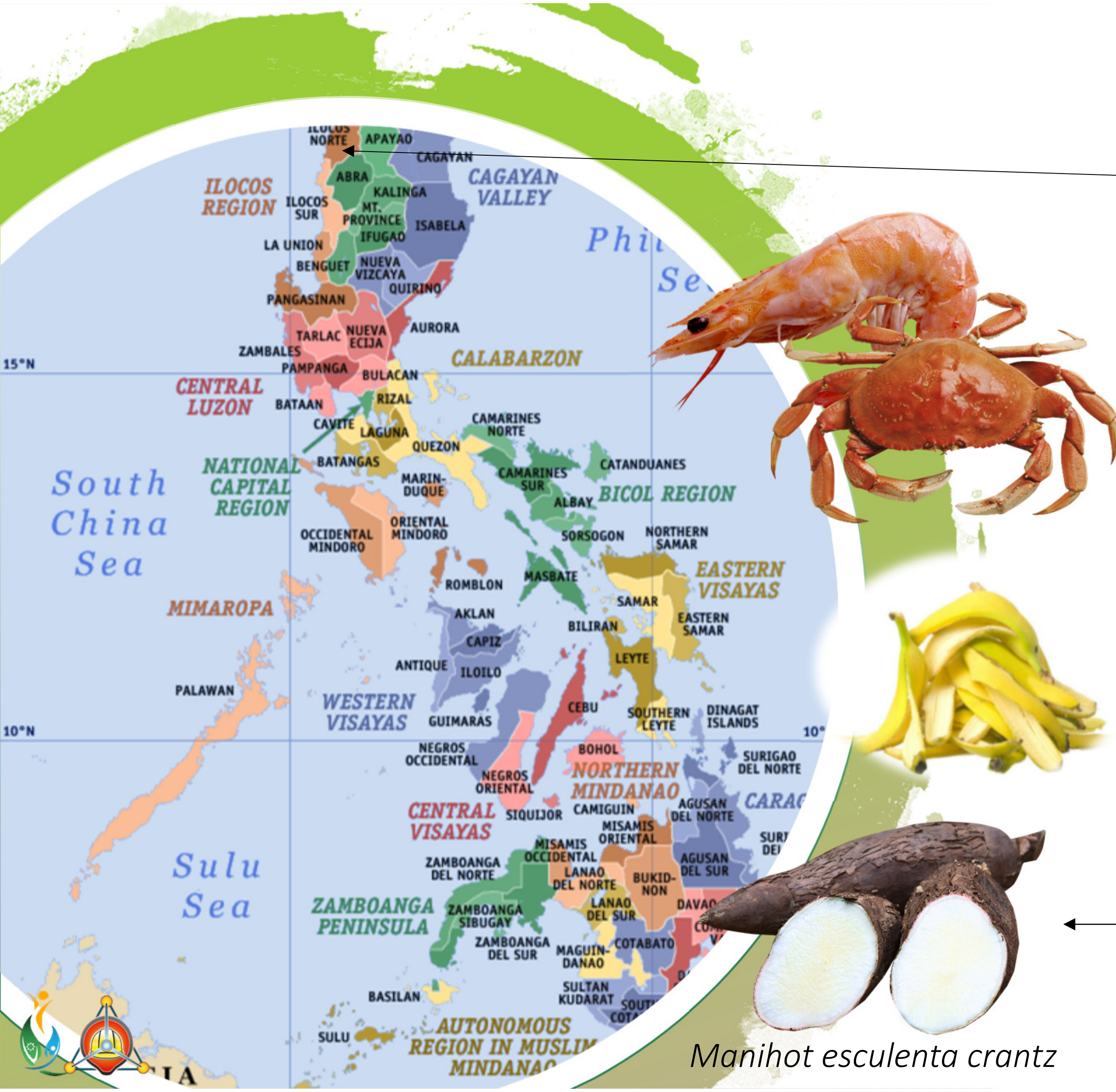
Extracellular matrix

✓ Extracellular Matrix

- *Non-cellular component present within all tissues*
- *Act as a scaffold*
- *Provides conditions for cell attachment, proliferation, migration, and differentiation*

✓ Wound dressing

- *Must have fiber diameter between 50 – 500 nm*
- *Promotes hemostasis and amenable for surface functionalization*
- *Facilitates cell respiration, gas permeation, wound dehydration prevention*
- *Prevents microbial infiltration and cell ingrowth*
- *Must have mechanical strength similar to natural skin*



Manihot esculenta crantz

nanoclay

chitin

cellulose

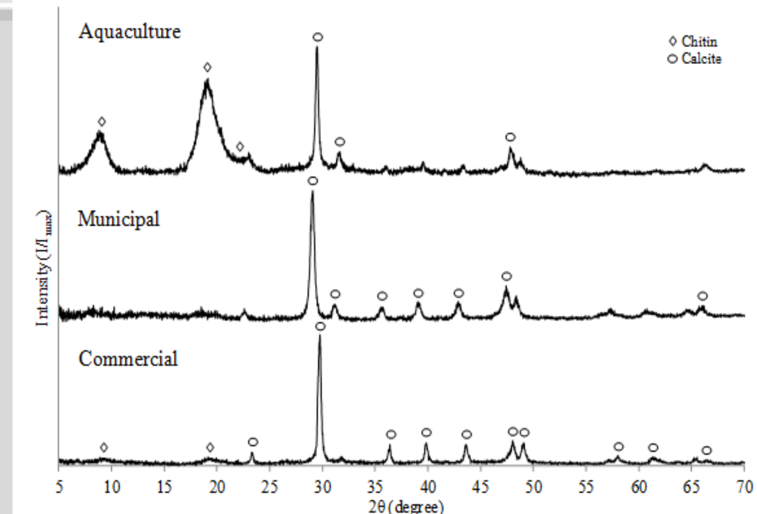
starch

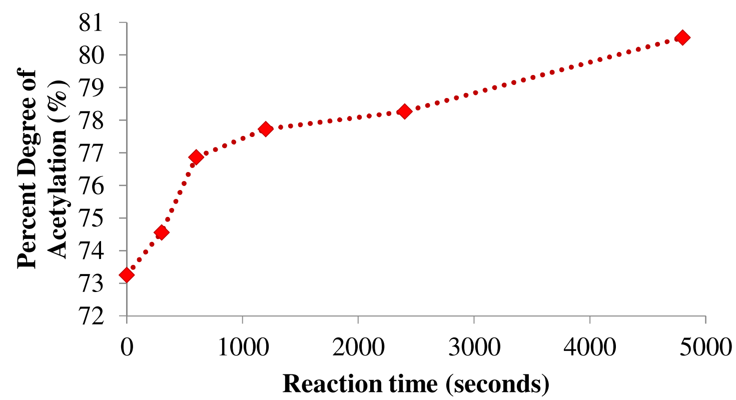
Synthesis of Chitin derived from Shells of Philippine Blue Swimming Crab (*Portunus pelagicus*)

Aileen Grace Ongkiko, MS MSE 2013, UPD

Bench-scale Chitin Extraction from Philippine Blue Swimming Crab (*Portunus pelagicus*)

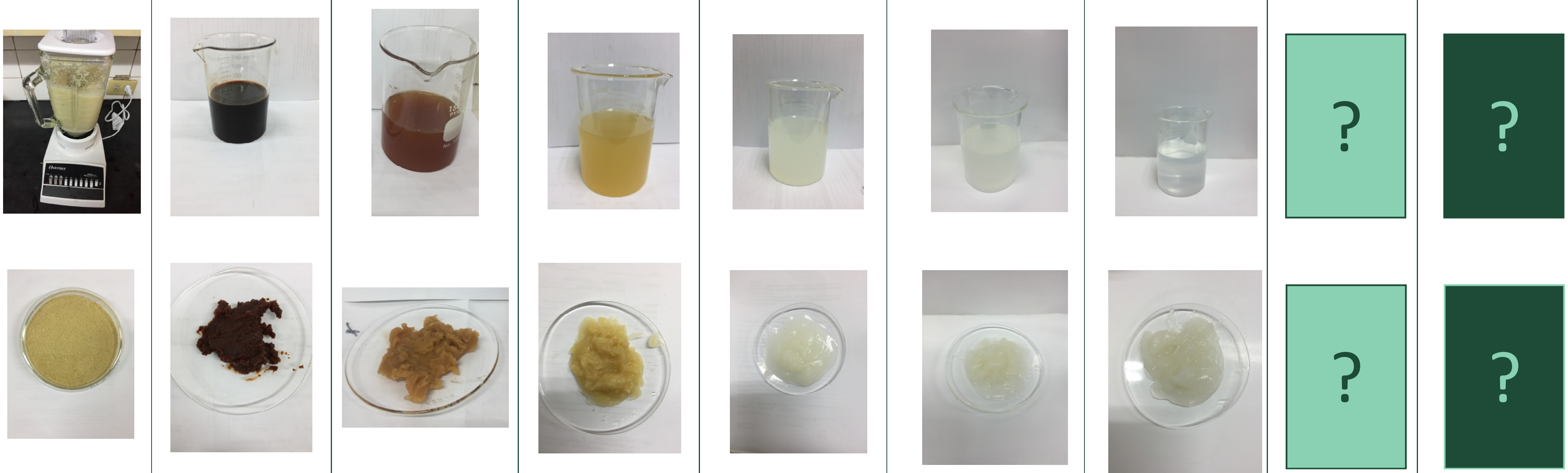
Lorenz Anthony Fernando, MS MSE 2014, UPD





Optimization of chemical and mechanical treatment conditions for the isolation of cellulose nanofibers (CNFs) from banana peels

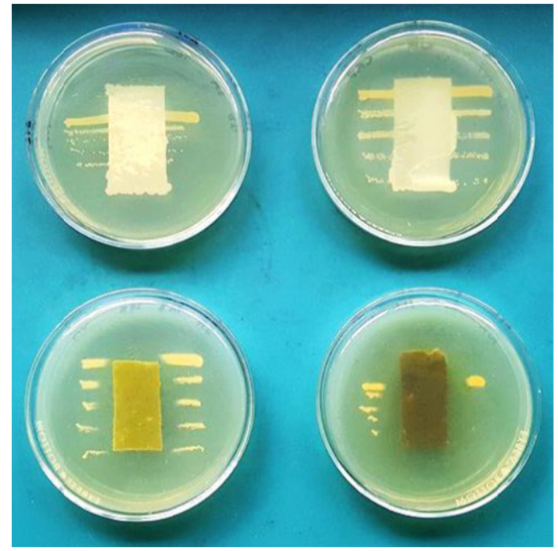
Kenneth Dognidon, on-going MS EnE student, UPD

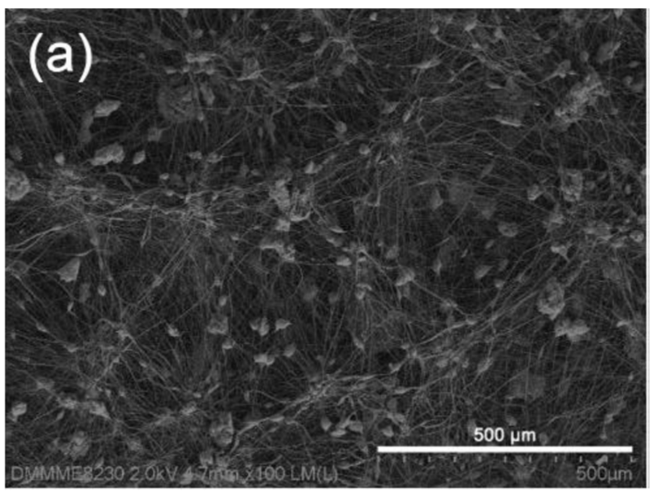


Banana Peel Bran	1st alkaline treatment (7 hrs)	1st alkaline treatment (7 hrs)	1st bleaching treatment	2nd bleaching treatment	2nd alkaline treatment (7 hrs)	2nd alkaline treatment (7 hrs)	Acid Hydrolysis	Mechanical Treatment

Fabrication and Characterization of Electrospun Cellulose-Reinforced Polycaprolactone Nanofibrous Membrane Filled with *Moringa oleifera* Leaf Powder

James Nicolas Pagaduan, MS MSE 2018, UPD





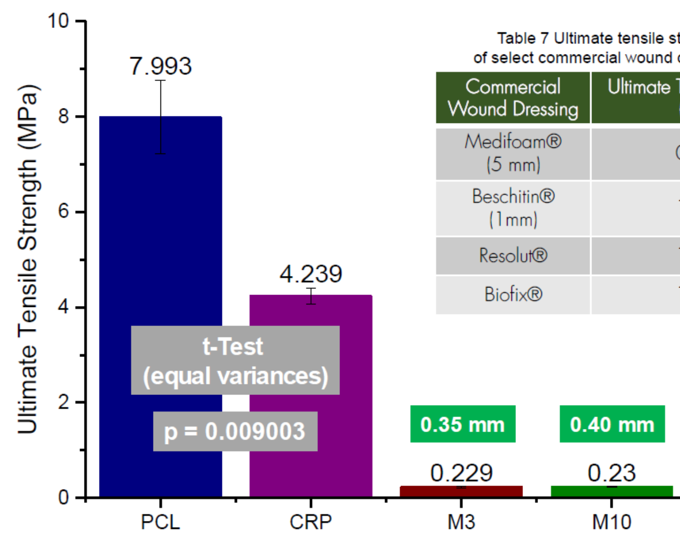


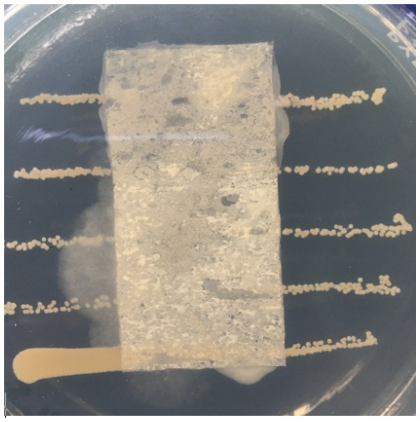
Table 7 Ultimate tensile strength of select commercial wound dressings.

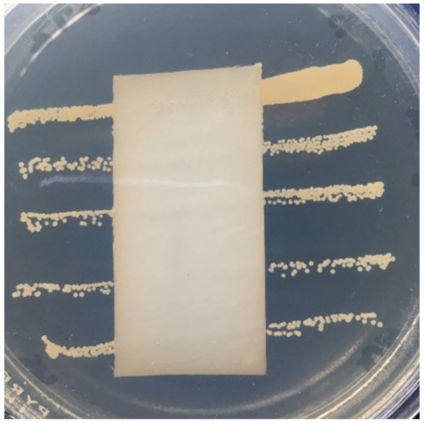
Commercial Wound Dressing	Ultimate Tensile Strength (MPa)
Medifoam® (5 mm)	0.324
Beschitin® (1mm)	15.89
Resolut®	11.72
Biofix®	14.50

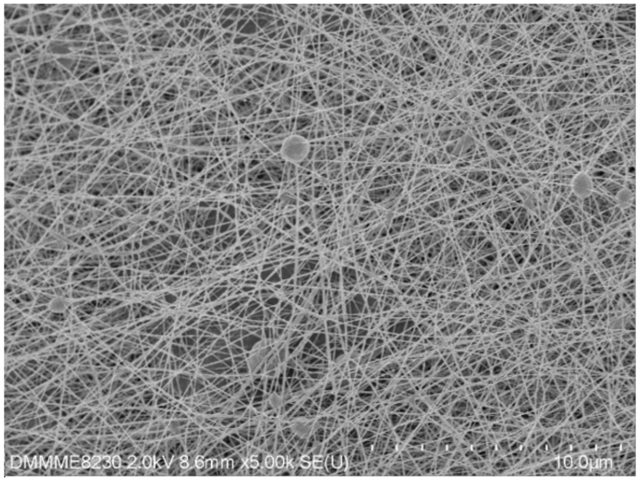
Fig. 31 Ultimate tensile strength of PCL, CRP, M3, and M10.

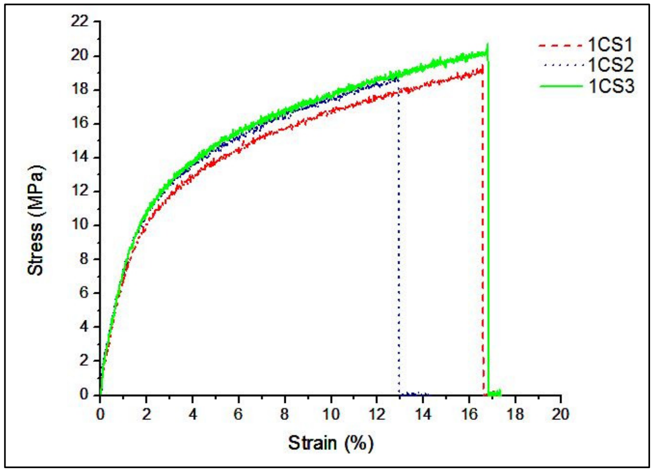
Electrospinning polycaprolactone-chitosan blend in acetone-acetic acid solvent system

Daffny Yvonne Fangonil & Renzes Anne Gaerelle Gualberto, BS MatE 2018, UPD







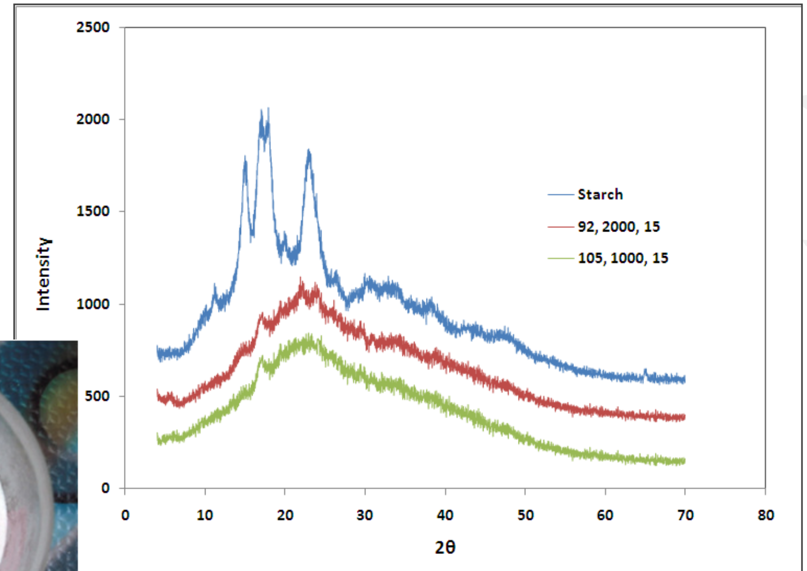


	Tensile Strength (MPa)	Maximum Strain (%)
PCL	1.480	3.230
PCL-1wt% CS	19.752	15.46
PCL-2wt% CS	17.642	7.148

Development of Packaging Material

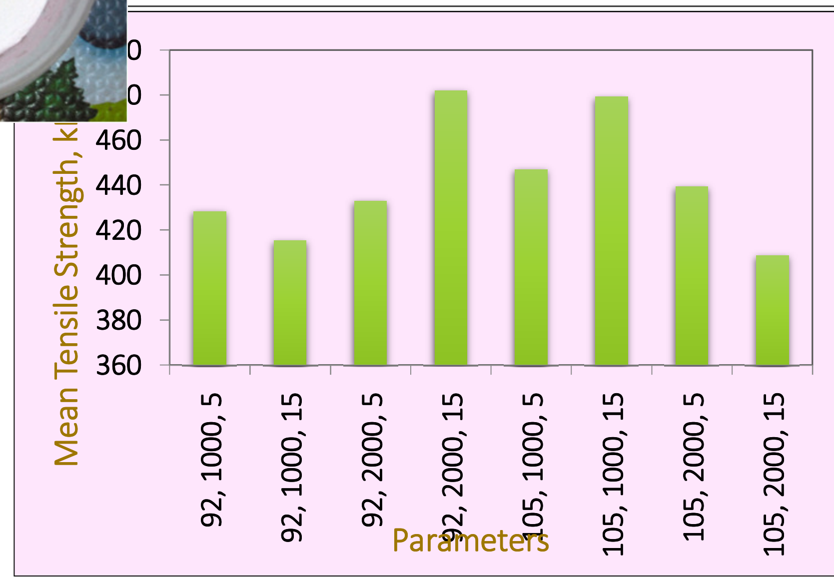
Unidirectional Abaca Fiber Reinforced Bitter Cassava based (*Manihot esculenta crantz*) Thermoplastic Starch Composite

Jasmine Vasquez, MS MSE 2014, UPD



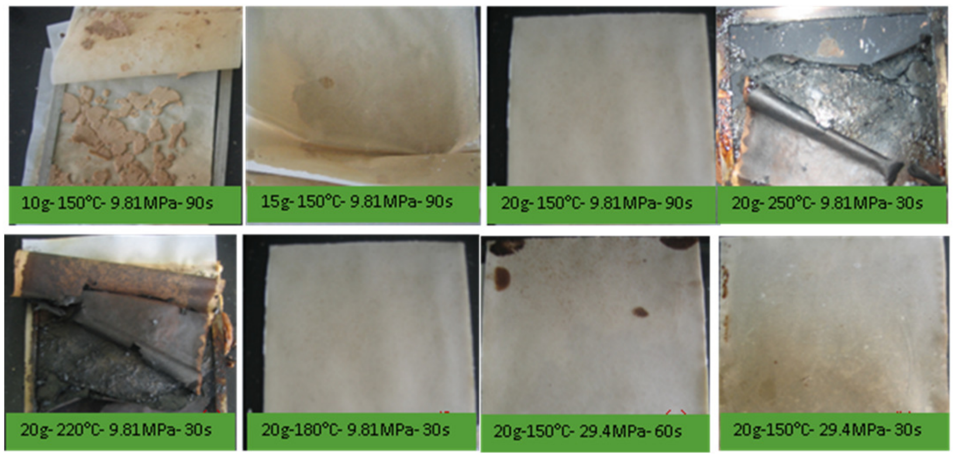
1000 psi

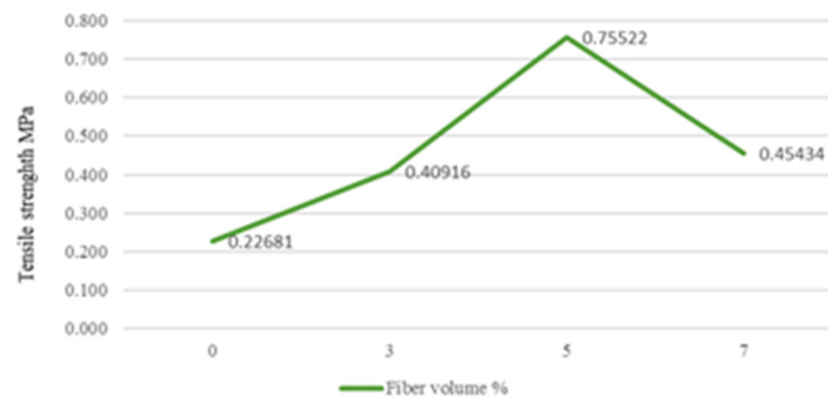
2000 psi

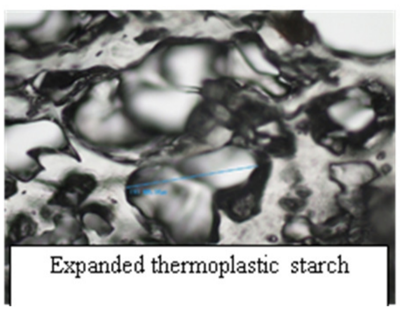


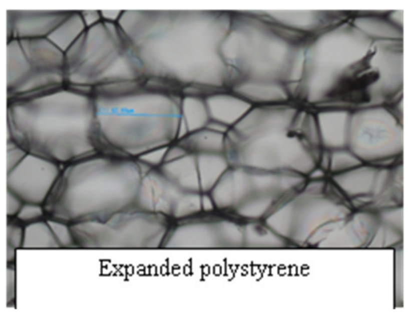
Fabrication of Expanded Thermplastic Starch Reinforced by Randomly Oriented Short Abaca Fibers

Anniver Ryan Lapuz, MS MSE 2016, UPD

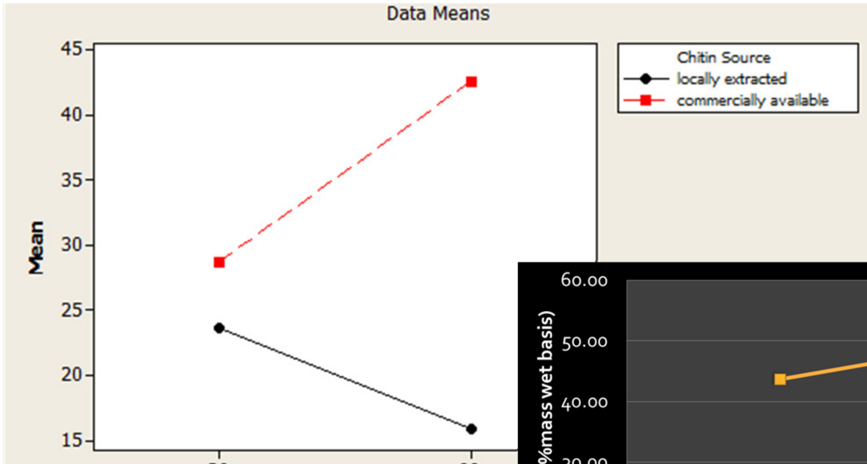


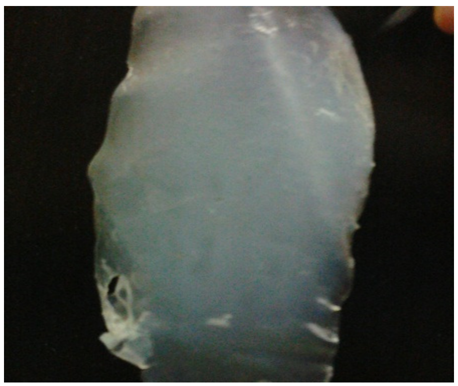


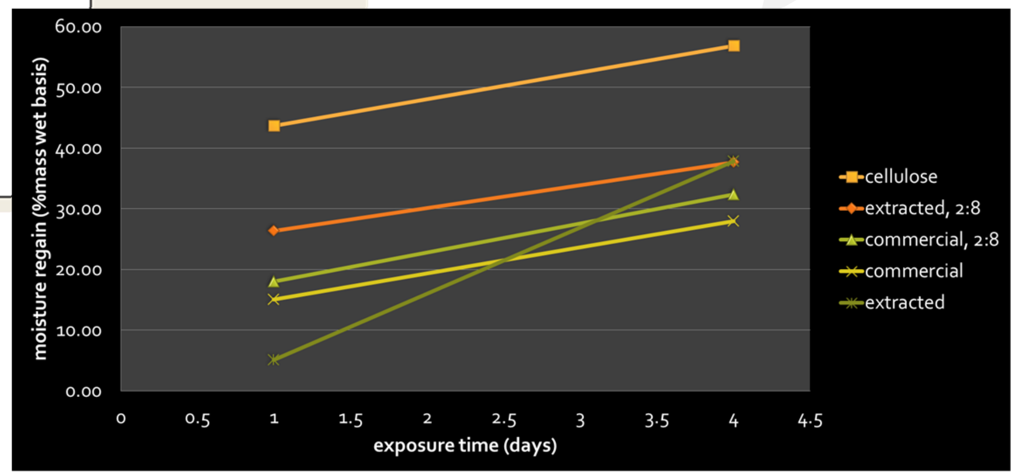

Expanded thermoplastic starch

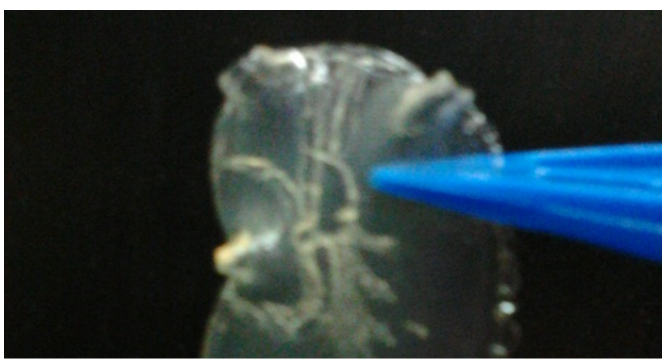

Expanded polystyrene

Condition	Actual (MPa)			Theoretical (MPa)
	Fiber Length		Average:	
	10mm	20mm		
Fiber volume, 0%	-	-	0.227	0.227
Fiber volume, 3%	0.2975 ± 0.090	0.5288± 0.128	0.409[a]	30.605
Fiber volume, 5%	1.0339 ± 0.199	0.5322 ± 0.046	0.755[b]	50.858
Fiber volume, 7%	0.3599 ± 0.143	0.5425 ± 0.115	0.454[a]	71.110









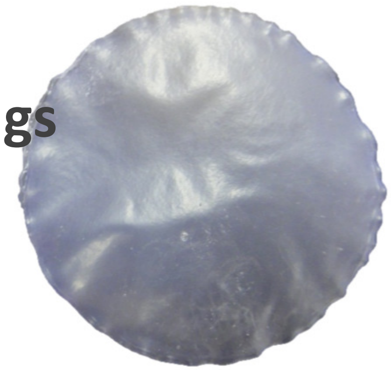
Synthesis of Biodegradable Cellulose-Chitin Polymer Blend Film from Recycled Agricultural Waste

Myra Ruth Poblete, MS EnE 2012, UPD

Local Research & Innovation

GOAL: To make a 100% bioplastic single-use plastic bags

Polymer	Tensile Strength (MPa)	Water Permeability* (kg*m/Pa*s*m^2)
Chitin: Cellulose	10 – 75	3.83×10^{-13}
Commercially Acquired Plastic Film (LDPE)	18.90	not determined
Polystyrene	40	8.00×10^{-13}
PET	55	1.06×10^{-15}



chitin-cellulose film

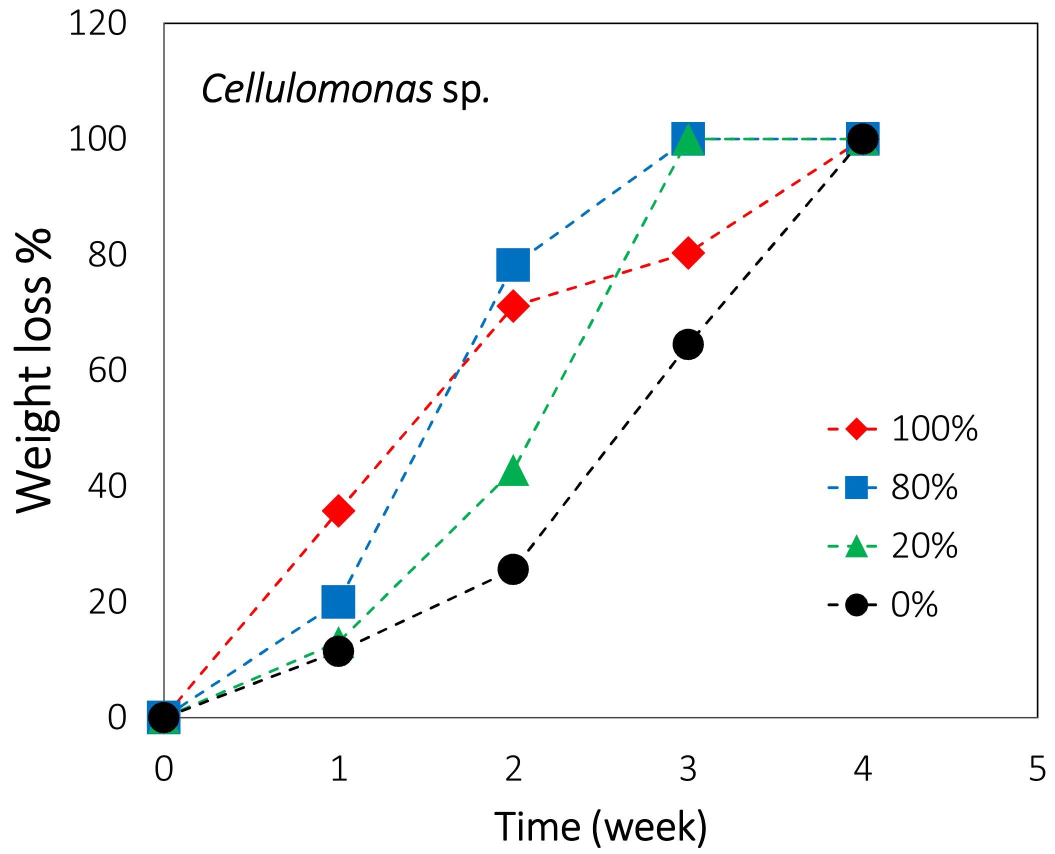
+ **Montmorillonite Nanoclay**

Poblete, Myra Ruth, and Leslie Joy Lanticse Diaz. "Synthesis of biodegradable cellulose-chitin polymer blend from portunus pelagicus." Advanced Materials Research 925 (2014): 379-384.

Lao, T L, L T Pengson, J Placido, and LJ L Diaz. "Synthesis of montmorillonite nanoclay reinforced chitin-cellulose nanocomposite film." 2018.

Biodegradation study of chitin-cellulose film

Moe Thazin Shwe,
PhD EnE 2014,
UPD



- Bioplastic Food Packaging -

A team effort between the industry and all research institutions is badly needed to save us all from destruction.

Search...

Engineering Research and Development for Technology

Serving the Nation through Human Resource Development

Thank You

Leslie Joy Lanticse-Diaz, Dr. Eng.

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