III SIAN – Simpósio de Alimentos e Nutrição

Nanoestruturas de resíduos agroindustriais para uso em embalagem de alimentos

Morsyleide de Freitas Rosa

18 e 19 de maio de 2017

Embrapa – Empresa Brasileira de Pesquisa agropecuária

Nanoestruturas de resíduos agroindustriais para uso em embalagem de alimentos

Embrapa

Polímeros sintéticos (plásticos)

Diversidade

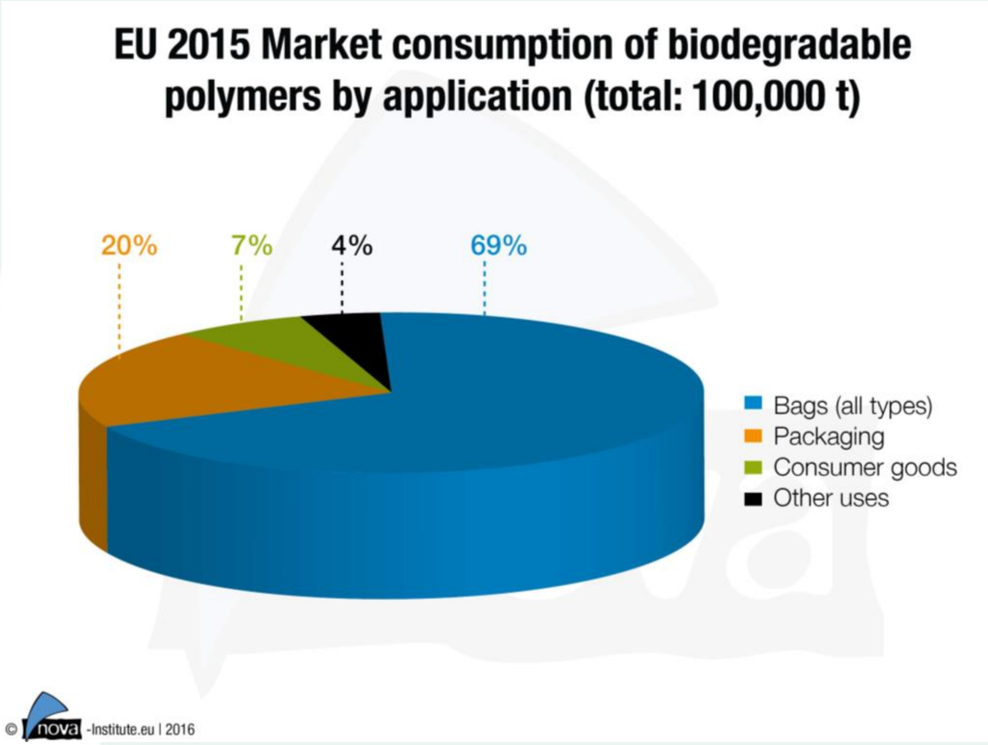
Baixo custo

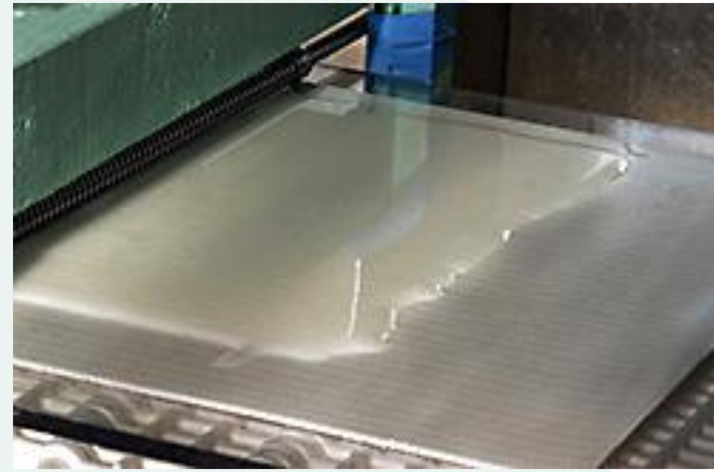
Alto apelo mercadológico

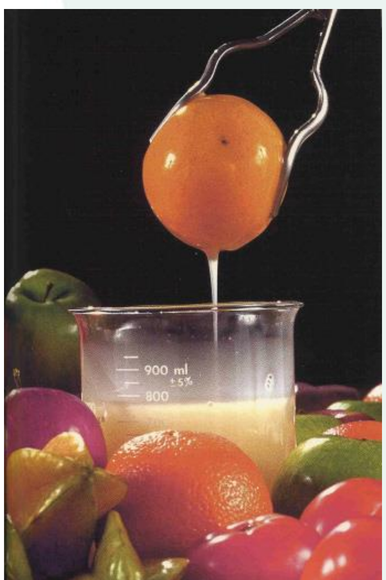
- transparência
- baixa densidade
- resistência a quebras

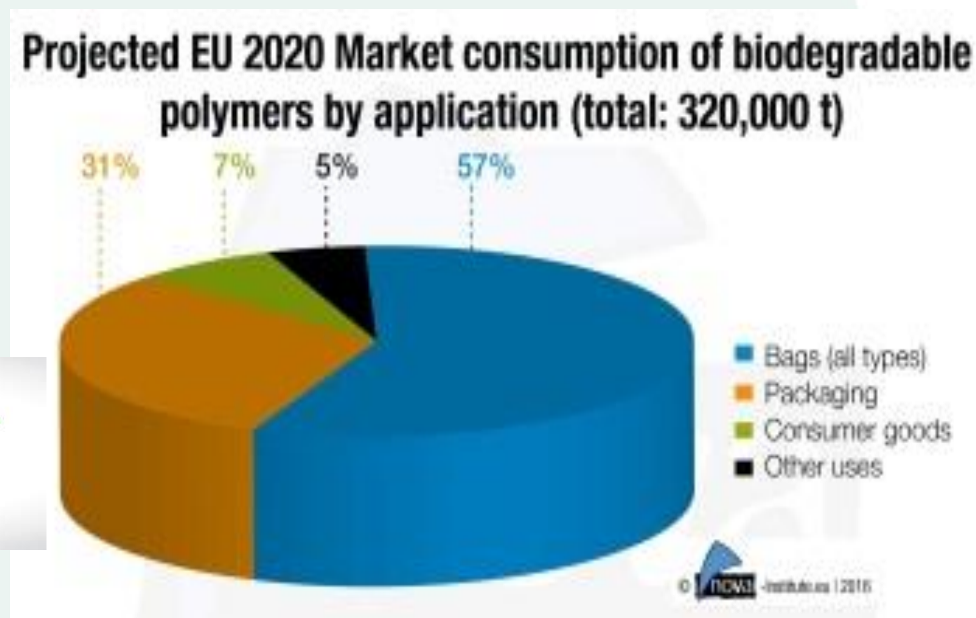
Não biodegradáveis

Dificuldades na reciclagem (diversidade de materiais)

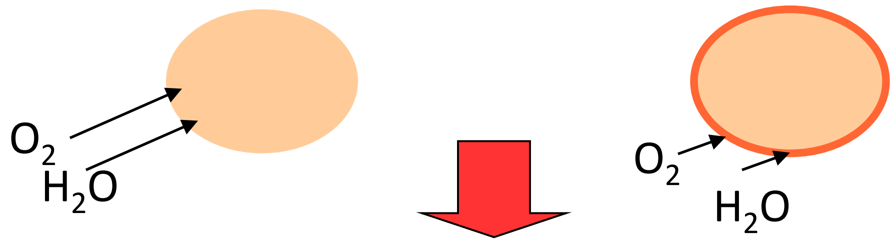

EU 2015 Market consumption of biodegradable polymers by application (total: 100,000 t)
20%
7%
4%
69%
Bags (all types)
Packaging
Consumer goods
Other uses
© nova-Institute.eu | 2016




900 ml
±5%
800


Projected EU 2020 Market consumption of biodegradable polymers by application (total: 320,000 t)
31%
7%
5%
57%
Bags (all types)
Packaging
Consumer goods
Other uses

Barreira (controle do transporte de O_2, CO_2, vapor de água)

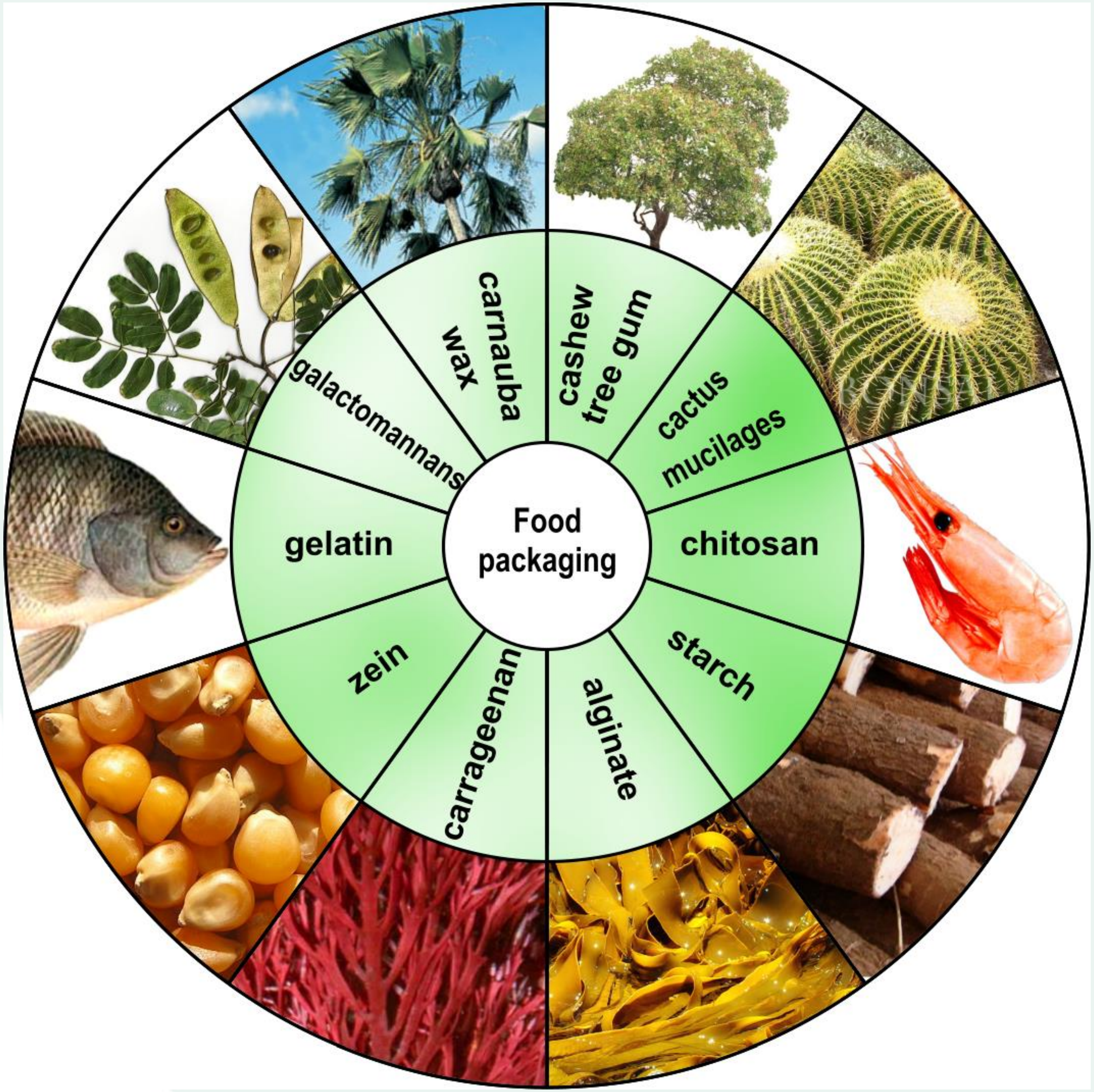


↓ taxas de oxidação, crescimento microbiano, alterações físicas

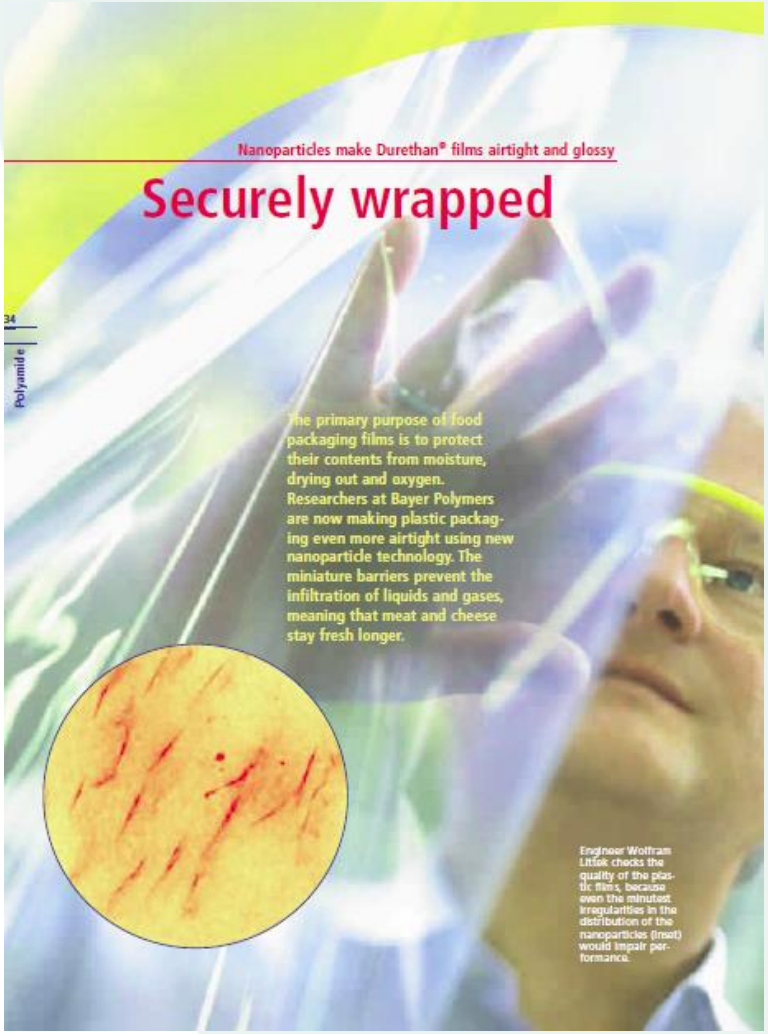
↓ volume necessário de embalagem sintética

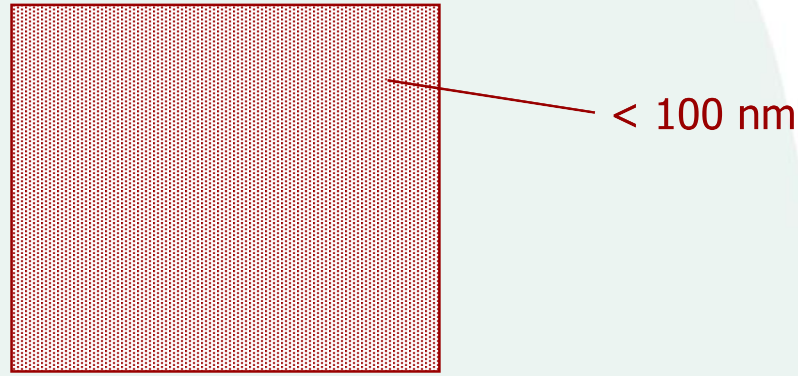
↓ **impacto ambiental**

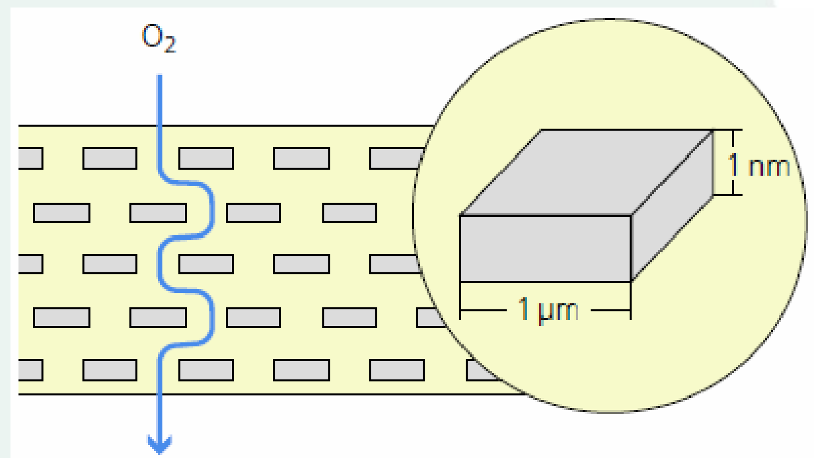
Azeredo, H.


Food packaging
carnauba wax
cashew tree gum
cactus mucilages
chitosan
starch
alginate
carrageenan
zein
gelatin
galactomannans

Nanocomposites







Embrapa

Nanocellulose is one of the major bio-nanomaterial as reinforcing filler in the polymeric nanocomposite industry, where annual global market size is projected to reach **$17.2 billion by 2025**.

Embrapa

Global Market for Nanocomposites (2017-2027) - Growing Use of Polymer Composites has Resulted in Increasing Demand for Nanomaterials - Research and Markets

May 17, 2017 05:07 AM Eastern Daylight Time

DUBLIN--(BUSINESS WIRE)--**Research and Markets** has announced the addition of the "The Global Market for Nanocomposites 2017-2027" report to their offering.

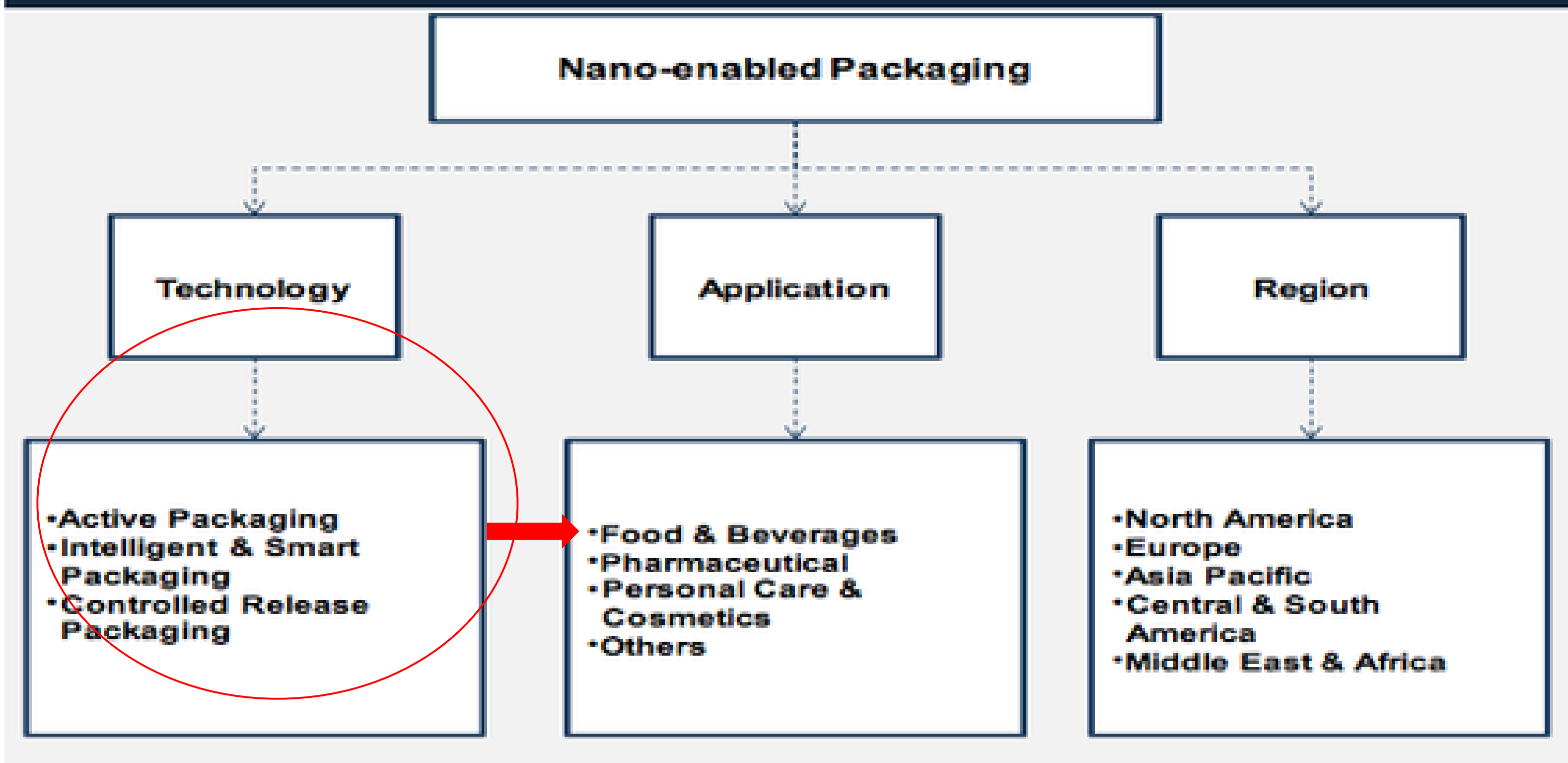
The growing use of polymer composites has resulted in increasing demand for nanomaterials, such as carbon nanotubes, graphene and nanocellulose, as companies seek alternatives to carbon fibre and petroleum-based packaging.

The need for continuous improvement in material performance is significant for engineering applications, with research focusing on new advanced materials with increased resistance to damage under operating conditions. This focus is more demanding in the case of structural composite materials, which are increasingly used in aeronautical/aerospace and automotive applications, as well as in civil infrastructure.

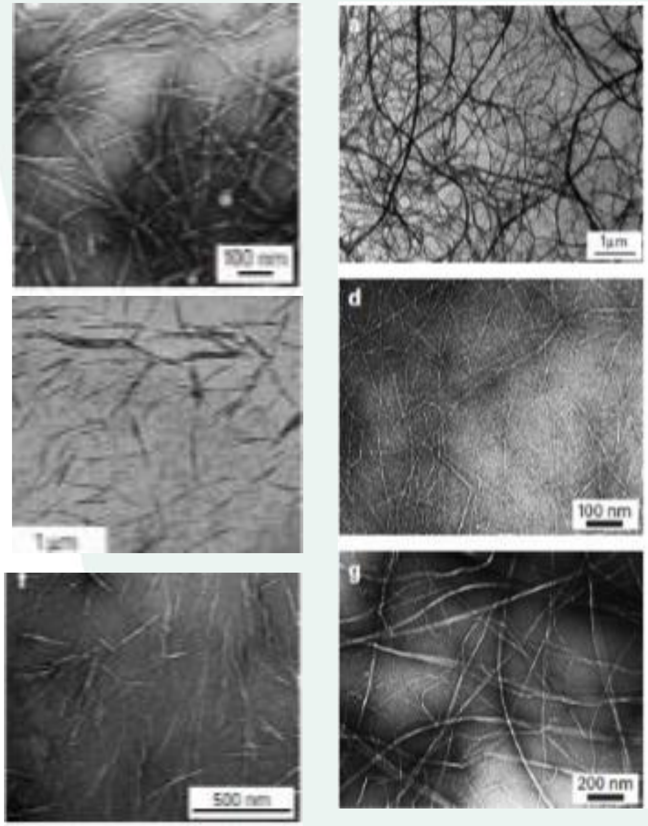
Global food packaging market $282.6bn in 2016

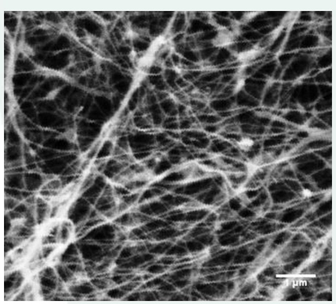
3.1 Market Segmentation

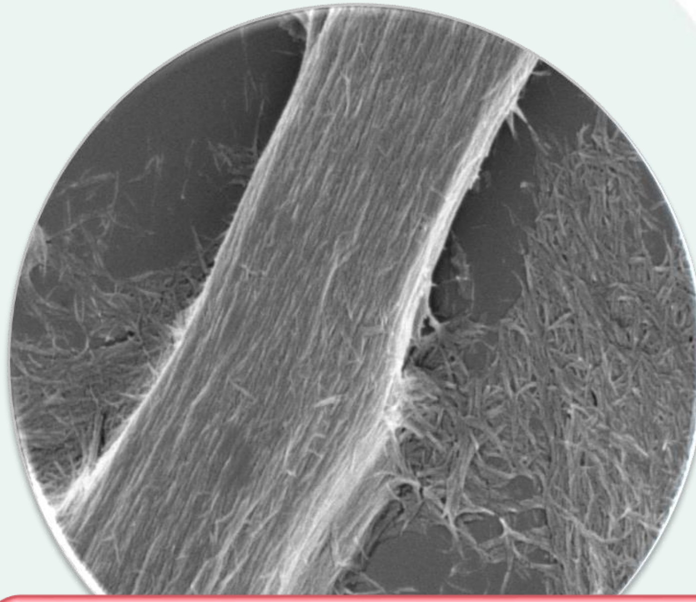
FIG. 1 Nano-enabled packaging market segmentation



Source: Nanotechnology Industries Association, PMMI, WHO, U.S. HHS, WPO, Company Publications, Primary Interviews, Grand View Research Inc.



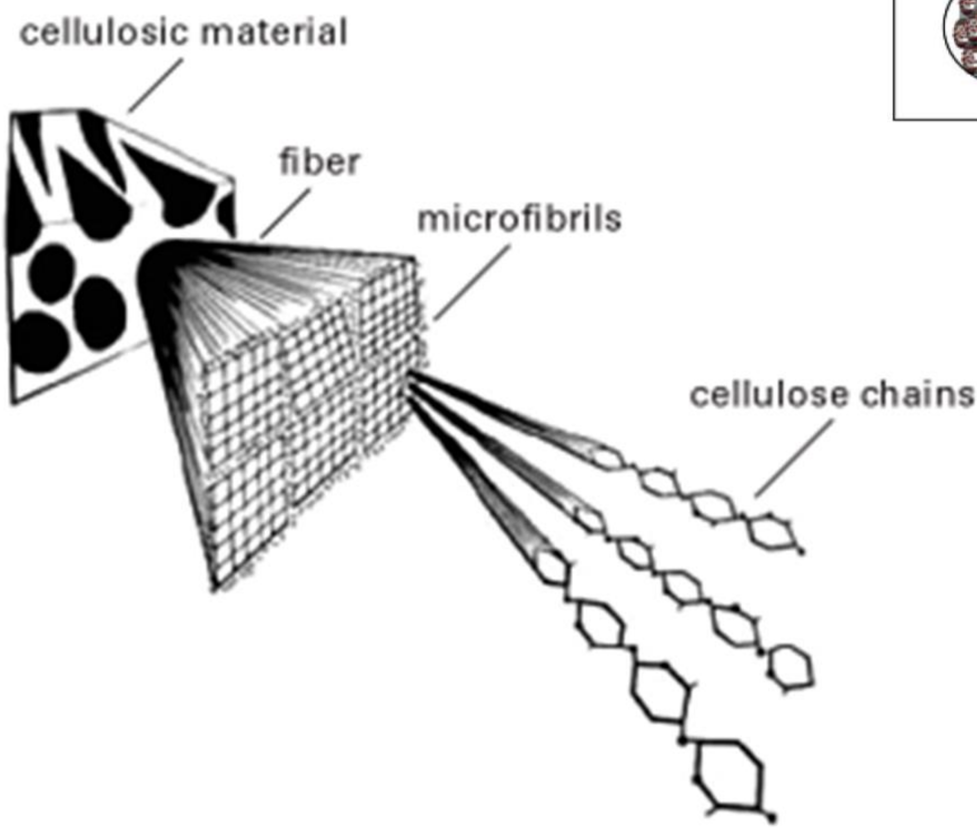




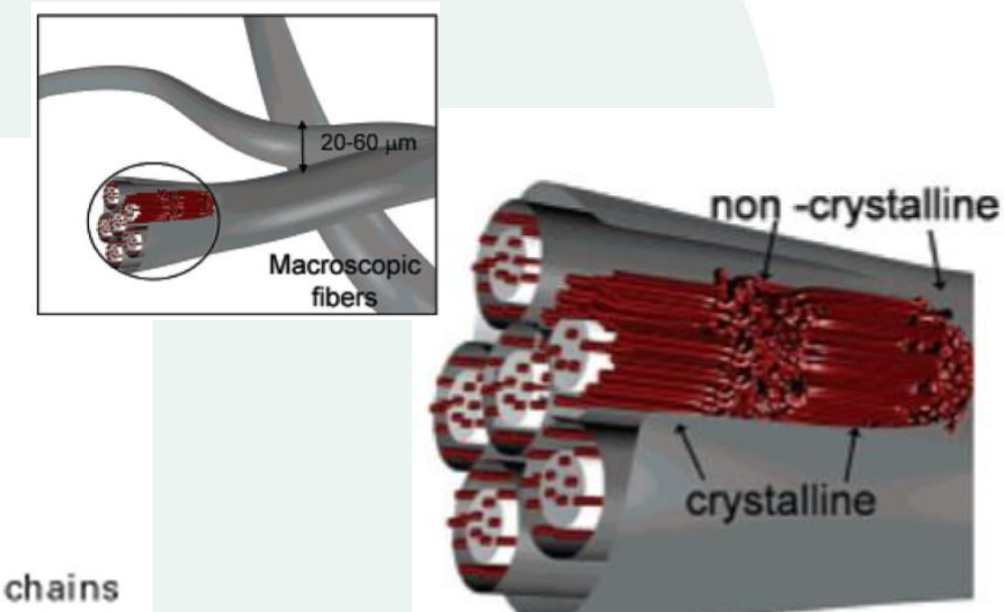
Nanocelluloses

Nanocelluloses

- ➢ Cellulosic nanoparticles



Schematic representation of the hierarchical structure of a lignocellulosic fiber. (Marchessault and Sundararajan, 1983)



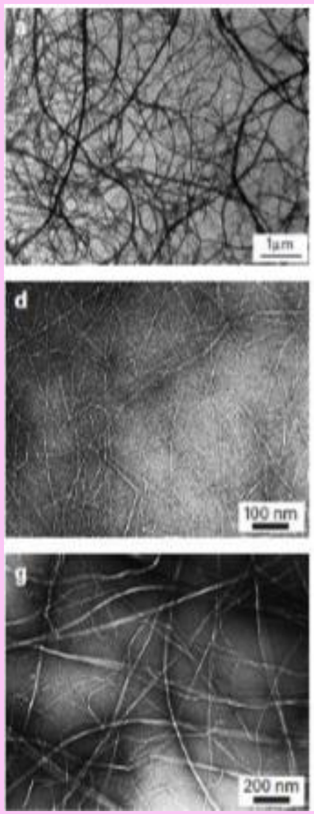
Paakko et al (2007)

Microfibrils have widths, lengths, shapes and crystallinities that may vary depending on the origin of cellulose.

Nanocelluloses

Top down approach

Mechanically
Cellulose nanofibrils (CNF)



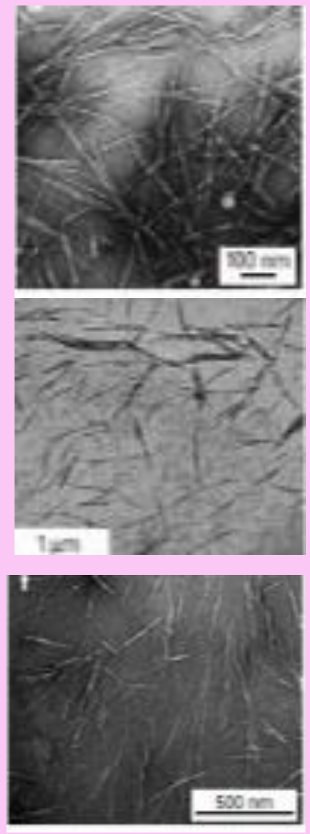
Width
5 – 30 nm

L/D > 50

(TAPPI, 2013)

Dufresne, 2012

Chemically
Cellulose nanocrystals (CNC)



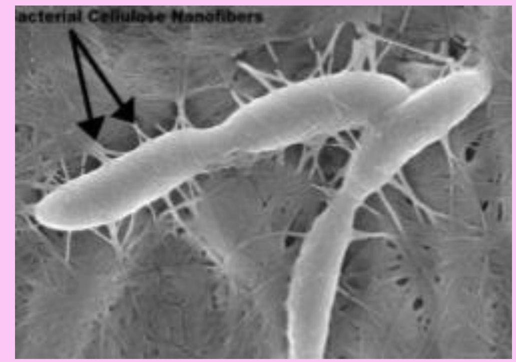
Width
3 – 10 nm

L/D > 5

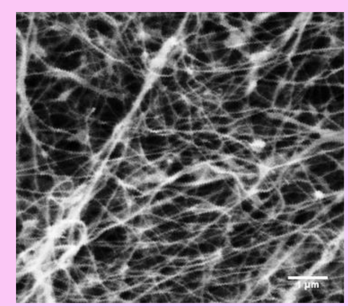
(TAPPI, 2013)

Bottom up approach

Biochemically
Bacterial cellulose (BC)

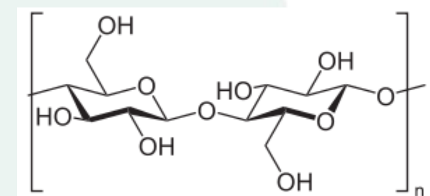


Width
24 – 28 nm



Why nanocelluloses?

Low density, low cost, high specific strength and modulus, renewability, biodegradability, availability in a variety of forms throughout the World, flexibility, non abrasive nature to processing equipment, non-toxicity, easiness to handle, high ability for surface modification.



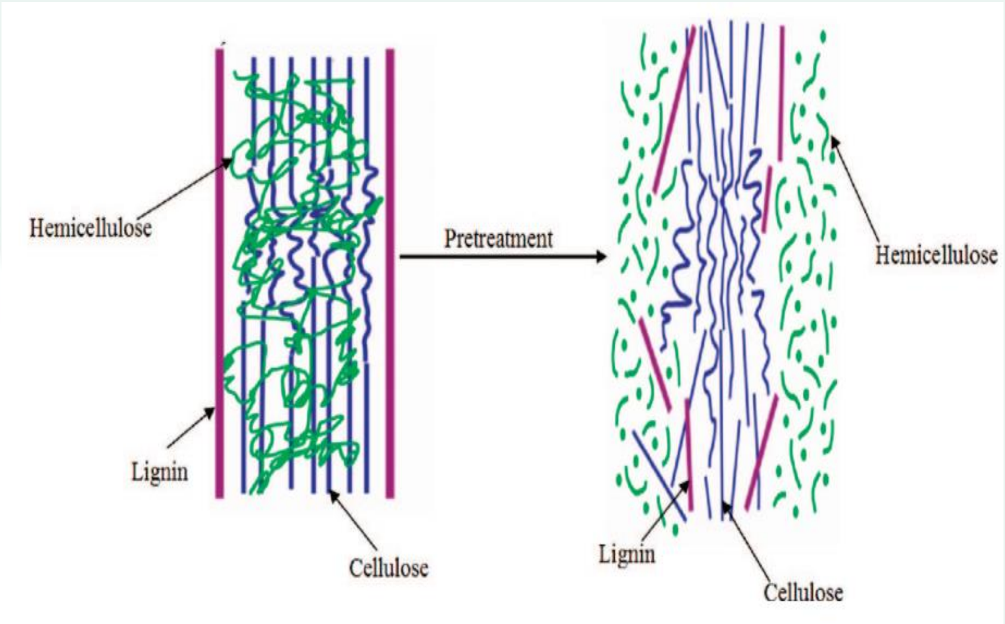
- Excellent mechanical properties
- High specific surface area
- **Low quantities → Huge effects**

Mechanical and barrier properties

Hydrophilic character :
poor adhesion and dispersion in non-polar matrix, high moisture absorption, limited thermal stability: low permissible temperatures of processing and use

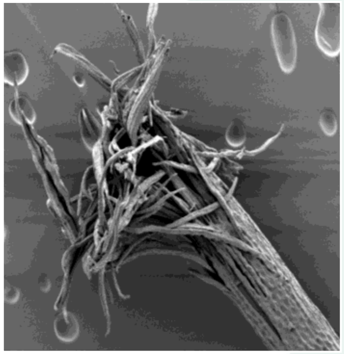
Dufresne, 2015

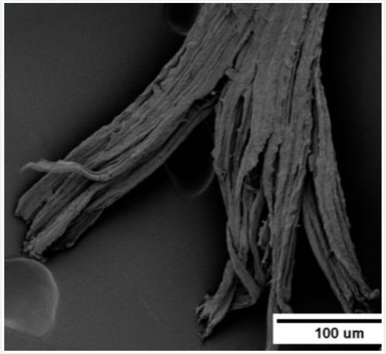
Preparation of nanocellulose: purification of cellulose

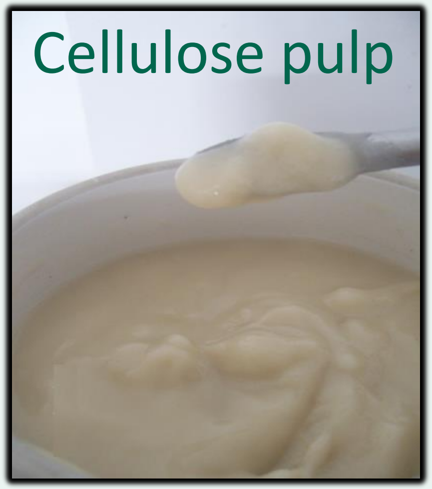


Pretreatments

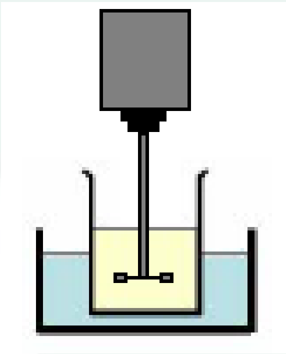
- Alkali extraction
- Bleaching
- Acetosolv
- Enzymatic hydrolysis
- Carboxymethylation
- TEMPO
- Cryocrushing
- Steam explosion



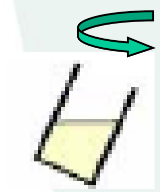




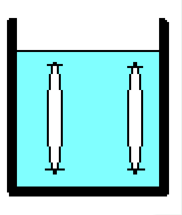
Preparation of cellulose nanocrystals – acid hydrolysis



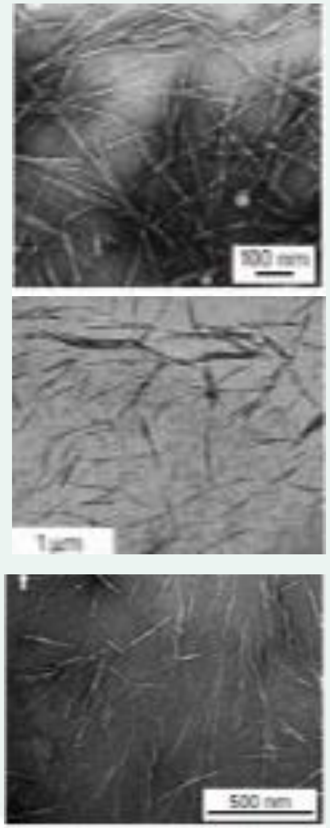
Cellulose pulp + acid sol. (t, T)

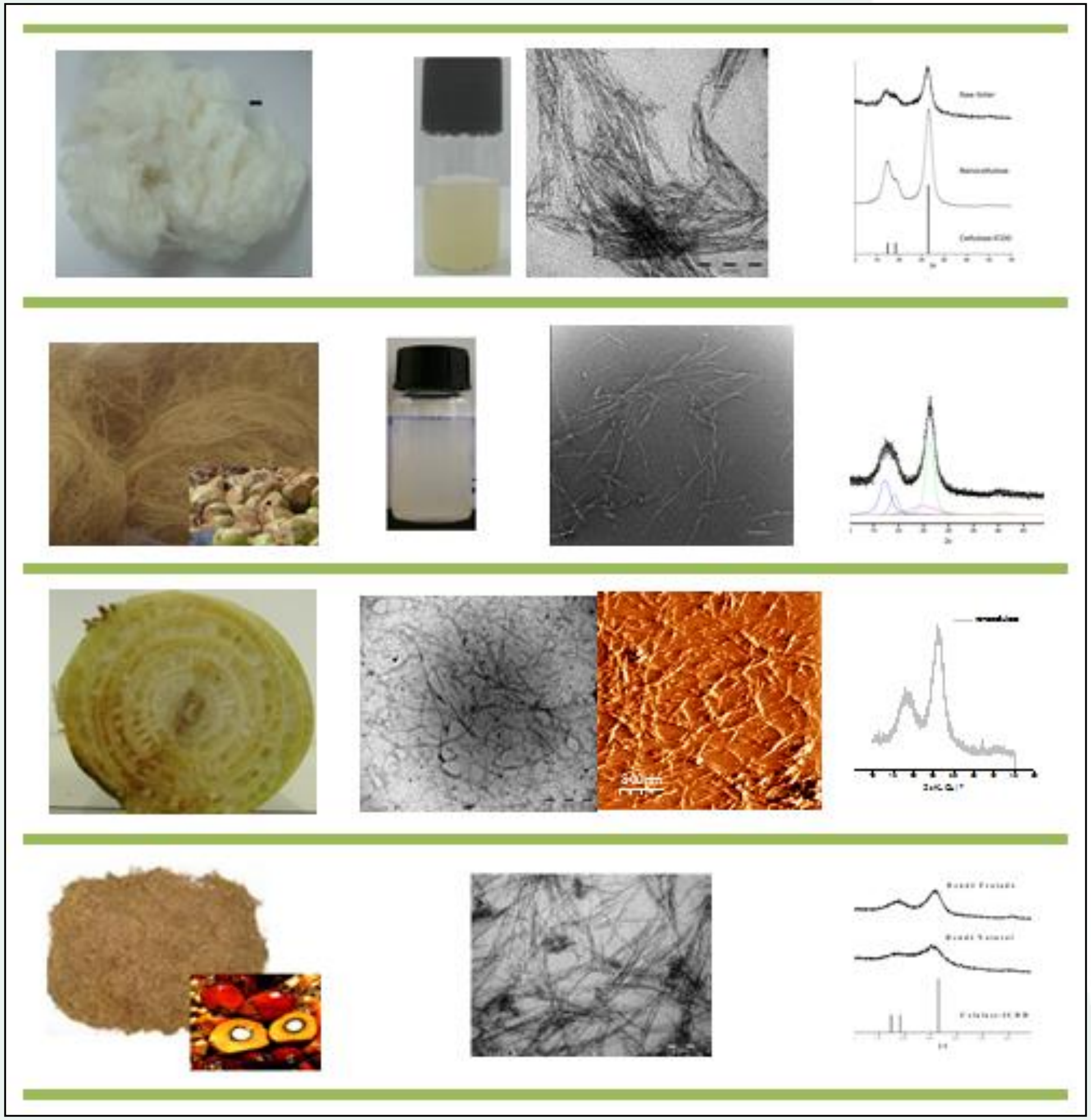


Centrifugation



Dialysis

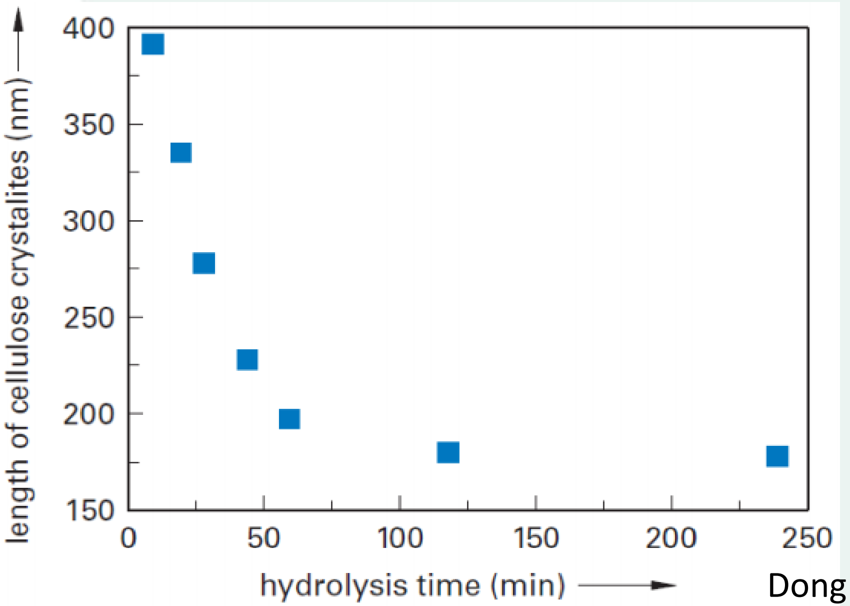




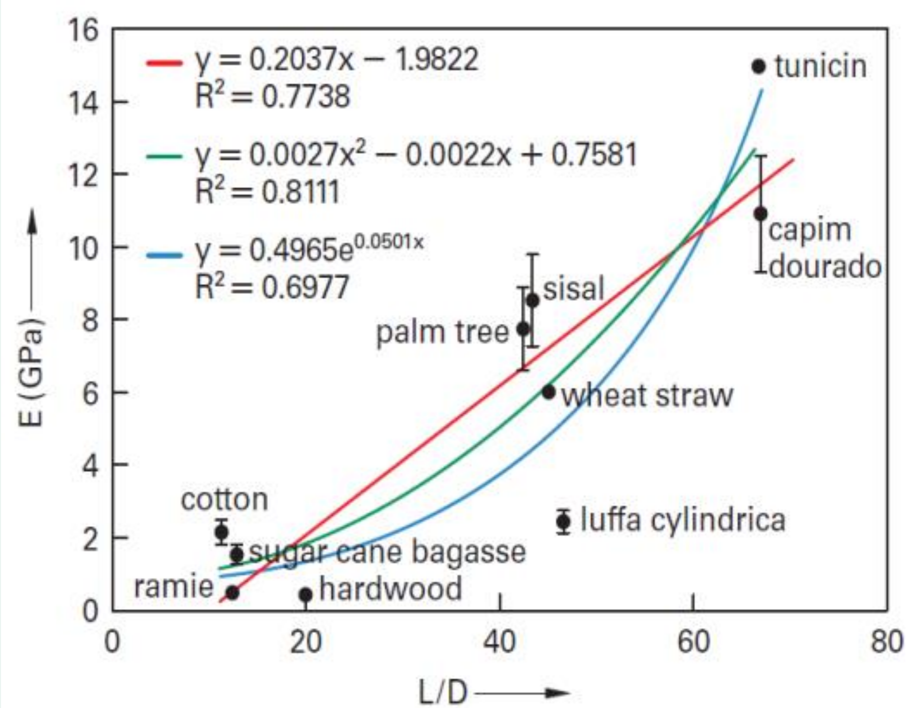
Bondeson et al, 2006

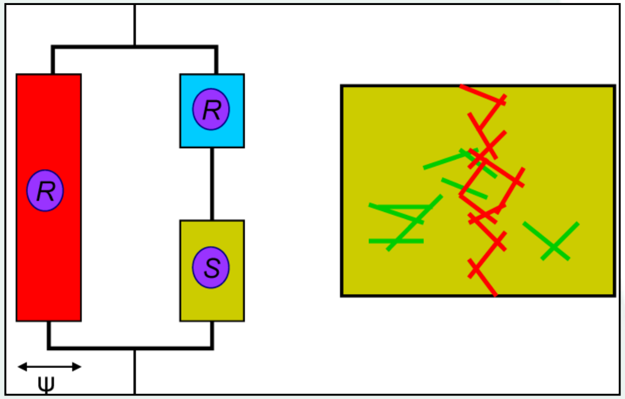
Preparation of cellulose nanocrystals – acid hydrolysis

Factors affecting performance of nanocellulose:
- aspect ratio: L/D
- percolation effects: φv = 0.7/(L/D)



Dong et al., 1998

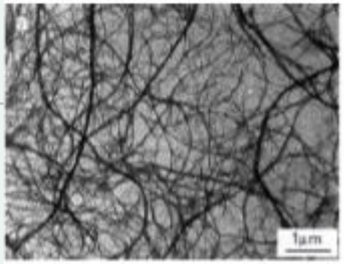




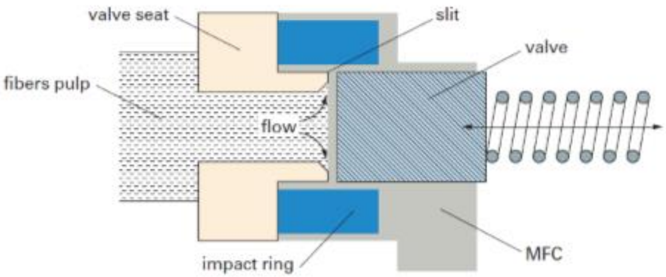
Dufresne, 2010

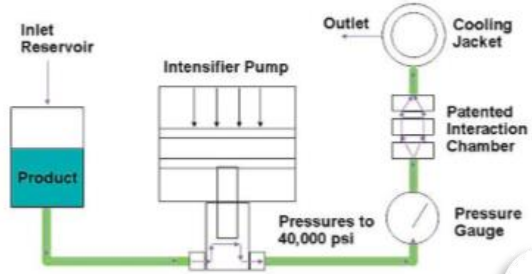
- Suspension stability (Zeta potential)
- Thermal stability - TGA

Preparation of cellulose nanofibrils

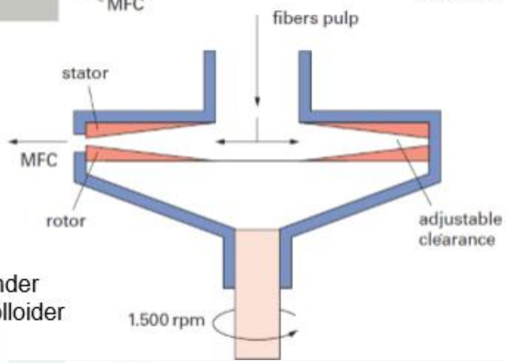


Scheme of the homogenizer





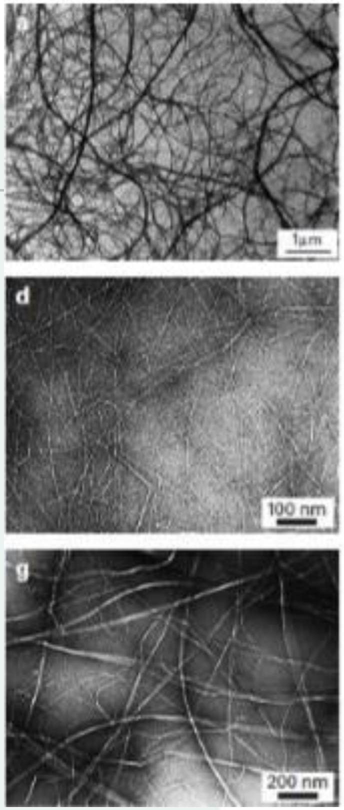
Microfluidizer (Microfluidics Inc., USA)

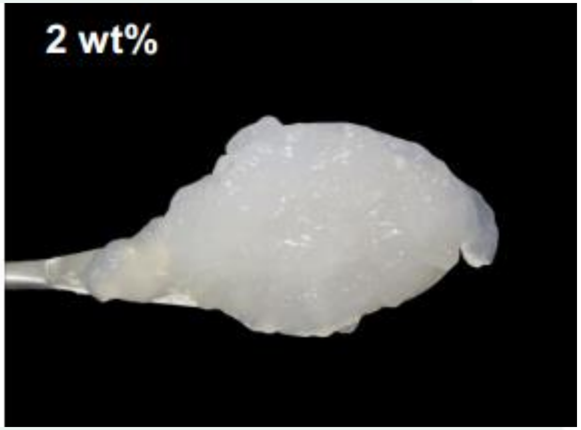


Ultra-fine friction grinder
Masuko Supermasscolloider

Cellulose nanofibrils - Degree of fibrillation

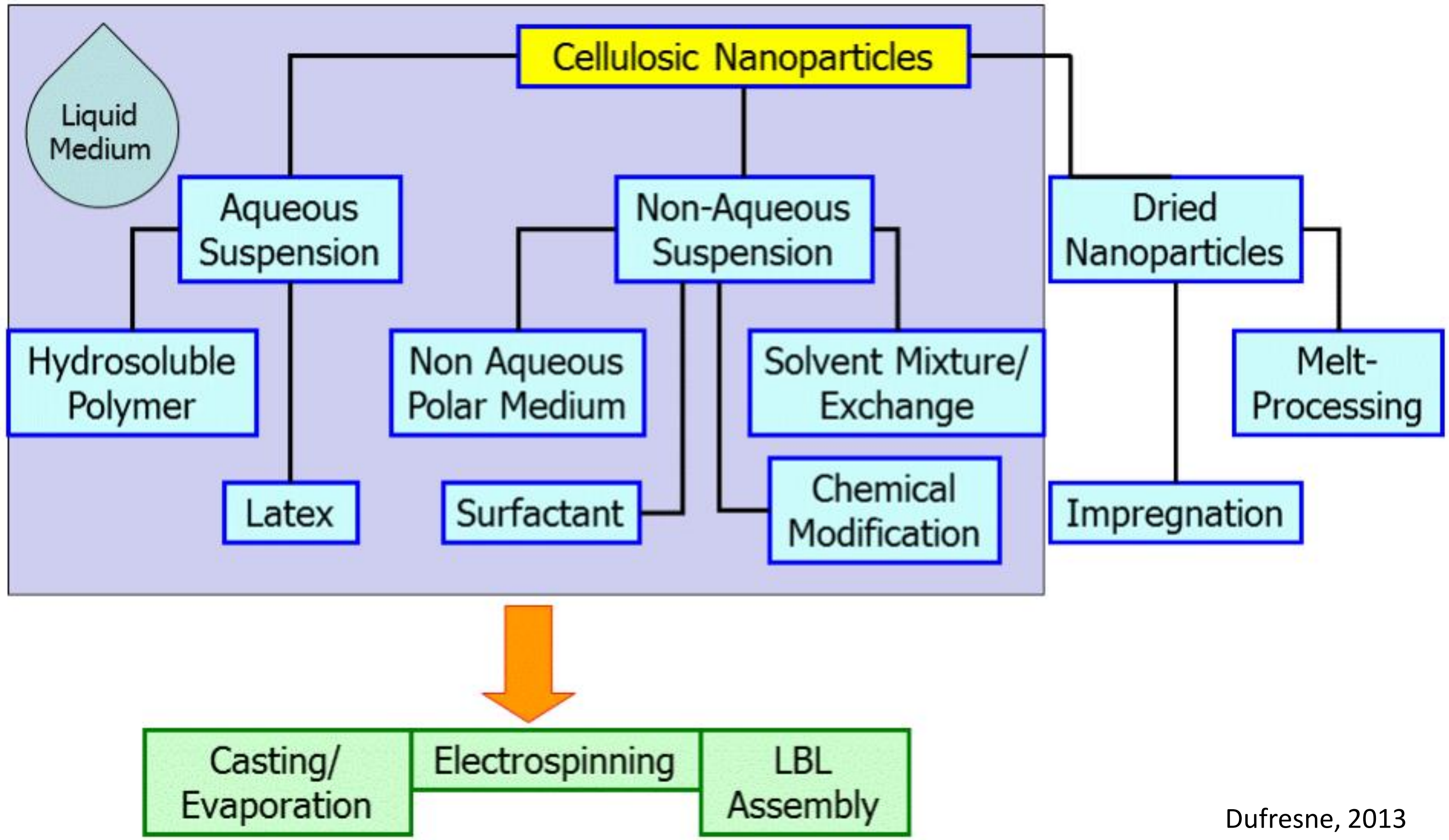
- Turbidity of the suspension (more transparent)
- Viscosity of the suspension (increase)
- Porosity of films (decrease) and density (increase)
- Mechanical strength of films (increase)
- Water retention (increase)
- Degree of polymerization (decrease)
- Specific surface area (increase)
- Degree of crystallinity (increase)





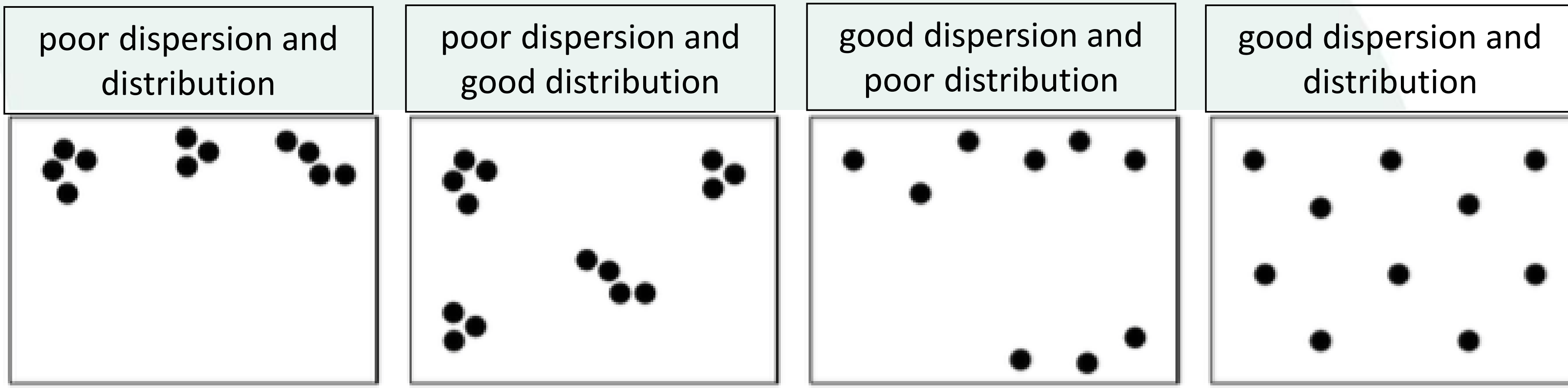
Lavoine et al.,2012

Processing of nanocomposites

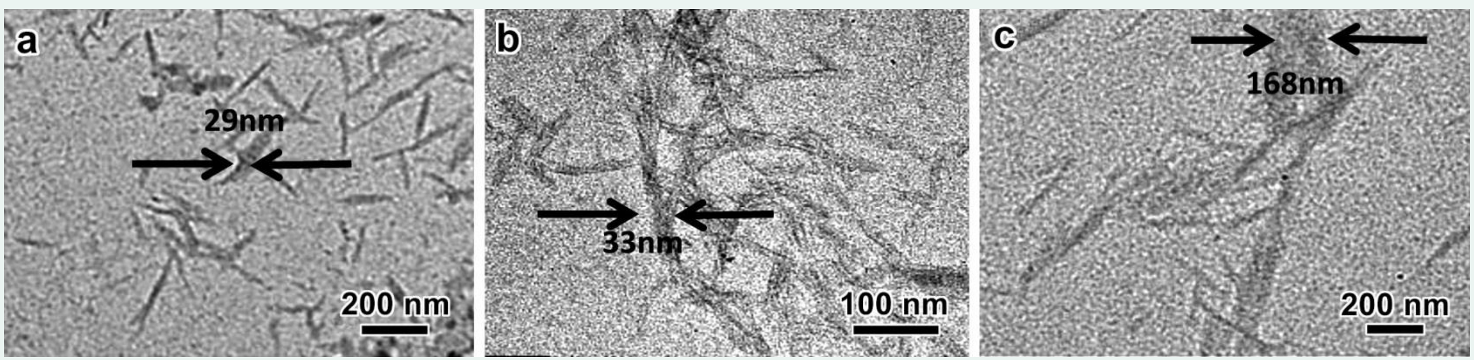


Dufresne, 2013

Concept of dispersion and distribution of nanoparticles in nanocomposites



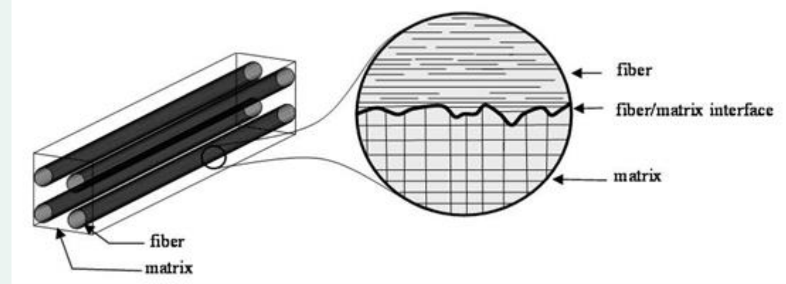
Dufresne, 2015

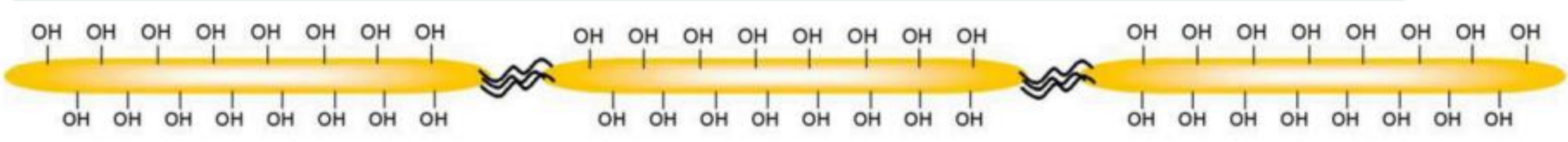


“hornification”

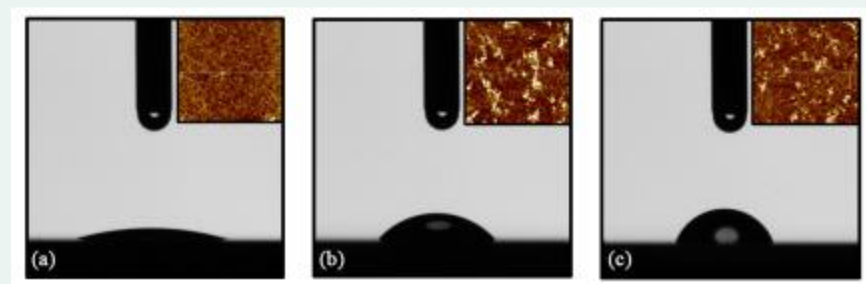
The main strategy to prevent this aggregation has been the introduction of a steric barrier or electrostatic groups to block cooperative hydrogen bonding of the cellulose chains

Compatibilization – Surface modification

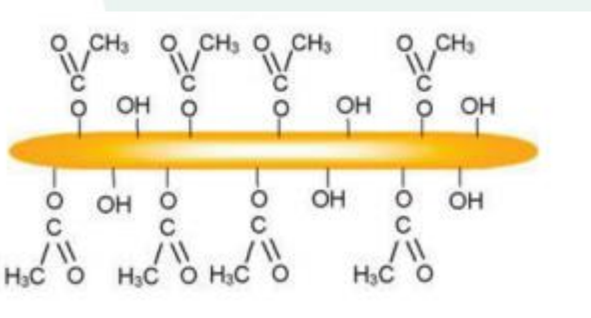




Abundance of hydroxyl groups at the surface of nanocelluloses makes it possible to adjust their hydrophilic–hydrophobic balance.



Acetylation



Braun, 2009

- Silylation
- Grafting
- TEMPO Mediated Oxidation
- ...

Embrapa

Nanocellulose from coconut fibers

Carbohydrate Polymers 81 (2010) 83–92

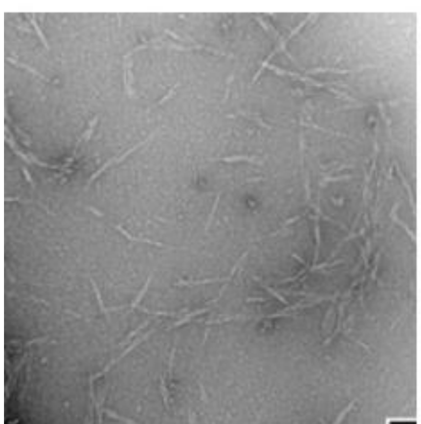
Contents lists available at ScienceDirect

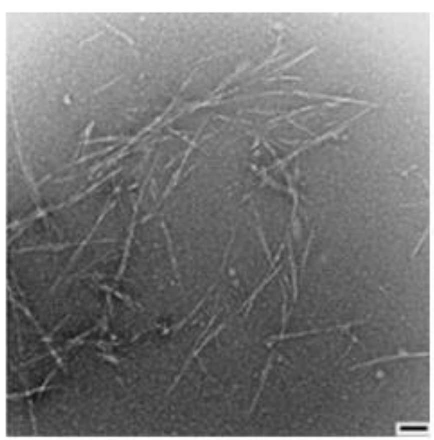
Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior

M.F. Rosa [a,b], E.S. Medeiros [b,c], J.A. Malmonge [d], K.S. Gregorski [b], D.F. Wood [b], L.H.C. Mattoso [c], G. Glenn [b], W.J. Orts [b], S.H. Imam [b,*]





CrI = 62 - 66%

L/D = 35 - 44

Contents lists available at ScienceDirect
Carbohydrate Polymers
journal homepage: www.elsevier.com/locate/carbpol

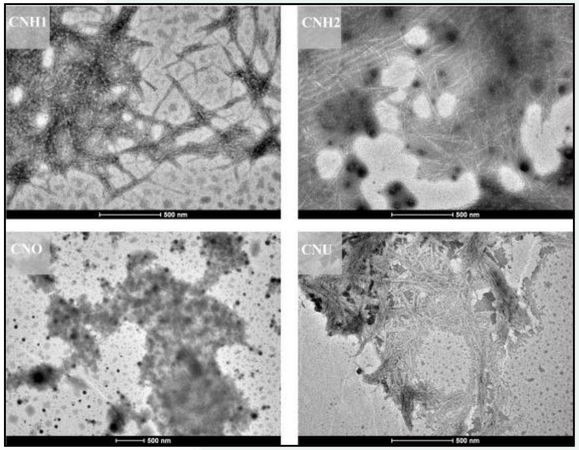
A novel green approach for the preparation of cellulose nanowhiskers from white coir

Diego M. Nascimento[a], Jessica S. Almeida[b], Amanda F. Dias[c], Maria Clea B. Figueirêdo[d], João Paulo S. Morais[e], Judith P.A. Feitosa[a], Morsyleide de F. Rosa[d,*]

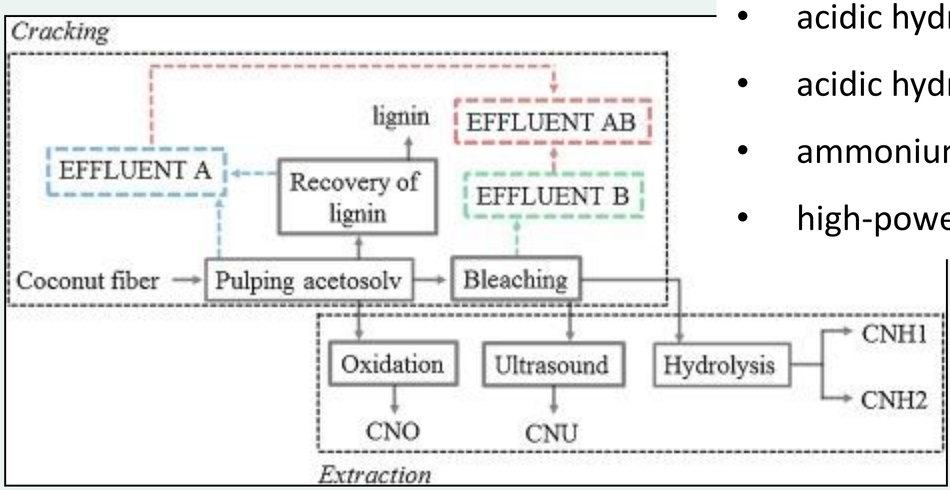
Products 93 (2016) 66–75
ilable at ScienceDirect
Industrial Crops and Products
journal homepage: www.elsevier.com/locate/indcrop

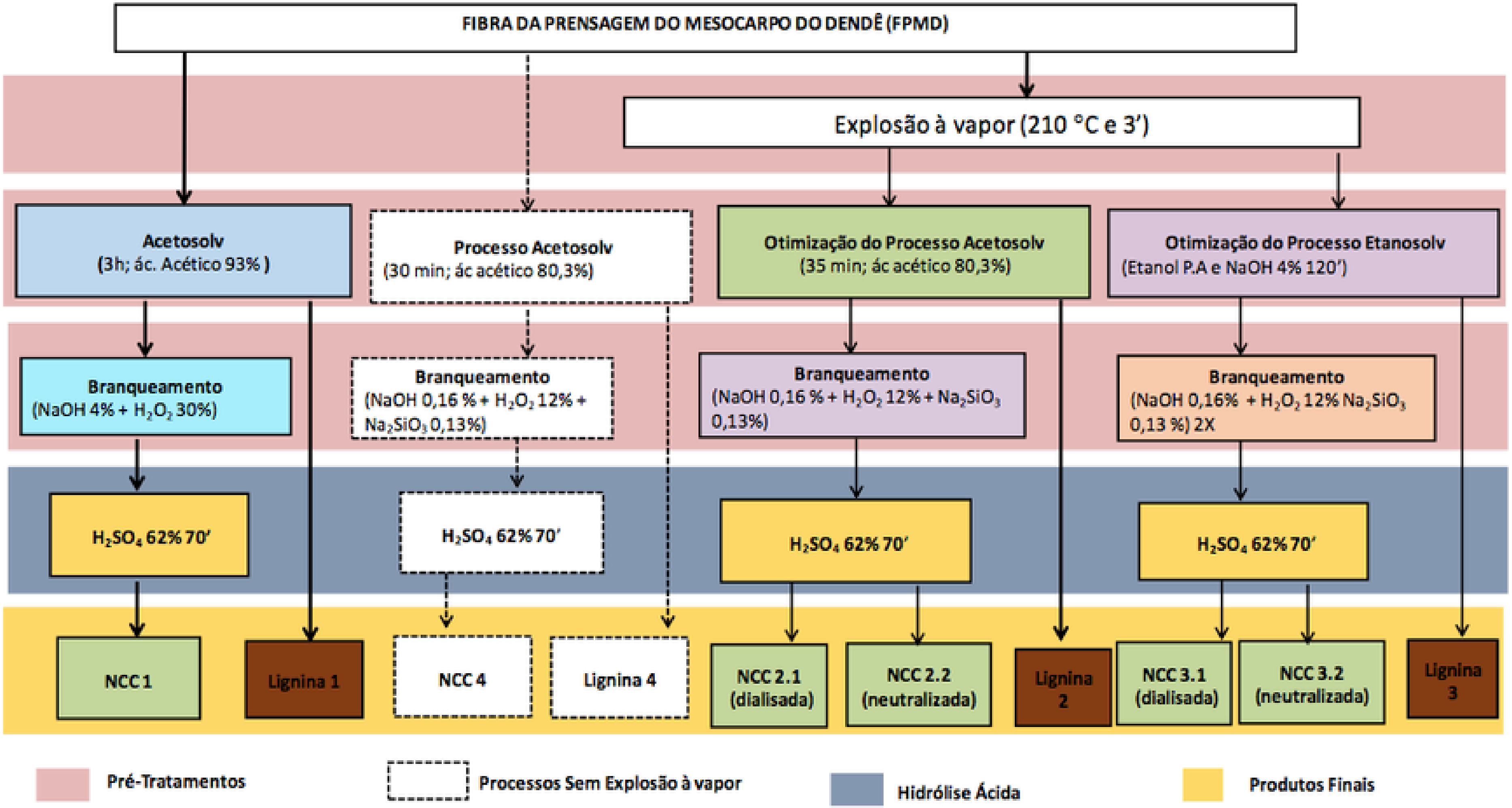
A comprehensive approach for obtaining cellulose nanocrystal from coconut fiber. Part I: Proposition of technological pathways

Diego M. do Nascimento[a,*], Jessica S. Almeida[b], Maria do S. Vale[c], Renato C. Leitão[c], Celli R. Muniz[c], Maria Clea B. de Figueirêdo[c], João Paulo S. Morais[d], Morsyleide de F. Rosa[c,*]



- acidic hydrolysis [H_2SO_4] ↑
- acidic hydrolysis [H_2SO_4] ↓
- ammonium persulfate oxidation
- high-power ultrasound





FIBRA DA PRENSAGEM DO MESOCARPO DO DENDÊ (FPMD)
Explosão à vapor (210 °C e 3')
Acetosolv (3h; ác. Acético 93%)
Processo Acetosolv (30 min; ác acético 80,3%)
Otimização do Processo Acetosolv (35 min; ác acético 80,3%)
Otimização do Processo Etanosolv (Etanol P.A e NaOH 4% 120')
Branqueamento (NaOH 4% + H_2O_2 30%)
Branqueamento (NaOH 0,16 % + H_2O_2 12% + Na_2SiO_3 0,13%)
Branqueamento (NaOH 0,16 % + H_2O_2 12% + Na_2SiO_3 0,13%)
Branqueamento (NaOH 0,16% + H_2O_2 12% Na_2SiO_3 0,13 %) 2X
H_2SO_4 62% 70'
H_2SO_4 62% 70'
H_2SO_4 62% 70'
H_2SO_4 62% 70'
NCC 1
Lignina 1
NCC 4
Lignina 4
NCC 2.1 (dialisada)
NCC 2.2 (neutralizada)
Lignina 2
NCC 3.1 (dialisada)
NCC 3.2 (neutralizada)
Lignina 3
Pré-Tratamentos
Processos Sem Explosão à vapor
Hidrólise Ácida
Produtos Finais

LWT - Food Science and Technology 46 (2012) 294–297

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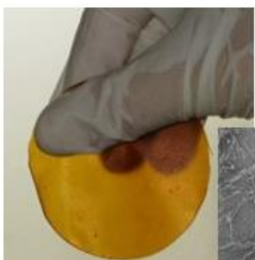
LWT - Food Science and Technology

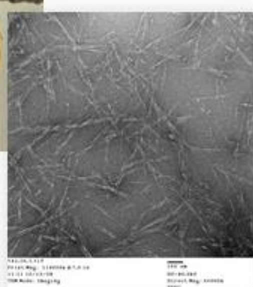
journal homepage: www.elsevier.com/locate/lwt

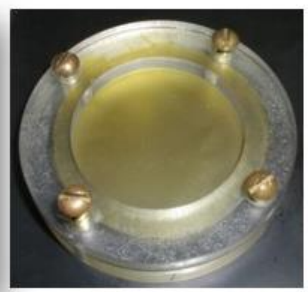
ELSEVIER

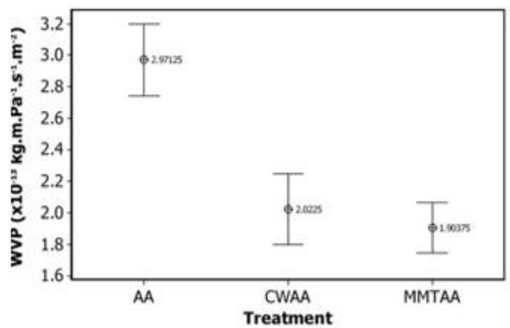
Edible films from alginate-acerola puree reinforced with cellulose whiskers

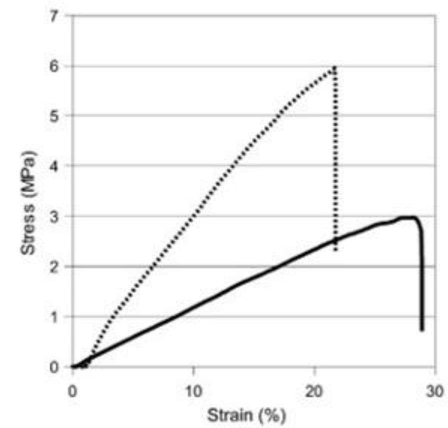
Henriette M.C. Azeredo [a,*], Kelvi W.E. Miranda [b], Morsyleide F. Rosa [a], Diego M. Nascimento [b], Márcia R. de Moura [c]

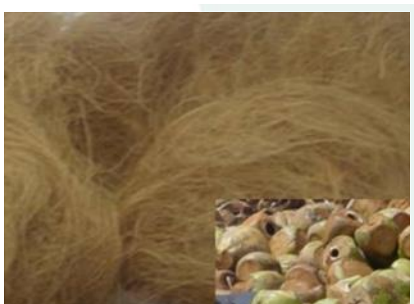












The incorporation of CNC to alginate-acerola films improved WV barrier, as well as tensile strength and modulus, indicating that CNC improves the film applicability as edible packaging.

Carbohydrate Polymers 91 (2013) 229–235

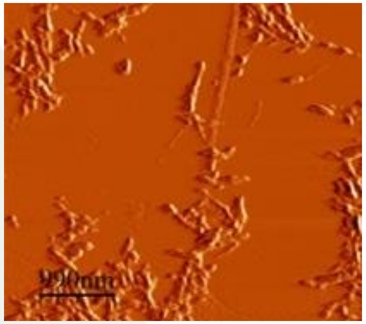
Contents lists available at SciVerse ScienceDirect

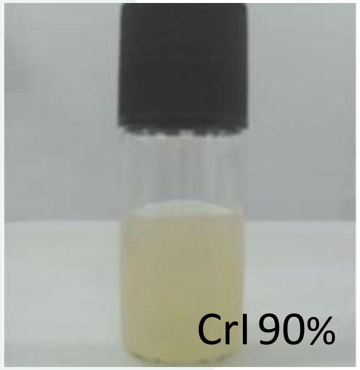
Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Extraction and characterization of nanocellulose structures from raw cotton linter

João Paulo Saraiva Morais[a,*], Morsyleide de Freitas Rosa[b], Men de sá Moreira de Souza Filho[b], Lidyane Dias Nascimento[a], Diego Magalhães do Nascimento[b], Ana Ribeiro Cassales[b]





L/D = 19

Zeta potential: - 45 mV

Food Hydrocolloids 41 (2014) 113–118

Contents lists available at ScienceDirect

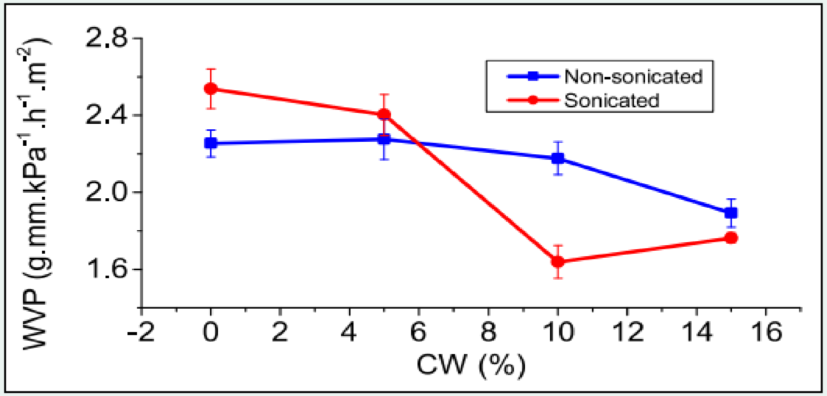
Food Hydrocolloids

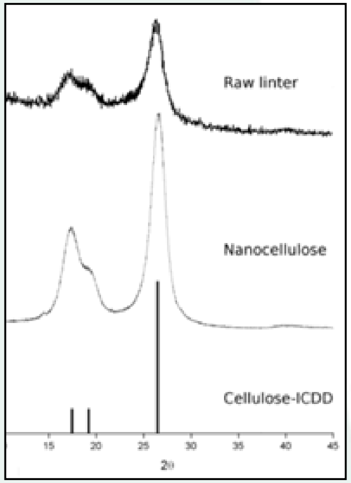
journal homepage: www.elsevier.com/locate/foodhyd

Fish gelatin films as affected by cellulose whiskers and sonication

CrossMark

Talita M. Santos[a], Men de Sá M. Souza Filho[b], Carlos Alberto Caceres[c], Morsyleide F. Rosa[b], João Paulo S. Morais[d], Alaídes M.B. Pinto[a], Henriette M.C. Azeredo[e,*]





Carbohydrate Polymers 112 (2014) 165–172

Contents lists available at ScienceDirect

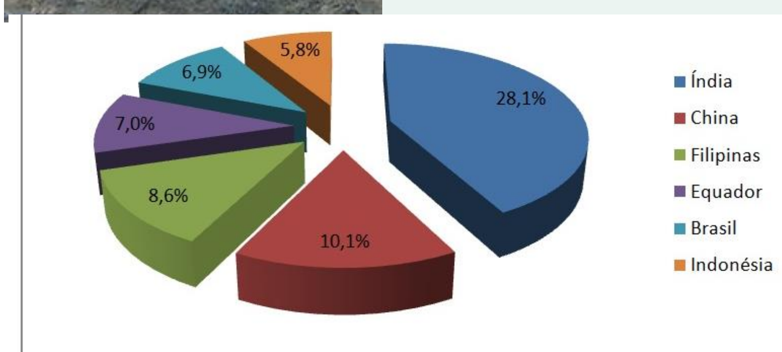
Carbohydrate Polymers

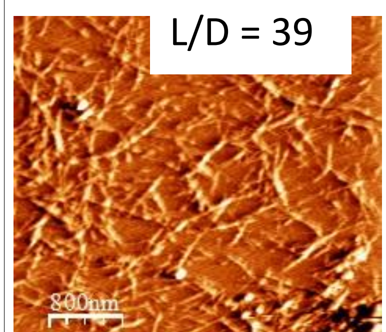
journal homepage: www.elsevier.com/locate/carbpol

Improvement of polyvinyl alcohol properties by adding nanocrystalline cellulose isolated from banana pseudostems

André Luís S. Pereira[a], Diego M. do Nascimento[b], Men de sá M. Souza Filho[c], João Paulo S. Morais[d], Niedja F. Vasconcelos[b], Judith P.A. Feitosa[b], Ana Iraidy S. Brígida[e], Morsyleide de F. Rosa[c,*]

1 billion tons of wasted banana





1% CNC → 100% tensile strength ↑

5% CNC → 30% WVP ↓

Carbohydrate Polymers 164 (2017) 317–324

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

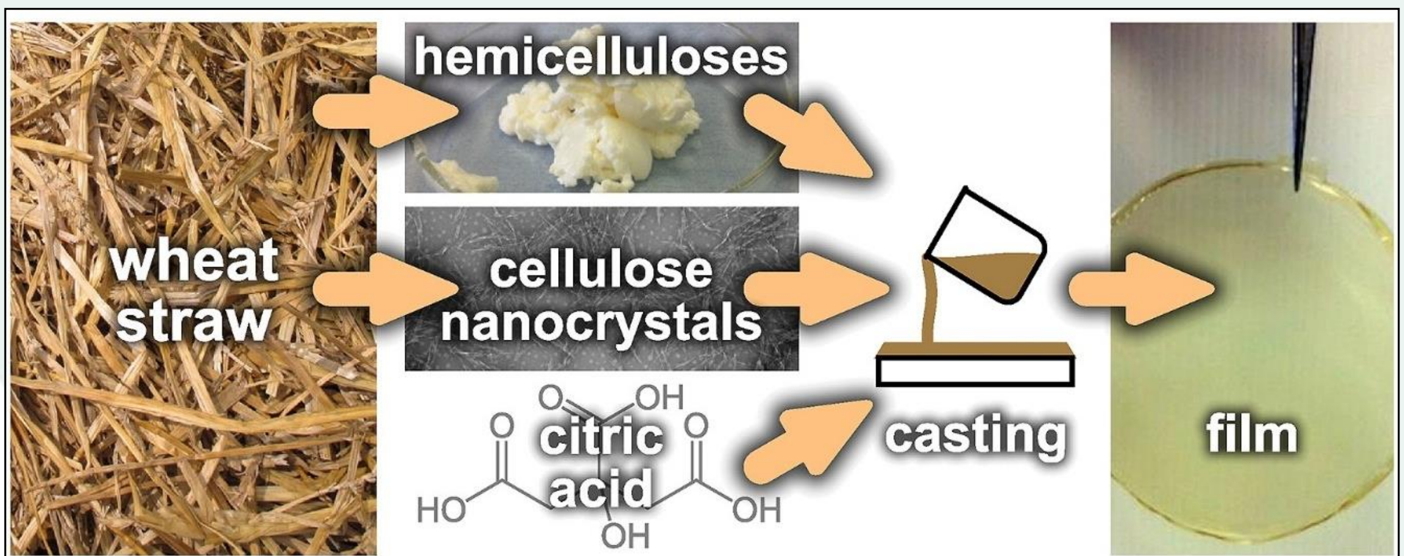
Wheat straw hemicelluloses added with cellulose nanocrystals and citric acid. Effect on film physical properties

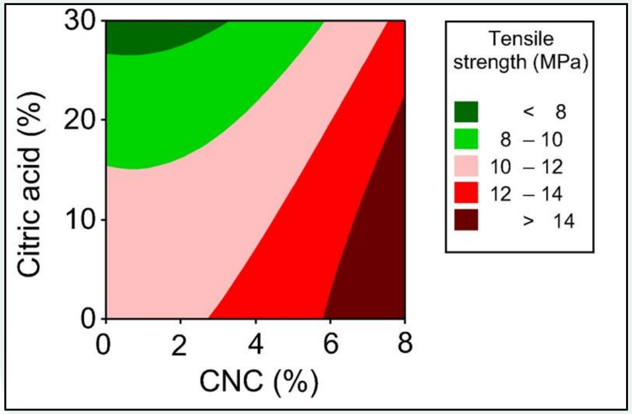
Paulo H.F. Pereira[a], Keith W. Waldron[b], David R. Wilson[b], Arcelina P. Cunha[c], Edy S. de Brito[d], Tigressa H.S. Rodrigues[d], Morsyleide F. Rosa[d], Henriette M.C. Azeredo[d,*]

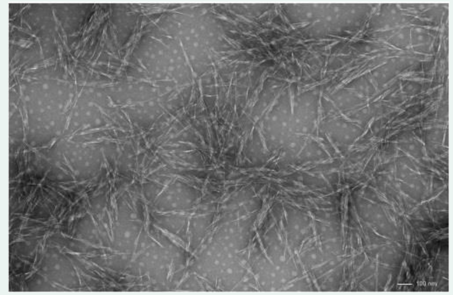
- World wheat consumption for 2015/2016: 710 million tons
- Wheat straw may be estimated as about 920 million tons

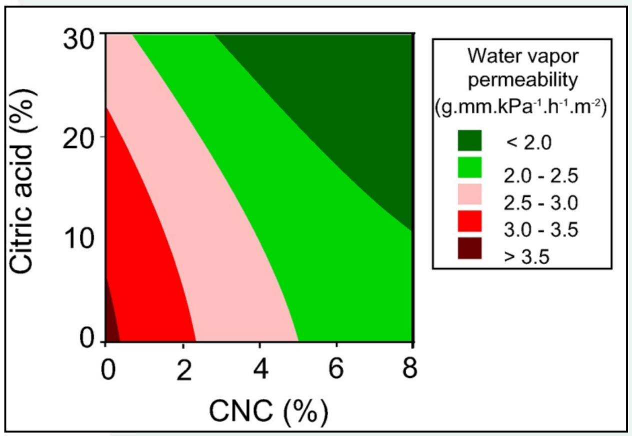
Polysaccharide films: poor tensile properties, highly permeable to water vapor and sensitive to water

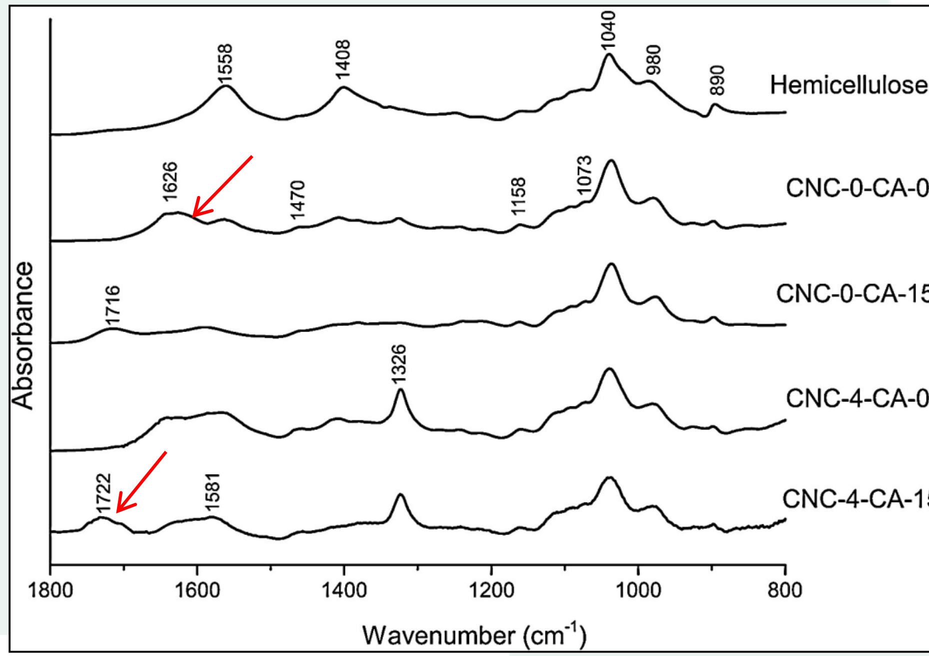
- 3 g WSH, 0.9 g glycerol
- CNC contents: 0–8 wt% on WSH
- Citric acid: 0–30 wt% on WSH







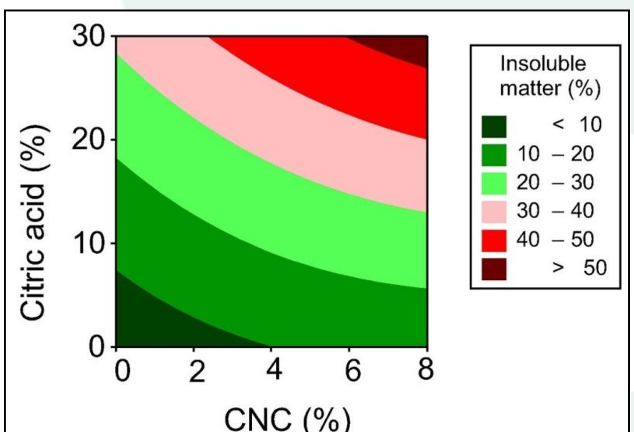




$L/D = 20$

$\varphi v = 0.7/(L/D)$

$\varphi v = 4.4$ wt%



1626 cm^{-1} - absorbed water

1710–1720 cm^{-1} - ester C=O stretching vibration

30% of fruit weight

International Journal of Biological Macromolecules 101 (2017) 1–8

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

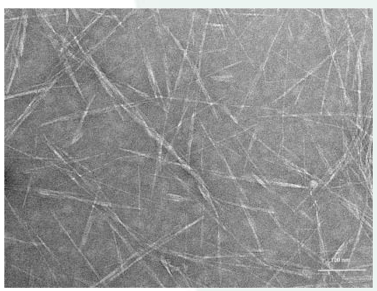
journal homepage: www.elsevier.com/locate/ijbiomac

Bionanocomposite films based on polysaccharides from banana peels

Túlio Ítalo S. Oliveira [a], Morsyleide F. Rosa [b], Michael J. Ridout [c], Kathryn Cross [c], Edy S. Brito [b], Lorena M.A. Silva [b], Selma E. Mazzetto [a], Keith W. Waldron [c], Henriette M.C. Azeredo [b,*]

CNC contents around **5 wt%** provided the films with improved tensile properties, water resistance, and water vapor barrier.

Even if the water solubility of the films has been decreased by CNC and citric acid, the obtained films still presented high water solubility, and should be used for applications which do not require a high water resistance – such as for primary packaging for products which will be protected from moisture by a secondary packaging.



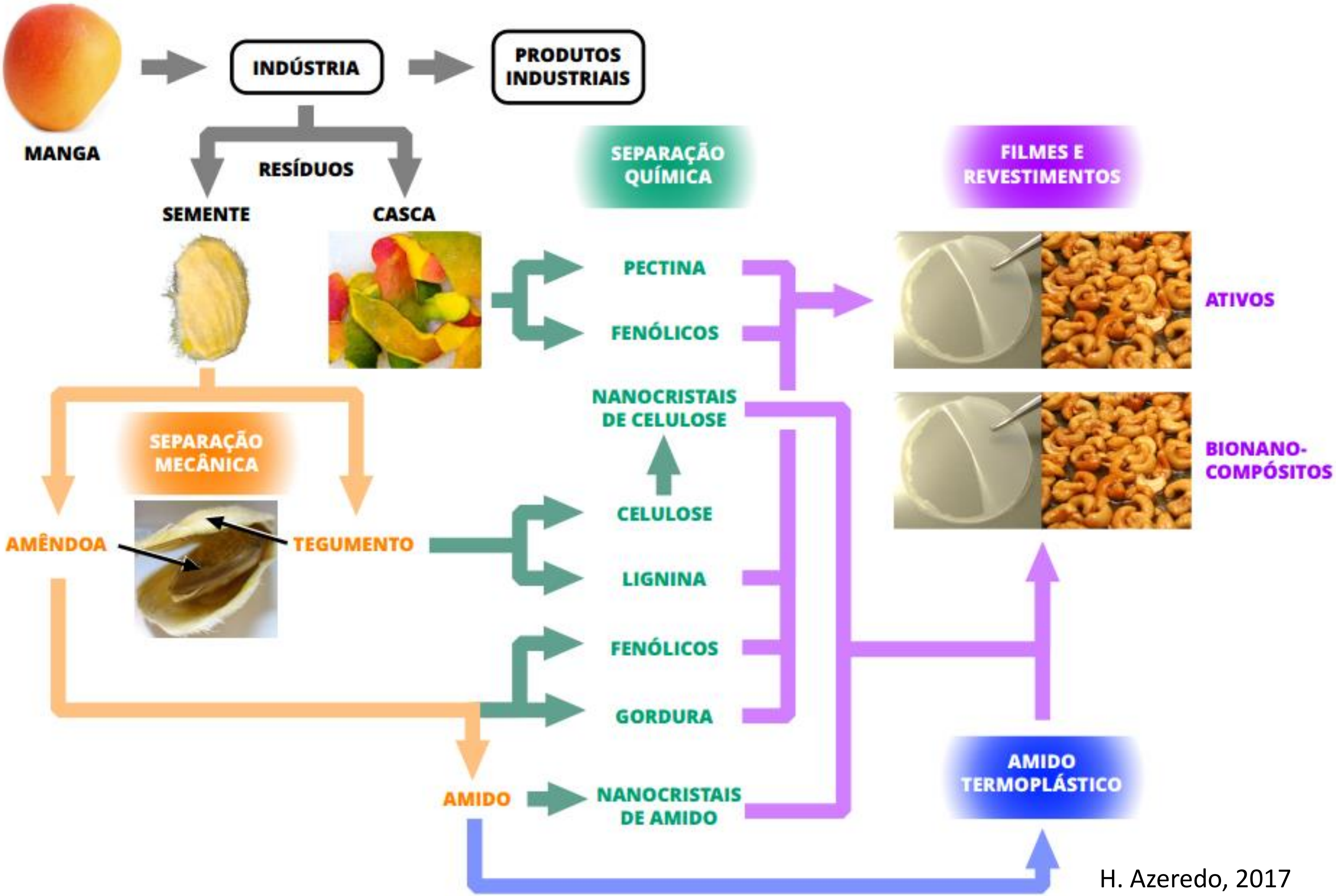
L/D = 54

$\varphi v = 0.7/(L/D)$

$\varphi v = 1.8$ wt%

Embrapa

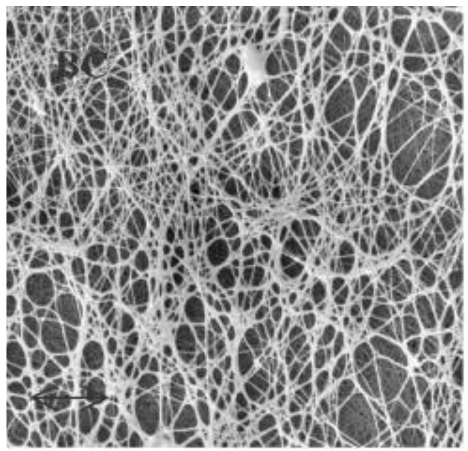
Aproveitamento integral dos resíduos do processamento da manga

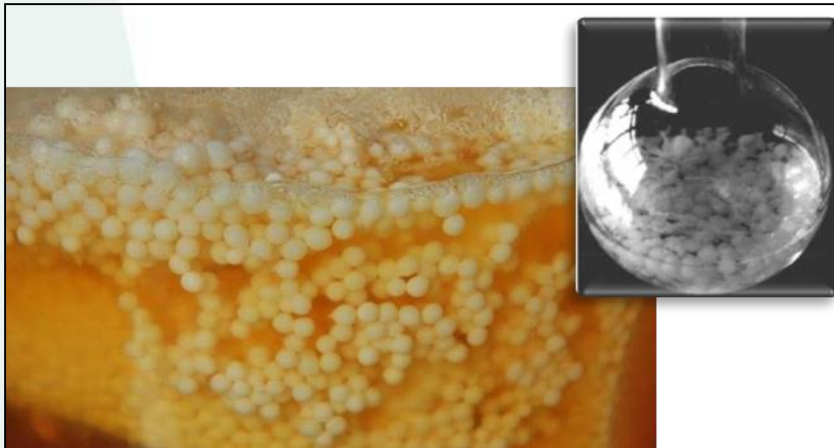


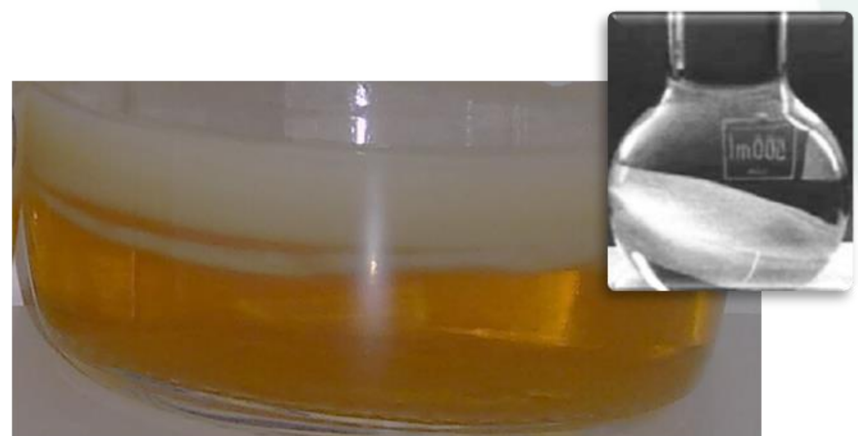
H. Azeredo, 2017

BACTERIAL CELLULOSE

- high porosity
- high water retention capacity
- high mechanical strength
- low density
- biocompatibility
- non-toxicity
- biodegradability







Bacterial cellulose from agroindustrial sources

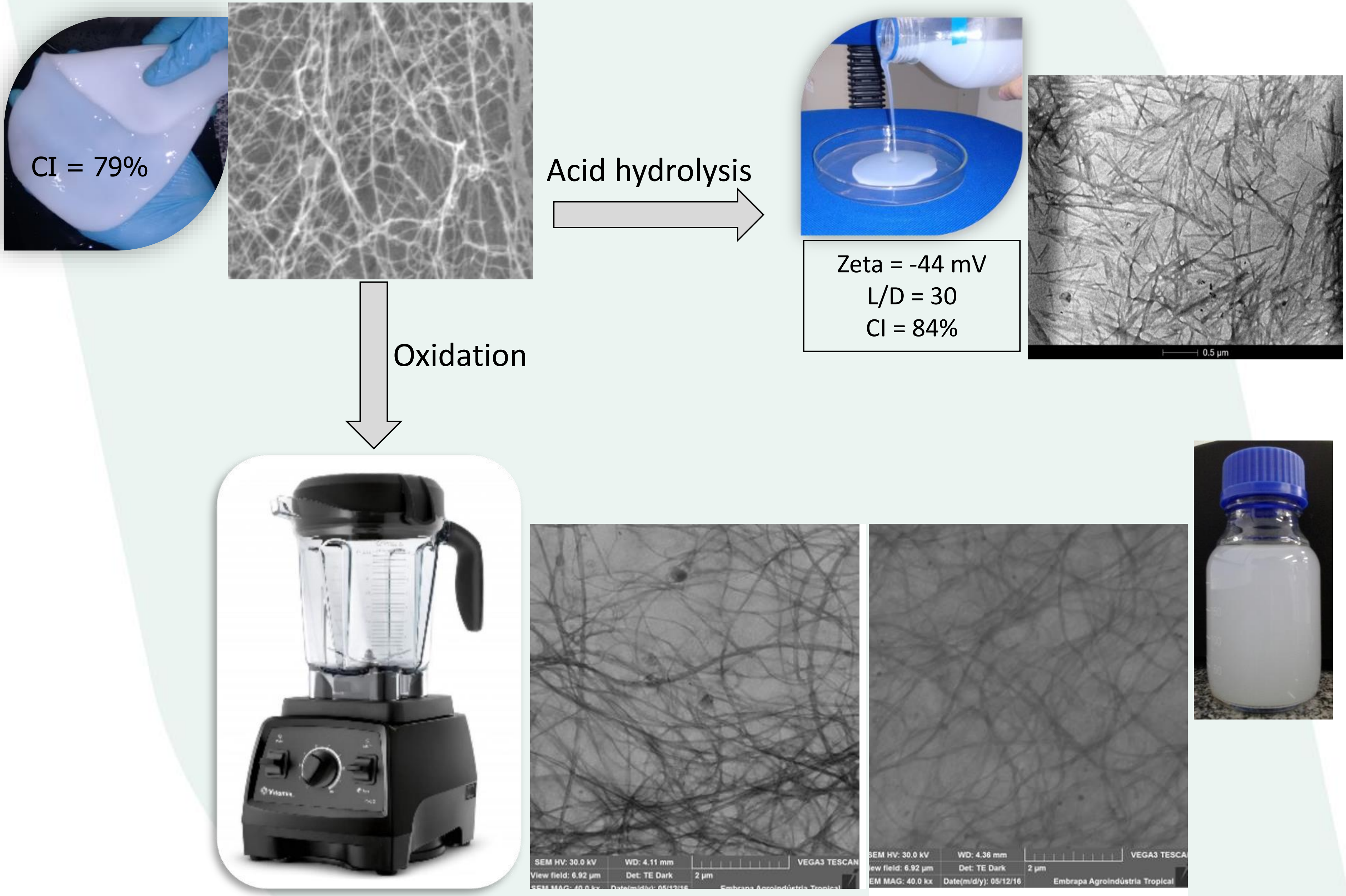
Crl 64%

Crl 81%

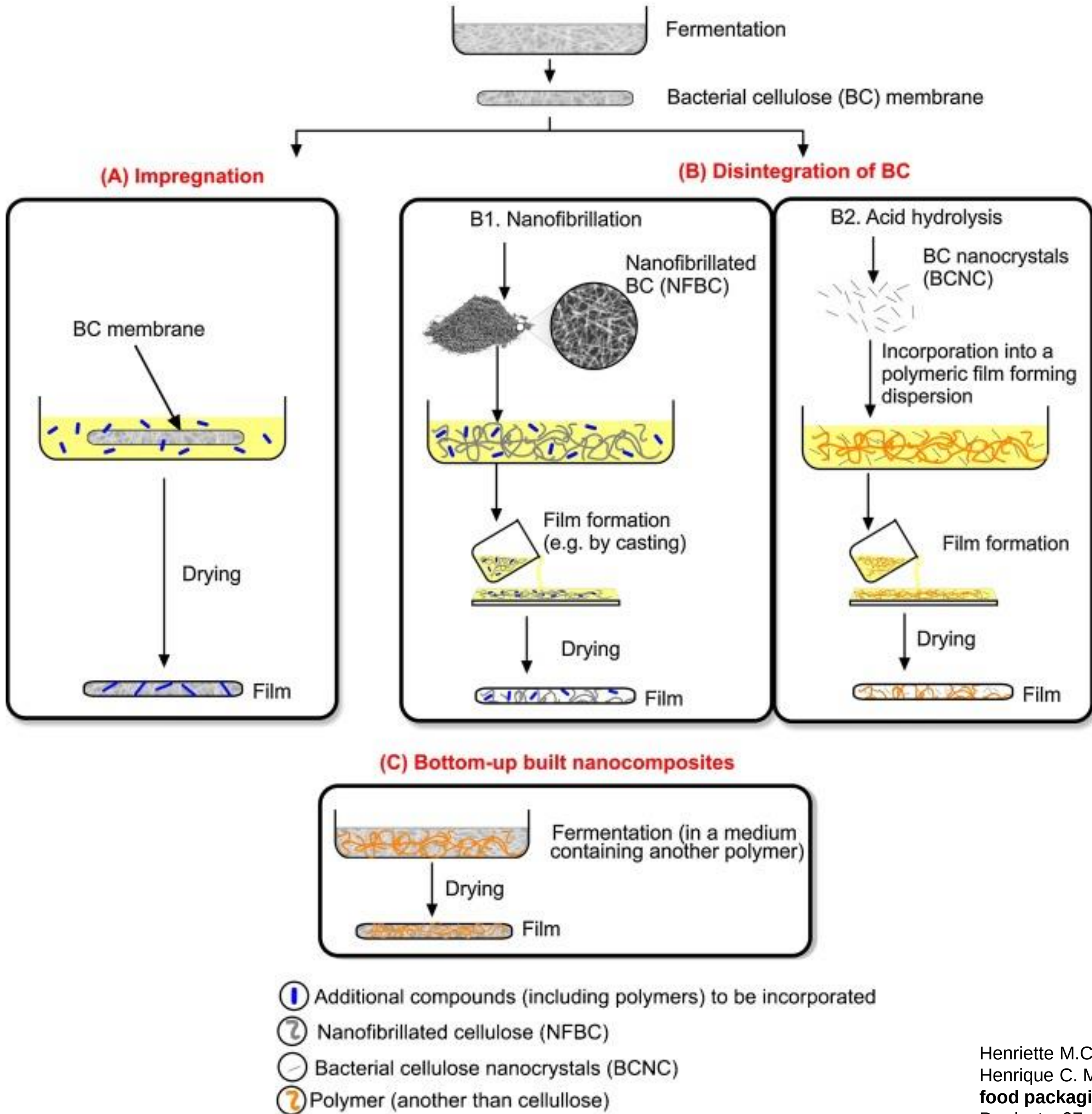
Crl 77%

Crl 70%

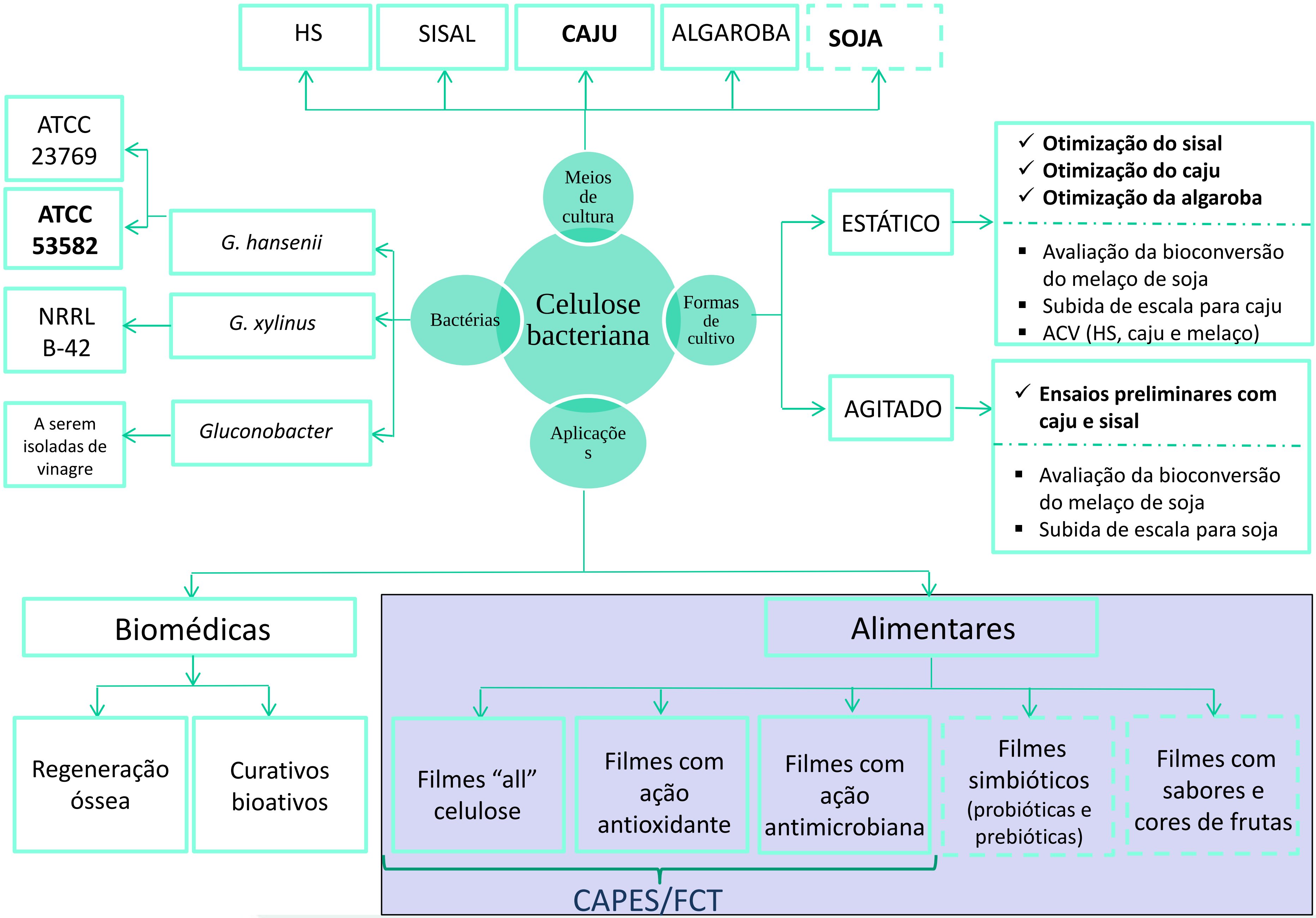
Bacterial nanocellulose



Films based on BC for packaging



Henriette M.C. Azeredo, Morsyleide F. Rosa, Luiz Henrique C. Mattoso. **Nanocellulose in bio-based food packaging applications,** Industrial Crops and Products, 97, 2017, 664–671



HS
SISAL
CAJU
ALGAROBA
SOJA
ATCC 23769
ATCC 53582
NRRL B-42
A serem isoladas de vinagre
G. hansenii
G. xylinus
Gluconobacter
Meios de cultura
Bactérias
Celulose bacteriana
Formas de cultivo
Aplicações
ESTÁTICO
AGITADO
✓ Otimização do sisal
✓ Otimização do caju
✓ Otimização da algaroba
▪ Avaliação da bioconversão do melaço de soja
▪ Subida de escala para caju
▪ ACV (HS, caju e melaço)
✓ Ensaios preliminares com caju e sisal
▪ Avaliação da bioconversão do melaço de soja
▪ Subida de escala para soja
Biomédicas
Regeneração óssea
Curativos bioativos
Alimentares
Filmes “all” celulose
Filmes com ação antioxidante
Filmes com ação antimicrobiana
Filmes simbióticos (probióticos e prebióticas)
Filmes com sabores e cores de frutas
CAPES/FCT

Rede AgroNano

Coordenação: Embrapa Instrumentação
158 pesquisadores / 53 Instituições

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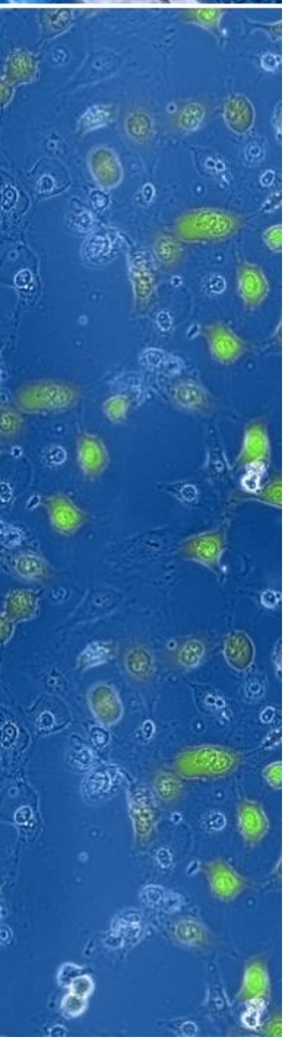
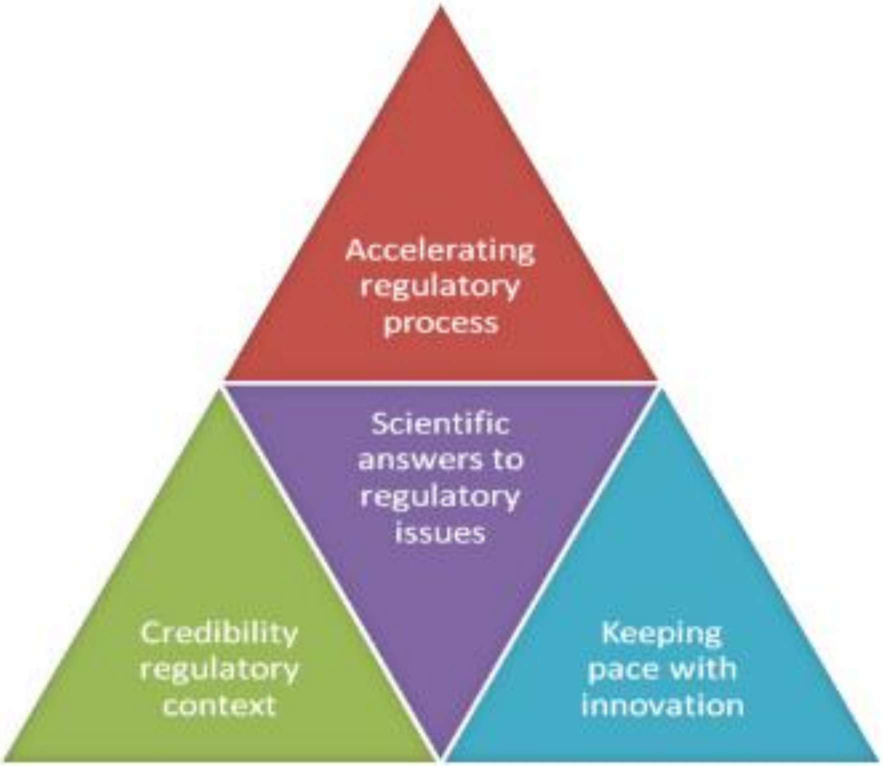
- Sensores e Biossensores
- Filmes finos comestíveis e embalagens ativas
- Bionanocompósitos
- Novos usos de nanomateriais sintéticos na agricultura
- Avaliação de Impactos em Nanotecnologia
- Aspectos regulatórios

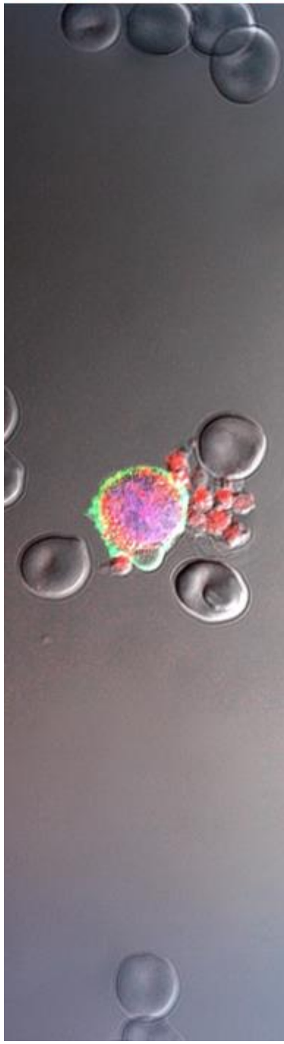
http://www.embrapa.br/nano

NANoREG

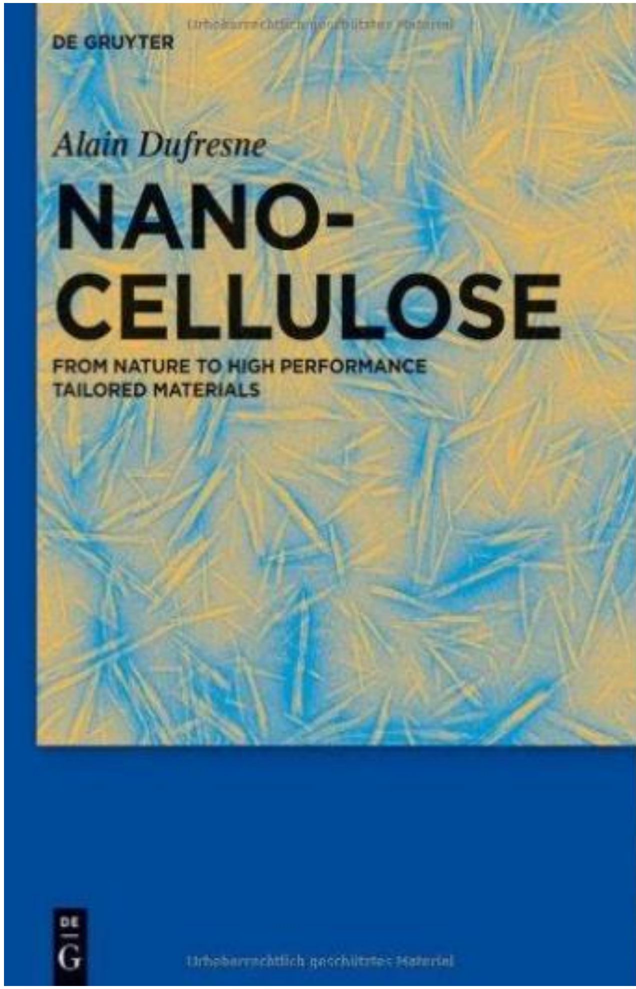
A common European approach to the regulatory testing of nanomaterials

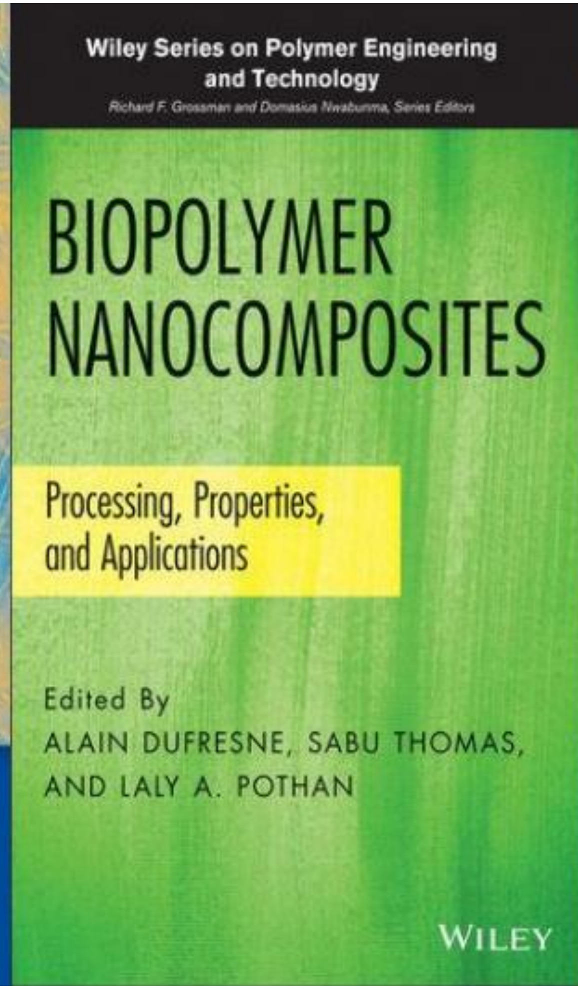






www.**nanoreg**.eu/


DE GRUYTER
Alain Dufresne
NANO-
CELLULOSE
FROM NATURE TO HIGH PERFORMANCE
TAILORED MATERIALS
DE G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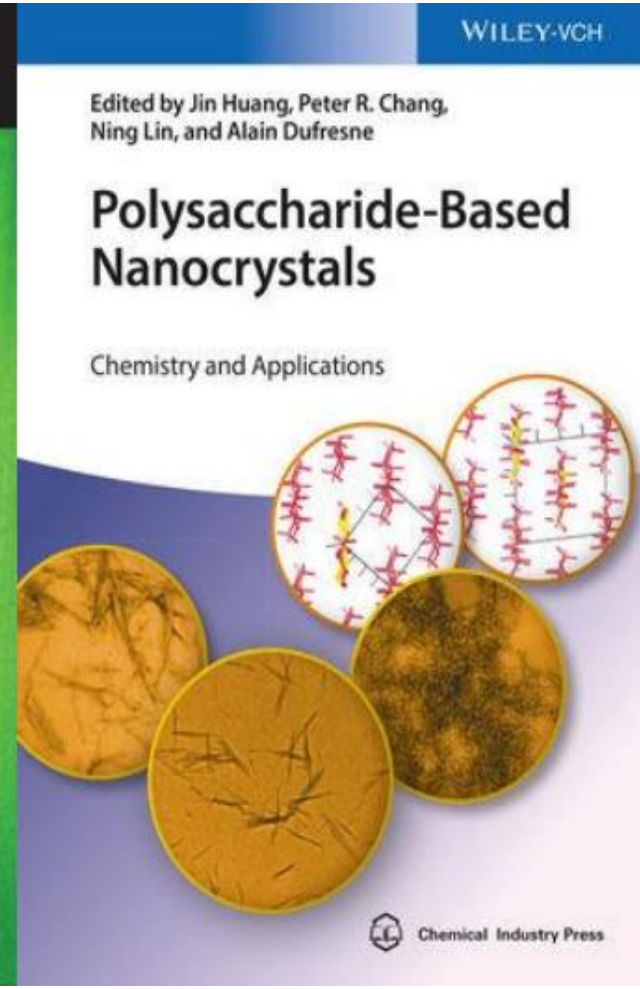
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Ning Lin, and Alain Dufresne
Polysaccharide-Based
Nanocrystals
Chemistry and Applications
Chemical Industry Press

Industrial Crops and Products 97 (2017) 664–671

Contents lists available at ScienceDirect

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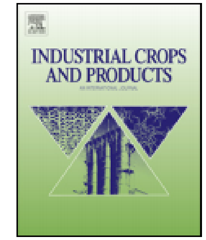

Nanocellulose in bio-based food packaging applications

Henriette M.C. Azeredo[a,*], Morsyleide F. Rosa[a], Luiz Henrique C. Mattoso[b]

[a] Embrapa Tropical Agroindustry, R. Dra. Sara Mesquita, 2270, Fortaleza, Ceará CEP 60511-110, Brazil
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ABSTRACT

Cellulose nanostructures have been widely studied as components of materials for a variety of applications including food packaging. They are usually incorporated as a reinforcement phase in nanocomposites (as cellulose nanocrystals or cellulose nanofibrils). In other cases, cellulose nanostructures have been used as matrices for films—bacterial cellulose (BC) deserving a special attention in this context, since it is produced as naturally nanostructured membranes, which may grow in a medium containing other biopolymers (producing bottom-up built bionanocomposites), be impregnated with other components, or be disintegrated into nanofibribils or even nanocrystals. This review summarizes findings and prospective applications of nanocellulose for bio-based materials to be used in food packaging (including active packaging).

Obrigada!

FUNCAP

CNPq

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