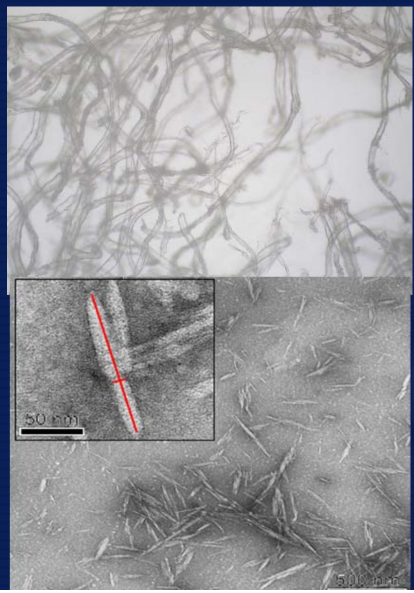
UNIVERSITÀ DEGLI STUDI DI MILANO

From Cellulose to Nanocellulose:
new opportunities for food packaging applications from the most abundant natural biopolymer

Luciano Piergiovanni, Ghislain Fotie, Luana Amoroso, Begum Akgun, Sara Limbo

DEFENS
DEPARTMENT OF FOOD, ENVIRONMENTAL AND NUTRITIONAL SCIENCES

PackLAB
UNIMI Food Packaging Laboratory



NewPack
New BioBased Film for Packaging
www.newpack-h2020.eu

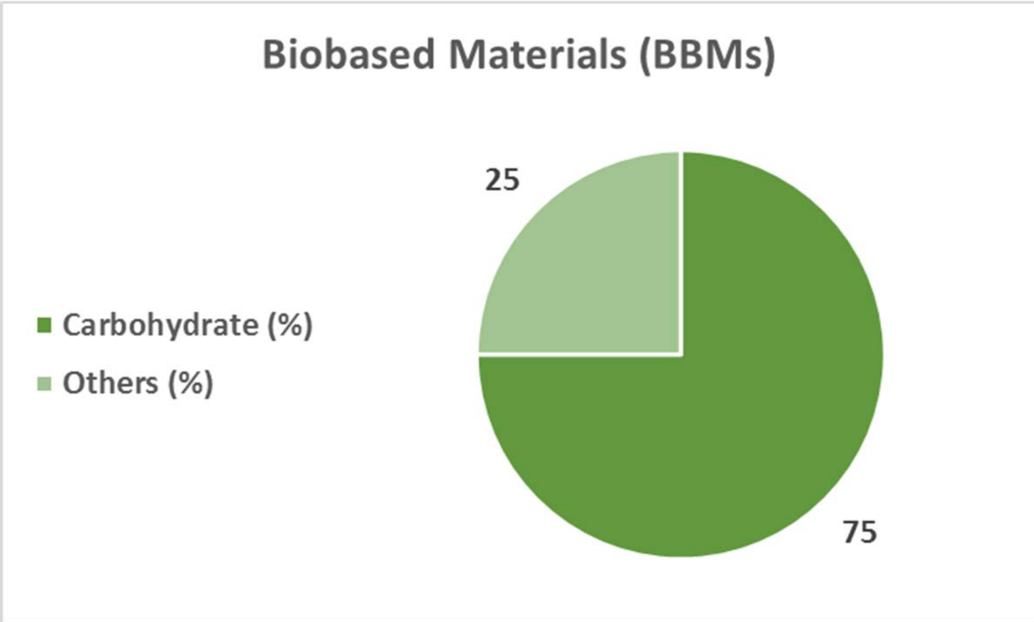
WORKSHOP

Piacenza, 19/11/2019

Development of innovative bioplastics for the food sector

Bio-based macromolecules

Every year about 170 x 10^9 metric tons biomass are produced by nature, of which only 3.5 % are utilized by mankind. Carbohydrate polymers are the most abundant renewable resources available in biomass (75%), being Cellulose the first.



Cellulose is the most ubiquitous and abundant renewable organic material in the biosphere.
Being renewable in the nature a mass of this biopolymer increases approximately on 100-200 billion tons annually as a result of the photo-biosynthesis

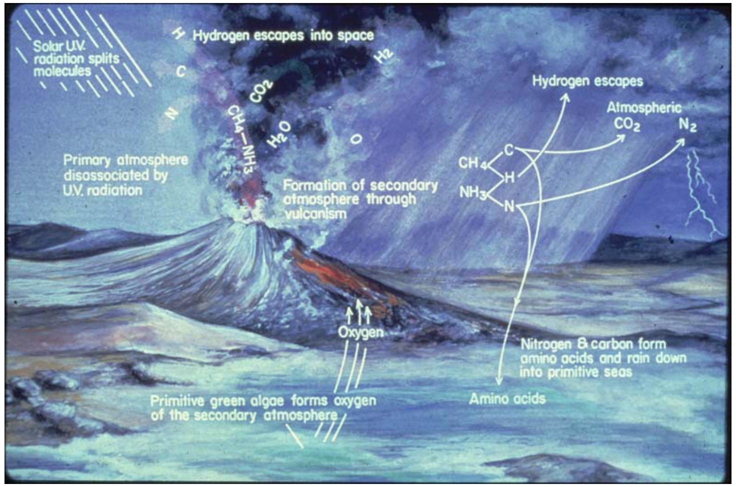
Michael Ioelovich. "Characterization of Various Kinds of Nanocellulose". Vol. 1, Chapter 2 in "Handbook of Nanocellulose and Cellulose Nanocomposites". H. Kargarzadeh, I. Ahmad, S. Thomas, A. Dufresne (eds.). John Wiley & Sons, 2017.

Bio-based macromolecules

Alexander Ivanovich Oparin (1894 –1980) was a Soviet biochemist notable for his theories about the origin of biopolymers, and for his book *The Origin of Life*.

Stanley Lloyd Miller (1930 – 2007) was an American chemist who made landmark experiments in the origin of life by demonstrating that a wide range of vital organic compounds can be synthesized by simple chemical processes from inorganic substances.

WIKIPEDIA
The Free Encyclopedia



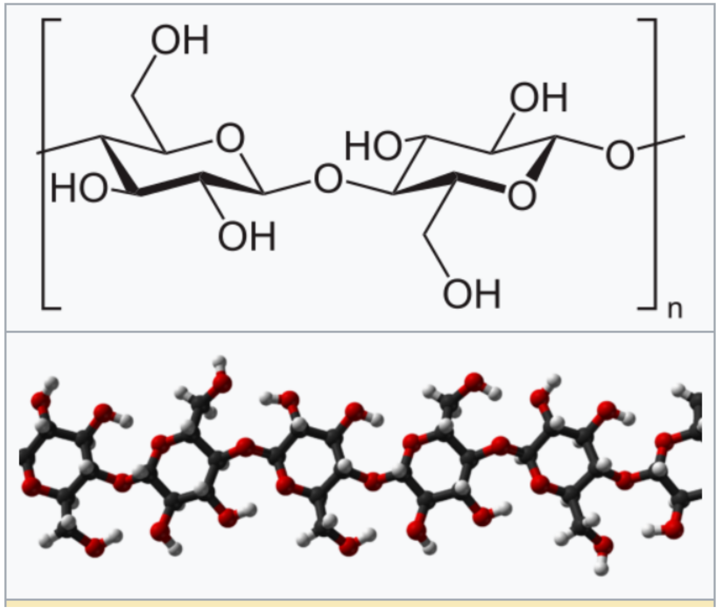
1998-2018 Robert W. O'Connell

However, Cellulose and carbohydrates are not the most ancient macromolecules on Earth, according to the Chemical Evolution theory.

Due to the primitive atmosphere composition, amines and amino acids are believed to be the building block of the first macromolecules.

Cellulose chemistry knowledge and exploitation

Anselme Payen (1795 –1871) was a French chemist, known for discovering the enzyme diastase and for isolating and naming the carbohydrate cellulose (1838).



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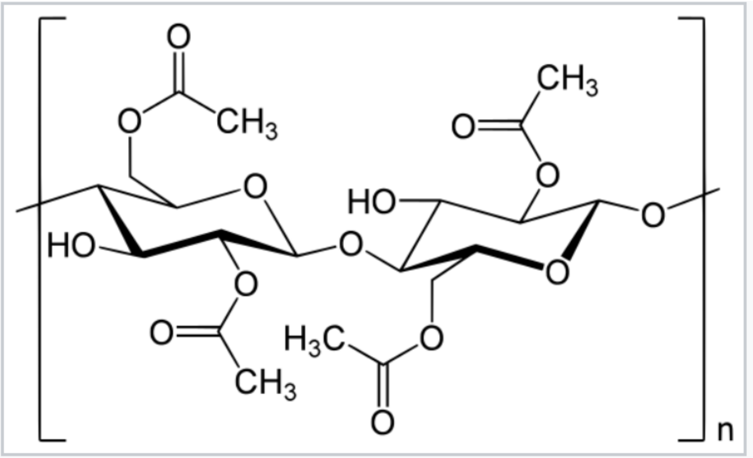
Anyway, cellulose has been well known for a long time.
Discovered more recently than starch and chitin but much earlier than glycogen, cellulose is certainly much more studied and investigated for practical purposes than whatever carbohydrate polymer.

Cellulose chemistry has been well known and used very positively for many years

Thermoplastic Cellulose

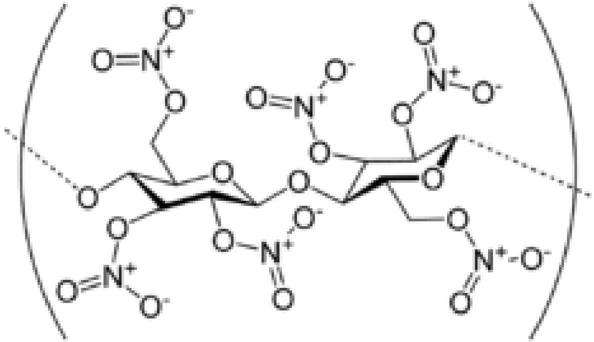


The acetate ester of cellulose (CA) was first prepared in 1865. It is used as a film base in photography, component in some coatings, frame material for eyeglasses, a synthetic fiber, in the manufacture of cigarette filters...

Cellulose octanate (cellulose C8),
Cellulose palmitate (cellulose C16),
Cellulose propionate (CP),
Cellulose acetate propionate (CAP),
Cellulose nitrate (CN)...............

Thermoplastic cellulose offers 100% bio-based, not-biodegradable bioplastics for manufacturing plastic products with existing plastic converting equipment.

Cellulose based solvents and low-order explosive

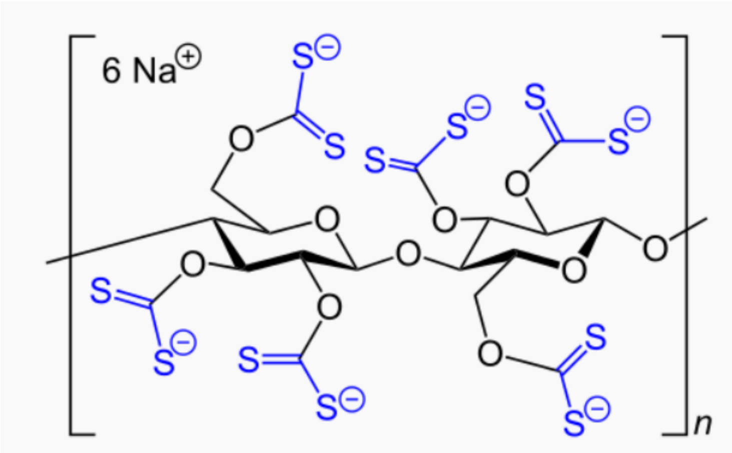


Nitrocellulose is a key component in many ink formulations and in many other applications.

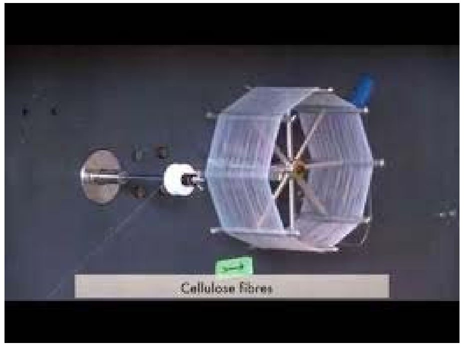
Nitrocellulose is a highly flammable compound formed by nitrating cellulose through exposure to nitric acid or another powerful nitrating agent. When used as a propellant or low-order explosive, it was originally known as guncotton.

Wikipedia
The Free Encyclopedia

Regenerated Cellulose - Cellophane



Regenerated cellulose is a class of materials manufactured by the conversion of natural cellulose to a soluble cellulosic derivative and subsequent regeneration, typically forming either a fiber (via polymer spinning) or a film (via polymer casting).



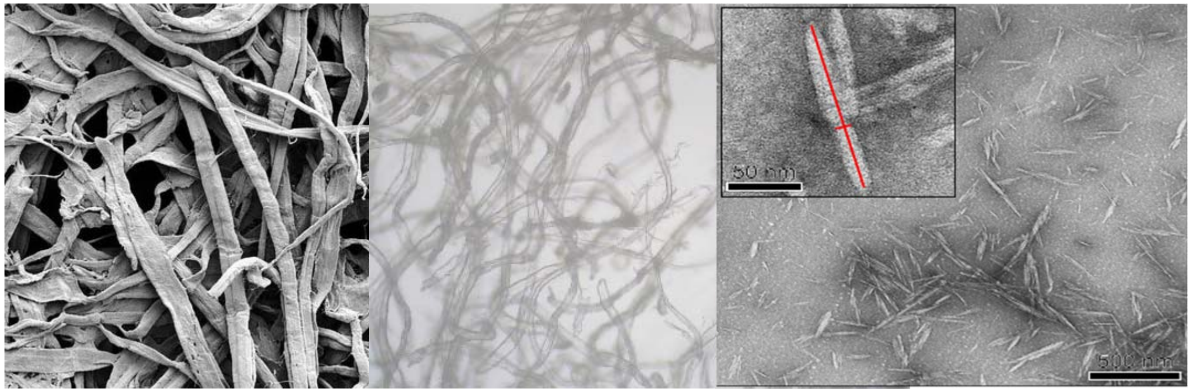
WIKIPEDIA
The Free Encyclopedia

Cellophane (*regenerated cellulose)* is the forerunner of all the **flexible packaging and all the artificial fibers.**

The British Patent Office granted the first patent for regerated cellulose in 1855 to the Swiss chemist George Audemars

From Cellulose to nano-cellulose

Beside the chemical changes of cellulose, a novel strategy to exploit cellulosic resources recently appeared: «Top-down» processes to reduce cellulose to the nanoscale.

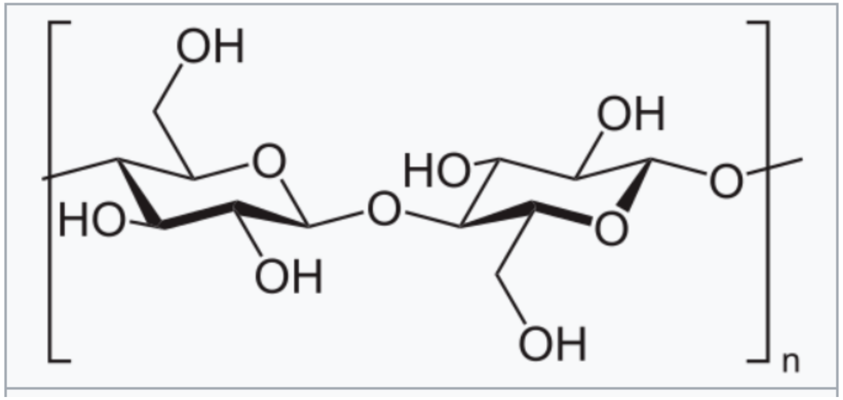


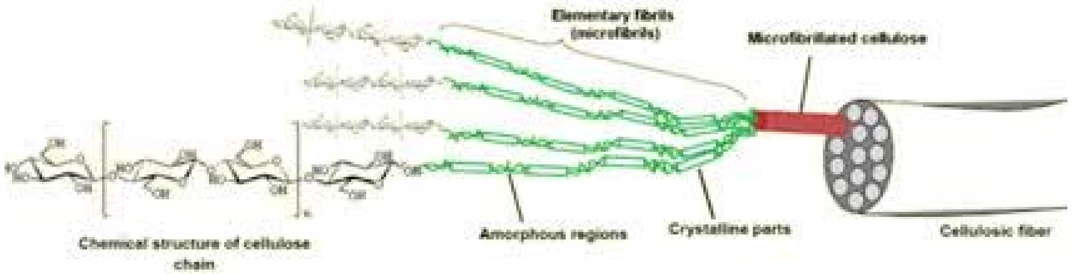
Nothing extraordinary or artificial, actually, if we consider that native cellulose itself is a nanostructured material

From Cellulose to nano-cellulose

Cellulose is a linear, stereoregular, semicrystalline polysaccharide composed of D-glucopyranose units linked by chemical ß-1,4-glycosidic bonds. The glucopyranose units (cellobiose) have a "chair" conformation. Macromolecules of natural celluloses of various origins may include from 2,000 to 30,000 elementary units with a molecular weight in the range 360,000 - 5,400,000

Michael Ioelovich. "Characterization of Various Kinds of NanocelluloseJohn Wiley & Sons, 2017.

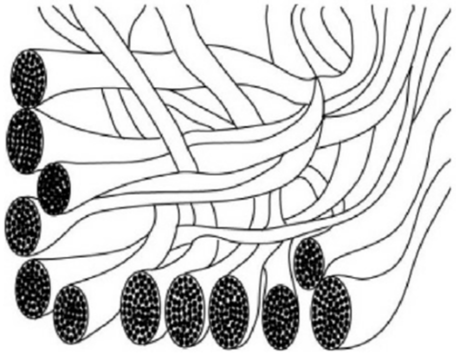




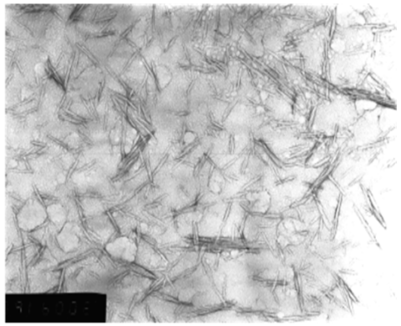
The linear macromolecules joined by hydrogen bonds form supramolecular structure of cellulose that consists of thread-like elementary nanofibrils which bundle in microfibrils and then in fibers

From Cellulose to nano-cellulose

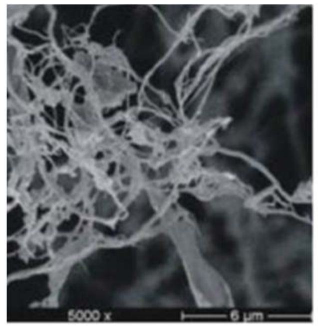
Adequate fragmentation of cellulose leads to cellulose nanoparticles (CNs) whose properties may be really interesting for packaging applications. Their different aspect ratio and cristallinity degrees address their use as possible mechanical reinforcement and for a gas barrier enhancement



Single fiber network



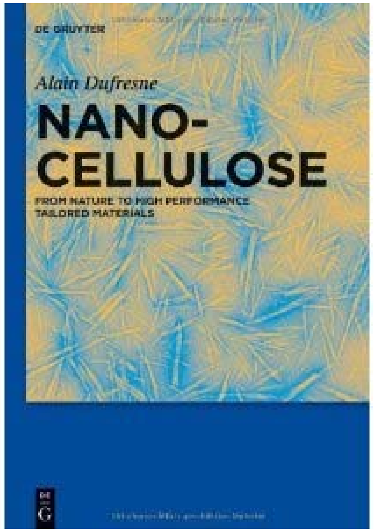
Cell. Nanocrystals (CNCs)

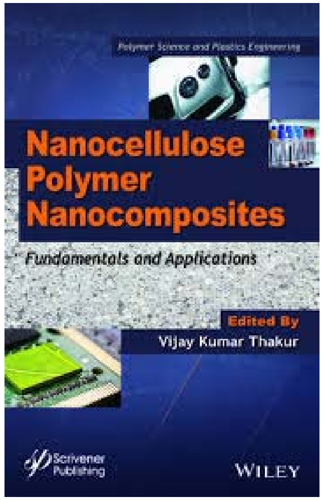


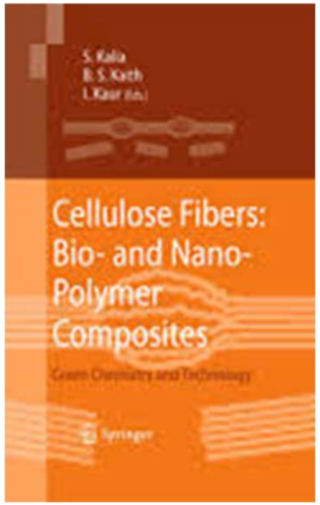
Micro-Nanofibrillated Cell. (MFC-CNFs)

From Cellulose to nano-cellulose

At nano dimension, cellulose particles revealed outstanding and somehow, unexpected properties which led to a fast growing interest within the scientific community







A fast growing interest in scientific research

From Cellulose to nano-cellulose

A fast growing interest in practical applications

CELLULOSE NANOPARTICLES (CNCs/CNFs)
CURRENT CAPACITY (2018)

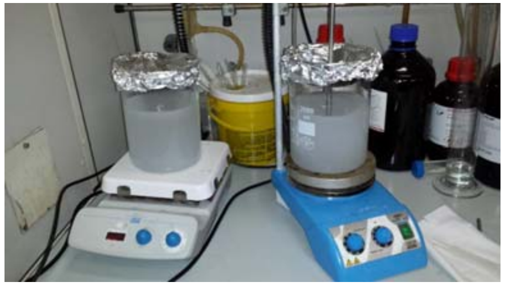
Country	Capacity (ton/year) CNCs/CNFs
USA	183 / 391
Canada	307 / -
EUROPE	35 / 113
Japan	- / 751
TOTAL	525 / 1255

Nanocellulose: Producers, Products, and Applications, A Guide for End Users, TAPPI, 2017. Updated, Biobased Markets, Sept. 2018.

Our research on nano-cellulose

We started to investigate on possible applications of cellulose nanoparticles, in particular CNCs.

After a preliminary literature review, we focused our interest about the hydrolytic and oxidative processes to obtain CNCs and their application to different sources and biomasses



Packaging Technology and Science
An International Journal

PACKAGING TECHNOLOGY AND SCIENCE
Packag. Technol. Sci. (2015)
Published online in Wiley Online Library (wileyonlinelibrary.com) DOI: 10.1002/pts.2121

The Potential of NanoCellulose in the Packaging Field: A Review

By Fei Li, Erika Mascheroni and Luciano Piergiovanni*

Cellulose (2016) 23:779–793
DOI 10.1007/s10570-015-0853-2

CrossMark

ORIGINAL PAPER

Comparison of cellulose nanocrystals obtained by sulfuric acid hydrolysis and ammonium persulfate, to be used as coating on flexible food-packaging materials

Erika Mascheroni · Riccardo Rampazzo · Marco Aldo Ortenzi · Giulio Piva · Simone Bonetti · Luciano Piergiovanni

Packaging Technology and Science
An International Journal

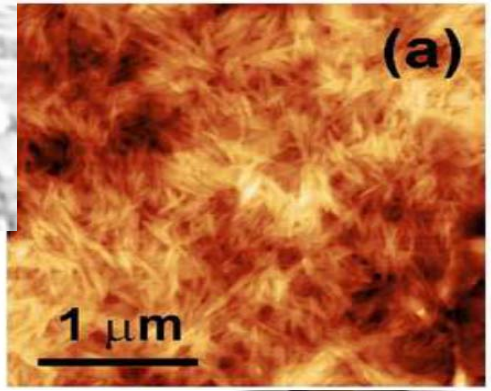
PACKAGING TECHNOLOGY AND SCIENCE
Packag. Technol. Sci. 2017;
Published online in Wiley Online Library (wileyonlinelibrary.com) DOI: 10.1002/pts.2308

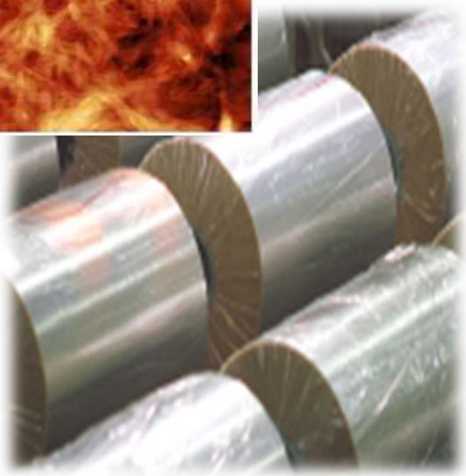
Cellulose Nanocrystals from Lignocellulosic Raw Materials, for Oxygen Barrier Coatings on Food Packaging Films

By Riccardo Rampazzo,[1,3†] Derya Alkan,[1†] Stefano Gazzotti,[2,3] Marco A. Ortenzi,[2,3] Giulio Piva[4] and Luciano Piergiovanni[1,3]*

Our research on nano-cellulose

CNCs coatings, 600-800 nm





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

Tunable green oxygen barrier through layer-by-layer self-assembly of chitosan and cellulose nanocrystals

Fei Li[a], Paolo Biagioni[b], Marco Finazzi[b], Silvia Tavazzi[c], Luciano Piergiovanni[a,*]

Cellulose (2013) 20:2491–2504
DOI 10.1007/s10570-013-0015-3

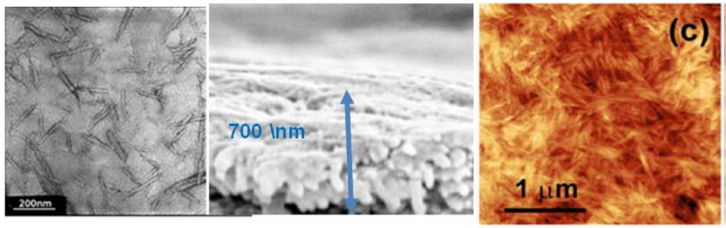
ORIGINAL PAPER

Multi-functional coating of cellulose nanocrystals for flexible packaging applications

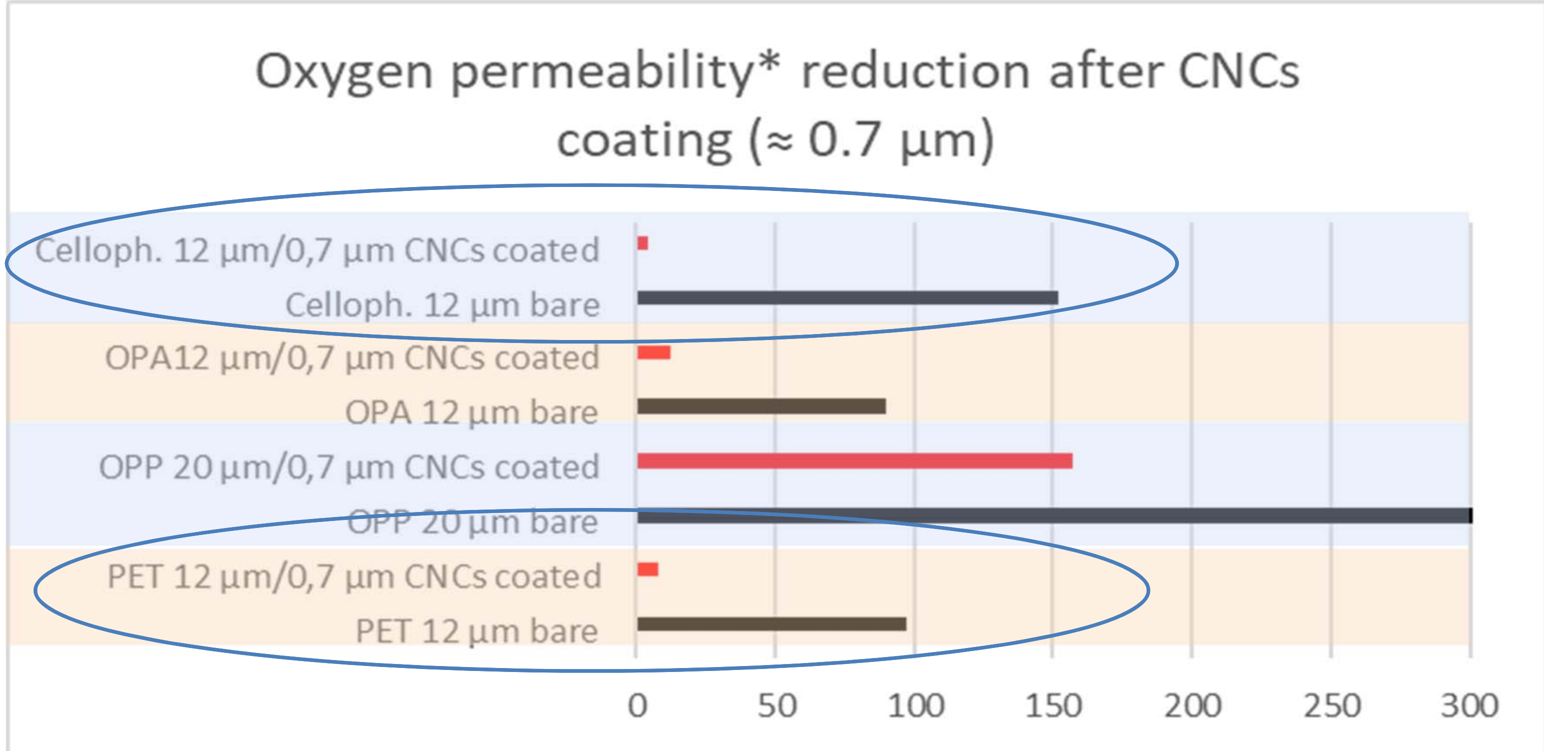
Fei Li · Paolo Biagioni · Monica Bollani · Andrea Maccagnan · Luciano Piergiovanni

Our main goal was to develop possible functional coatings for flexible films to increase the gas barrier properties by means of a bio based, biodegradable thin layer

Our research on nano-cellulose



Cellulose nanocrystals have been tested as very thin coatings onto various polymer films, with very good results at low RH values.



* $cm^3\ m^{-2}\ d^{-1}\ bar^{-1}$ at 25 °C; 0% RH

Li F, Biagioni P, Bollani M, Maccagnan A, Piergiovanni L (2013) Multi-functional coating of cellulose nanocrystals for flexible packaging applications Cellulose 20 2491-2504

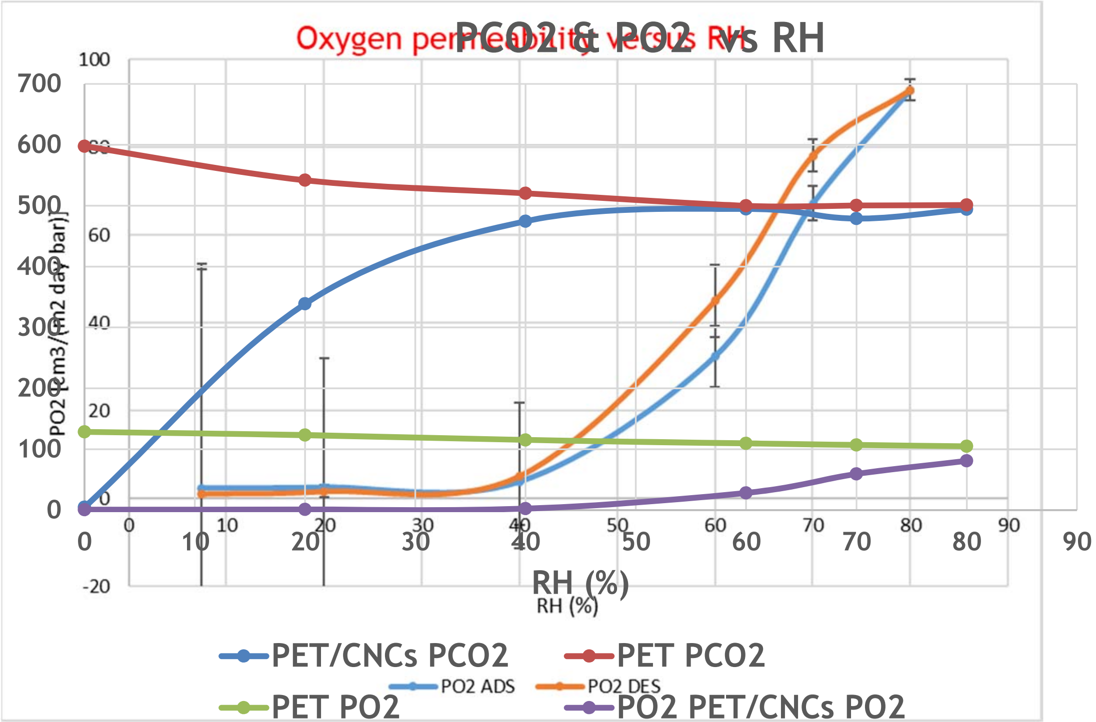
◊ poly(ethylene terephthalate) PET, 12 ± 0.5 μm

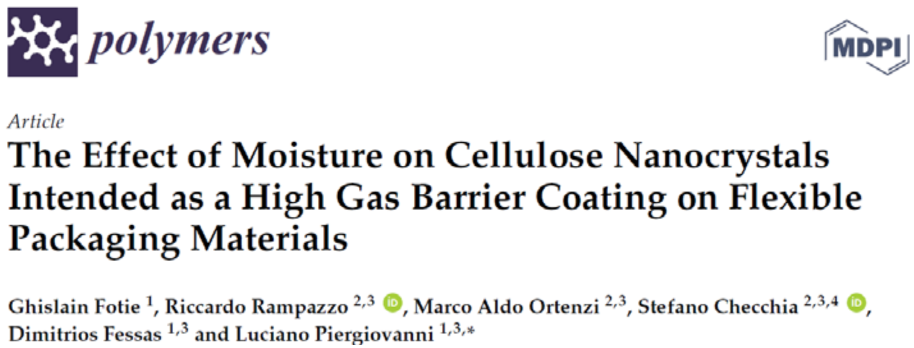
◊ oriented polypropylene OPP, 20 ± 0.5 μm

◊ oriented polyamide OPA, 12 ± 0.5 μm

◊ cellophane 12 ± 0.5 μm

Our research on nano-cellulose





polymers

MDPI

Article

The Effect of Moisture on Cellulose Nanocrystals Intended as a High Gas Barrier Coating on Flexible Packaging Materials

Ghislain Fotie [1], Riccardo Rampazzo [2,3], Marco Aldo Ortenzi [2,3], Stefano Checchia [2,3,4], Dimitrios Fessas [1,3] and Luciano Piergiovanni [1,3,*]

Contents lists available at ScienceDirect

Food Packaging and Shelf Life

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

ELSEVIER

Carbon dioxide diffusion at different relative humidity through coating of cellulose nanocrystals for food packaging applications

Ghislain Fotie[a], Luana Amoroso[b], Giuseppe Muratore[b], Luciano Piergiovanni[a,*]

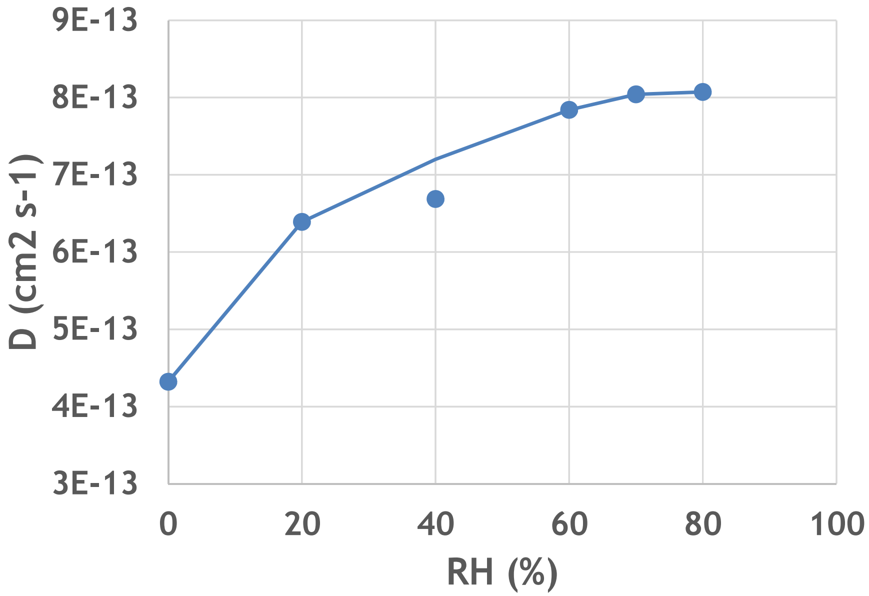
[a] DeFENS, Department of Food, Environmental and Nutritional Sciences, PackLAB Università degli Studi di Milano, Via Celoria 2, 20133, Milan, Italy
[b] Department of Agricultural, Food and Environment (Di3A), Università degli Studi di Catania, Via Santa Sofia 100, 95123, Catania, Italy

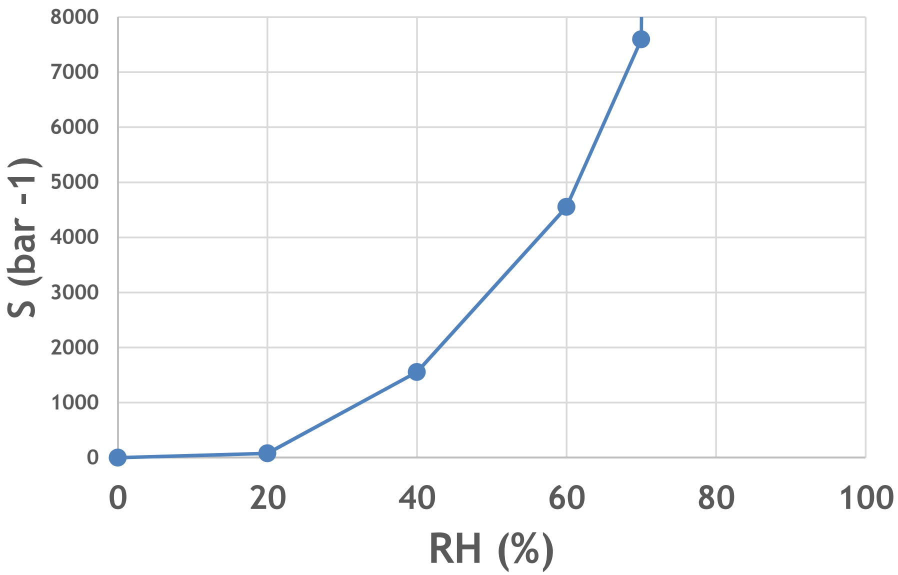
The coatings, however, lose their barrier properties to oxygen at 80% relative humidity and that of CO_2 even at low humidity

Our research on nano-cellulose

In the same range of RH values, CO_2 diffusion and solubility coefficients show different trends.

The increase of $D_{CO2/CNCs}$ is slow and stops around 50-60 %RH,





While the apparent solubility coefficient $S_{CO2/CNCs}$ increases more than 1000 times in an approximately exponential way.

Our research on nano-cellulose

The possible use of cellulose nanocristals as barrier coating against gas transmission, to extend the shelf life of perishable products, seems promising but requires technological developments, such as lamination of the coated films with hydrophobic and sealable layers

A comparative Shelf Life test using conventional and novel/biocompostable laminates

	Conventional laminate (EVOH)	**Novel, compostable laminate (CNCs)**
Thickness	72 μm	81 μm
Structure	PET (28μm) / Adhesive (1.2μm) / **EVOH** (3.3μm) / Adhesive (1.2μm) / PET (25μm) / Adhesive (1.2μm) / PE (12μm)	Cellophane (19μm) / Metallization (<< 1 μm) / Adhesive (2μm) / **CNCs** (1μm) /Adhesive (3μm) / PLA (55μm)

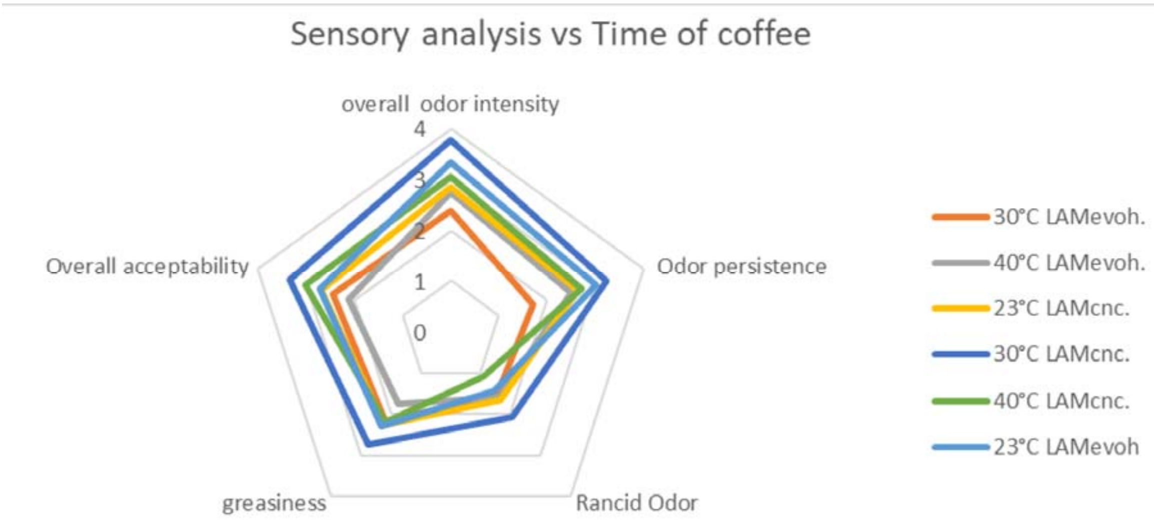
Our research on nano-cellulose

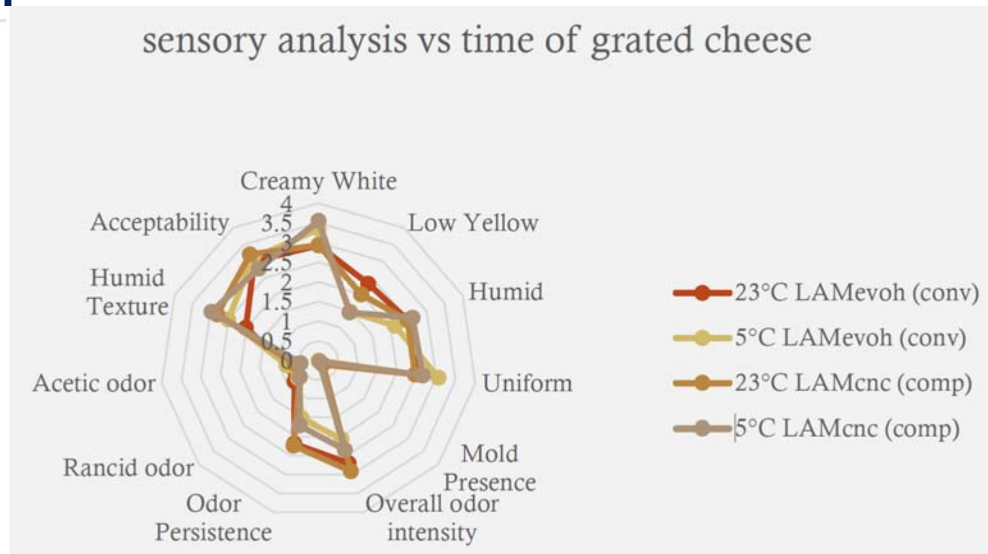
Biocomplack, the Fast-Track EU project for the implementation of a Cellulose Nanocrystals barrier in fully compostable novel laminates
June 2016 - May 2019

Our research on nano-cellulose

A comparative two-month food shelf-life assessment was designed by using the two types of laminates to fabricate identical-sized pouches and filled with **ground coffee and grated cheese** then, sealed under 100% N2 to be finally stored at 23° C/30° C/40° C and 5° C/23° C respectively.

From the findings, CNCs laminates were equivalent or even better in the shelf-life extension of food products.





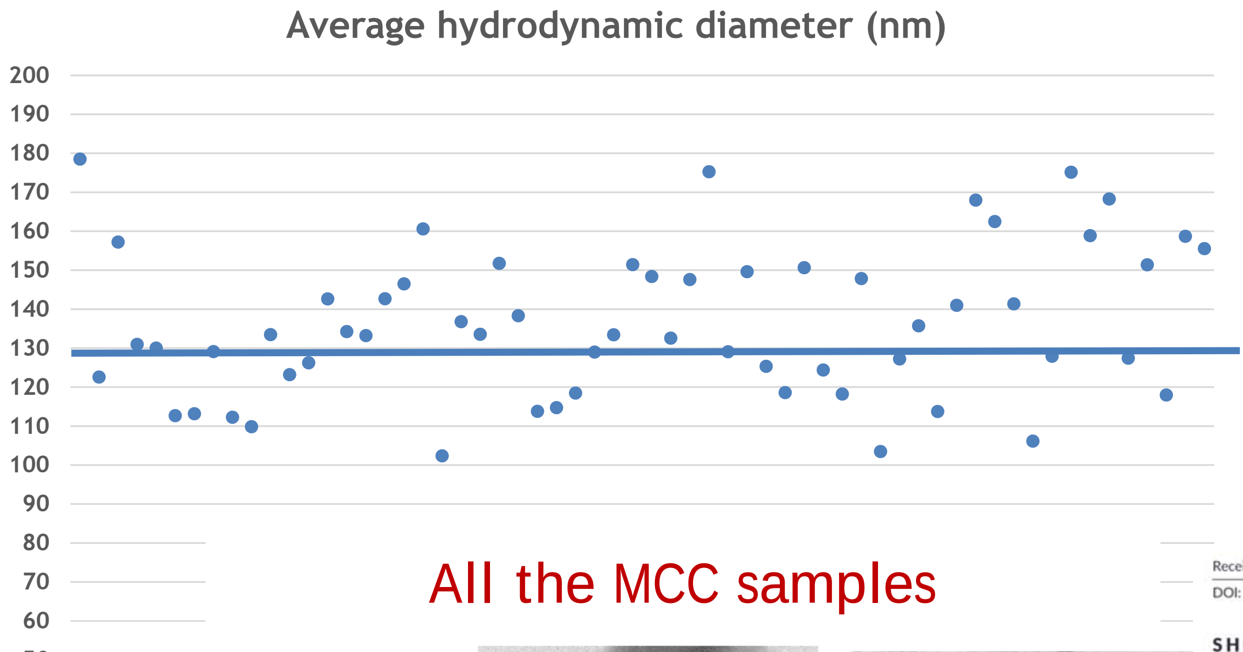
CNCs as Food Contact Material

Unfortunately, a strong prejudice on the use of nanomaterials in food contact materials (FCM) persists all around the world and, since 2011, the European legislation established that in the manufacture of FCM:

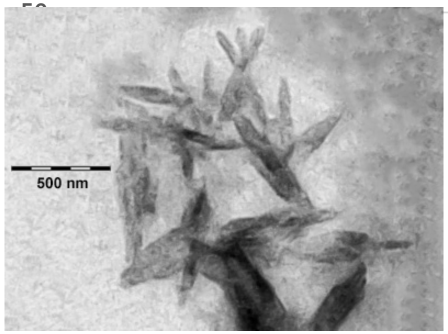
…substances in nanoform should be used only if explicitly authorized… they should not be covered by the functional barrier concept…substances in nanoform shall only be used if explicitly authorized and mentioned in the specifications in Annex I. ….

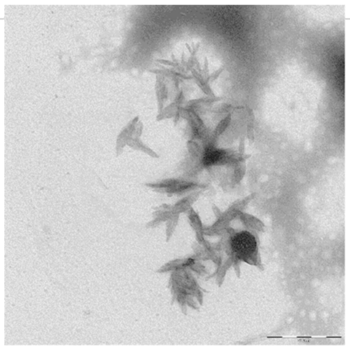
However, in foods and in pharmaceutical products, the presence of cellulose is very common because a wide group of cellulose-based additives are authorized worldwide as thickening, filler and functional agents.

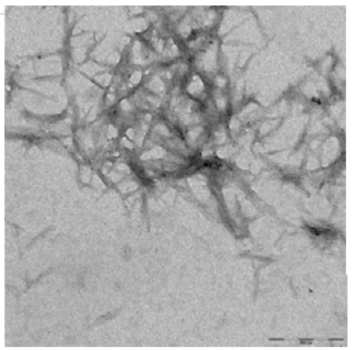
CNCs as Food Contact Material



All the MCC samples







MCC Pharmaceutical Grade (USP EP)
for tablet eccipient

MCC Pharmaceutical Grade
for tablets manufacture

MCC Food Grade
for emulsifier, stabilizer, thickener additives

MCC Laboratory Grade
for column chromatography

Received: 28 March 2019 | Revised: 18 July 2019 | Accepted: 22 July 2019
DOI: 10.1002/pts.2477

SHORT COMMUNICATION

WILEY Packaging Technology and Science

Are cellulose nanocrystals "alien particles" to human experience?

Luciano Piergiovanni[1] | Ghislain Fotie[1] | Luana Amoroso[2] | Begum Akgun[1] | Sara Limbo[1]

The foods and the pharmaceuticals we have been consuming so far do indeed contain traces of CNCs to such an extent that this wide presence in consumed products should be taken into account when considering possible limitations of the use of such useful nanoparticles in food contact materials manufacture.

Thanks for your kind attention !!