UNIVERSITÀ DEGLI STUDI DI MILANO
University of Milan

DEFENS
DEPARTMENT OF FOOD, ENVIRONMENTAL AND NUTRITIONAL SCIENCES

Potenziali applicazione della nano-cellulosa nell'imballaggio flessibile per alimenti

Luciano Piergiovanni, Erika Mascheroni, Riccardo Rampazzo, Fei Li

PACKAGING SOSTENIBILE: I materiali e le tecnologie innovative per il design in carta e cartone

Milano, 16 settembre 2014

Comieco
Consorzio Nazionale Recupero e Riciclo degli Imballaggi a base Cellulosica

UNIVERSITÀ DEGLI STUDI
DI MILANO

DEPARTMENT OF
FOOD, ENVIRONMENTAL AND
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University of Milan

Dipartimento di Scienze per gli Alimenti, la Nutrizione e l'Ambiente

Department of Food, Environmental and Nutritional Sciences

DeFENS

(formerly DiSTAM, Dept. of Food Science & Microbiology)

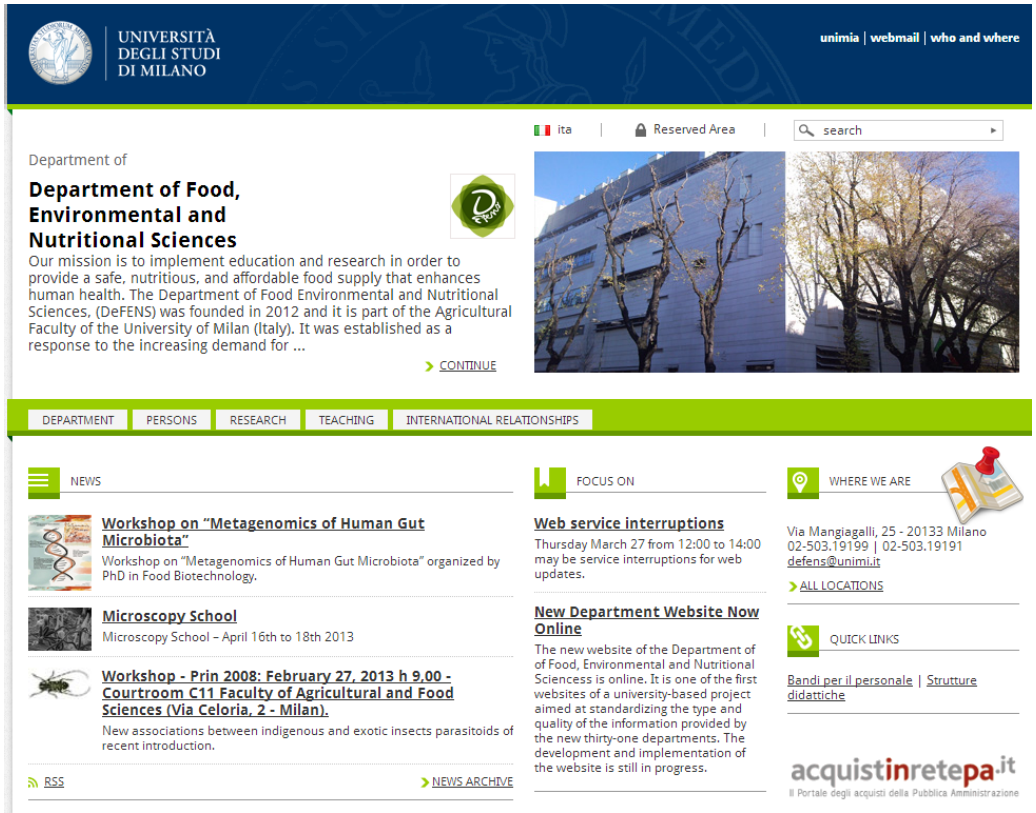
Packlab

The Department of Food, Environmental and Nutritional Sciences - *DeFENS*

5 Sections (or Divisions) belong to the Department:

http://www.defens.unimi.it

- Chemical and Biomolecular Sciences
- Agro-Environmental Systems
- Food Microbiology and Bioprocesses
- Human Nutrition
- Food Technology



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DEPARTMENT OF FOOD, ENVIRONMENTAL AND NUTRITIONAL SCIENCES

Packlab history

A laboratory exclusively devoted to packaging research (the Packlab) has been established in the Department of Food Science and Microbiology (DISTAM) since 1985. At that time, the first course of Food Packaging and Distribution was offered in our Country, within the curriculum of Food Science and Technology in the Faculty of Agriculture of University of Milan.

From then on an intense activity of both applied research and specialist teaching begun in the Packlab. Due to the very fast and worldwide growing importance of the food packaging sector, also Packlab grew quickly. In these almost 25 years several collaborations have been established with companies in the food as well as in the packaging sector and many relationships have been instituted with other Universities and Research Centers in Italy and abroad. A list of the main significant partnerships is reported in the section "Facts & Figures" of this web site.

A fundamental driving force for Packlab growth during these years, however, has been provided by the great number of students, post graduated, PhD students and post docs

http://users.unimi.it/packlab/default.htm

An Operative Unit exclusively devoted to food packaging (the Packlab) has been established in our University since 1985.

Packlab is the only unit in the University of Milan engaged in research, teaching and testing in the Food Packaging field

FOOD PACKAGING RESEARCH at PACKLAB

FOOD CONTACT COMPLIANCE

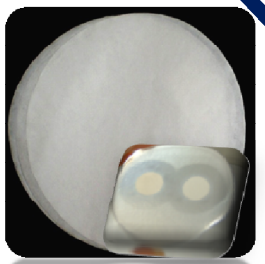
ACTIVE PACKAGING SYSTEMS

INNOVATIVE BIOBASED MATERIALS

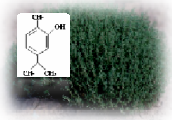
SHELF LIFE TESTING & MODELLING

Antimicrobial proteins (LZ and LF) controlled release from paper sheets

The figure shows the activity of paper sheets against food spoilage microorganisms.

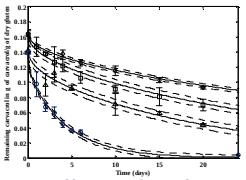


Incorporation and diffusion of natural volatile antimicrobials from bio-coating



Essential oil of carvacrol

Cyclodextrin

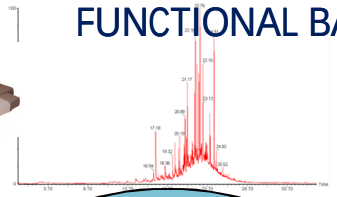


Studies of release of carvacrol from biocoating at different RH

NIAS (non intentionally added substances)

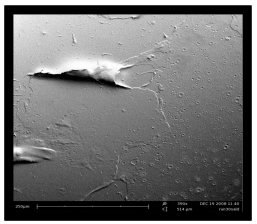
Transference of contaminants from cellulosic packaging and innovative approach for food contact material safety

FUNCTIONAL BARRIERS



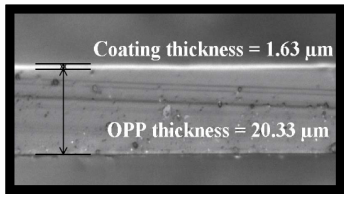
Sealable bio-coatings

SEM image shows a polypropylene coated films after rupture of sealed strips



Barrier bio-coatings

A very thin bio-coating can improve the oxygen barrier property of a plastic film.



Nano-Cellulose applications

Cellulose properties including hydrophilicity, biocompatibility, stereoregularity, biodegradability, chemical stability, multi-chirality, reactive hydroxyl groups and the ability to form superstructures.

Beverages

Effects of light exposure and protection efficacy of packaging

Meat & Processed Meat

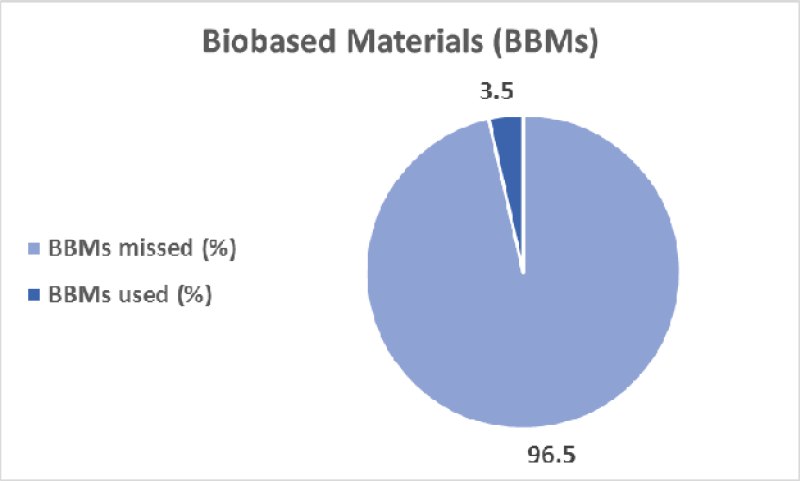
Optimization of active packaging solutions

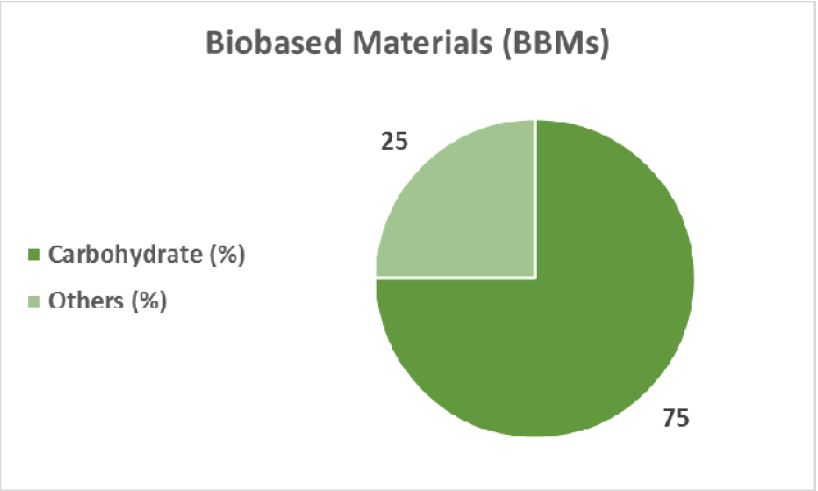
Low -moisture and dried foods

Modelling of moisture diffusion across the packaging material

Bio-based materials

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





http://en.european-bioplastics.org/multimedia/PROBIP2009_Final_June_2009.pdf

Cellulose

- Cellulose is the most ubiquitous and abundant renewable organic material in the biosphere

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- **It is a linear homopolymer of ß-1,4-linked anhydro-D-**glucose, with a MW around 20-30,000 kDa and a DP in the range 3000-15,000; it is biodegradable and/or biocompatible

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- It comes from several different sources, mainly nonfood agricultural based sources; It has low cost and low energy consumption; it is *Carbon neutral*, having a net zero carbon footprint

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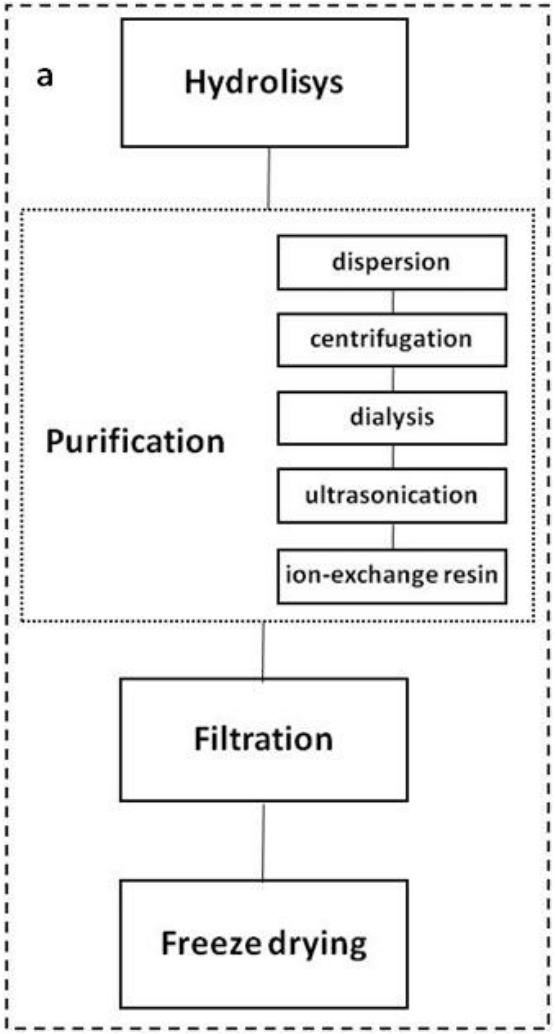
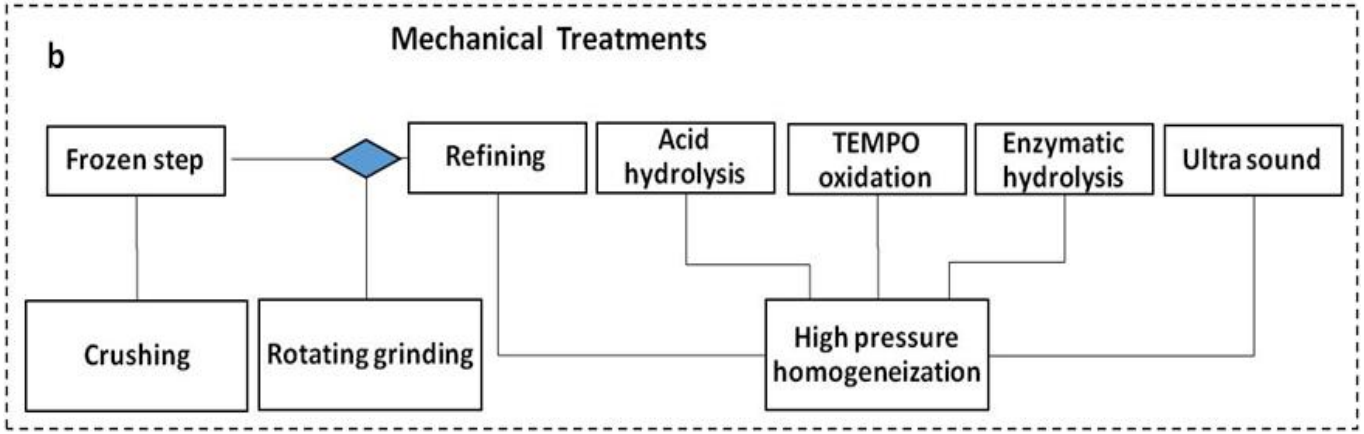
- **At nano dimensions it reveals outstanding and, somehow, unexpected properties**

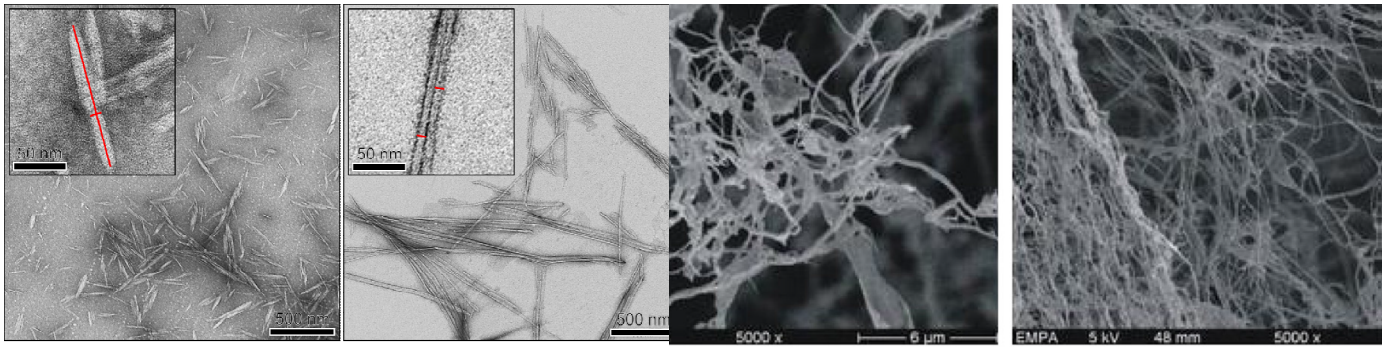
From Cellulose to nano-cellulose





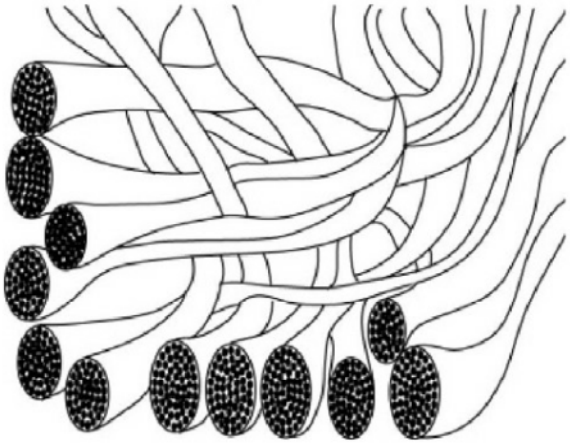
Various methods are known to obtain CNs, high pressure homogeneization and acid hydrolysis are the most common and used.

Different morphologies and dimensions of CNs are obtained.



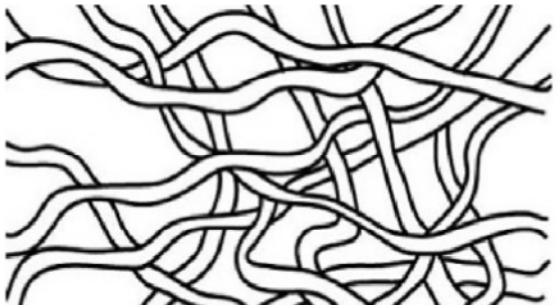
From Cellulose to nano-cellulose

Fragmentation of native fibers and fibrils of cellulose lead to cellulose nanoparticles (CNs) whose properties may be really interesting for packaging applications



Single fiber network

Cell. Nanocrystals (CNC)



Nanofibrillated Cell. (NFC)

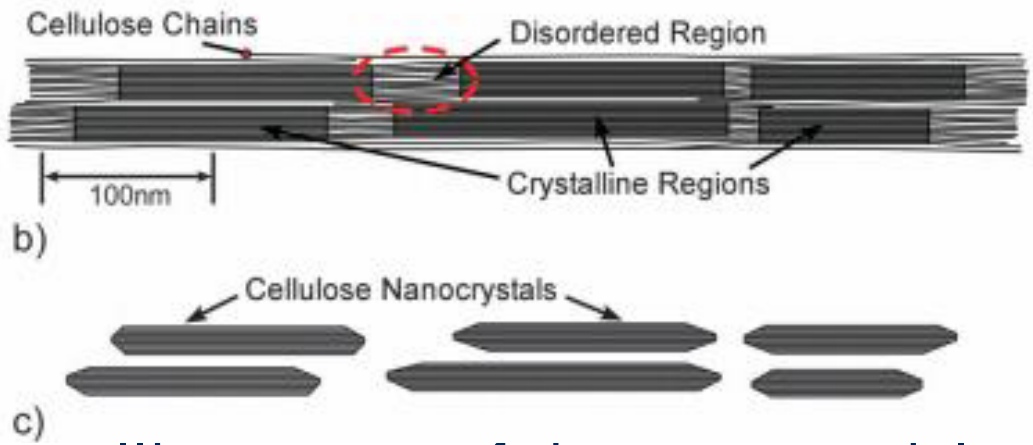
Their use as possible mechanical reinforcement of various materials has been largely investigated

Component	Single fiber	Microfibril	Nanocrystals (CNC)	Nanofibrillated (NFC)
Young's Module (GPa)	40	70	50-143	145-150

H.P.S. Abdul Khalil et al. / Carbohydrate Polymers *99 (2014) 649– 665*

From Cellulose to nano-cellulose

The acid attack occurs preferentially on the amorphous parts of native cellulose which are also the less dense ones, leaving more dense and crystalline particles with shorter chains (Cellulose nanocrystals, CNC)



The prevalent crystalline nature of the nano-particles obtained by acid hydrolysis lead to new materials with high compactness and tortuous free path, which should result in a decrease of permeability and migration.

Crystallinity (CRI%) of the native fibers (source)	69 (Flax)	73 (wood pulp)	79 (MCC)	56 (Hemp)	59 (Bacterial Cell.)
Crystallinity (CRI%) of the CNC obtained	75	81	83	73	70

Alfred C. W. Leung et al. / Small (2011) 7 (3):302

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The crystalline portion makes a fraction of polymeric volume unavailable for transport

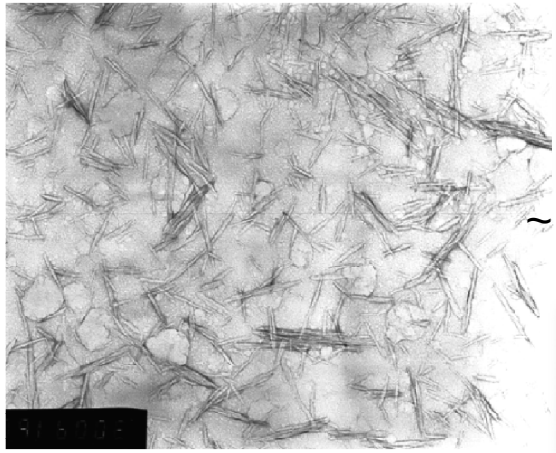
Effect of crystallinity on permeability of polyethylene

% Crystallinity in HDPE	$P(O_2) \times 10^{14}$ (cm^3 (STP) cm/cm^2 S Pa)
60	41.25
69	15.75
78	8.25
81	7.95

Progress in Organic Coatings 50 (2004) 28–39

The Research on CNC at our Lab

The basic idea is to use CNC water suspensions as novel coating of conventional flexible packaging, in order to enhance properties useful for Shelf Life extension



~1% w/w CNC dispersion

Freeze-dryed CNC

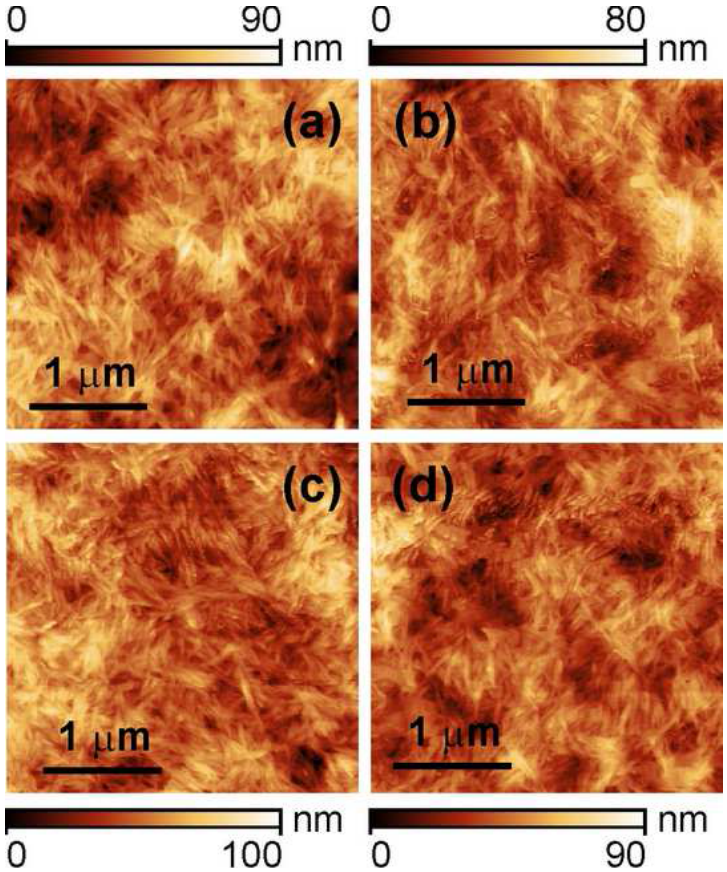
Milled cotton linters were hydrolyzed by 64 wt% sulfuric acid at 45 ° C for 45 minutes to obtain 1 wt% Cellulose nanocrystals dispersion. After further purification the suspension was sonicated, adjusted to pH ~7, freeze-dried and used to prepare a given concentration of cellulose nanocrystals for coating operations

F. Li, P. Biagioni, M. Bollani, A. Maccagnan, L. Piergiovanni. 2013 Multi-functional coating of cellulose nanocrystals for flexible packaging applications *Cellulose 20* (5): 2491-2504

The Research on CNC at our Lab

The corona-treated sides of 4 different plastic films were coated (1-1.5µm thick) with CNC obtained from Cotton linters using acid hydrolysis, using an automatic film applicator at a constant speed:

Polyethylene terephthalate (PET, 12µm, a)
Oriented polypropylene (OPP, 20µm, b),
Oriented polyamide (OPA, 12µm, c)
Cellophane (CELL,12 **µ**m, d)



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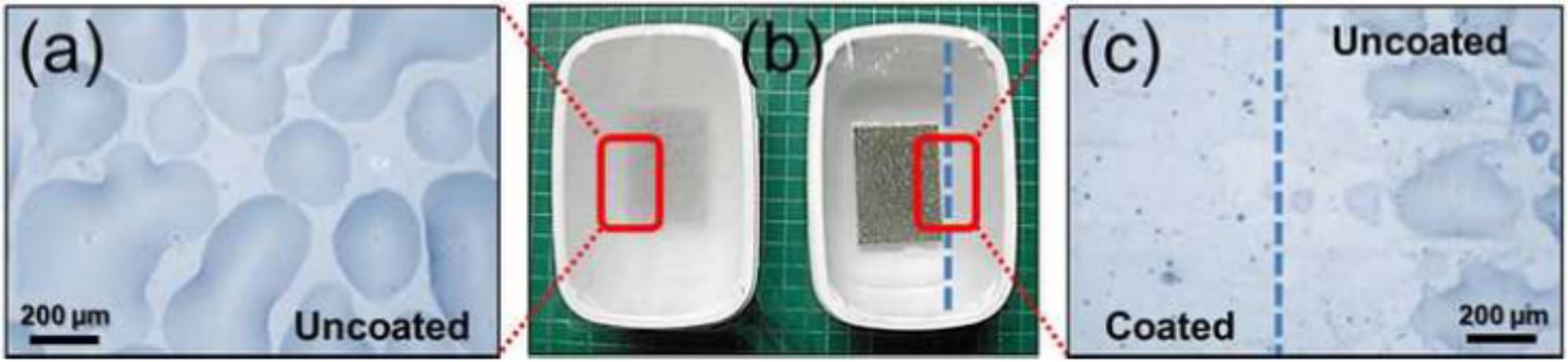
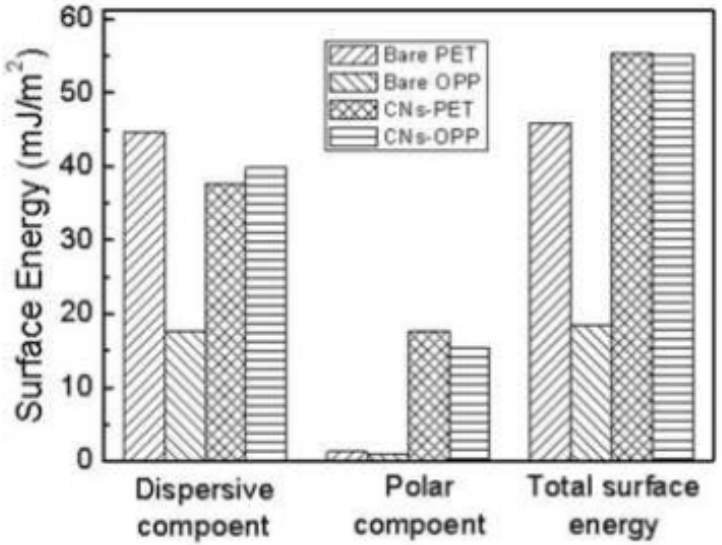


The goal was to investigate the possible enhancement of coefficient of friction, anti-fog, optical, oxygen barrier and water vapor barrier properties of the various coated films



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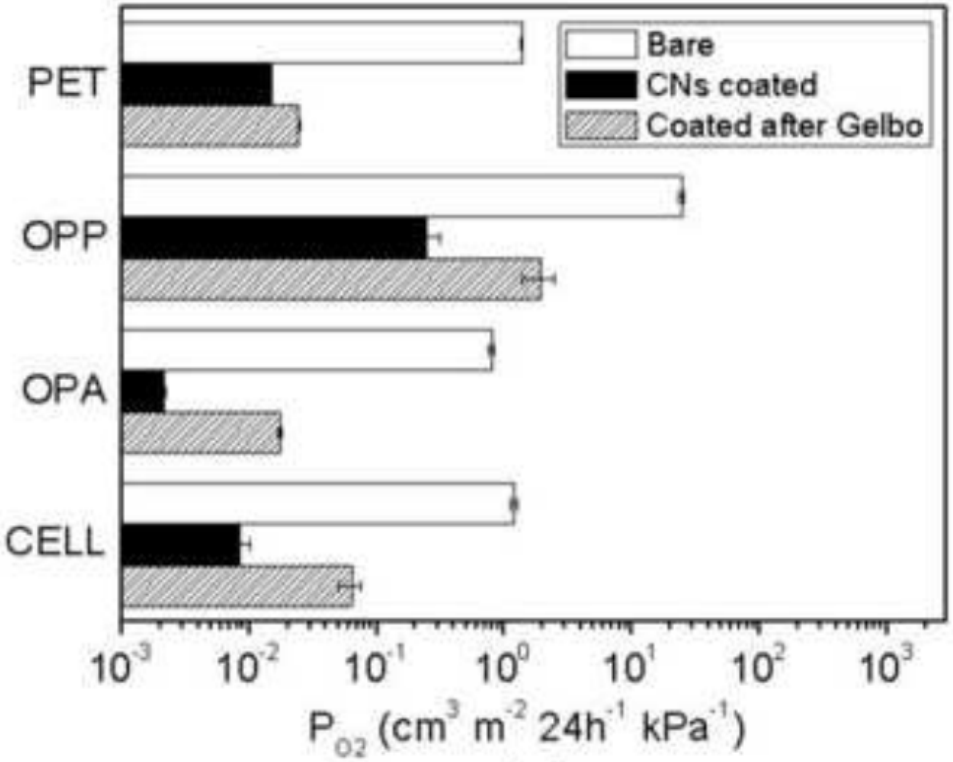
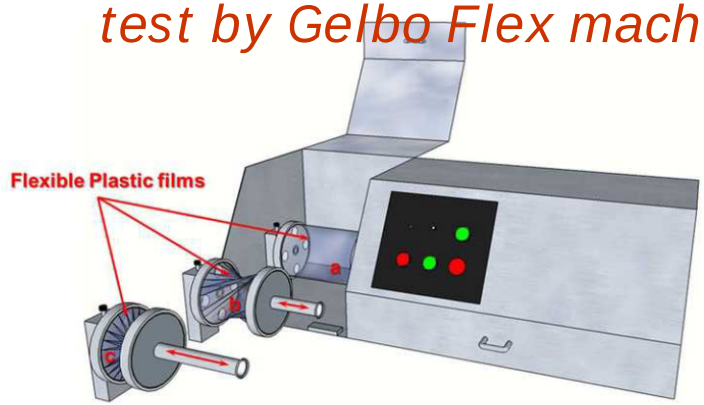


Very good final performance were obtained for all the coated films, but different according to the substrates used, denoting different degree of adhesion.

Oxygen permeability, in particular, was clearly reduced, remaining much lower than the bare films even after an abuse test by Gelbo Flex machine



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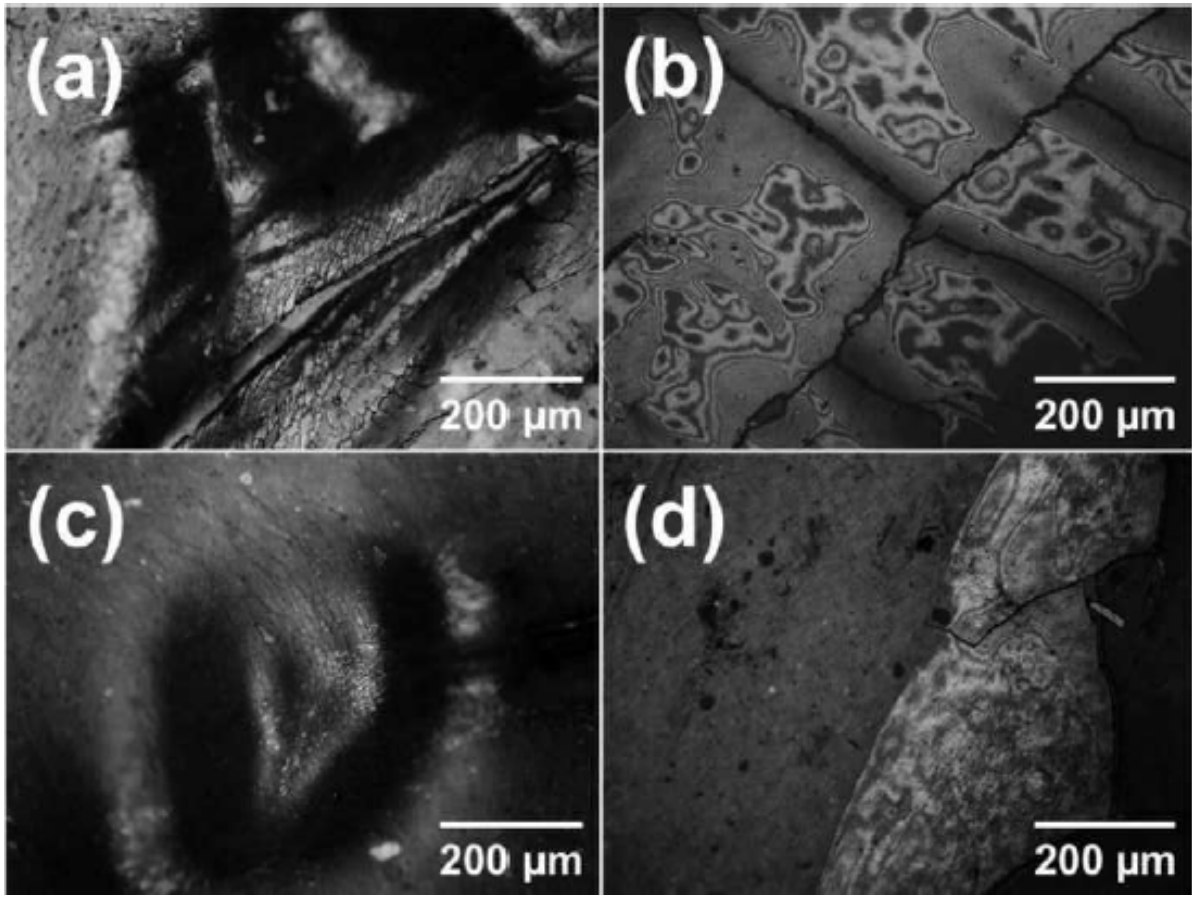
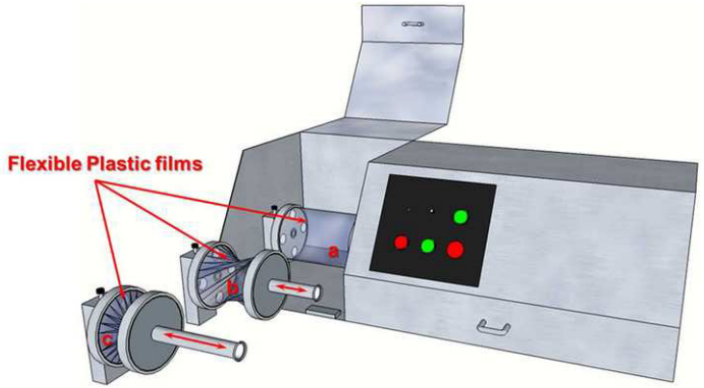




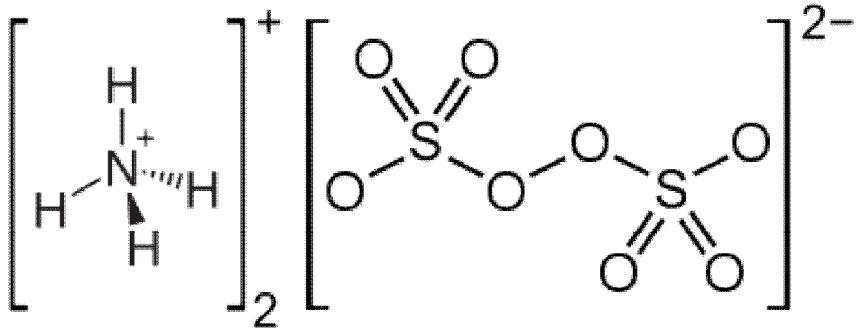
Strong distortions led to some destructions of CNs coating and reduce the oxygen barrier properties not in same way for all the substrates, probably due to different adhesion

The Research on CNC at our Lab

As a logical consequence of the previous works, we tried to substitute concentrated Sulfuric acid with Ammonium persulfate (APS)
Leung et al. Small (2011) 7 (3):302.

APS is a strong oxidizing agent commonly used in polymer chemistry as an etchant, as a cleaning and bleaching agent.

APS has low long-term toxicity, high water solubility, low cost and easier handling. The absence of sulfate groups in the CNC obtainad leads to a higher thermal stability.



Molar mass	228.18 g/mol
Appearance	white to yellowish crystals
Density	1.98 g/cm^3
Melting point	120 °C (393 K) decomp.
Solubility in water	80 g/100 cm^3 (25 °C)

The Research on CNC at our Lab

Moreother, APS action is double, being able to release, when heated, both free acid radicals ($SO_4^{\bullet -}$) and oxidant species (H_2O_2), leading to a deep penetration in amorphous regions and achieving, due to the carboxylation of primary alcohols (C6) of cellulose molecules, higher cristallinity and higher charge density.
Two achievement that might be useful to increase barrier properties and **coating adhesion respectively**.

The process to obtain CNC is easier, modulable according to the cellulose source, applicable to complex raw materials (opens lignin aromatic rings)

Sheets of Cotton Linters (CL)

70 ° C, 16-18 h
1M APS, 1g CL in 100 mL

Centrifugation
8000 RPM 20min
(3 times)

Filtration, 2-3 µm

Freeze drying

CNC yield
≈ **50%**

CNC by APS treatment

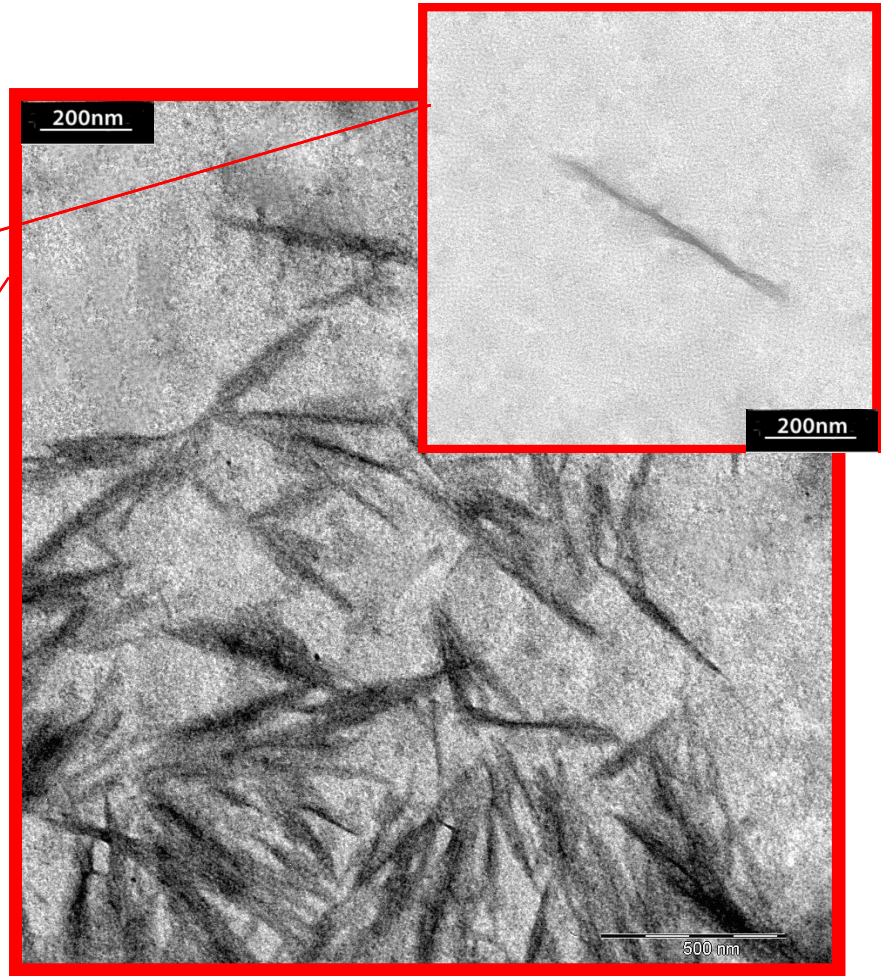
The goal was to investigate the differences between CNC obtained by the two methods and to compare the final properties of coated PET and OPP films

Morphology by TEM

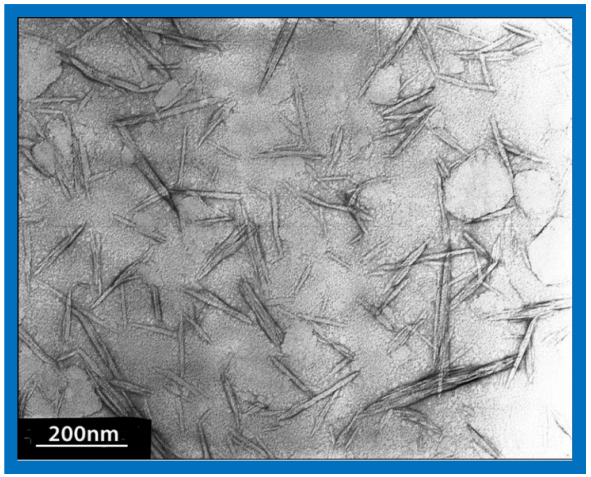
The morphology of CNC nanoparticles obtained were quite similar. Nanocristals by acid hydrolysis were generally shorter and thinner. The highest Aspect Ratio in the APS CNC was ≅ 200 (Inset)

Single cellulose nano-crystal by APS treatment

CNC by APS treatment



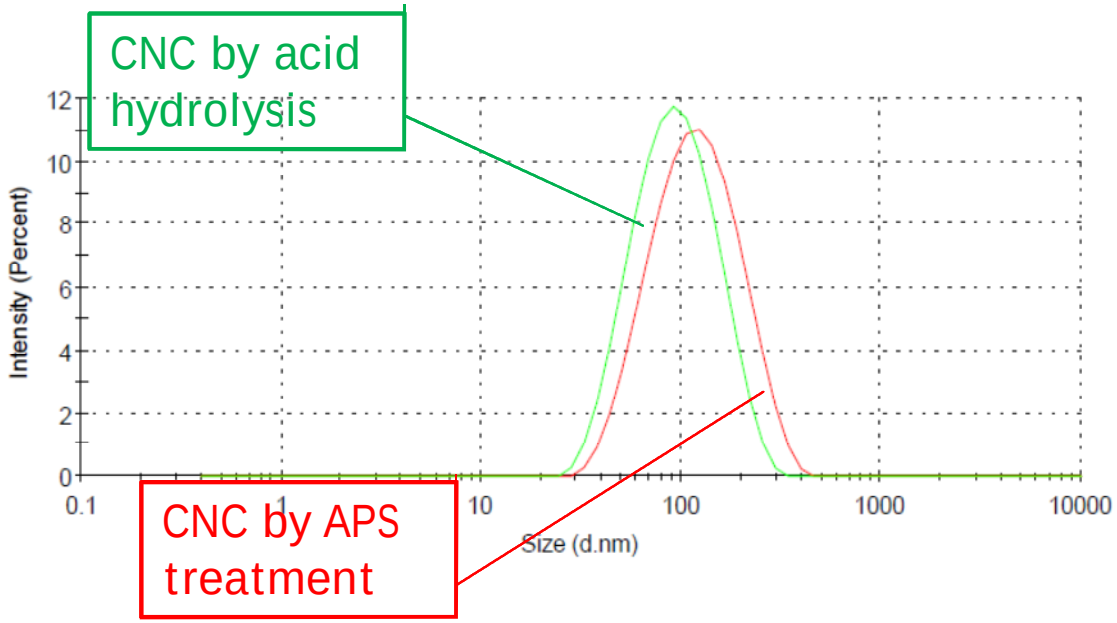
CNC by acid hydrolysis



CNC by APS treatment

Size Distribution by Laser diffraction

The distributions obtained by a Mastersizer equipment were quite similar. Nanocristals by acid hydrolysis were lightly smaller and a little more uniform.

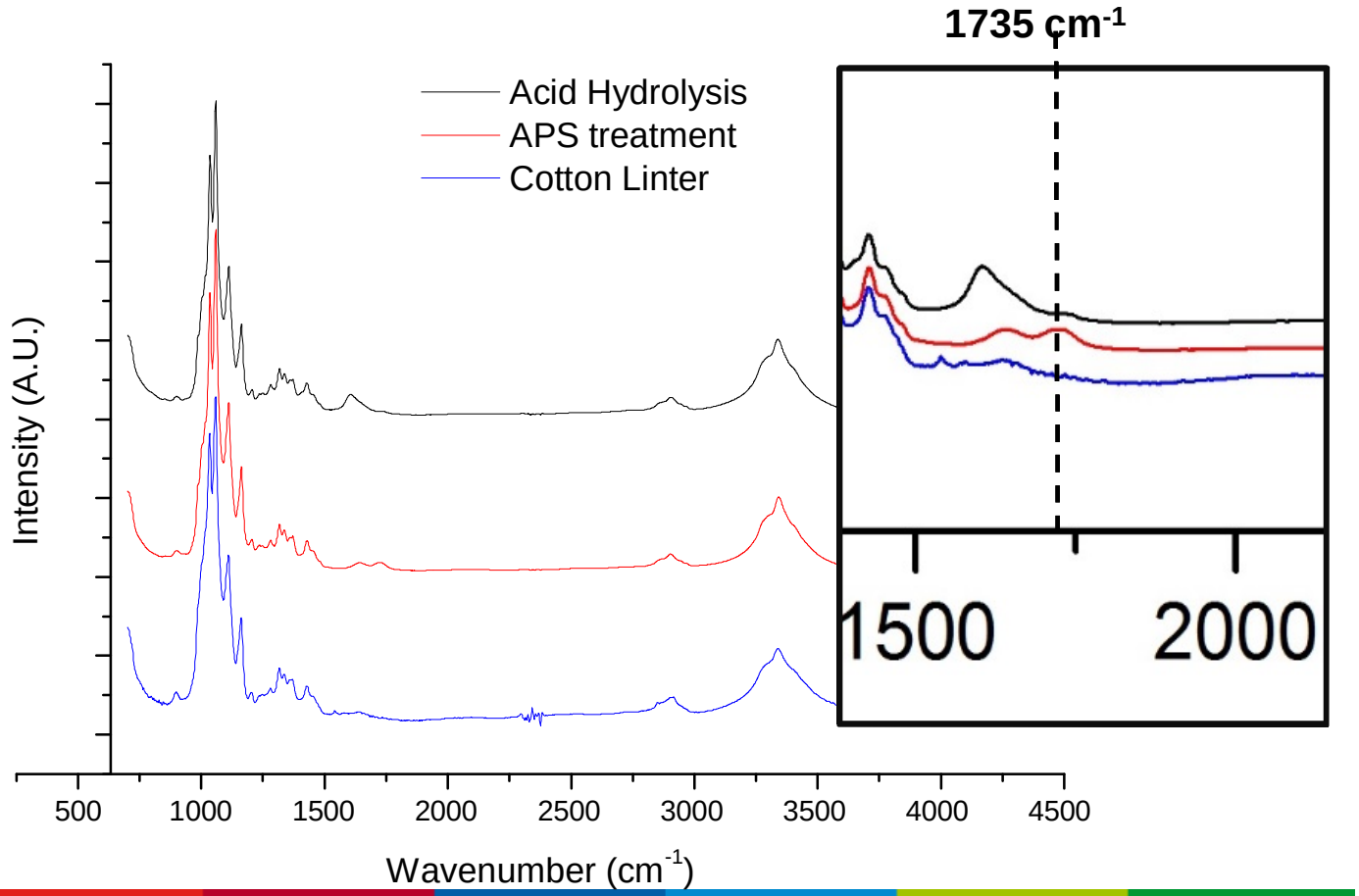


	Maximum dimension (nm)	Dispersity (Đ)
CNC by acid hydrolysis	80.8	0.19
CNC by APS treatment	101.2	0.23

CNC by APS treatment

Molecular Structure by FT-IR

The typical FT-IR spectrum of celllulose showed by the original source (cotton linters) were mantained in the two kind of CNC produced. In the CNC by APS treatment a signal from carboxylic groups at 1735 cm^{-1} was also detected, while in nanocrystal from acid hydrolysis it was absent.

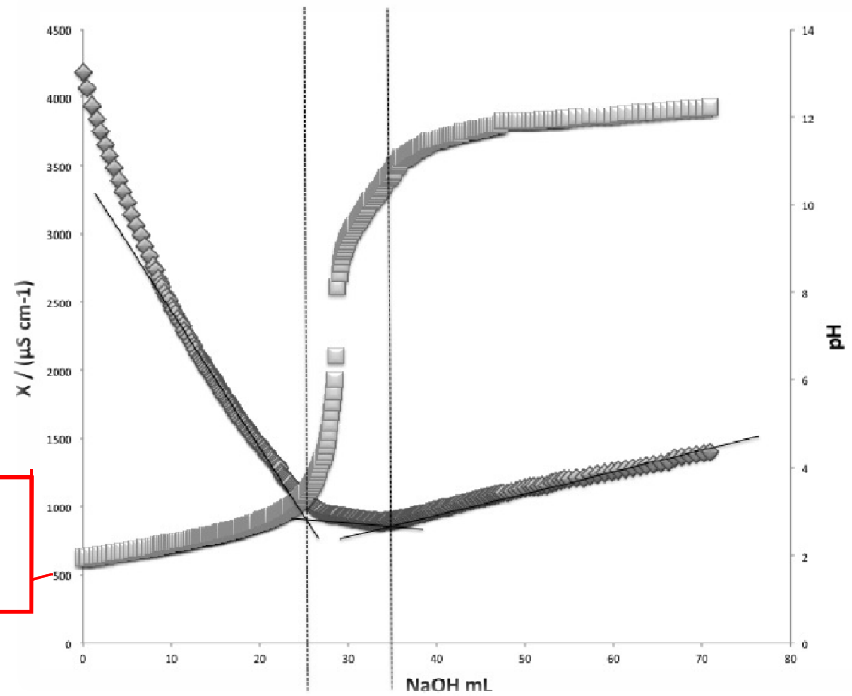


CNC by APS treatment

Charge Density by titration

The curves of titration allowed to calculate the amount of carboxyl groups and therefore the degree of oxidation (DO). The charge density of CNC obtained by APS treatment is more than 4 times the one showed by acid hydrolysis

CNC by APS treatment



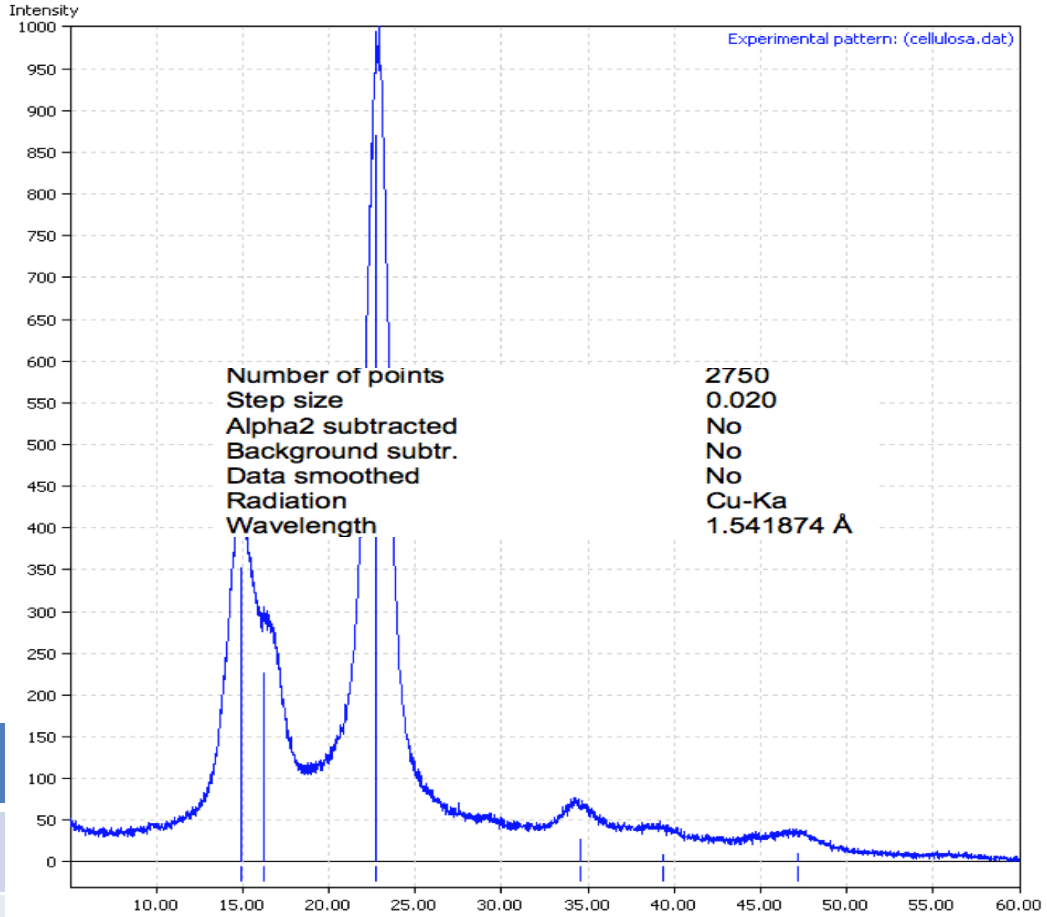
	Charge density (mEq/kg)	Degree of oxidation
CNC by acid hydrolysis	220	-
CNC by APS treatment	905	0.15

CNC by APS treatment

Cristallinity by XRD

The typical X-ray diffraction spectum of crystalline cellulose was obtained after APS treatment.
The CRI (crystallinity index) was calculated by «peak height method» resulting in 87%. The value is in accordance with literature reports and little higher than the value obtained previously on the same source, by **acid hydrolysis** (close to 85% by NMR).

	Crystallinity (CRI%)
CNC by acid hydrolysis	**≈85**
CNC by APS treatment	87.0
Cheng *et al.* (2014) J. Mater. Chem. A 2,251	87.5

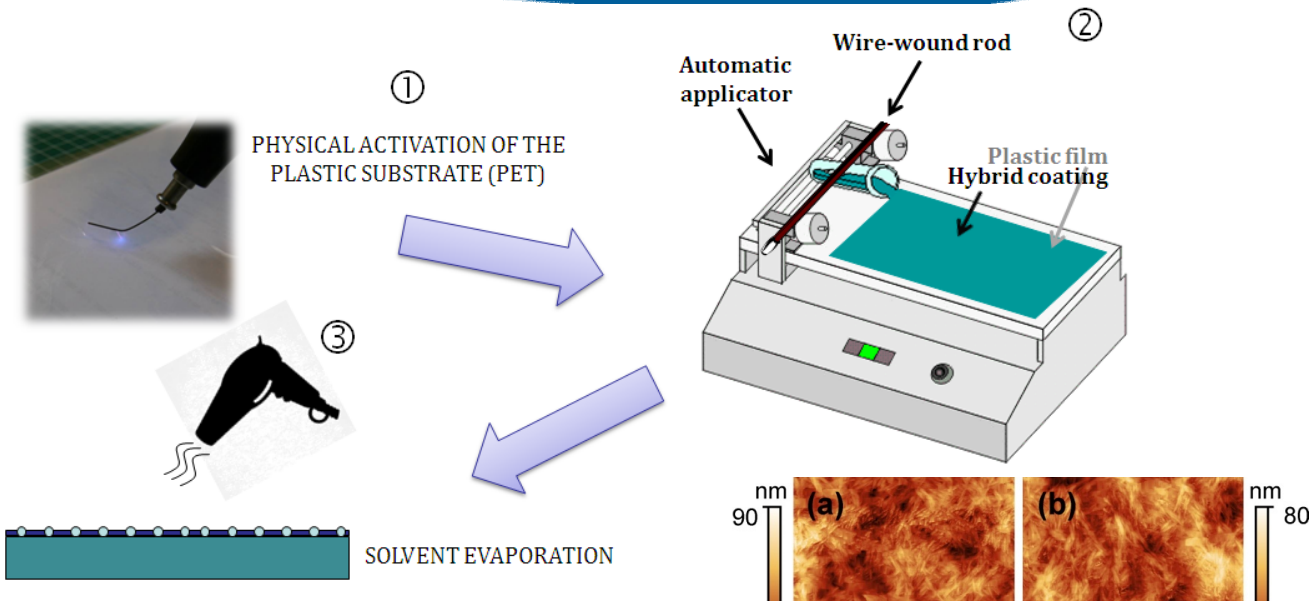


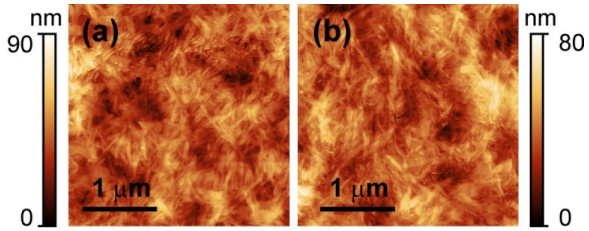
$$crI(\%) = \left[\frac{(I_{200} - I_{am})}{I_{200}}\right] \times 100$$

PET and OPP coating by APS-CNC

Film coating

A 8% m/m suspension in water at pH 7 of CNC obtained by APS treatment, was used to coat the corona treated sides of PET 12 μm and 20 μm OPPcoex films. Both the two films, after the surface activation, were succesfully coated, resulting in a nanocellulose thickness of about 600-800 nm, quite clear and stable.

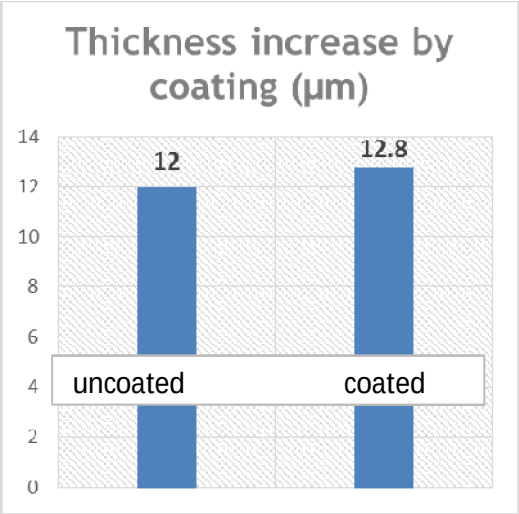


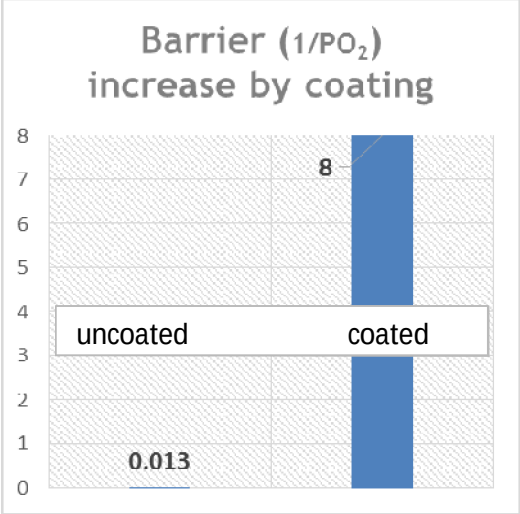


AFM pictures of CNC coatings by acid hydrolysis of PET(a) and OPP (b)

PET Coatings	Thickness (μm)	Transparency (T%, 550nm)		Haze (%)	
CNC by acid hydrolysis	0.8-1.5	89.4±0.2	PET bare 88.0±0.2	5.10±0.20	PET bare 2.7±0.1
CNC by APS treatment	0.6-0.8	86.1±0.01	PET bare 84.2 ±0.02	5.28±0.00	PET bare 2.8 ±0.01

OTR of coated films





PET film coated with CNC by APS treatment

Oxygen Permeability

The oxygen permeability of the two films were strongly reduced in comparison with the un-coated films and also with similar substrates coated with CNC obtained by acid hydrolysis.The PO2 reduction was estimated, at 23 C and 0% of RH, to be 99.8 and 99.3% respectively for PET and OPP film

	PO2 of PET coated [ml m^{-2} d^{-1} bar^{-1}) 23°C 0% RH	PO2 of PP coex coated [ml m-2 d -1 bar-1) 23°C 0% RH
CNC by acid hydrolysis	1.51	24.7
CNC by APS treatment	0.125	6.64

Conclusions

Coating technology can be really useful in implementing enhanced properties provided by biobased materials on flexible packaging materials.

The perspective use of cellulose nanocristals as barrier coating against oxygen transmission to extend the shelf life of perishable products, seems promising and feasible and goes towards a higher sustainability of packaging materials.

CNC obtained by APS treatment demonstrated to have better barrier performance and adhesion capacity, due to higher crystallinity and charge density

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DEFENS
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Grazie per la vostra attenzione!

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Milano, 16 settembre 2014