Structure and properties of extruded bio-nano-composites based on bio-polyesters and chitin nanofibrils

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SEA FOOD WASTE

Worldwide chitin based waste material from the fishing industry, exceeds 250 billion tons/year

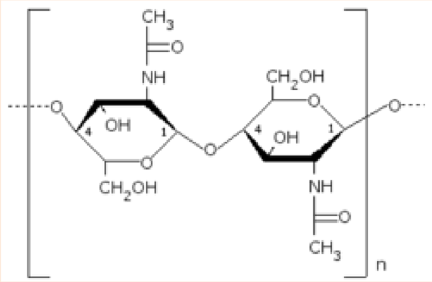
The processing of 1 kg of shrimp produces 0,75 kg of waste (e.g: chitin containing shells) and 0,25 Kg of final food [1]

High availability of chitin based waste from shrimp and crabs[2] as food industry produces them in huge amount

1. P Morganti, G Morganti, A Morganti, Nanotechnology, Science and Application, 2011:4, 123-129
2. JG Fernandez et al., Adv. Funct. Mater. 2013, 4454-4466
3. M Mincea et al., Rev. Adv. Mater. Sci. 30, 2012, 225-242

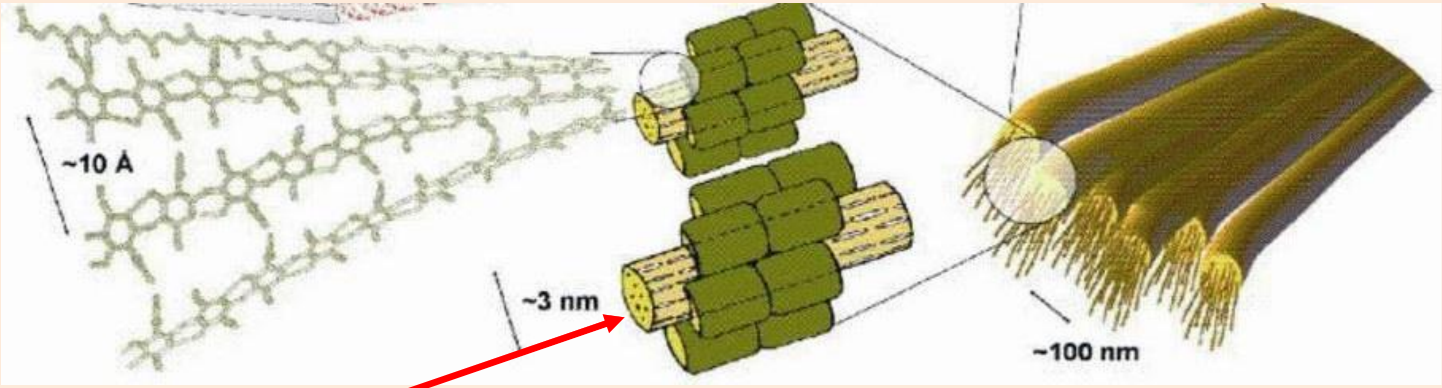
CHITIN

structure



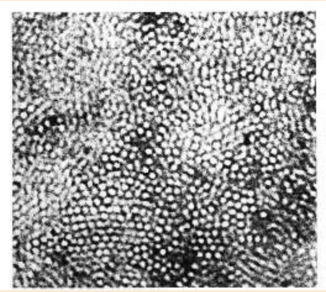
Inter-macromolecolar hydrogen bonding

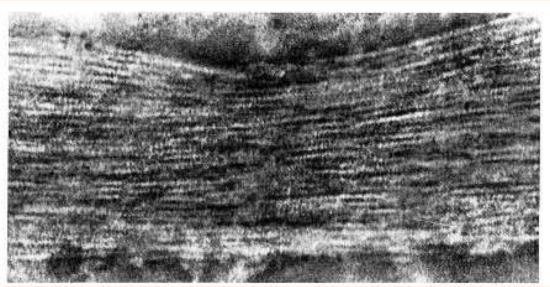
nano-assembly



Each chitin nano-crystallite is composed of about 20 linear chains of poly(N-acetyl glucosamine)

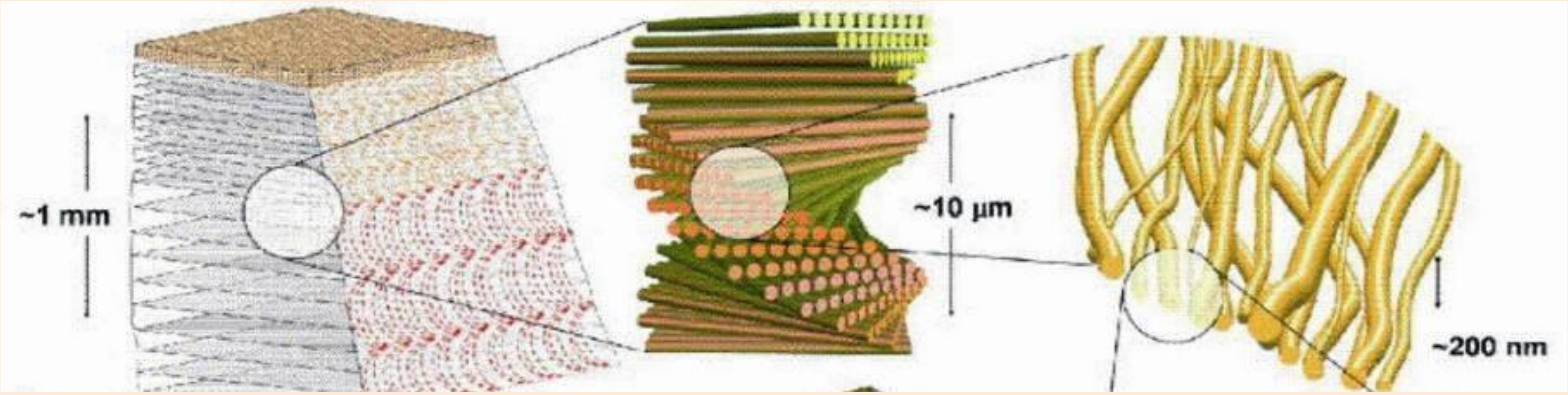
micro-assembly





the chitin resulting rigid substance is ***immersed in a matrix*** of proteins and calcium carbonate

Interestingly, the microfibers form layers producing a plywood-like structure

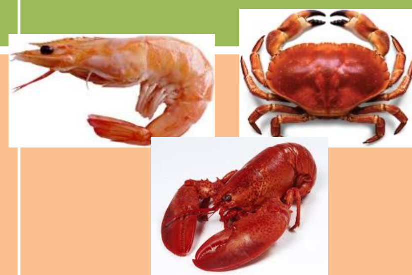


On each layer a different orientation of the microfibers is achieved, thus making the material highly resistant.

[The traditional production of glass reinforced composites for structural application in building or ships was unconsciously following a biomimetic approach!]

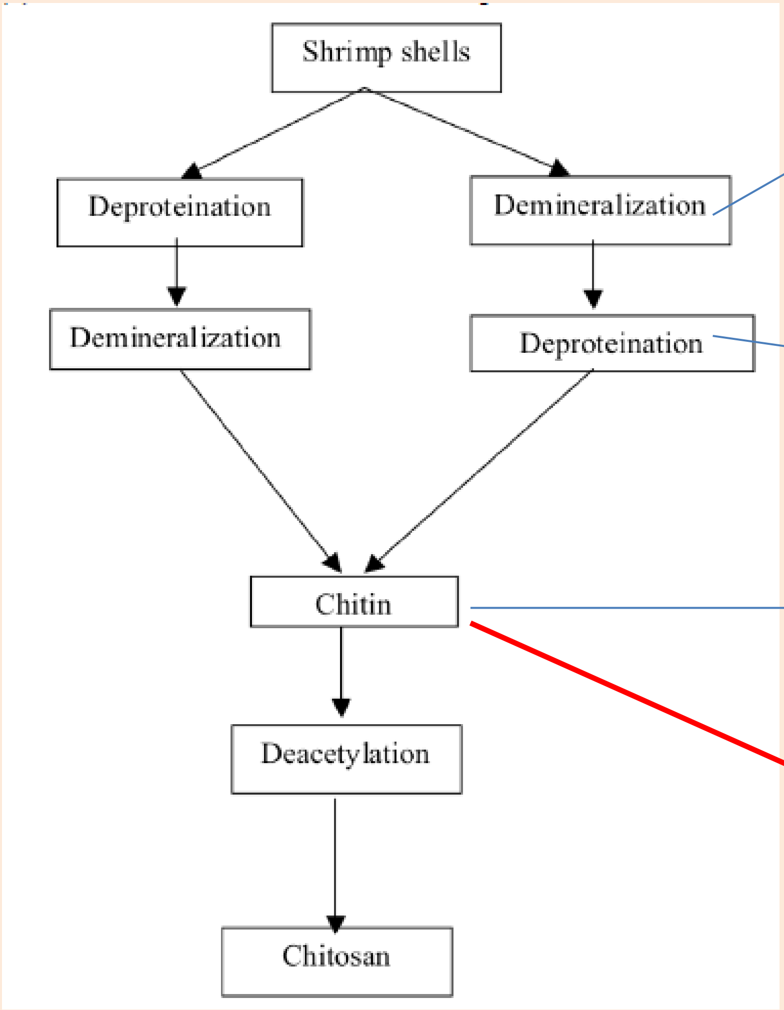
Chitin microfibrils are constituted of alternating crystalline and amorphous domains.

The most abundant kind of crystalline chitin is the α-chitin

CHITIN CRYSTALS	where	Structural features
α-CHITIN	 krill, insect cuticle, fungal and yeast cell walls	Molecules arranged in antiparallel fashion (strong H bonding)
β-CHITIN	 Squid pens  Tube worms	Molecules arranged in parallel fashion
γ-CHITIN	 Beetle cocoons	Molecules arranged in both parallel and anti-parallel fashion

M Mincea et al., Rev. Adv. Mater. Sci. 30, 2012, 225-242

CHITIN PURIFICATION



Acid treatment

Basic treatment

Acetylation degree should be higher than 0,9 and molecular weight in the range 1-2,5*10 ^{6}

MNV Ravi Kumar, React. Funct. Polym, 46, 2000, 1-27

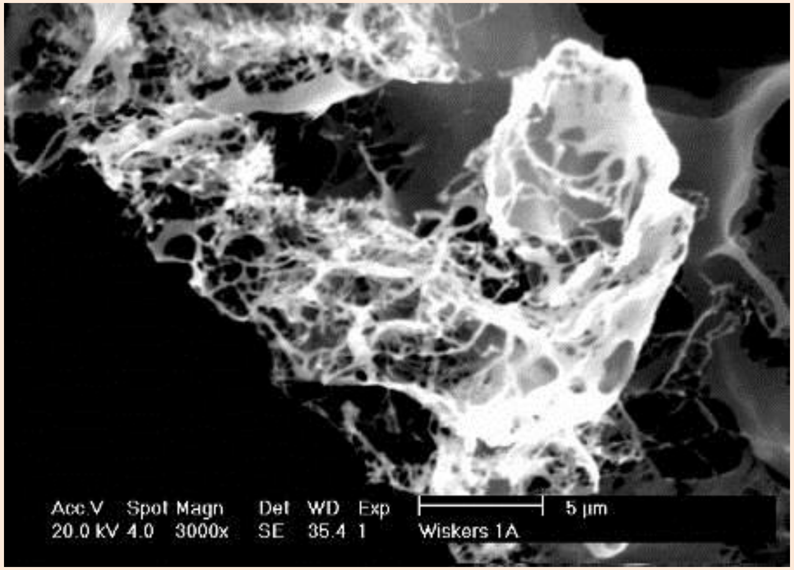
Microfibers based materials

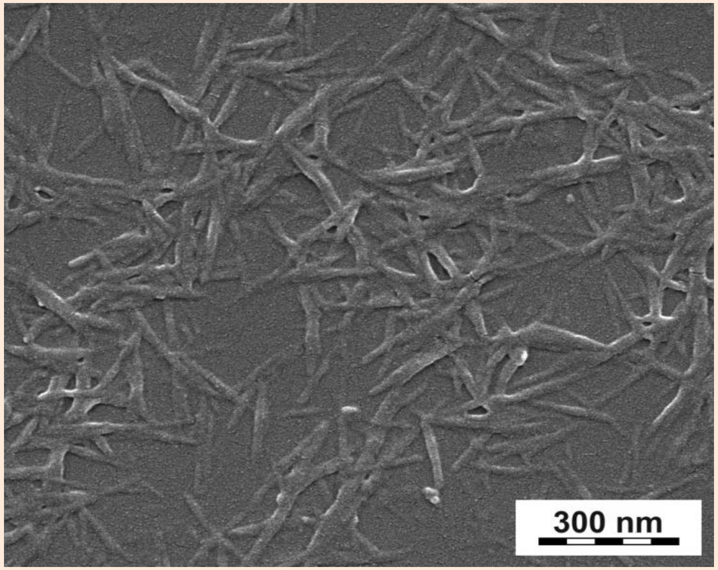
N. Van Toan, The Open Biomaterials Journal, 1, 2009

FROM CHITIN TO NANO-CHITIN

The microfibers contain crystalline nano-fibers. It is possible to produce chitin nano-whiskers by chemical treatment of microfibers.

MAVI SUD plant, Aprilia, (Italy) patented this process. Nano-chitin is thus available in diluted water suspension for cosmetic applications.

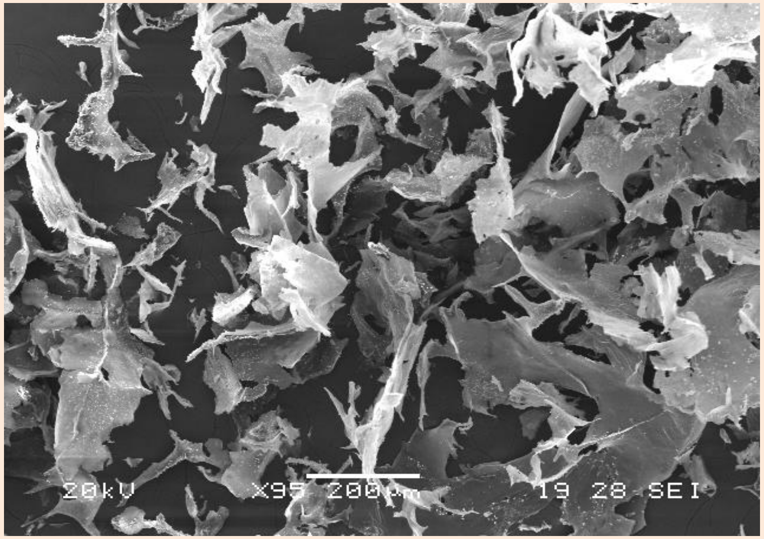




300 nm long and 10 nm wide nano-fibrils

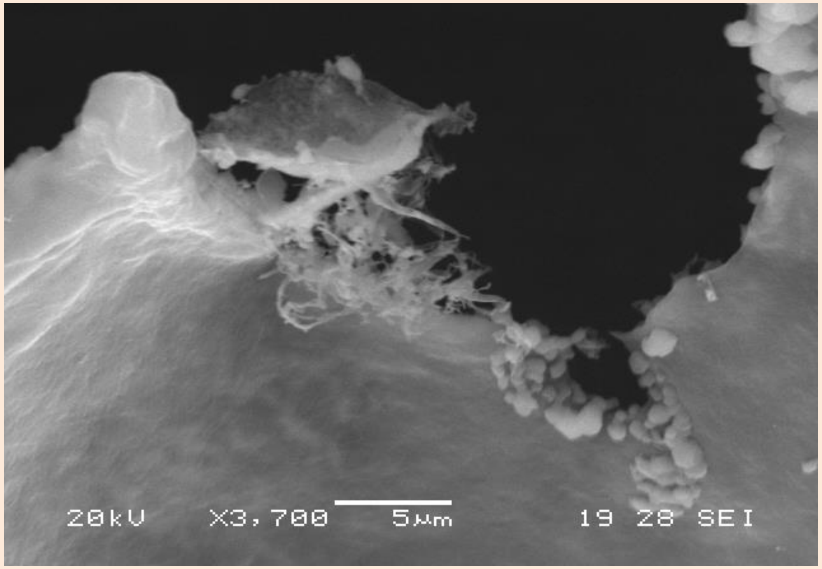
Aspect ratio = 30

STRUCTURE OF DRIED NANO-CHITIN

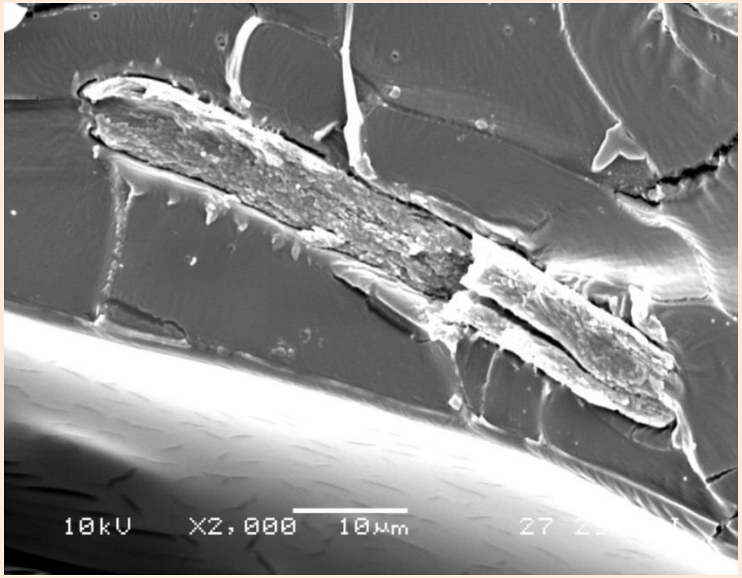


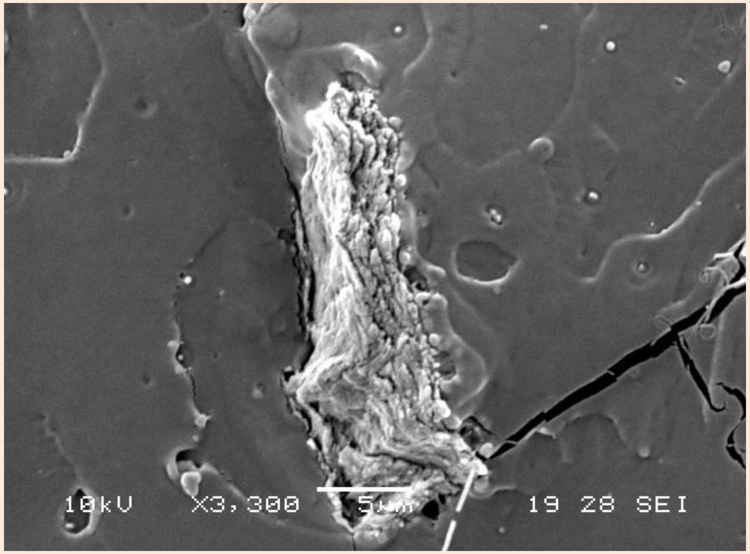
Dried nano-chitin agglomerates in sheets

The original nanostructure can be observed only on the edge of the sheets



The dispersion after drying in a poly(lactic acid) PLA matrix in discontinuous mixer resulted in the morphology described by the micrographs below.



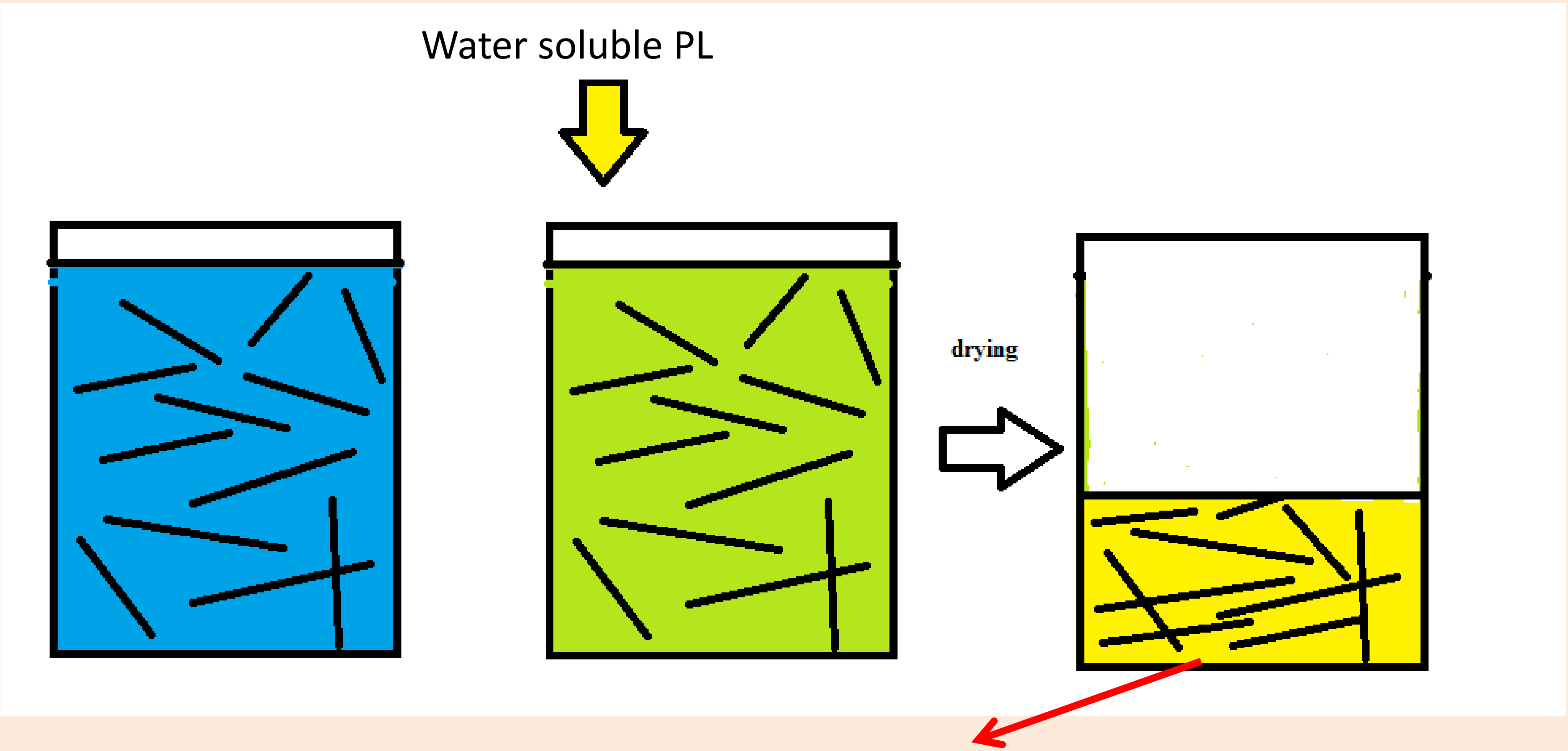


PLA NC 2%

The presence of big agglomerates resulted in material brittleness

MASTER-BATCH APPROACH

The preparation of a NC suitable for dispersing in PLA requires to keep separated nanofibrils during the drying.
Different additives were added to these water based suspensions.

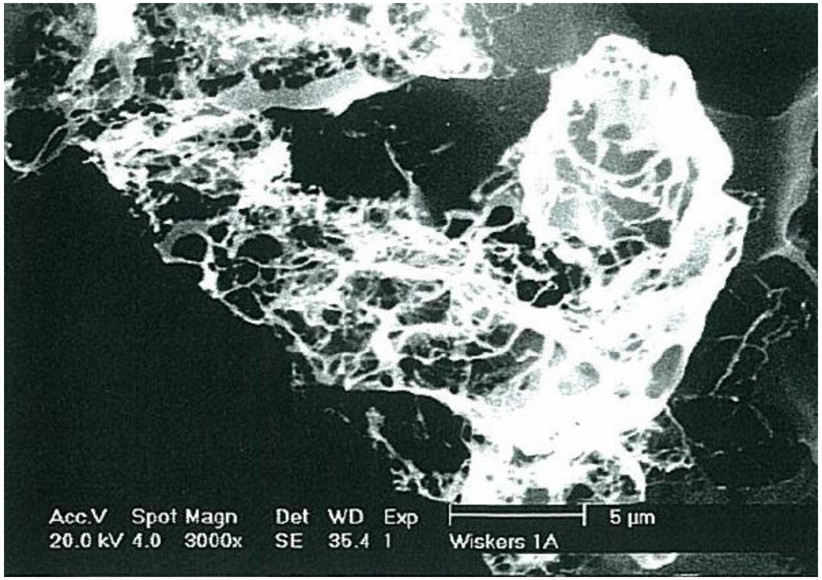


Solid or semi-solid composites with CN maintaining nano-dispersion

Lab- Preparation of master-batches

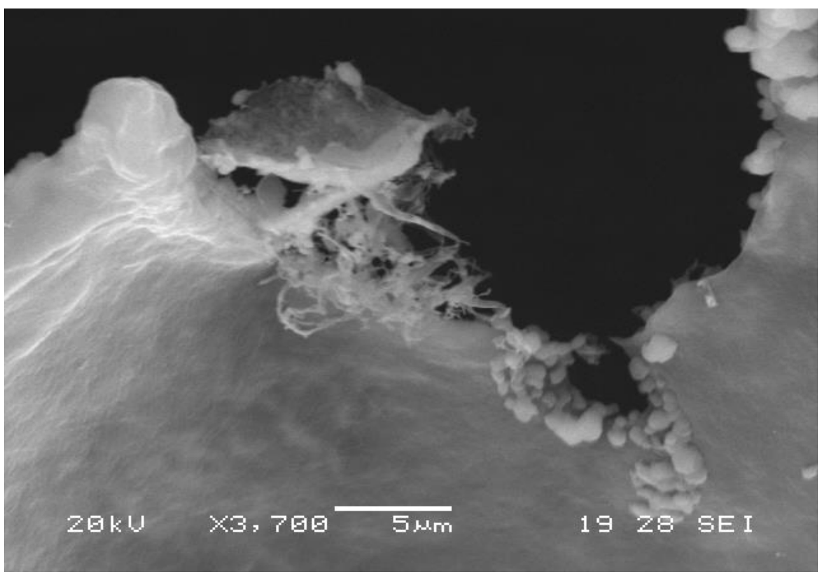
Preparation in water suspension with final drying step

	PL MW	Quality of dispersion (By SEM analysis)
PL8000_NC	8000	OK
PL6000_NC	6000	OK
PL4000_NC	4000	OK
PL1500_NC	1500	OK
PL400_NC	400	Not detectable

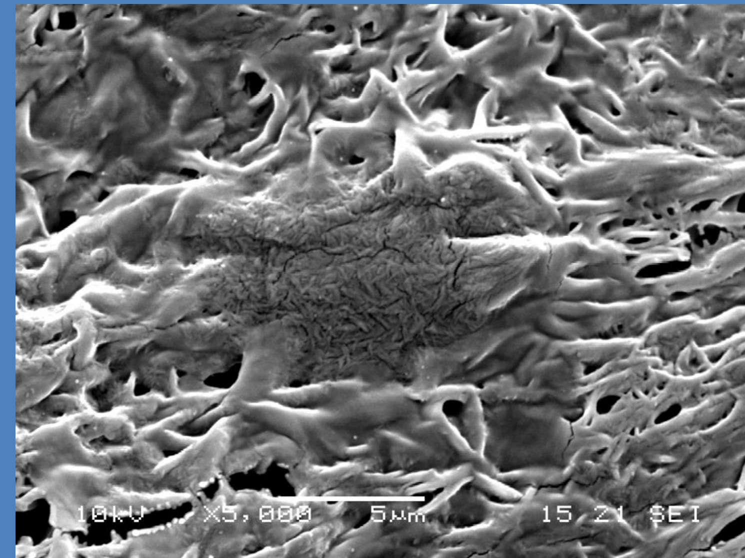


Starting nanofibrils (240 x 5 x 7 nm)

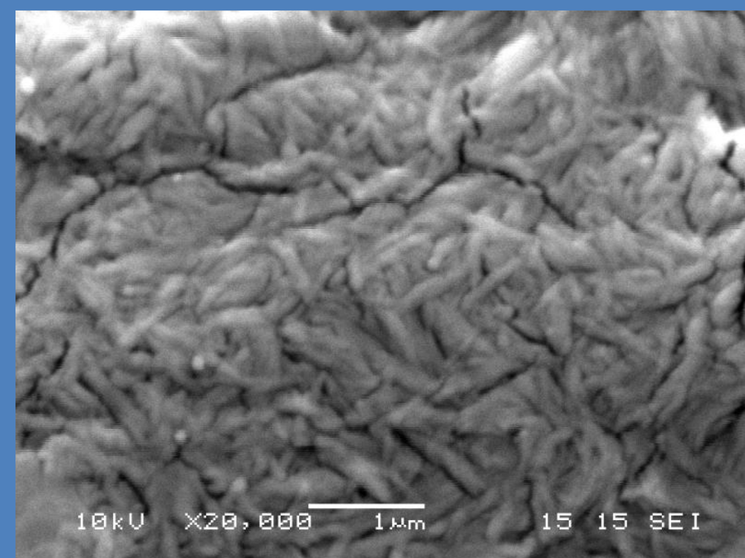
P. Morganti et al., Clinics in Dermatology (2008) 26, 334–340



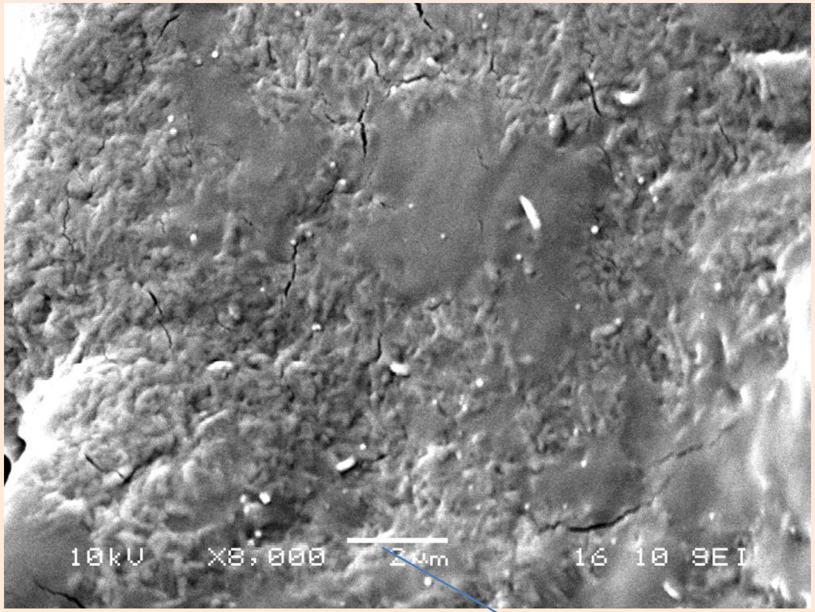
Agglomerated nanofibrils (after drying suspension)



PL 8000_NC

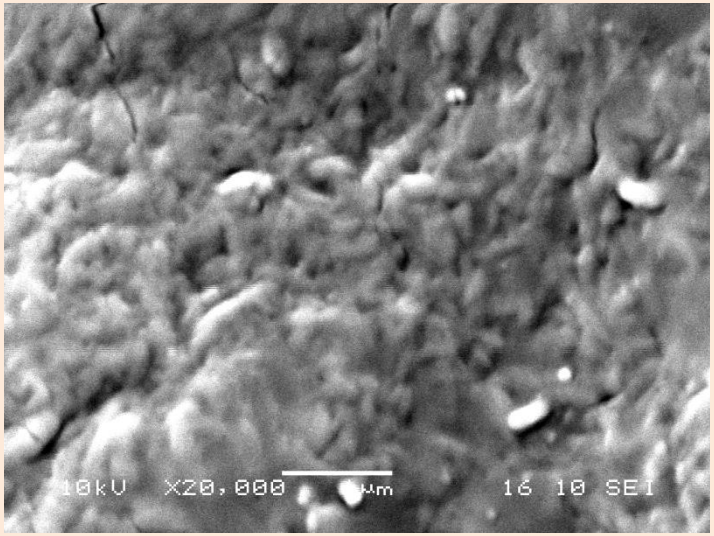


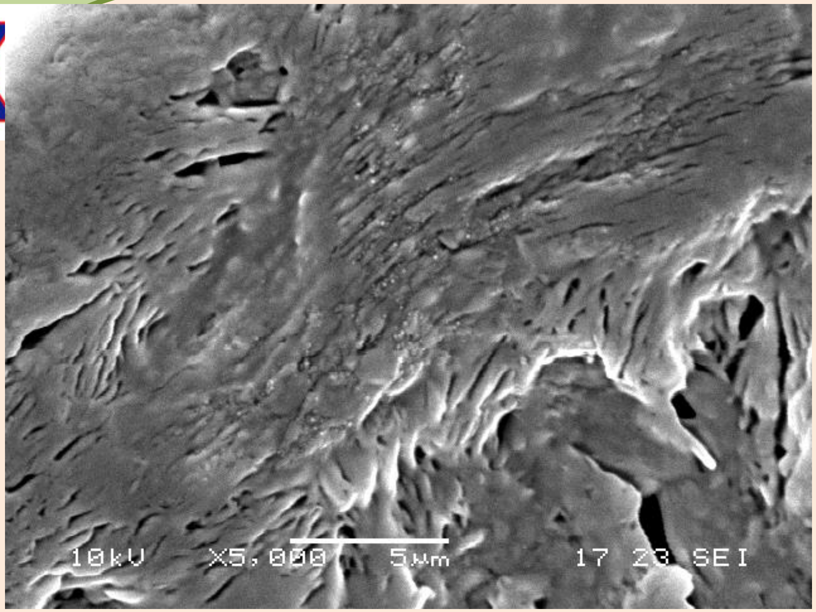
General view

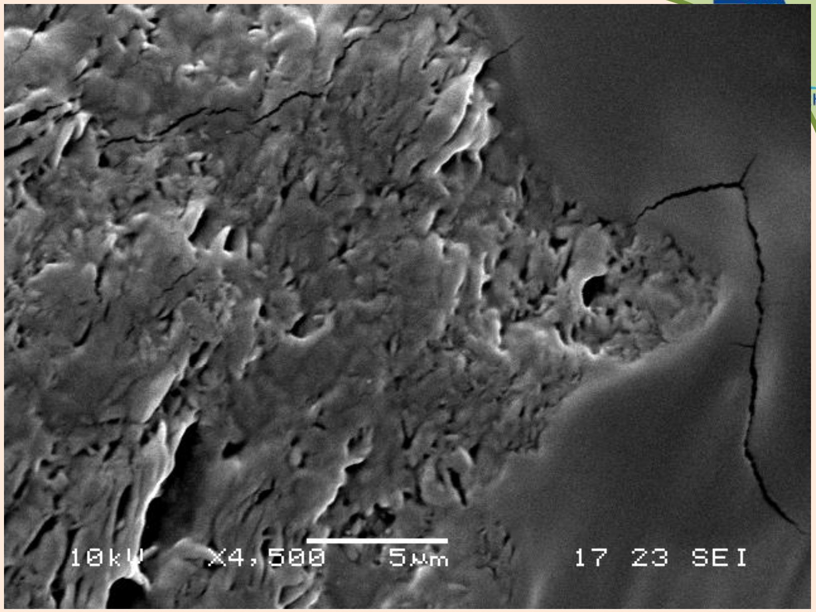


PL 6000_NC

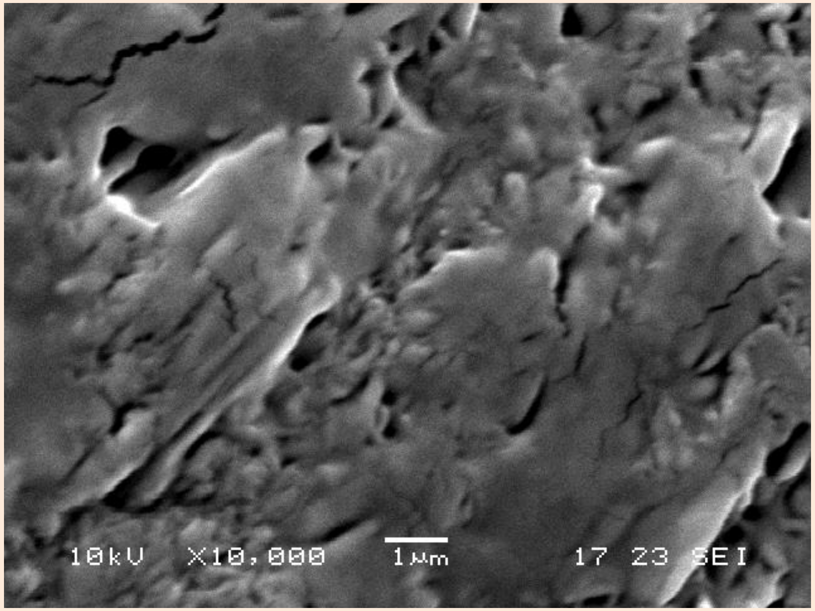
Enlergment 20000X







PL 4000 + chitin nanofibers



PREPARATION OF BIOPOLYESTER COMPOSITES

PLA

masterbatch

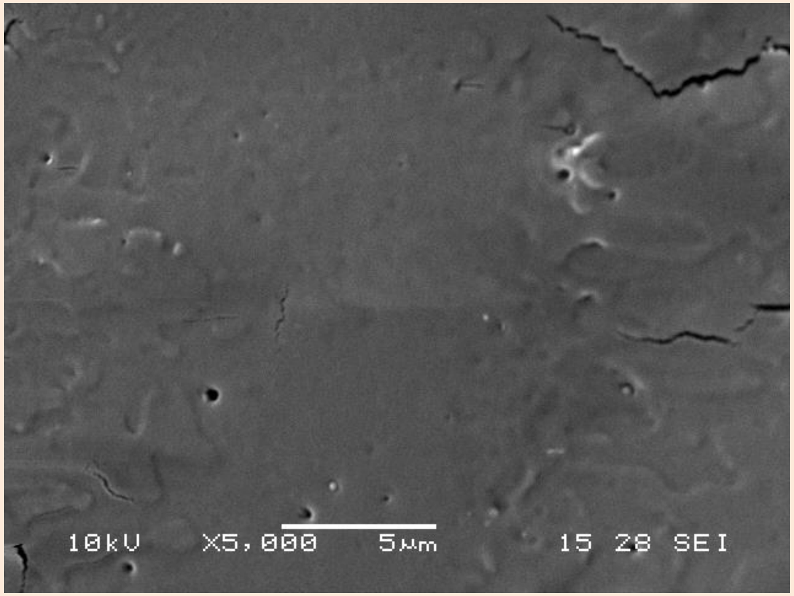
plasticizer

Minilab II Haake Reomex twin-screw extruder

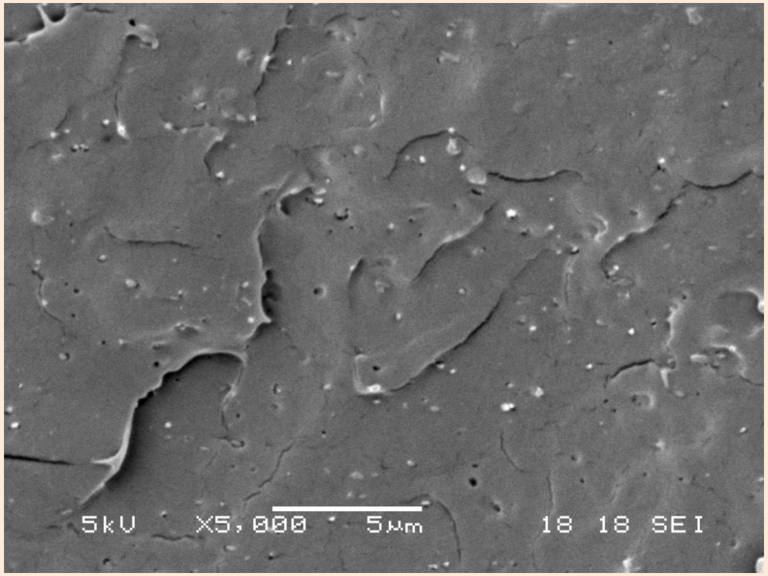
Preheated cylinder

Haake MiniJet II mini injection molder

Haake type 3 specimen (557-2290)



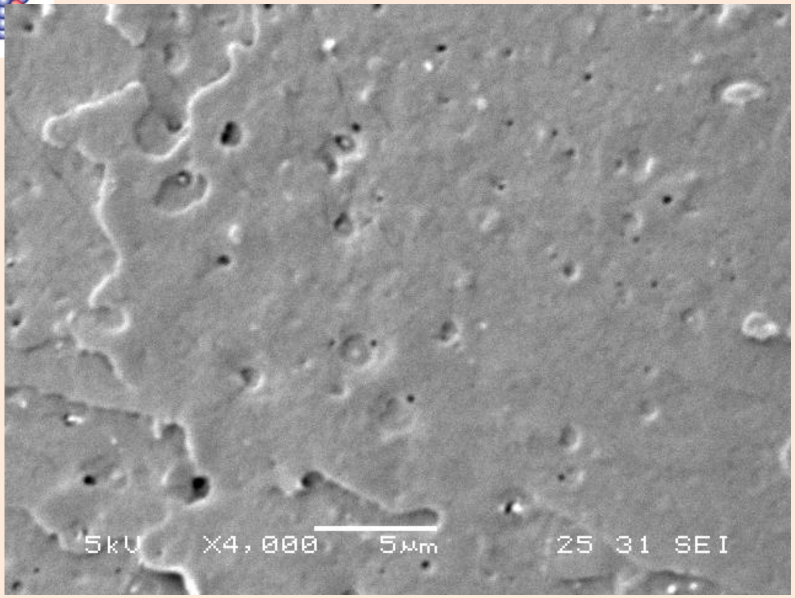
Plasticized PLA
PLA_PLlow

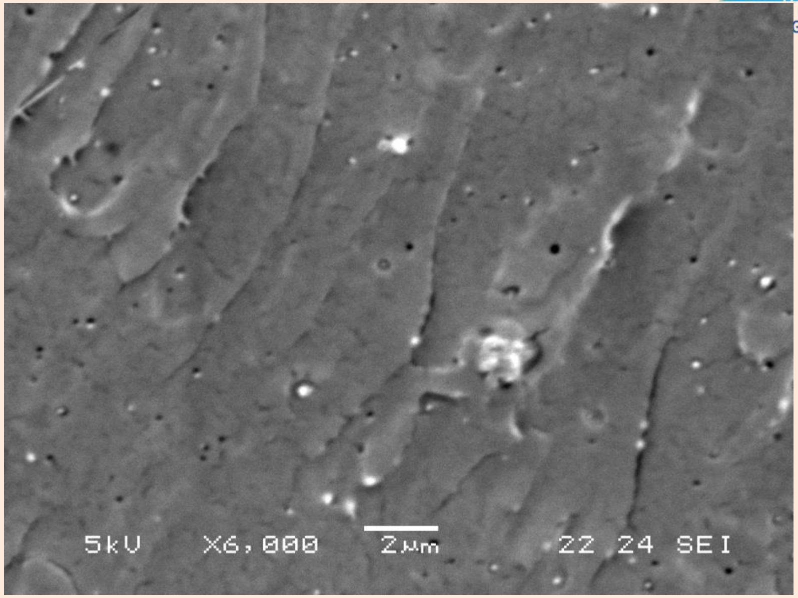


PLA_PLlow_NC

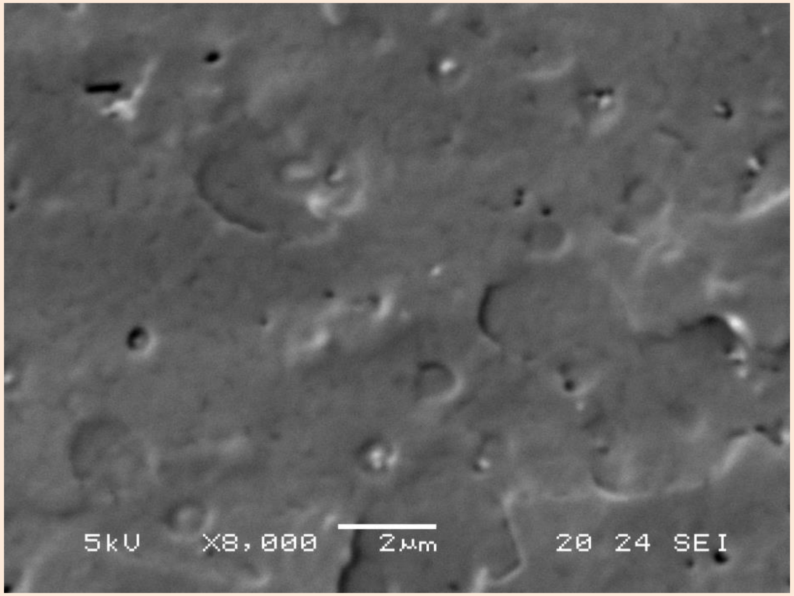
The micro-morphology, with PE dispersed domains, did not change because of NC addition.

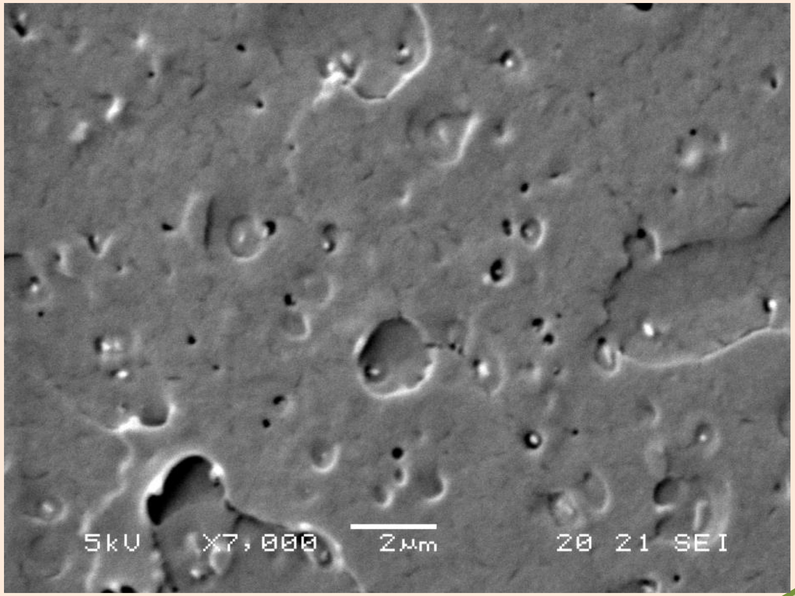
The agglomerates are not present at all in the material





PLA + PLhigh NC

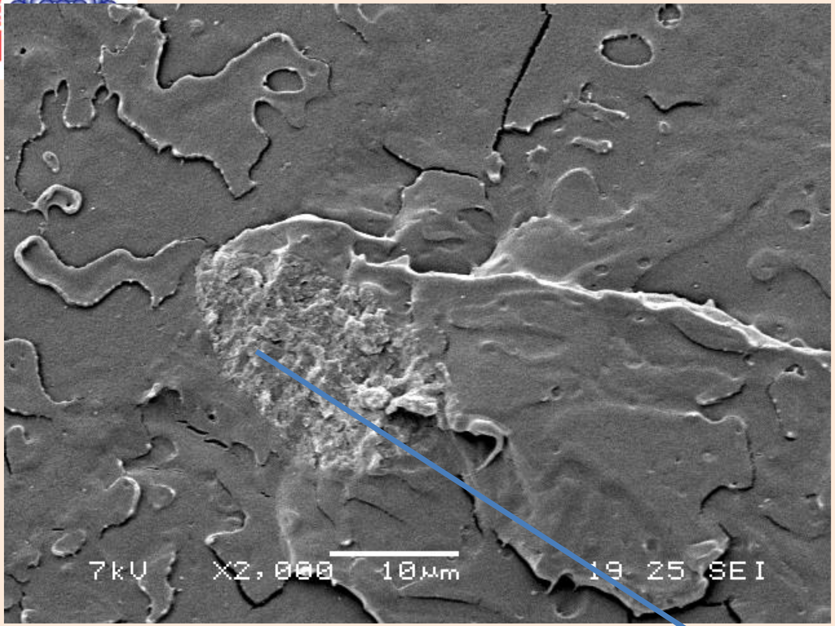


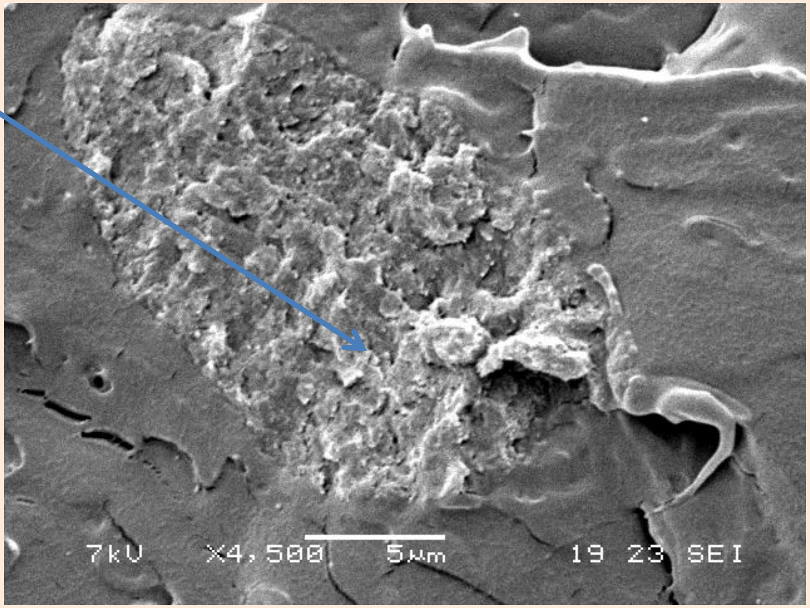


Tensile tests results

	E (GPa)	σ_y(MPa)	ε_b (%)
PLA	3,5 ± 0,1	60,4 ± 0,3	4,1± 0,5
PLA+2%NC	2,9 ± 0,1	-	2,3 ± 0,4
PLA +lowPL10%	2,3 ± 0,3	26 ± 0,3	180± 10
PLA+lowPL10%+2%NC	1,8 ± 0,3	23 ± 5	160 ± 10
PLA+highPL10%+2%NC	2,5 ± 0,1	45 ± 5	160 ± 10
PLA+lowPL1%+2%NC	3,2 ± 0,8	52 ± 6	10 ± 2
PLA+lowPL5%+2%NC	2,8 ± 0,8	47 ± 3	11,4 ± 0,9
PLA +lowPL10%+5%NC	1,8 ± 0,3	34 ± 2	160 ± 10
PLA +lowPL10%+12%NC	1,7 ± 0,3	23 ± 5	181 ± 6

PLA+2% NC





The presence of such agglomerates can be avoided thanks to the master-batch strategy!!!

Nano-dispersion vs micro-dispersion: subtracting the effect of plasticizer

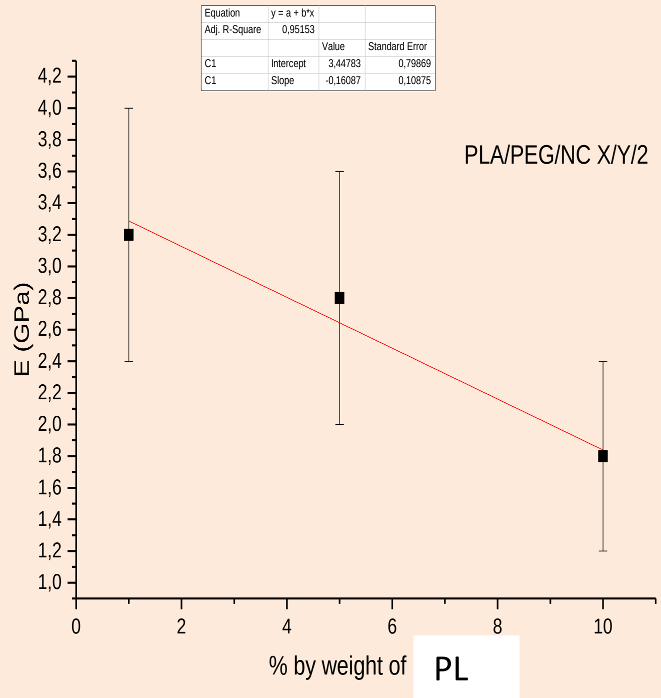
Trials at different content of PL and constant content of NC : extrapolation of modulus at PL= 0.

E_{extrap} = 3,4 GPa

E_{agglom} = 2,9 GPa

E agglom was obtained for the composites obtained without PL(with agglomerates!!!).

An improved dispersion can favor reinforcement, but the NC can not allow reaching a modulus higher than the one of PLA (3,5 GPa).



A similar evaluation can be made by considering the $\varepsilon_{bextrap}$ and the $\varepsilon_{bagglom}$.

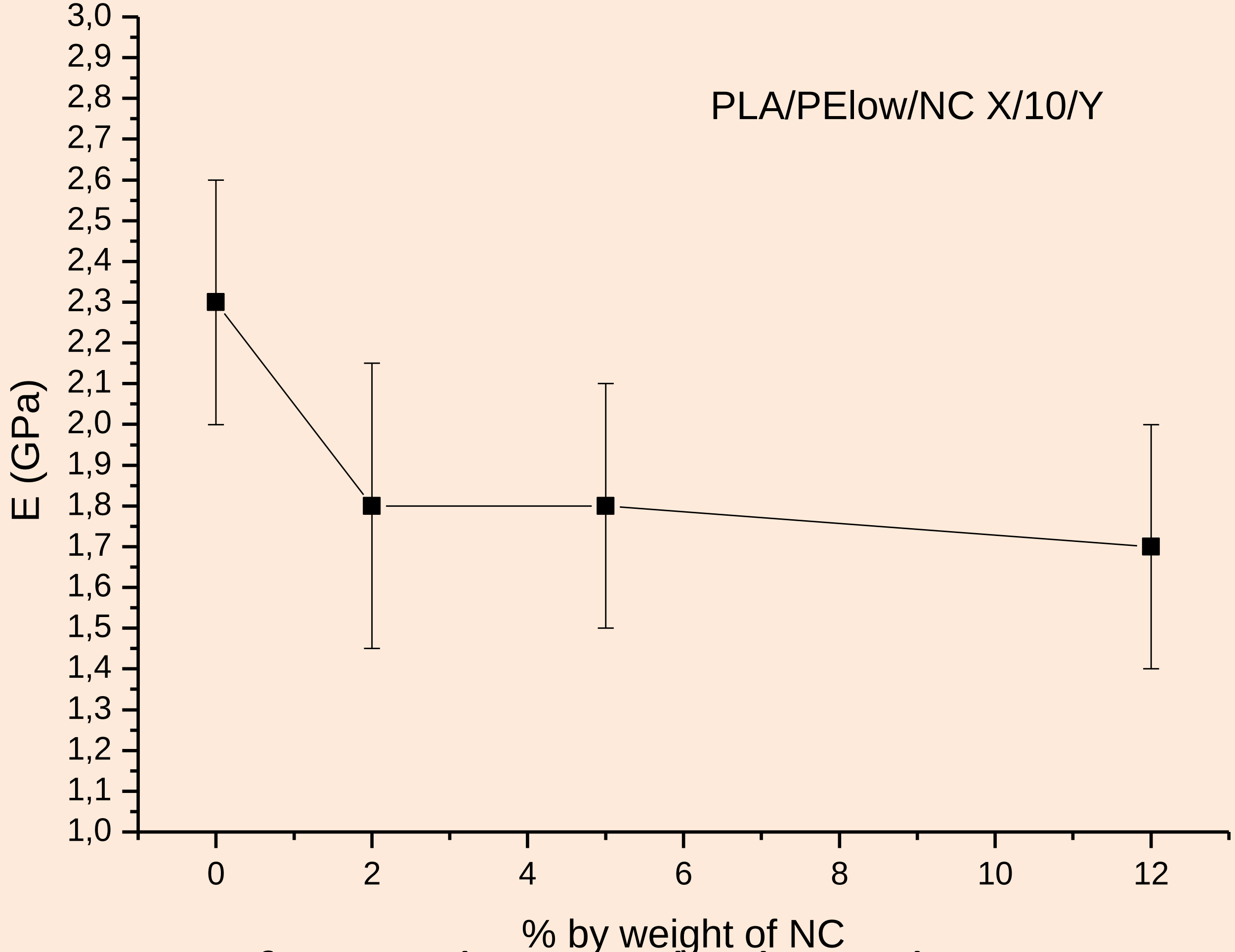
$$\frac{\varepsilon_{bextrap}}{\varepsilon_{bagglom}} = 4$$

The increase in the extrapolated value of ε_b is related to the absence of agglomerates.

The extrapolated value is twice the value of pure PLA

E as a function of NC content

Trials carried out by maintaining the PL low content at 10% by weight



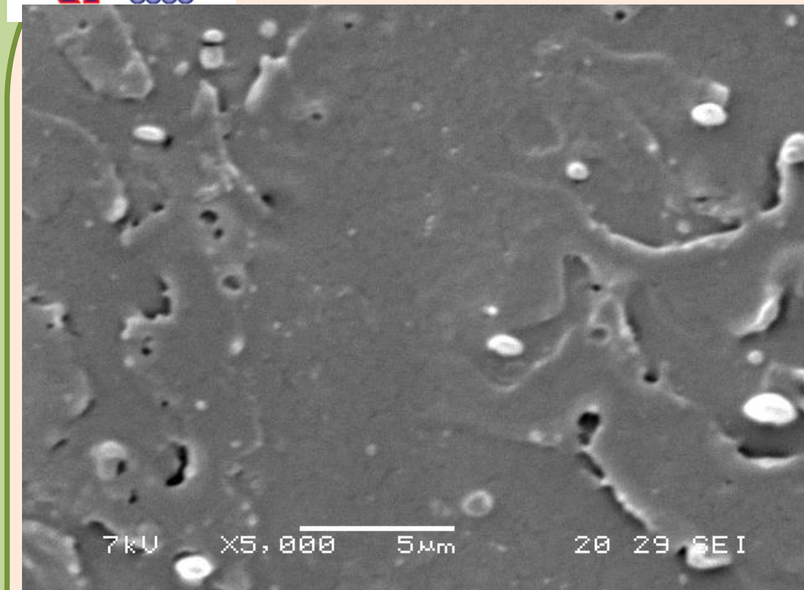
The presence of NC and PL resulted in a decrease in modulus

DSC analysis results

	T_g (°C)	X_c (%)
PLA	58	0
PLA+2%NC	57	3
PLA + lowPL10%	42	10
PLA+lowPL10%+2%NC	40	8

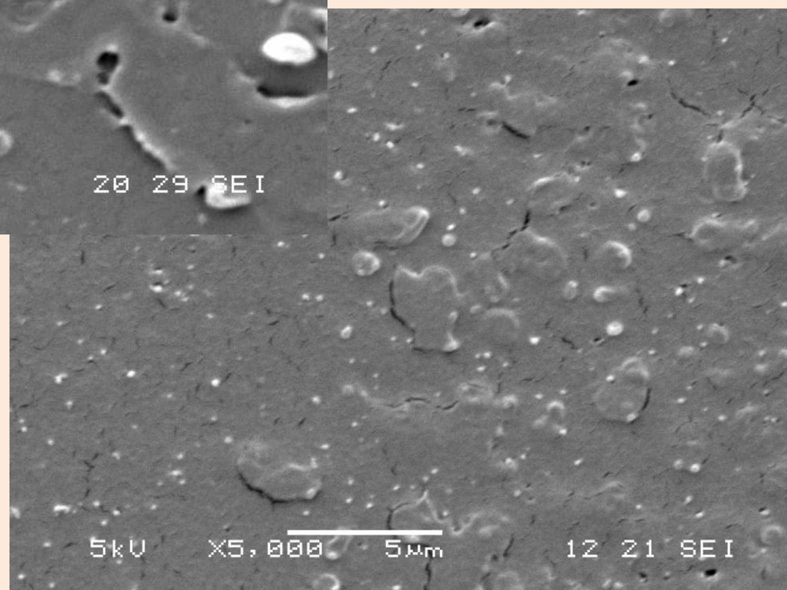
The addition of nano-dispersed nano-fibrils leads to a slight crystallinity reduction

PLA_PLlow1_NC

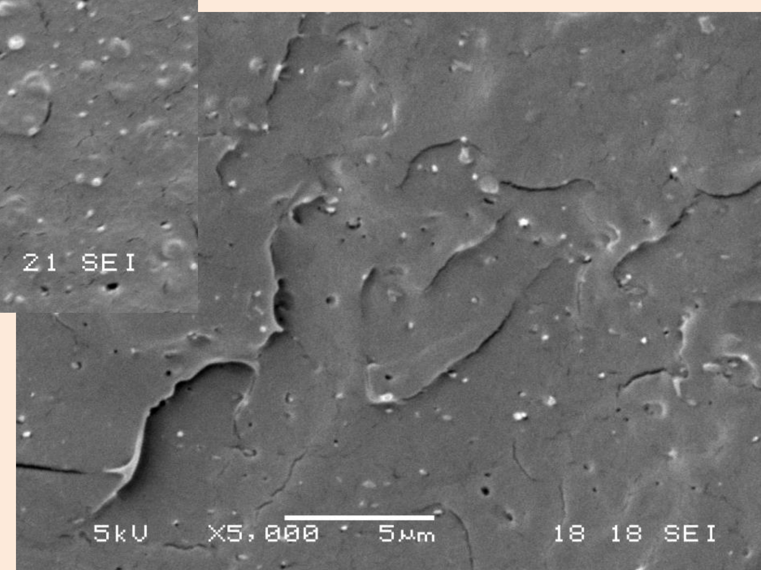


Increasing amount of PE

PLA_PLlow5_NC

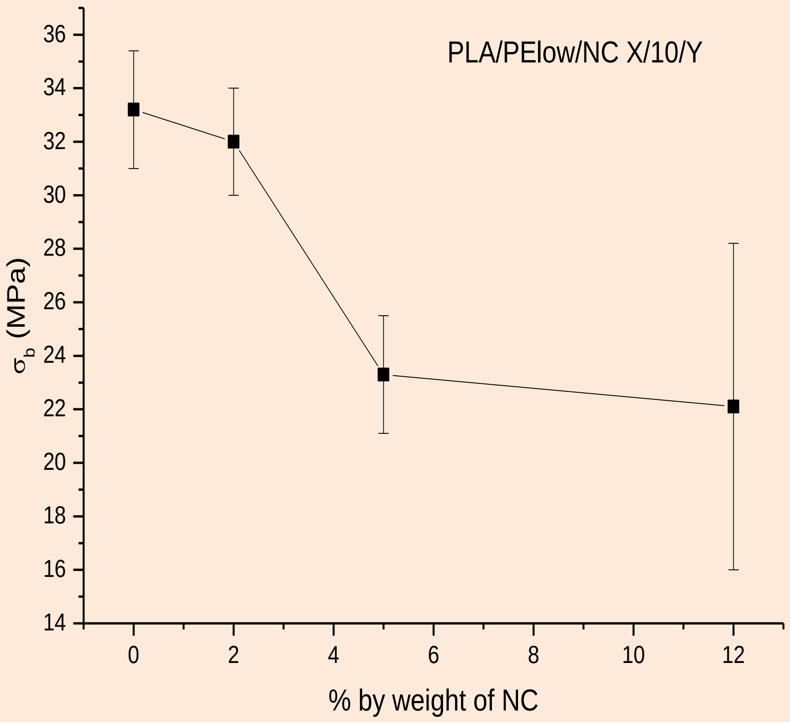


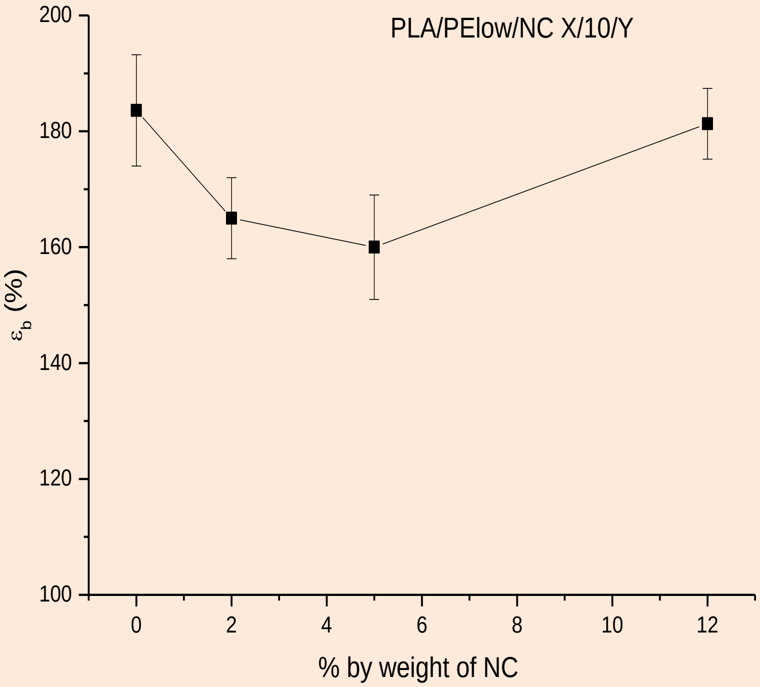
PLA_PLlow10_NC



PL is active in allowing the achievement of a better morphology (lower dispersed phase diameter and lower diameter value dispersion)

Breaking behavior as a function of NC content





In the presence of PL with different molecular weight it was possible to have a dispersion of NC in much concentrated (about 50% of NC) composites .

These pre-composites, added to PLA during extrusion, allowed to obtain both plasticized and nano-filled materials.

Properties can be modulated as a function of PE and NC composition as a result of balancing between plasticization effect, crystallinity content and reinforcement effect.

SEVENTH FRAMEWORK PROGRAMME

Thanks to:

n-chitopack

Sustainable technologies for the production of biodegradable materials based on natural chitin-nanofibrils derived by waste of fish industry, to produce food grade packaging

mavi

INSTM

macro PRAGUE

AROMA

MICROTEC SRL Plastics Masterbatch Compound

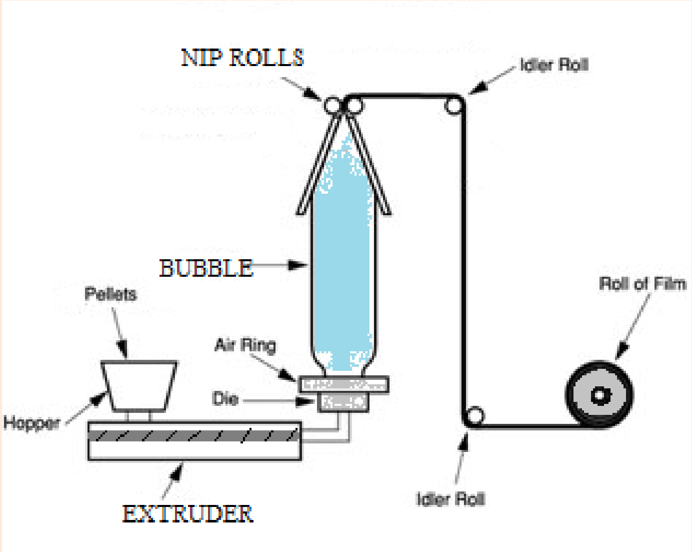
Nofima

RODAX IMPEX SRL

biozoon food innovations gmbh

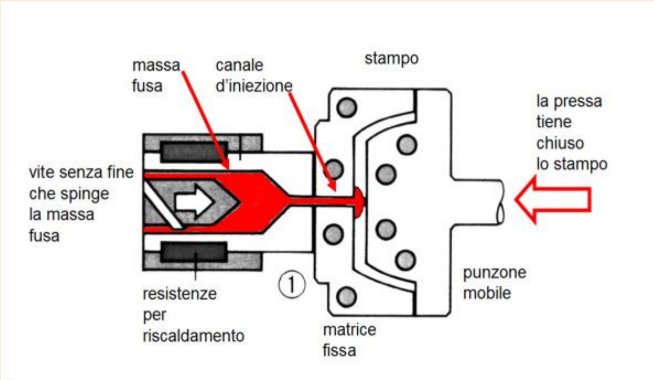
Flexible packaging

Blown film extrusion

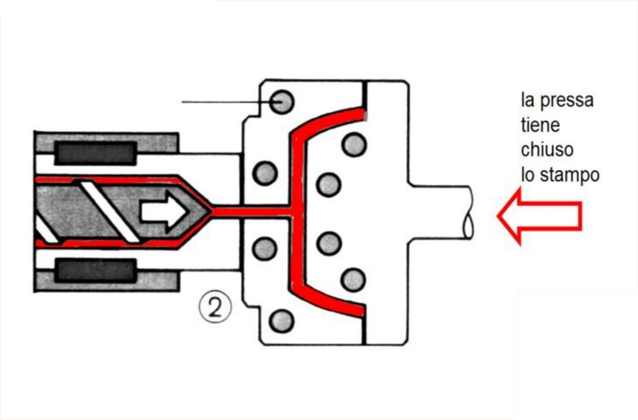


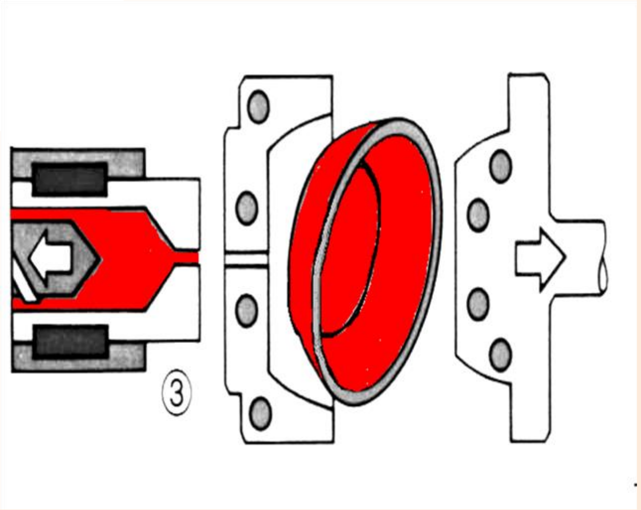
Trial carried out by using a bio-nano-composite based on biodegradable polyesters and n
Chitin nano-fibrils.

Rigid packaging



Injection molding testst





Conclusions

It was possible to disperse chitin nano-fibrils at nano-scale in biodegradable polyester matrices thanks to a method based on the preparation of a master-batch

The chitin-nanofibrils reinforcement of the material was evidenced by comparing the properties of agglomerates and nano-dispersed PLA/NC nano-composites.

The mechanical properties were modified only slightly for the addition of chitin nano-fibrils. to the plasticized polyester. The decrease in Modulus can be attributed to the thermal behavior of the composites.

The bio-nano-composites can be imployed in rigid and flexible packaging.