SUSTAINABILITY OF BIOPOLYESTER COMPOSITES CONTAINING NANO-CHITIN FROM SEA FOOD WASTE

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INSTM- National Interuniversity Consortium of Materials Science and Technology c/o University of Pisa, Department of Civil and Industrial Engineering

Workshop "Natural Biodegradable Polymers for cleaner Planet",
17th October 2014
Prague, *Czech Republic*

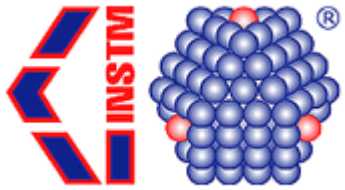
n-CHITOPACK

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

SME-2012-1

http://www.n-chitopack.eu

INSTM – Pisa University



INSTM ACTIVITY

- ***Key activities***
  - *INSTM Consortium of Italian Universities for the Science and Technology of Materials, groups 45 Italian Universities where research on Materials is carried out.*
  - *The group of Prof. Lazzeri, INSTM- Research unit of Pisa University, is active in the chemical and physical characterisation of nanomaterials, polymers, and ceramics as well as in processing, composite, production, microwave processing, green polymeric materials from renewable and sustainable matters, development of new tough and stiff nanocomposite materials.*
- ***Key figures***

  The Research Unit from INSTM-Pisa University consist of 2 full Professor, 1 researcher, 1 technicians , 1 contract researcher, 1 Post Doc, several PhD and Master Degree students

- ***Localisation(s)***

  INSTM administrative offices of INSTM are located at Florence (http://www.instm.it)
  UNIPI Research Unit is located in Pisa (http://materials.diccism.unipi.it

- ***Background/experience***
  - *highly skilled in nanoparticles production of precipitated calcium carbonate coated with fatty acids and characterization of fillers for the application into both traditional petroleum-based polymers and PLA:…as well as in the production of nanocomposite and composites with biodegradable polymeric matrices (PHB, CDA, PLA, Ecoflex, etc) and recycled polymers.*
  - *Study of materials properties: thermal, thermo mechanical, mechanical (tensile, impact, creep, fatigue), structure and environmental impact.*

- ***Collaborative – industrial projects participation and/or leaderships (National, European, technology platforms…)***
  - ***FORBIOPLAST**, Forest Resource Sustainability through Bio-Based-Composite Development KBBE-2007-Large , Coordinator, end 30.06.2012*
  - ***WHEYLAYER** Whey protein-coated plastic films to replace expensive polymers and increase recyclability, BSG Research for the benefit of specific groups, concluded 31.10.2011, Partner*
  - ***DIBBIOPACK** "Development of injection and blow extrusion molded biodegradable and multifunctional packages by nanotechnology improvement of structural and barrier properties, smart features and sustainability " NMP2011.Large, Started 01.03.2012**,** www.dibbiopack.eu*
  - ***Oli-PHA** "A novel and efficient method for the production of polyhydroxyalkanoatepolymer-based packaging from olive oil waste water" NMP2011.Small , negotiation, Partner, start 01.06.2012,*
  - ***HELM**, High-frequency ELectro-Magnetic technologies for advanced processing of ceramic matrix composites and graphite expansion, NMP2011.Large, negotiation, Coordinator*
  - ***PERFORMANCE** "Development of Personalised Food using Rapid Manufacturing for the Nutrition of elderly Consumers", KBBE-2012-6, negotiation, partners*
  - ***EVOLUTION** ""The Electric Vehicle revOLUTION enabled by advanced materials highly hybridized into lightweight components for easy integration and dismantling providing a reduced life cycle cost logic" **FP7-2012-GC-MATERIALS ,** negotiation, partner*
  - ***WHEYLAYER2** "barrier biopolymers for sustainable packaging" FP7-SME-2012_BSG-DEMO, negotiation*
  - ***BIOBOARD** "Development of sustainable protein-based paper and paperboard coating systems to increase the recyclability of food and beverage packaging materials" FP7-SME-2012-SME-AG, negotiation*

INSTM-UNIPI

Products/services/R&D axis activity…

Polymer processing (laboratory and pilot scale) and characterization; Green synthesis polyurethane, Nano materials, Ceramics . Materials characterization. Life Cycle Analysis.

- PROCESSING AND CHARACTERIZATION

BIOPLASTIC

Biobased:
The term “biobased” means that the material or product is (partly) derived from biomass (plants). Biomassused for bioplastics stems from e.g. corn, sugarcane, or cellulose.

-Biodegradable:
Biodegradation is a chemical process during which micro-organisms that are available in the environment convert materials into natural substances such as water, carbon dioxide, and compost (artificial additives are not needed).
The process of biodegradation depends on the surrounding environmental conditions (e.g. location or temperature), on the material and on the application.

Biobased PE
Triunfo, Braskem, Brasil

biodegradable

http://en.european-bioplastics.org/bioplastics/

CEN TC 261/SC4 - Packaging & Packaging Waste

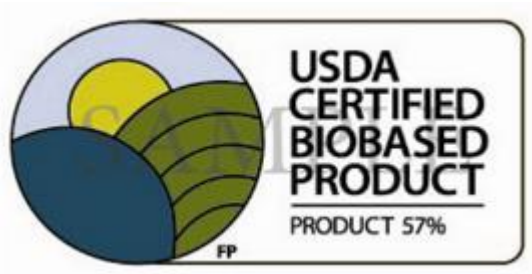
- **EN 13431:2000** - Packaging. Requirements for Packaging Recoverable in the Form of **Energy Recovery** Including Specification of Minimum Inferior Calorific Value.
- **EN 13432:2000** - **Packaging. Requirements for Packaging Recoverable Through Composting and Biodegradation. Test Scheme and Evaluation Criteria for the Final Acceptance of Packaging.**
- **CR 13695-1** - Packaging. Requirements for Measuring and Verifying the Four Heavy Metals (Cr, Rd, Hg, Pb) and Their Release into the Environment, and Other Dangerous Substances Present in Packaging.
- **EN 13427:2000** - Packaging. Requirements for the Use of European Standards in the Field of Packaging Waste ("Umbrella Norm").
- **EN 13428:2000** - Packaging. Requirements Specific to Manufacturing and Composition. Prevention by Source Reduction.
- **EN 13429:2000** - **Packaging. Reuse**
- **EN 13430:2000** - Packaging. Requirements for Packaging Recoverable by **Material Recycling.**

BIOPLASTIC

Biodegradable and Compostable Polymers according to:
EN 13432, ASTM 6400 (ISO methods)

Bio based Polymers from “Renewable Resources”

Compostable

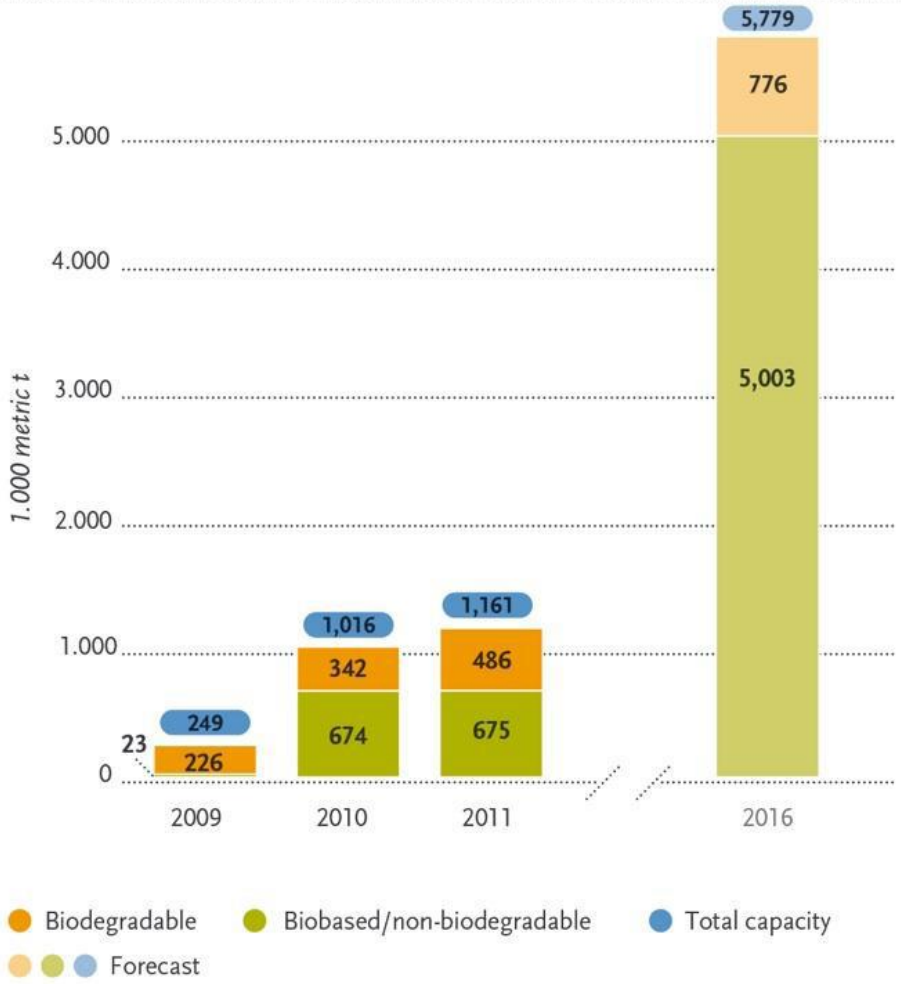


Certification in USA

Bio Based

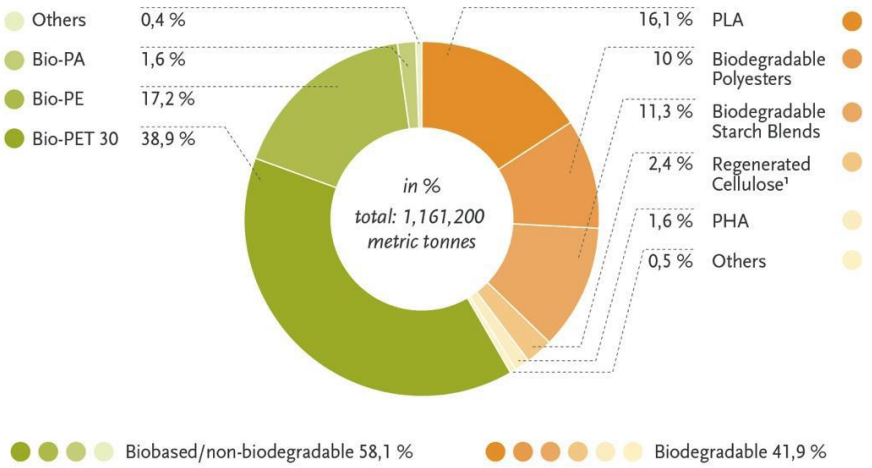
http://en.european-bioplastics.org/wp-content/uploads/2011/04/fs/Bioplastics_eng.pdf

Global production capacity of bioplastics



Source: European Bioplastics | Institute for Bioplastics and Biocomposites (October 2012)

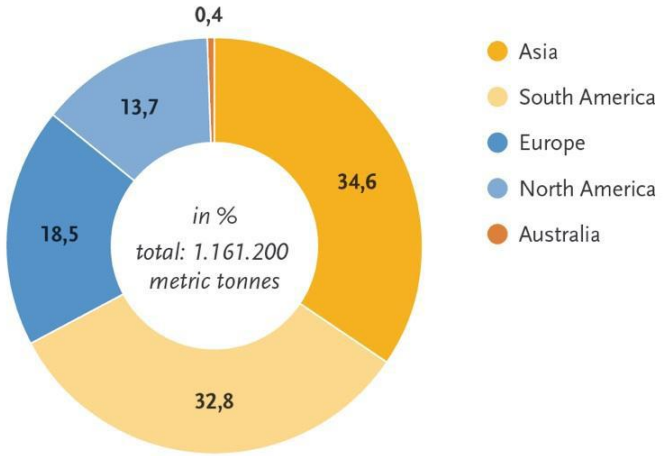
Bioplastics production capacity 2011 (by type)



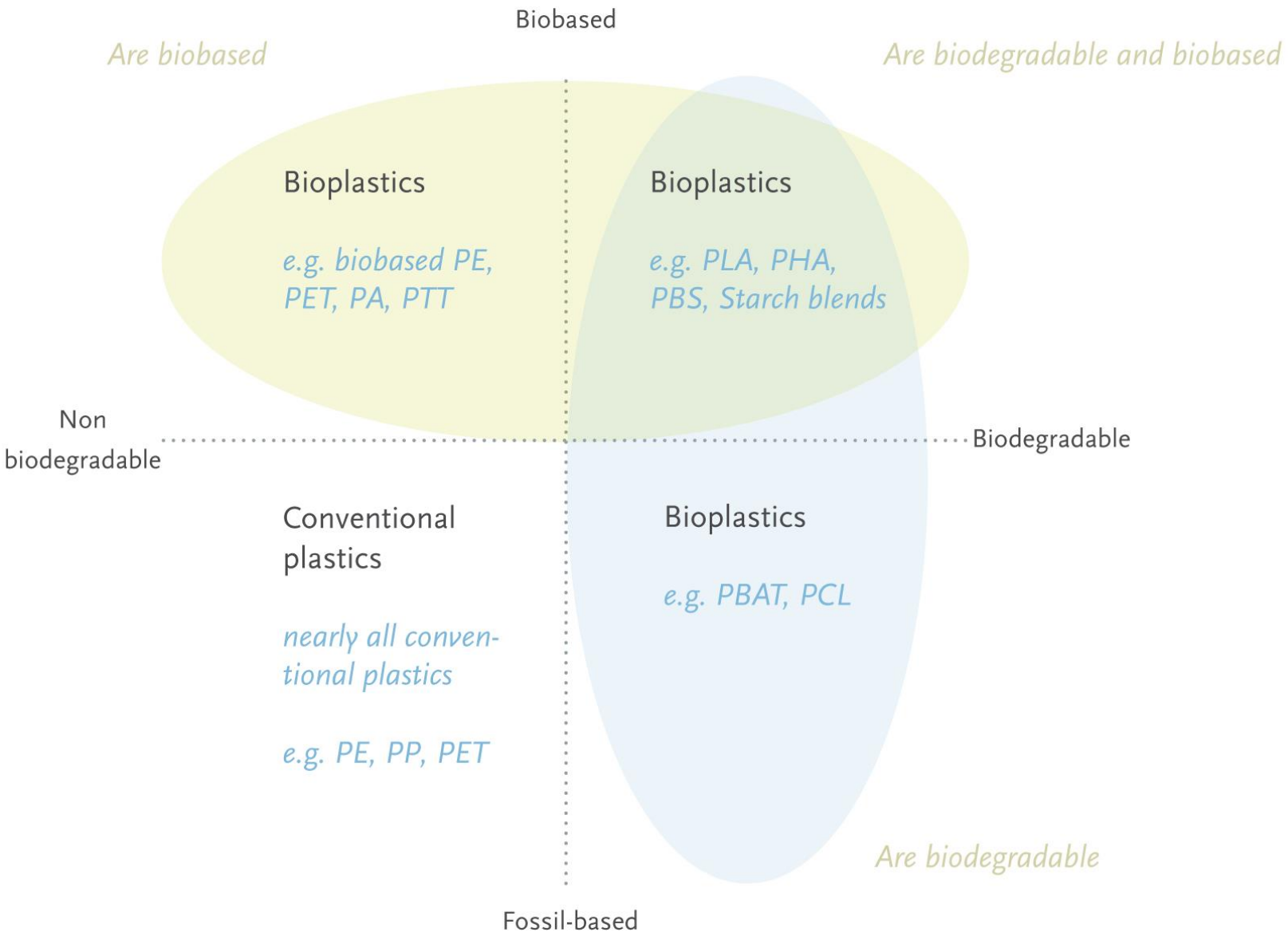
Source: European Bioplastics | Institute for Bioplastics and Biocomposites (October 2012)

¹ only hydrated cellulose foils

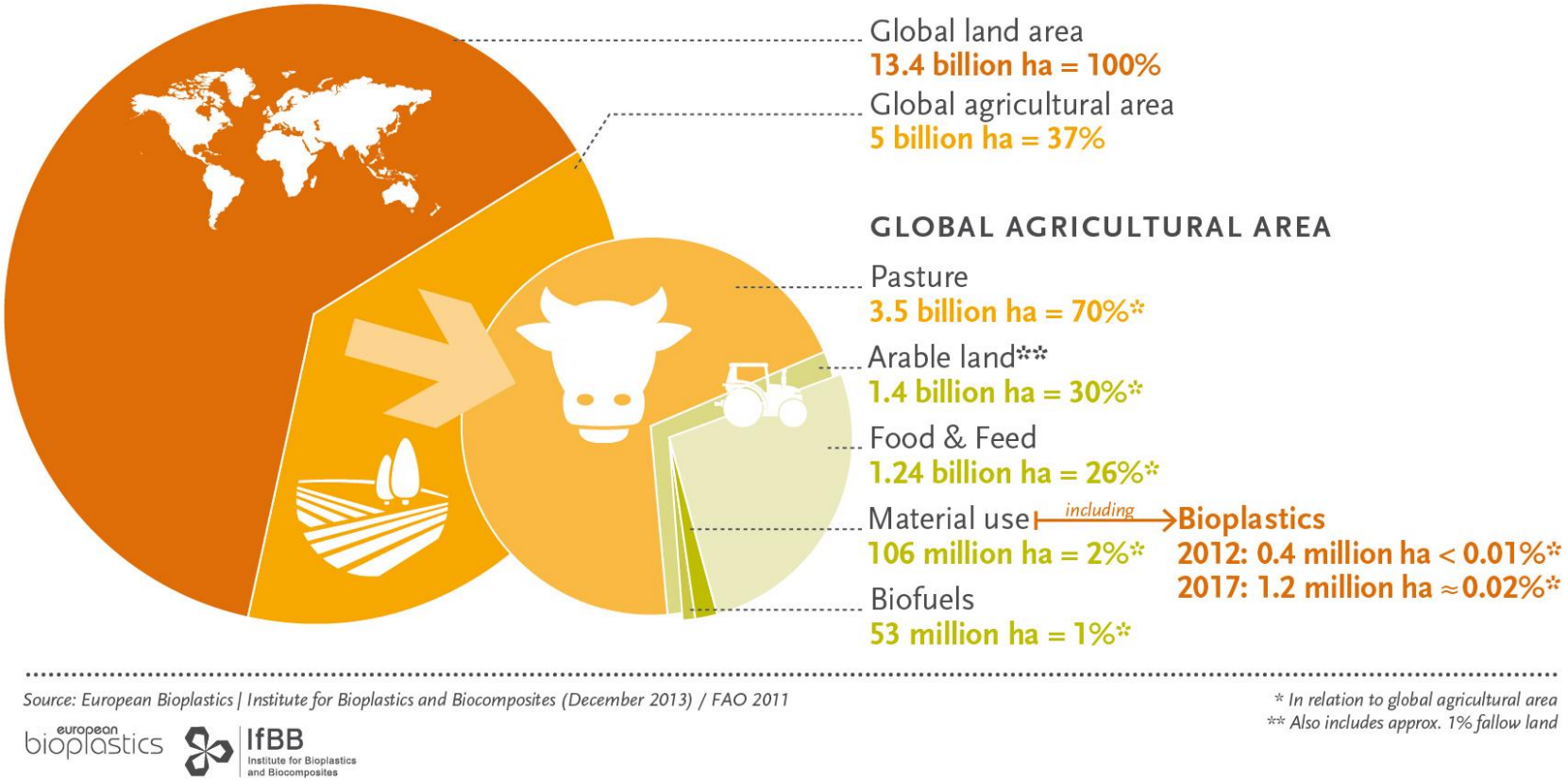
Global production capacity of bioplastics in 2011 (by region)



Source: European Bioplastics | Institute for Bioplastics and Biocomposites (October 2012)


Biobased
Are biobased
Are biodegradable and biobased
Bioplastics
e.g. biobased PE, PET, PA, PTT
Bioplastics
e.g. PLA, PHA, PBS, Starch blends
Non biodegradable
Biodegradable
Conventional plastics
nearly all conventional plastics
e.g. PE, PP, PET
Bioplastics
e.g. PBAT, PCL
Are biodegradable
Fossil-based

Land use for bioplastics 2012 and 2017



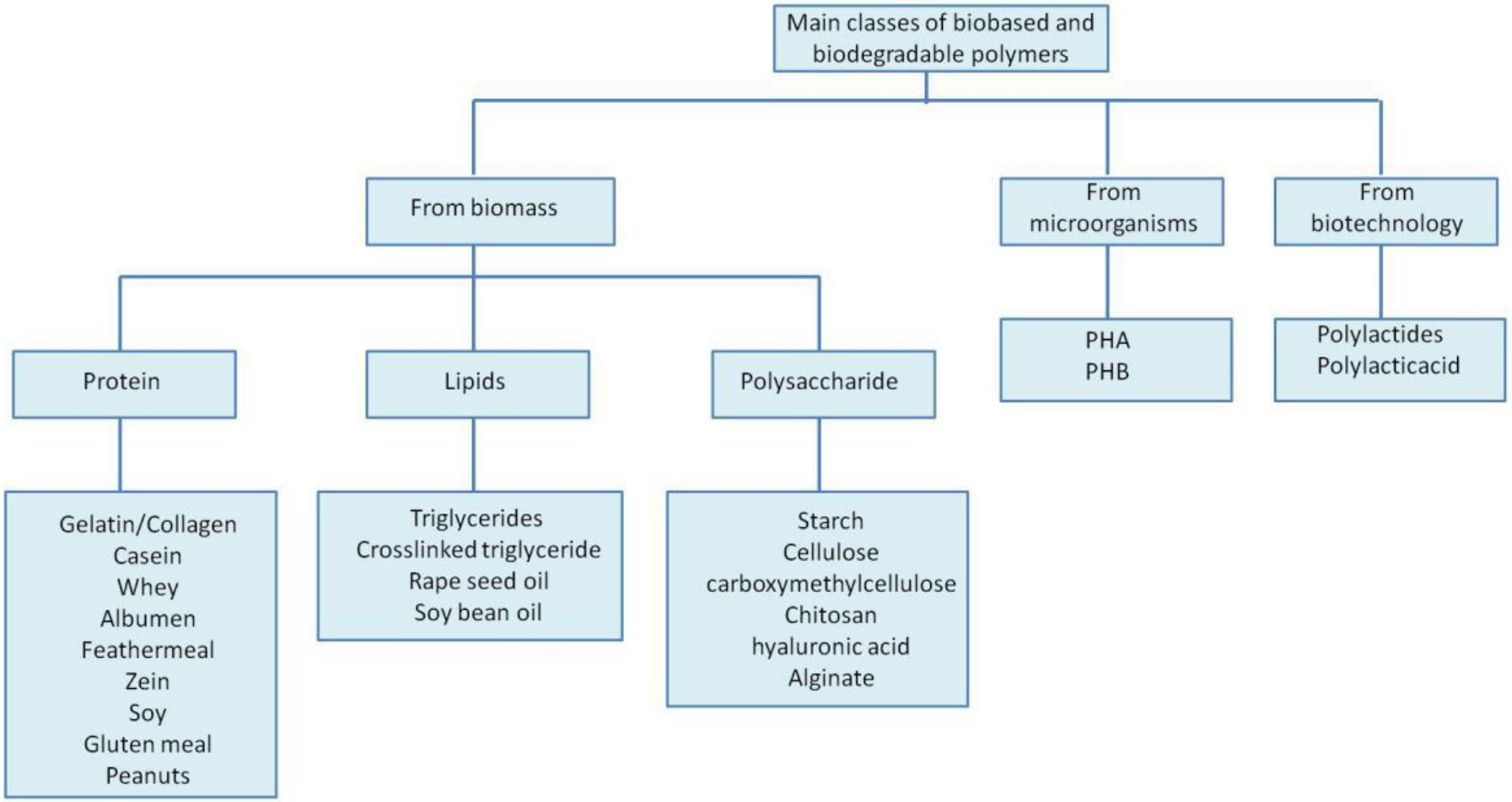
Source: European Bioplastics | Institute for Bioplastics and Biocomposites (December 2013) / FAO 2011

** In relation to global agricultural area*
*** Also includes approx. 1% fallow land*

european bioplastics | IfBB Institute for Bioplastics and Biocomposites

http://en.european-bioplastics.org/

BIOPLASTIC

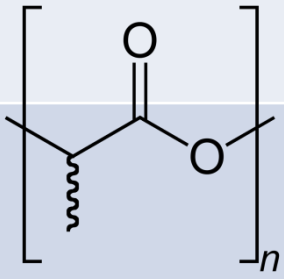


Different classes of polymers which are biobased and biodegradable (therefore not including biodegradable plastics from petrochemical resources and non biodegradable partly or fully biosourced plastics)

Polymer Letters, 2014, 8(11), 791-808, Polyhydroxyalkanoate (PHA): Review of synthesis, characteristics, processing and potential applications in packaging, E. Bugnicourt, P. Cinelli, A. Lazzeri, V. Alvarez

STARCH BASED

Producer	Tradename	Type of Starch plastics	Biode-gradable	Capacity 2007
BIOP (Germany)	BioPar	Starch Blend	X	3.500 t
	BioPar TPU	Starch/PUR		
	BioParen	Starch Blends Starch acetate	X	
Biome (UK)	Biome		X	
Biotec (Germany)	Bioplast TPS	TPS	X	20.000 t
	Bioplast	Starch Blends	X	
Cardia Bioplastics (Australia)	Compostable Biohybride	Starch Blends	X	
Cereplast (USA)	Cereplast Compostable	Starch Blends	X	22.500 t
	Cereplast Hybrid			
FuturaMat (France)	Bioceres	Starch Blends	X	
Guangdong (China)	BOR	Starch Blends	X	
Japan Corn Starch (Japan)	Evercorn		X	
Limagrain (France)	Biolice	Starch Blends	X	15.000 t
Livan (China)	Livan	Starch Blend	X	10.000 t
Novamont (Italy)	Mater-Bi	Starch Blends	X	60.000 t
PaperFoam (Netherlands)	PaperFoam	Starch Composites	X	
Plantic (Australia)	Plantic	Starch Blends	X	5.000 t
Rodenburg (Netherlands)	Solanyl	Partially fermented starch	X	40.000 t
Vegeplast (France)	Vegemat	Starch blends Starch composites	X	
Wuhan Huali (China)	Plastarch	Starch Blends	X	

Biodegradabile/ Compostabile	Biodegradabile/compostabile a Base Bio	Base Bio
Synthetic polyesters (BASF, Mitsubishi, ..)	Polylactic (PLA) NatureWork, Purac/Synbra, Futerro)	Bio-PDO (DuPont)
	Starch Based (Novamont, Speher-Biotec, Plantic, ..)	PE from bioethanol (Braskem, DOW)
	Cellulose Based (Innovia, Acetato di Cellulosa, ..)	PET from bioethanol (Coca Cola)
Poly Lactic Acid	Copolymers of PLA (BASF, Fkur, etc..)	Poliamide (Arkema, BASF)
	Polydroxyalkanoatie(PHA) (Biomer, Telles, Mirel)	

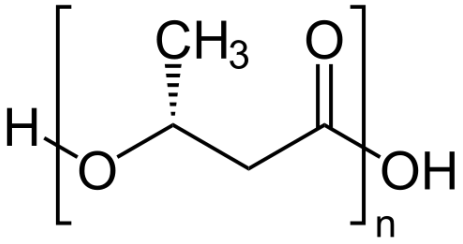
PE= Polyetilene, PA= Polyamide, PET= Polyethylenetherephtalate

PLA PRODUCERS

Producer	Tradename	Capacity in 1000 t (estimated)	
		2007	2020
Futerro, Belgium	Futerro		
Hisun, China	Renova	0,03	5
Mitsui, Japan	Lacea	0,5	
Natureworks LLC, USA	Ingeo	70	450
Purac, Netherlands	Puralact	75	300
Pyramid, Germany	Pyramid		60
Shanghai Tong-jie-liang China			
Teijin, Japan	Biofront	0,2	10
Toyobo, Biologics, Japan			
Unitika	Terramac		

PHA PRODUCERS

Producer	Tradename	Types of PHA
BioMatera, Canada	BioMatera	P(3HB-co-3HV)
Biomer, Germany	Biomer	P(3HB)
Beijing Tianzhu, China	PHBH	P(3HB-co-HHx)
Green Bio/DSM, China	Green Bio	P(3HB-co-4HB)
Kaneka, Japan	Kaneka BHPH	P(3HB-co-3HHx)
Mitsubishi Gas, Japan	Biogreen	P(3HB)
PHB Industrial, Brazil	Biocycle	P(3HB) P(3HB-co-HV)
Shenzhen-Ecomann, China	EM	P(3HB-co-4HB)
Telles, USA	Mirel	PHB co-polymers
Tianan, China	Enmat	P(3HB-co-HV)



Poly hydroxyAlkanoate

INSTM c/o University of Pisa is Scientific coordinator of:

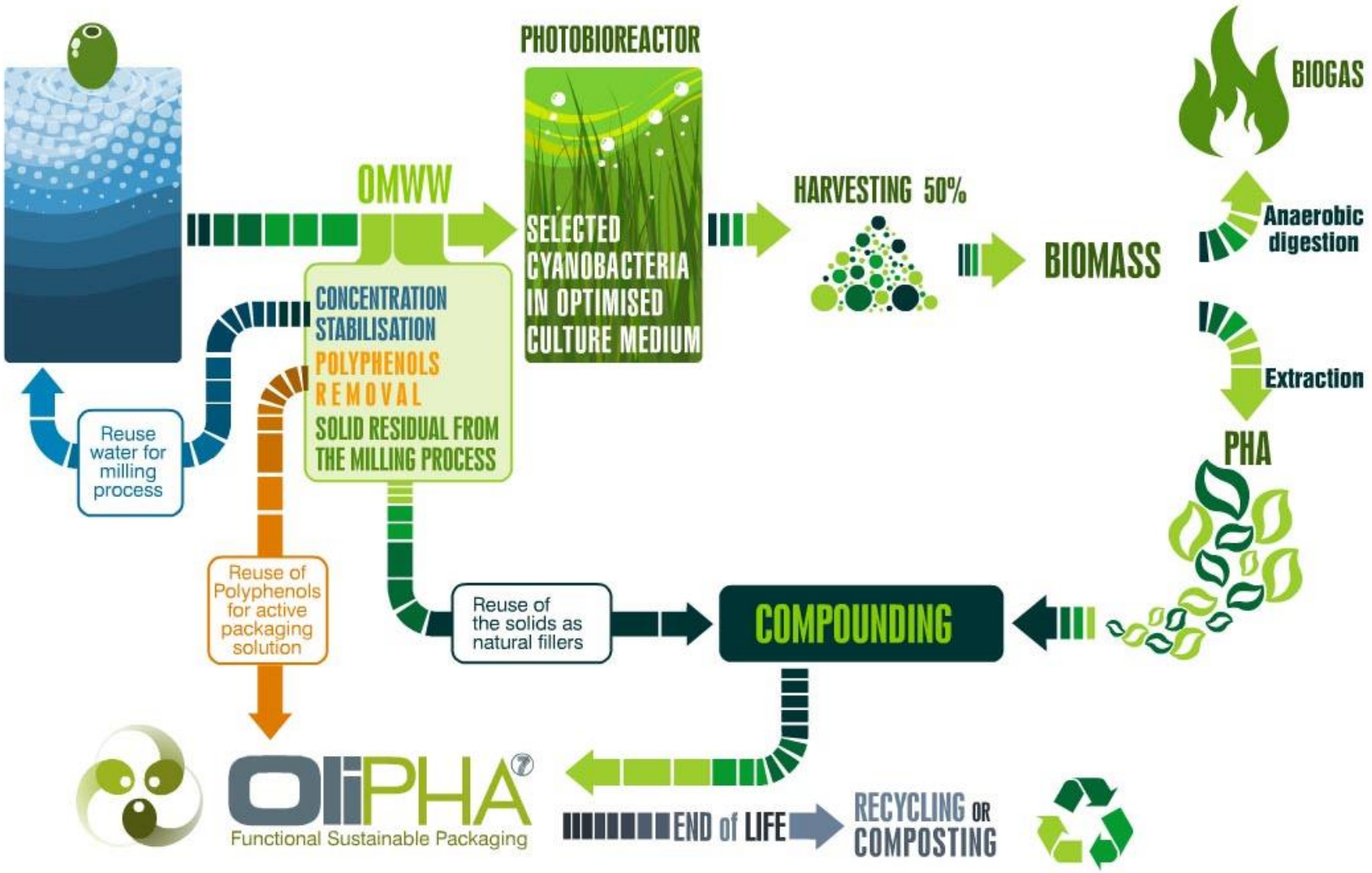
A novel and efficient method for the production of polyhydroxyalkanoate polymer-based packaging from olive oil waste water

OliPHA

Collaborative Project
Small or medium-scale focussed research projects - Specific International Cooperation Actions (SICA) to promote the participation of emerging economies and developing countries: Latin America.

Work programme topics addressed: NMP.2011.2.3-1 Advanced packaging materials from renewable biogenic resources

Coordinated by IRIS, Innovacio i Recerca Industrial i Sostenible, Spain,
Coordinator Contact : Elodie Bugnicourt ebugnicourt@iris.cat

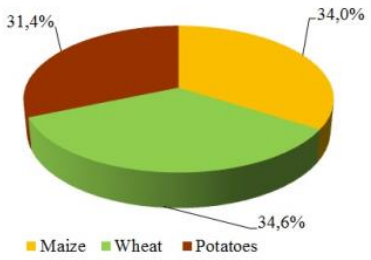


http//:www.olipha.eu

Starch production in the EU – 2011

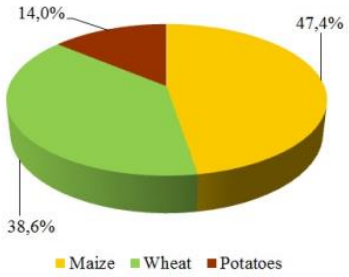
Association des Amidonniers et Féculiers
European Starch Industry Association

Processed raw materials



Total : 22 Mio tonnes

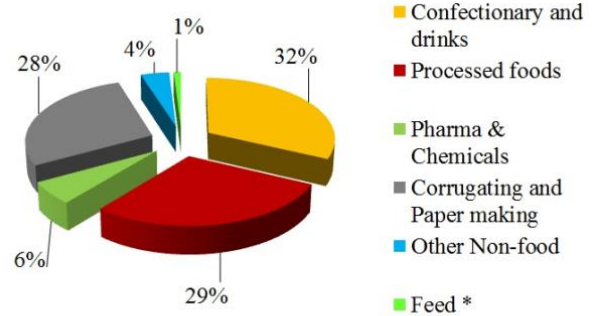
Starch products in starch equivalent



Total : 10 Mio tonnes

Applications of starch and starch derivatives (EU market segments - 2011)

Association des Amidonniers et Féculiers
European Starch Industry Association



Total Market : 8,9 mio tonnes

* Excluding co-products amounting to about 5 million tonnes

http://www.aaf-eu.org/european-starch-industry/ (AAF – Association des Amidonniers et Féculiers)

BLENDS OF POLYMERS

- **PBS/A (Polybutylene succinate/adipate)**

Tradename: Bionolle®, supplied by Showa Highpolymer

- **PBSL (Polybutylene succiante-co-lactate)**

Tradename: GS Pla®, supplied by Mitsubishi Chemical

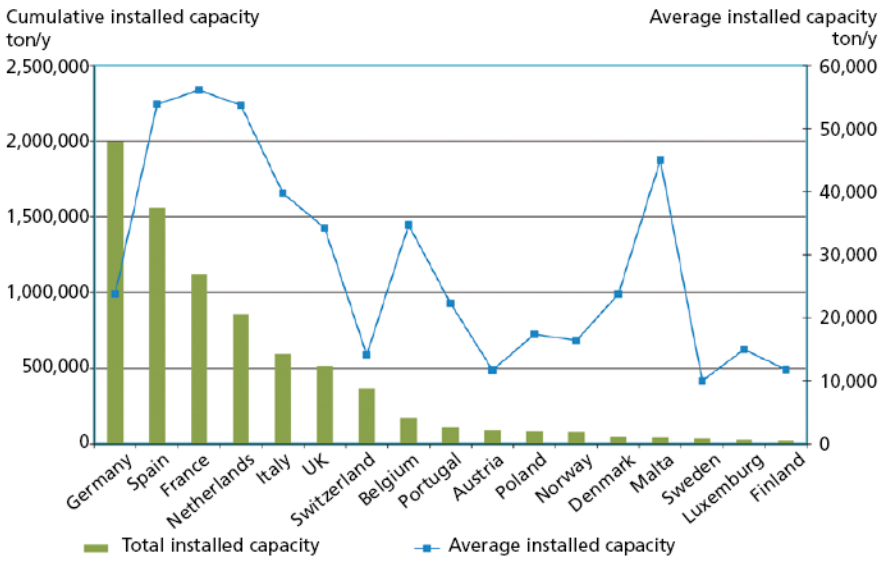
- **PBAT (Polybutyleneadipate-co-terephtalate)**

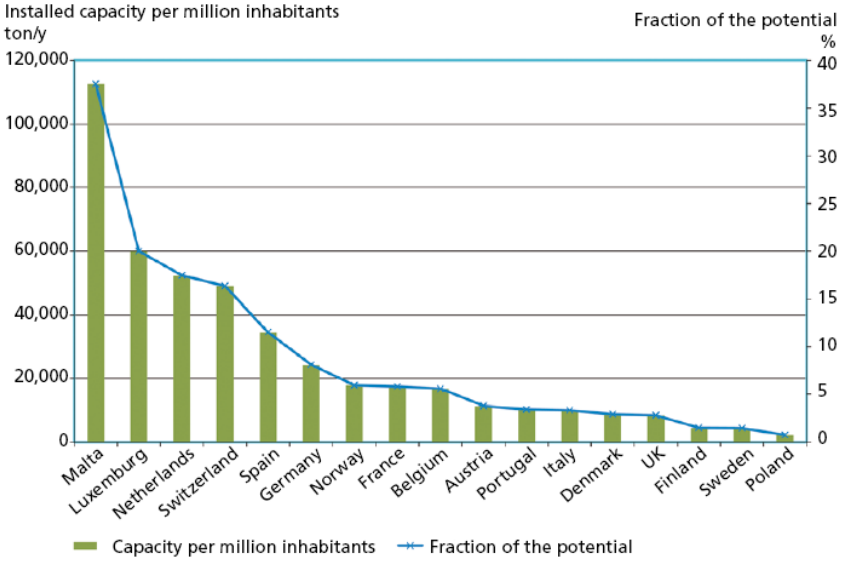
Tradename: Ecoflex®, supplied by BASF
Biomax®, supplied by DuPont

- **PCL (Poly-ε-caprolacton)**

Tradename: CAPA®, supplied by Perstorp UK Ltd.
Celgreen®, supplied by Daicel

ANAEROBIC DIGESTION





Luc De Baere and Bruno Mattheeuws Anaerobic Digestion of the Organic Fraction of Municipal Solid Waste in Europe – Status, Experience and Prospects –From: Anaerobic Digestion of the Organic Fraction of Municipal Solid Waste in Europe, pp.517-526 (http://www.ows.be/downloads/Anaerobic%20Digestion.pdf)

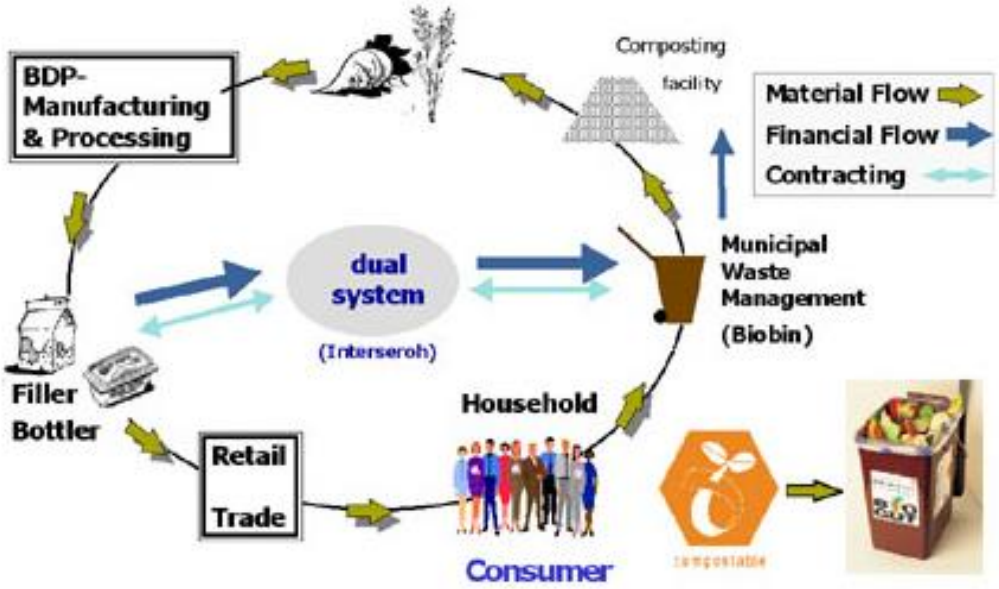
Dunja-Manal Abou-Zeid, Rolf-Joachim Muller , Wolf-Dieter Deckwer, Degradation of natural and synthetic polyesters under anaerobic conditions, Journal of Biotechnology 86 (2001) 113–126

J. J. Kolstad, E.T.H. Vink, B. De Wilde, L. Debeer, Assessment of anaerobic degradation of Ingeo™ polylactides under accelerated landfill conditions, Polym.Deg.Stab. 2012, 97, pp. 1131-1141

BIODEGRADABILITY

DISINTEGRATION IN COMPOST
ISO 20200

Plastics — Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test.



COMPOST DISINTEGRATION TEST

Table 1. **Samples tested in compost degradation tests**

Sample	PLA/Plasticizer (%)	BioComp (%)	Chitin Nanofibrils (%)
1	100	-	-
2	98	-	2
3	-	98	2

COMPOST DISINTEGRATION TEST

– ISO 20200 – Plastics- Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test.

Table 1 — Composition of synthetic solid waste

Material	Dry mass %
Sawdust	40
Rabbit-feed	30
Ripe compost	10
Corn starch	10
Saccharose	5
Cornseed oil	4
Urea	1
Total	100

NOTE 1 Sawdust from untreated wood shall be used. It is preferable to use wood from deciduous trees. Sawdust shall be sieved through a 5 mm sieve before use.

NOTE 2 The rabbit-feed shall be a commercial product based on alfalfa (lucerne) (*Medicago sativa*) and vegetable meal. If a product with a different composition is used, the composition shall be given in the test report. The protein content of the rabbit-feed shall be approximately 15 % and the cellulose content approximately 20 %.

COMPOST ANALYSIS

	Compost
Dry weight (%w/w)	53,3
Ashes at 550° C (%w/w)	26,5
Carbon content (%w/w)	29,5
Nitrogen content (%w/w)	1,9
Ratio C/N	15,5

CERMEC SpA Consorzio Ecologia e Risorse di Massa e Carrara
www.cermec.it/

COMPOST DISINTEGRATION TEST

Closed Polypropylene containers, two holes for air circulation
10g Test material / 1 Kg wet synthetic waste
58 °C for 90 days

Test materials:

PLA based film
PLA based film with 2% NC
BIOCOMP with 2% NC
Pure compost

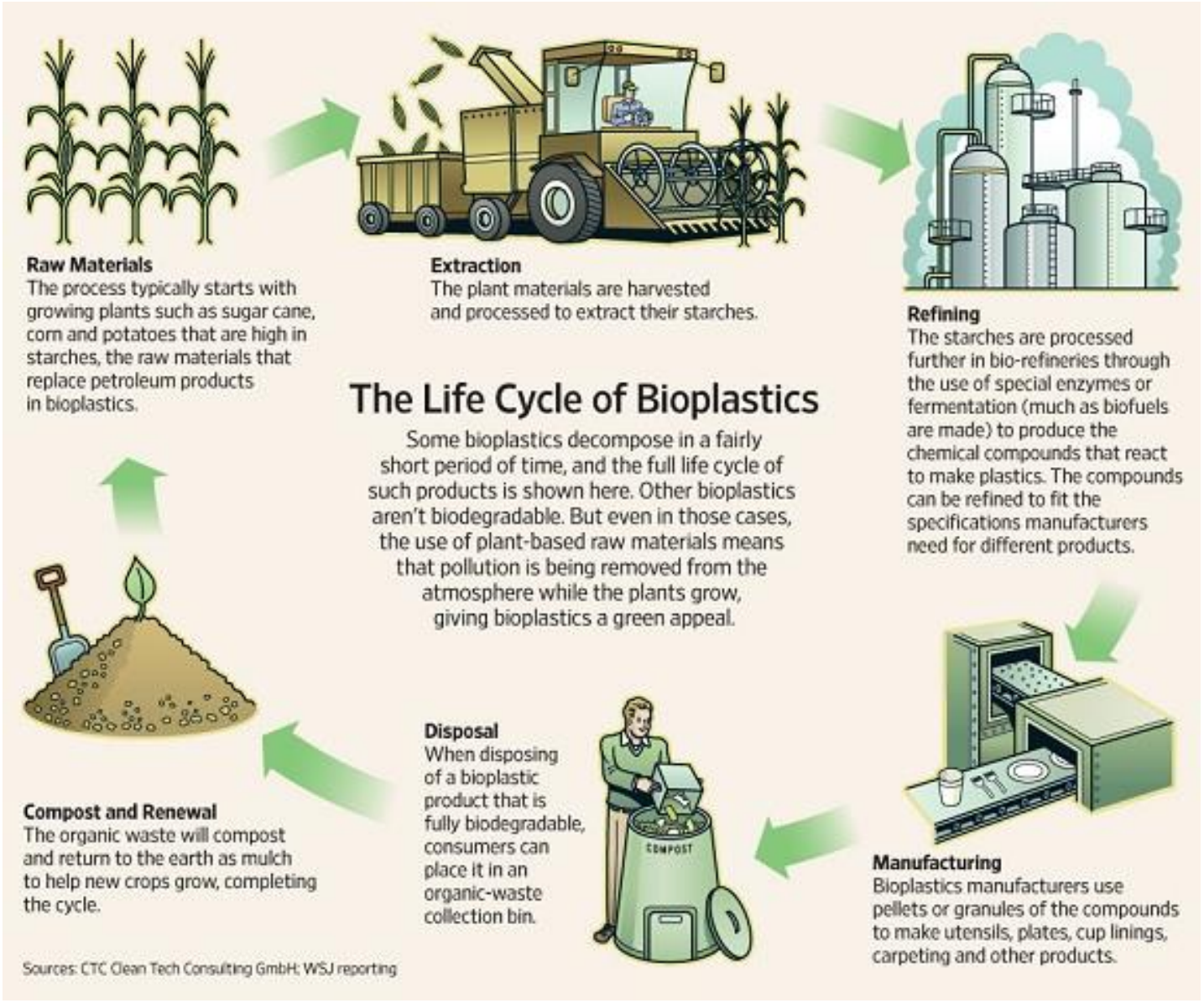
Table 3 — Composting procedure (thermophilic incubation period)

Time from start days	Operation
0	Record initial mass of reactor
1, 2, 3, 4, 7, 9, 11, 14	Weigh reactor and add water to restore the initial mass, if needed. Mix the composting matter.
8, 10, 16, 18, 21, 23, 25, 28	Weigh reactor and add water to restore the initial mass, if needed. Do not mix the composting matter.
30, 45	Weigh reactor and add water to restore the mass to 80 % of the initial mass, if needed. Mix the composting matter.
From 30 till 60, twice a week	Weigh reactor and add water to restore the mass to 80 % of the initial mass, if needed. Do not mix the composting matter.
From 60 onwards, twice a week	Weigh reactor and add water to restore the mass to 70 % of the initial mass, if needed. Do not mix the composting matter.

COMPOST DISINTEGRATION TEST

COMPOST DISINTEGRATION TEST

- Disintegration started after 15 days and was significant after 30 days
- Samples broken in small pieces
- PLA and PLA/NC completely disappeared after 20 days
- BIOCOMP/NC started to disintegrate later but still meet the Normative



http://www.natural-biodegrade.com/bioplastics/

LCA General information

- The procedure for the calculation of an LCA can be divided into 5 steps:
- 1. Definition of functional unit, investigated system and system boundaries.

One Square meter for film, one coffee caps. Cradle to grave.

- 2. Data collection: production energy and fuels, electricity mix, transport distances, effects in use-phase (cleaning), waste management conditions
- 3. Transformation of life-cycle-data into CO2-equivalent figures
- 4. Total balance of CO2—equivalent emissions in total life-cycle
- 5. Comparison of results, sensitivity analyses, optimization and conclusions

CHITIN as a Waste

Worldwide chitin based waste material from the fishing industry, exceeds 25 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] *JG Fernandez et al., Adv. Funct. Mater. 2013, 4454-4466*
[2] *M Mincea et al., Rev. Adv. Mater. Sci. 30, 2012, 225-242*

Waste Biomass from the seafood processing industry is not food competition

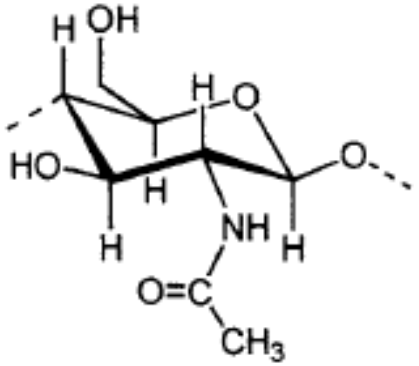
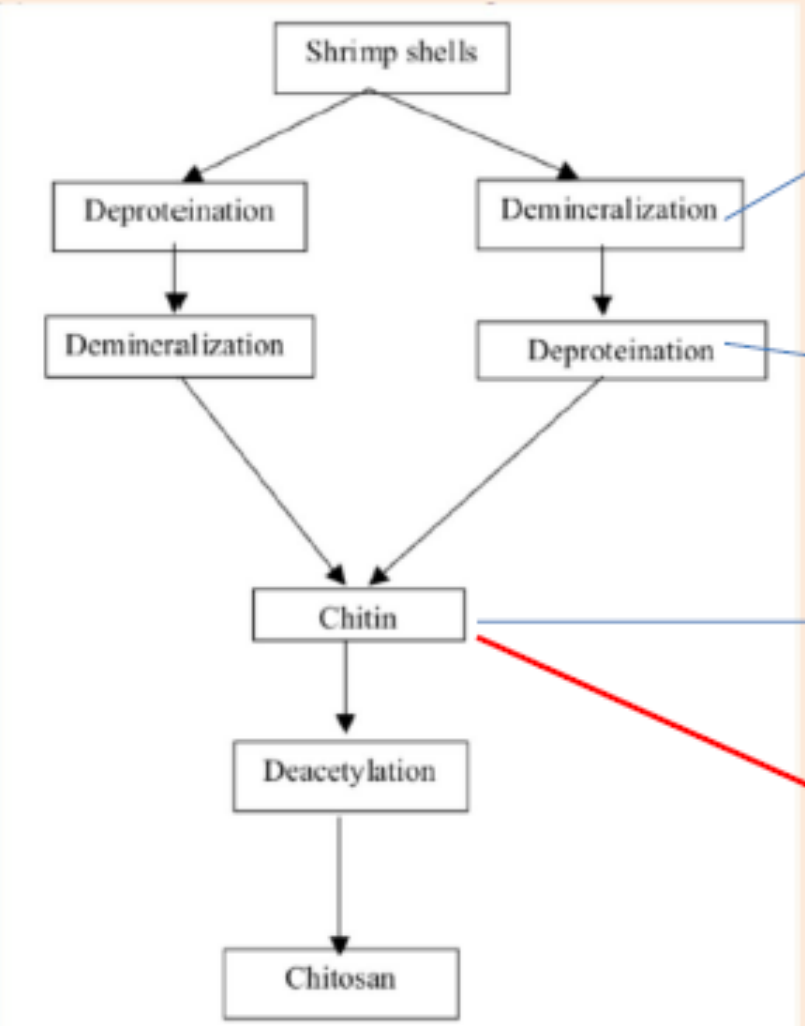


Figure 1. Monosaccharide repeating units of β(1→4)-linked N-acetyl-2-amino-2-deoxi-D-glucose (**A**-residue) in fully N-acetylated chitin chain.

Crustacean shell waste consists of protein (20-40%), calcium and magnesium salts -mainly carbonate and phosphate- (30-60%), chitin (20-30%) and lipids (0-14%). These proportions vary with species and season [24]. Therefore, isolation of chitin from crustacean biowaste, involves three basic operations:

1. Removal of residual protein
2. Removal of inorganic matter
3. Removal of lipid pigments (carotenoids)

CHITIN PRODUCTION



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

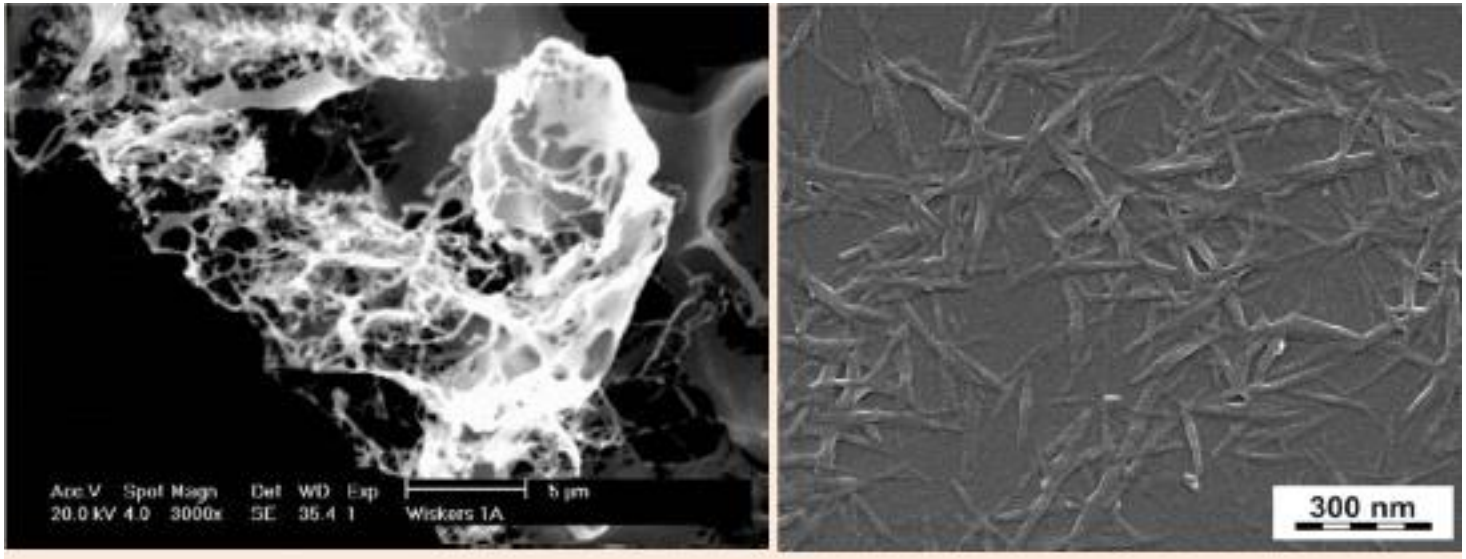
N. Van Toan, The Open Biomaterials Journal, 1, 2009

CHITIN PRODUCTION BY MAVI SUD (Aprilia, IT)

Production of diluted solution for applications as ingredients in cosmetics

Chitin nanofibrils for advanced cosmeceuticals
Pierfrancesco Morganti, Gianluca Morganti
Clinics in Dermatology (2008) 26, 334–340

"Spray-dried chitin nanofibrils, method for production and uses thereof" Patent 8552164 (issued 8.10.2013), Mavu Sud Srl, P.F.Morgnati, C. Muzzarelli.
Nano fibrils chitin : Chtin, water, HCl



300 nm length, 30 nm width

LCA ANALYSIS OF PROCESSES AND PRODUCTS

LCA compilation and evaluation of the inputs, outputs and potential environmental impacts of a product system throught its life cycle.

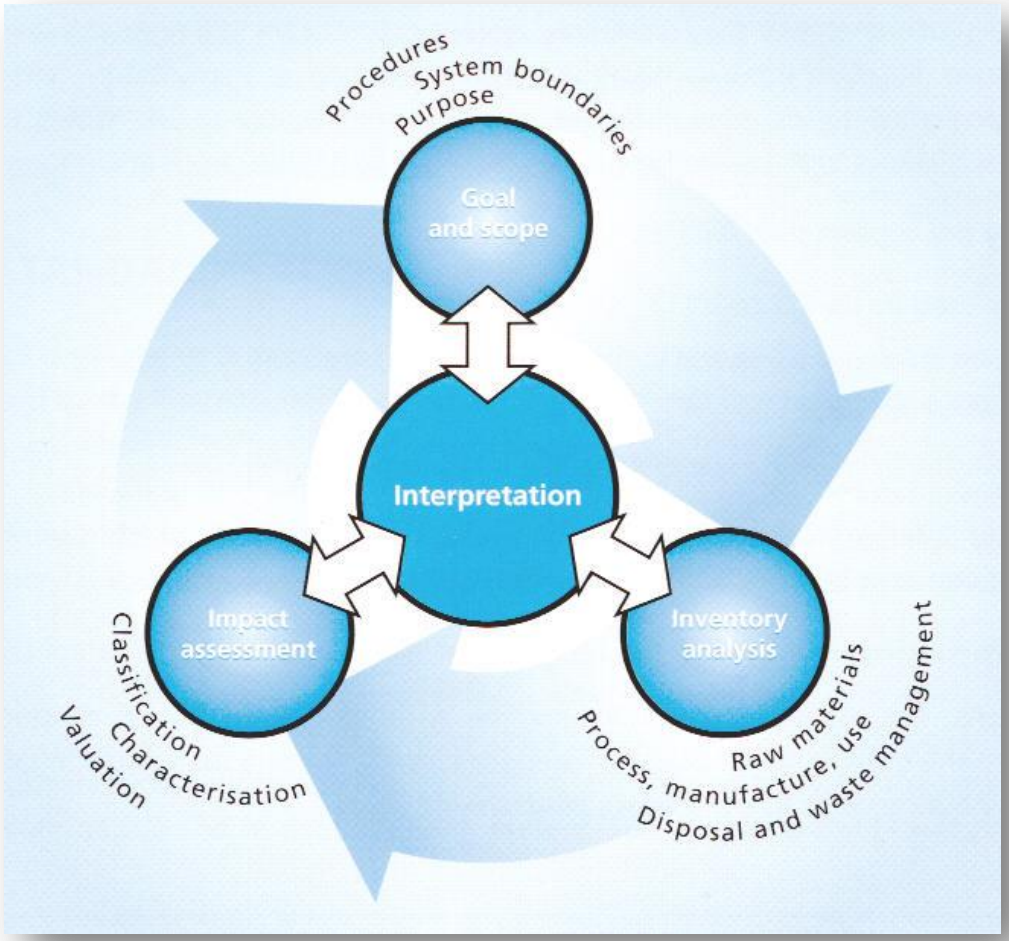
Objective and standardized criteria.
ISO 14040 and ISO 14044, 2006: impact of products on the environment. Their primary use in industry is to optimise process-engineering aspects of production with regard to the environment.

SIMAPRO7.3.3-Software,

ECOINVENT v2 Database

Fig 1: Structure of the Life Cycle Assessment (LCA)

Life Cycle Assessment Methodology

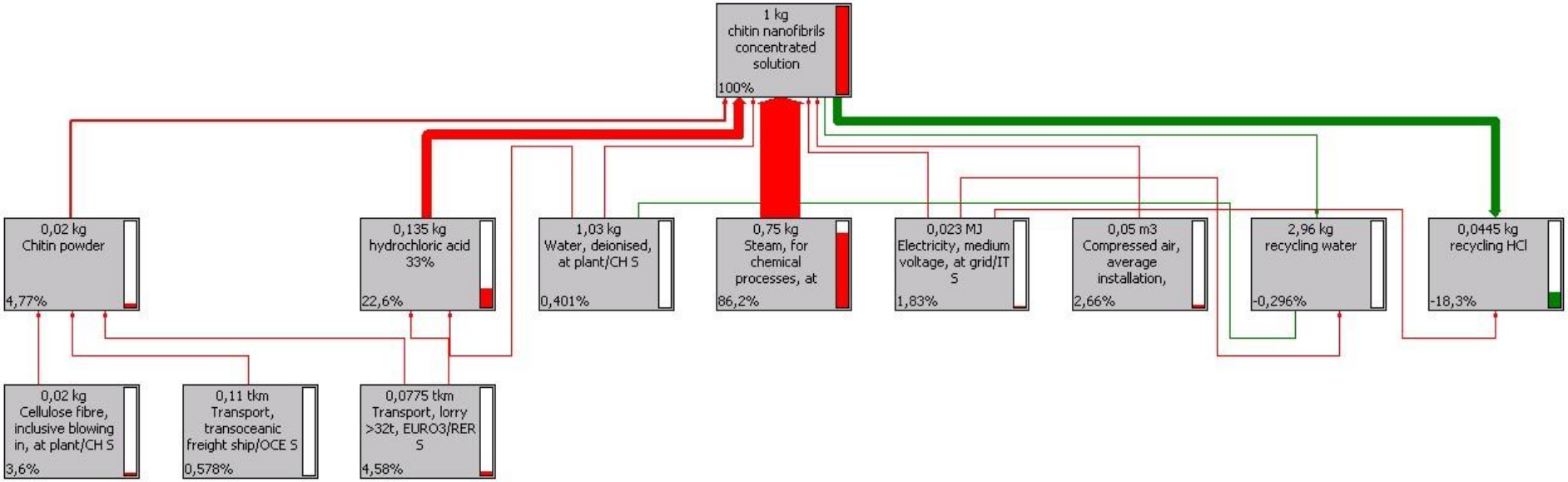


LCA calculations will include:

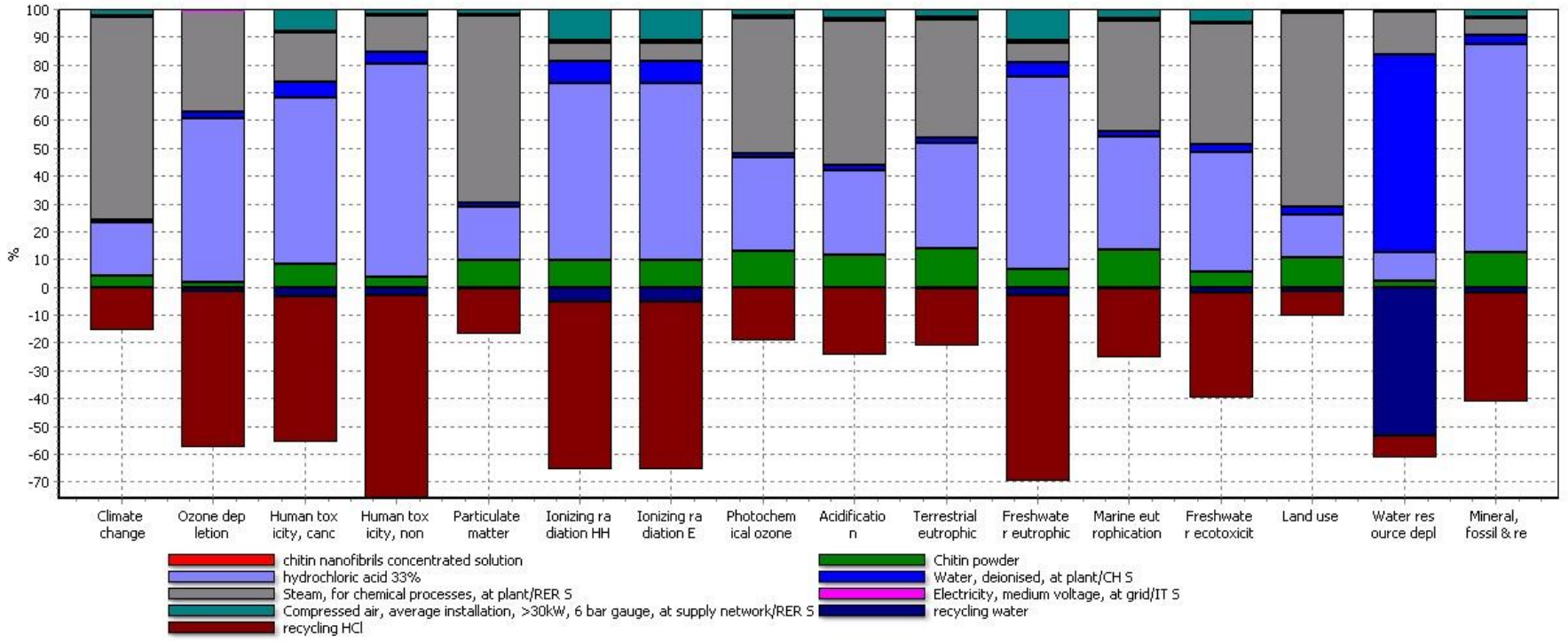
- Goal and scope
- Inventory analysis
- impact assessment
- interpretation of the results.

The essential characteristics of the basic materials, developed products and related technology should be defined in cooperation with other WP's in order to make the LCA data collection and calculation effective.

NETWORK of CHITIN NANO FIBRILS PRODUCTION

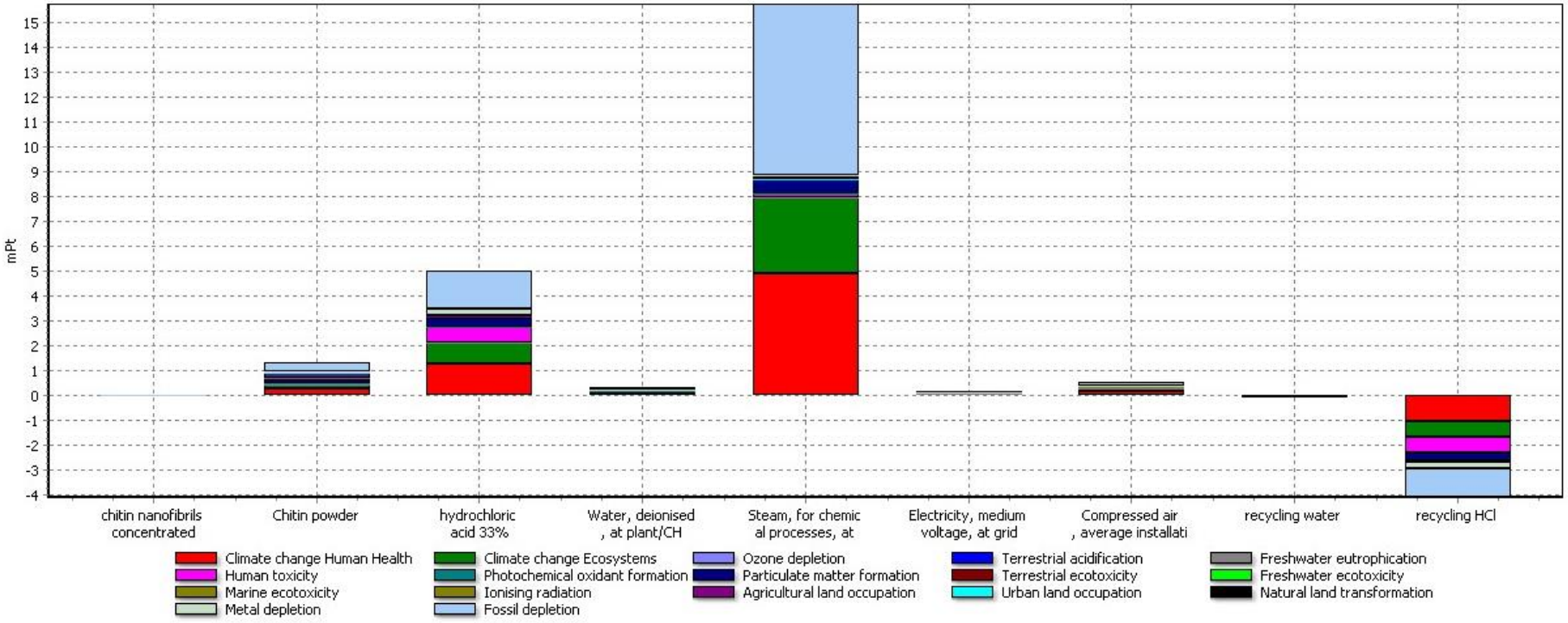


Impact by ILCD methods, considering the recovery and re use of chemicals



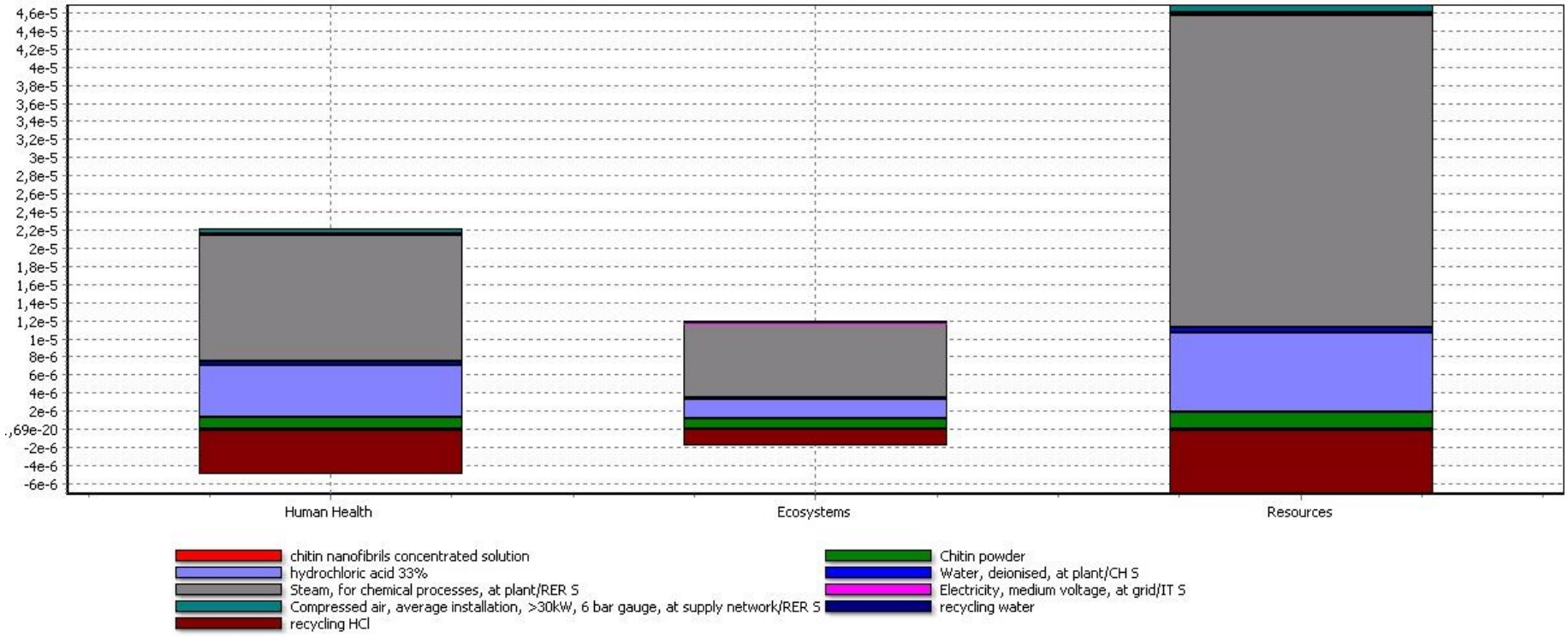
Analysing 1 kg 'chitin nanofibrils concentrated solution';
Method: ILCD 2011 Midpoint V1.01 / Characterisation

Impact by Recipe “Single score”



Analysing 1 kg 'chitin nanofibrils concentrated solution';
Method: Recipe Endpoint (H) V1.07 / Europe ReCiPe H/A / Single score

Impact by Recipe “Normalization”



Analysing 1 kg 'chitin nanofibrils concentrated solution';
Method: Recipe Endpoint (H) V1.07 / Europe ReCiPe H/A / Normalisation

CONCLUSIONS

Nano chitin fibrils (NC) are an interesting anno additive from renewable resources with anti oxidants and anti UV properties

Production of chitin nano fibrils is being optimized considering impact from LCA running studies , with particular focus on energy consumption and recovery –reuse of chemicals .

Nano chitin nano fibrils can be used for preparation of nano composites with PLA as polymeric matrix.

Thank your for your attention

n-CHITOPACK

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

SME-2012-1

http://www.n-chitopack.eu