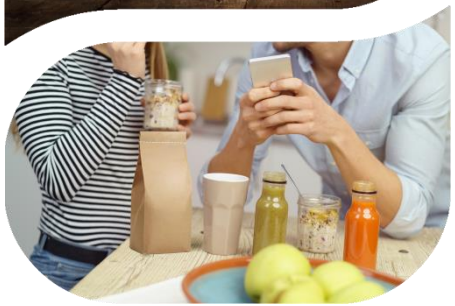
Sherpack Final Workshop

Biopolymer waterborne emulsion formulation and coating

Monica Bertoldo | ISOF

sherpack

Biopolymer waterborne emulsion formulation and coating



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Bio-based Industries Consortium

Horizon 2020 European Union Funding for Research & Innovation

BBI JU

Outlook

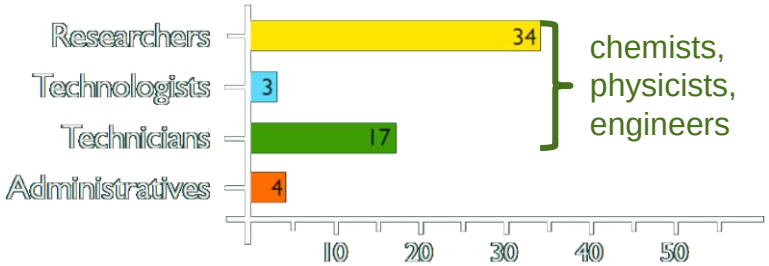
- ISOF and the other Sherpack's partners participating to the activity
- Introduction
- Results
  - Preparation of emulsions
  - Properties of the emulsions
  - Coating of the emulsions on paper
  - Characterization of the coatings
- Conclusion

National Research Council of Italy (CNR)

The Institute of Organic Synthesis and Photoreactivity (ISOF) belongs to the Department of Chemical Sciences and Materials Technologies of the National Research Council of Italy (**CNR**), the largest **public Research Institution** in Italy.

Consiglio Nazionale delle Ricerche

Permanent staff



What people do at ISOF

ChemNanoCARE
Chemistry & Nanotechnology for HealthCare & Environment

Research in the field of (bio)medicine, healthcare, biomedical engineering and environment sustainability.

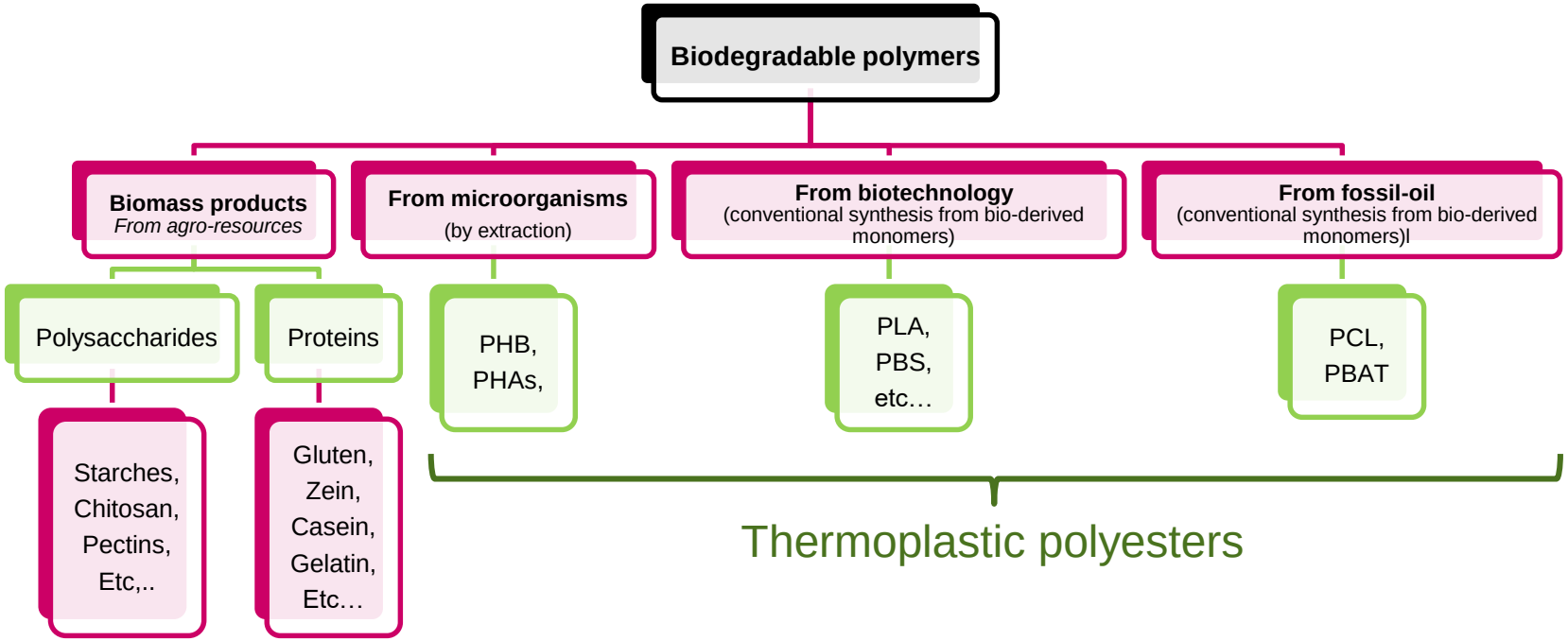
Research about materials for energy production and storage, optoelectronics, mechanics, environmental protection and biomedical devices

Photonics PHEEL
for Health, Energy & Environment Lab

Research about the light-matter interaction at the molecular, supramolecular and macromolecular level

ISOF research **activities are supported** by regional, national, European and international **funding through projects of industrial relevance** that address the societal challenges of the Europe 2020 strategy.

Biodegradable polymers

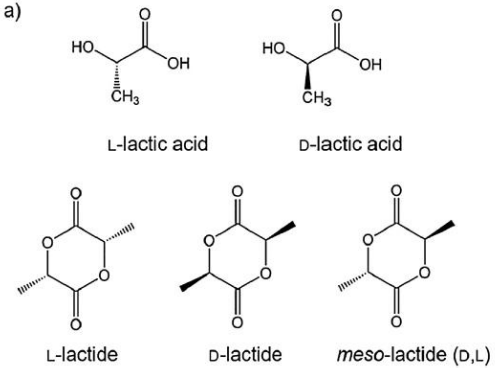


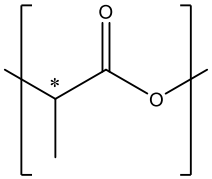
Adapted from: Avérous L. J. Macromol. Sci., Polym. Rev., C4 (3), 2004 , 231 – 274 .

Polylactic acid (PLA)

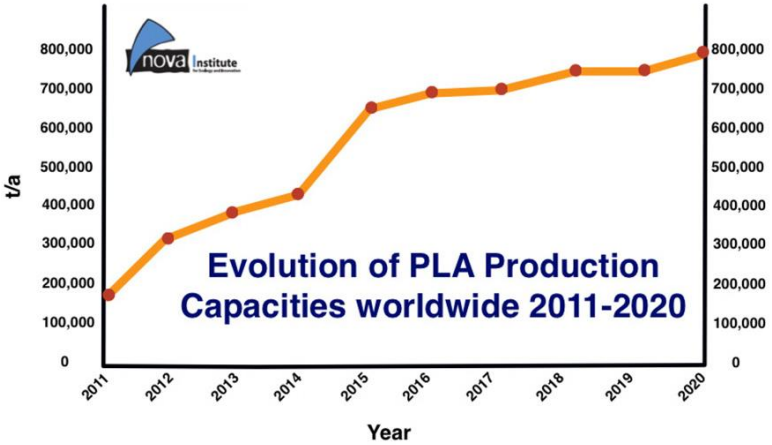
Biomass

a)





Polylactic acid
(PLA)



M. Murariu, P. Dubois, Advanced Drug Delivery Reviews 107 (2016) 17–46

PLA properties and applications

Thermal properties

Copolymer ratio	Glass transition temperature (°C)	Melting temperature (°C)
100/0 (L/D,L)-PLA	63	178
95/5 (L/D,L)-PLA	59	164
90/10 (L/D,L)-PLA	56	150
85/15 (L/D,L)-PLA	56	140
80/20 (L/D,L)-PLA	56	125

Degradation temperature ~ 200° C depending on moisture

Thermoplastic polymer, usually converted as polypropylene

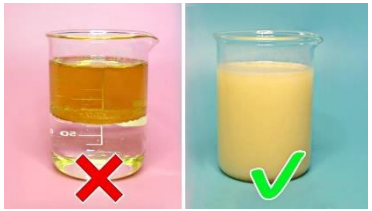
Applications

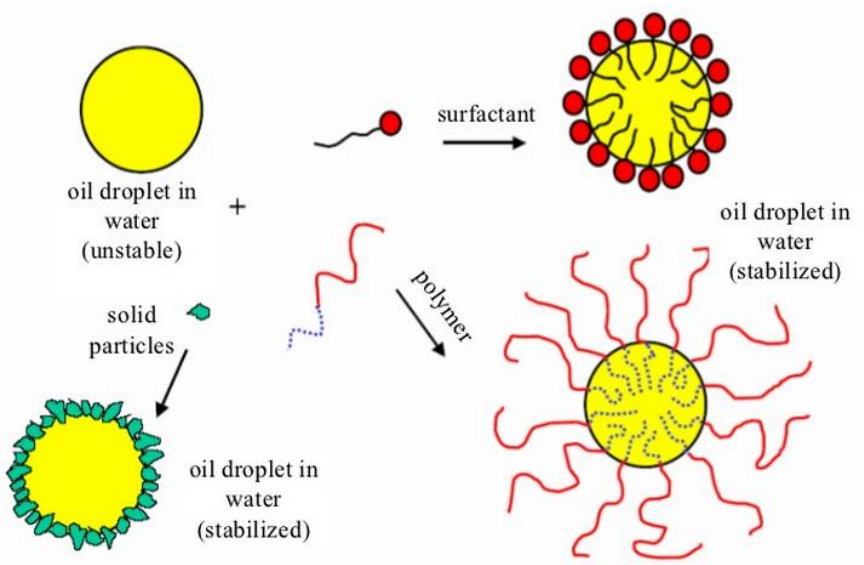
	MFI[a] (g/10 min)
Extrusion, thermoforming, sheets, films, fibers	3
Extrusion, thermoforming, sheets, films, fibers	6–7
Injection molding, staple fibers	14–15
Injection molding	30
Continuous yarns	6–7
Oriented films, bi-axially stretched, blown films	4
Extruded sheets for thermoforming, extrusion	3
Extruded sheets for thermoforming, extrusion	6–7
Amorphous parts, injection molding	22–23

M. Murariu, P. Dubois, Advanced Drug Delivery Reviews 107 (2016) 17–46

Emulsions

An **emulsion** is a special type of mixture made by combining **two liquids** that normally don't mix, such as for instance oil and water





www.thoughtco.com/definition-of-emulsion-605086 (accessed 10/09/2020)

Methods to prepare polymer emulsions

- Emulsion polymerization

Monomer

Water with **surfactants**

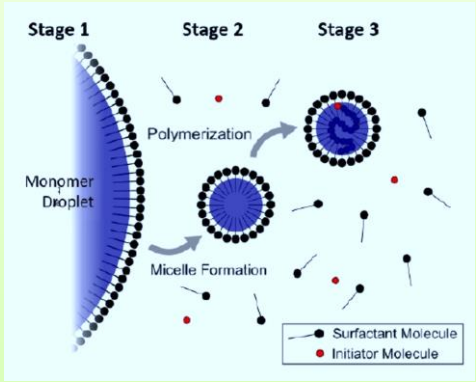
Oil

Water

non miscible

Energy

POLYMERIZATION



- Emulsification of polymers

polymer in organic solvent

Water with **surfactants**

Oil

Water

non miscible

Energy

Advantage and disadvantages of the two methods

Emulsion polymerization

+ No solvent needed with liquid monomers
+ High dry matter content values accessible

- Limited applicability (acrylates, methacrylates, vinyls, styrene, etc..)

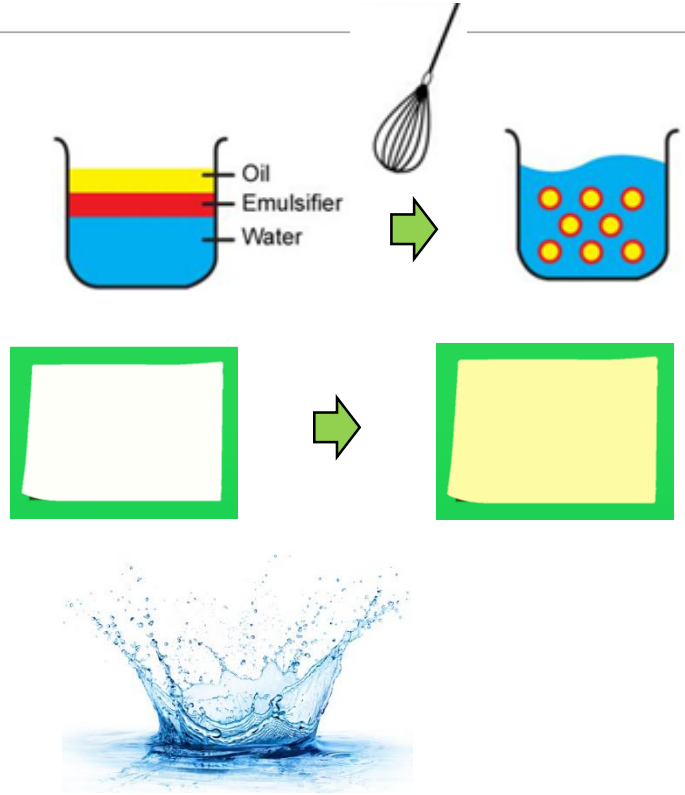
Emulsification of pre-formed polymers

+ Possible for all polymers

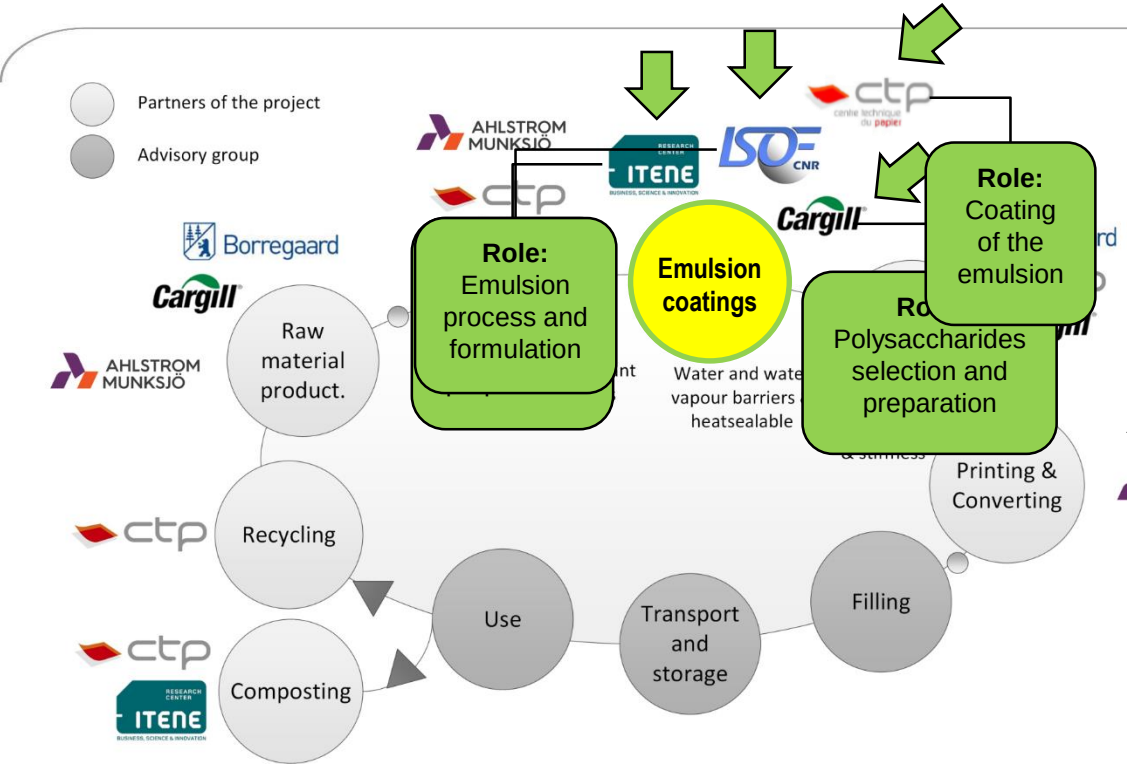
- Organic solvents needed to solubilize polymers
- Viscosity issues limiting the applicability

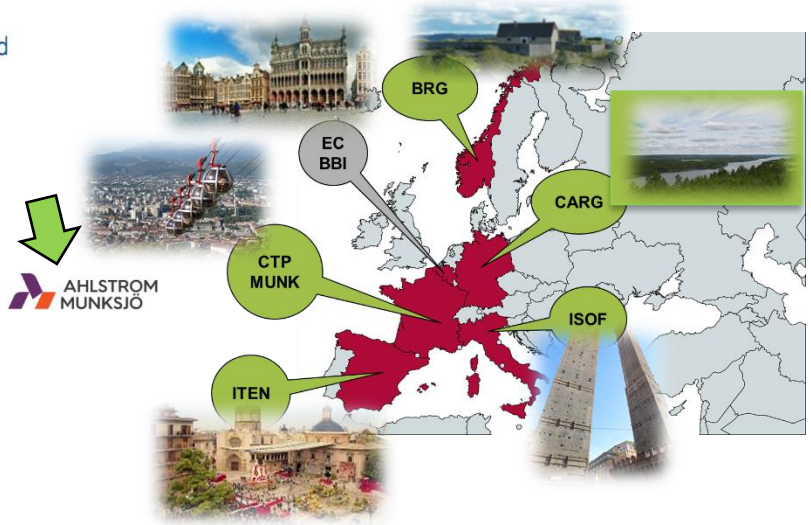
Aim of the study

1. Development of a method to obtain water emulsions of PLA and PLA blends
2. Coating of the emulsions on paper
3. Coated paper must be sealable and not permeable to water

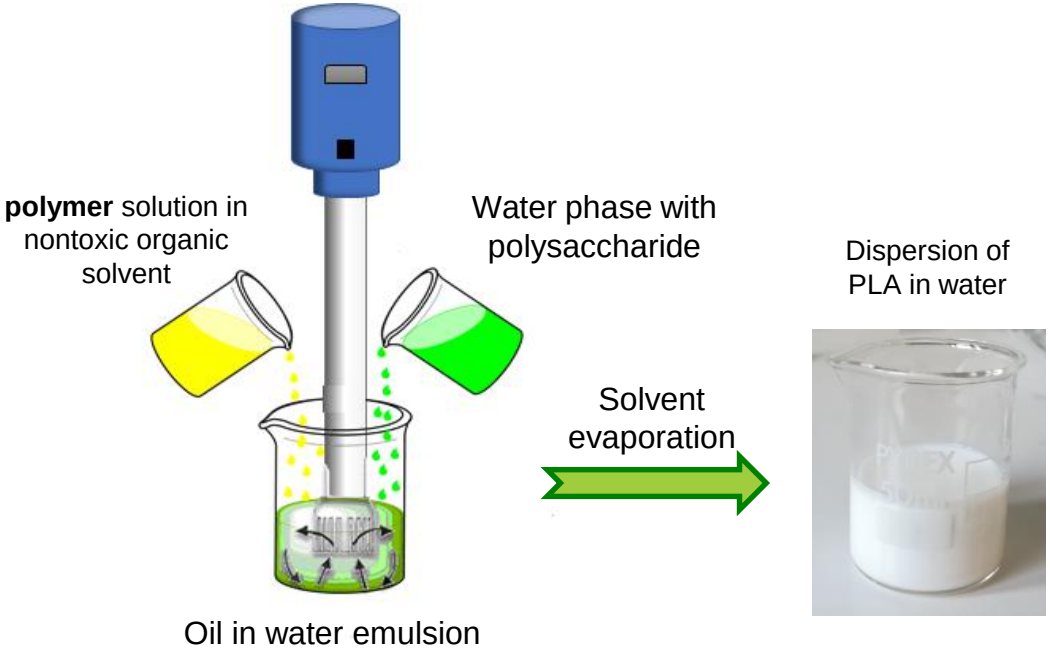


European Consortium





Preparation of the emulsion: concept



The parameters that were studied and optimized are:

- PLA grade
- Blend composition
- Organic solvent and polymer concentration
- Water phase composition
- Mixing method
- Solvent evaporation condition

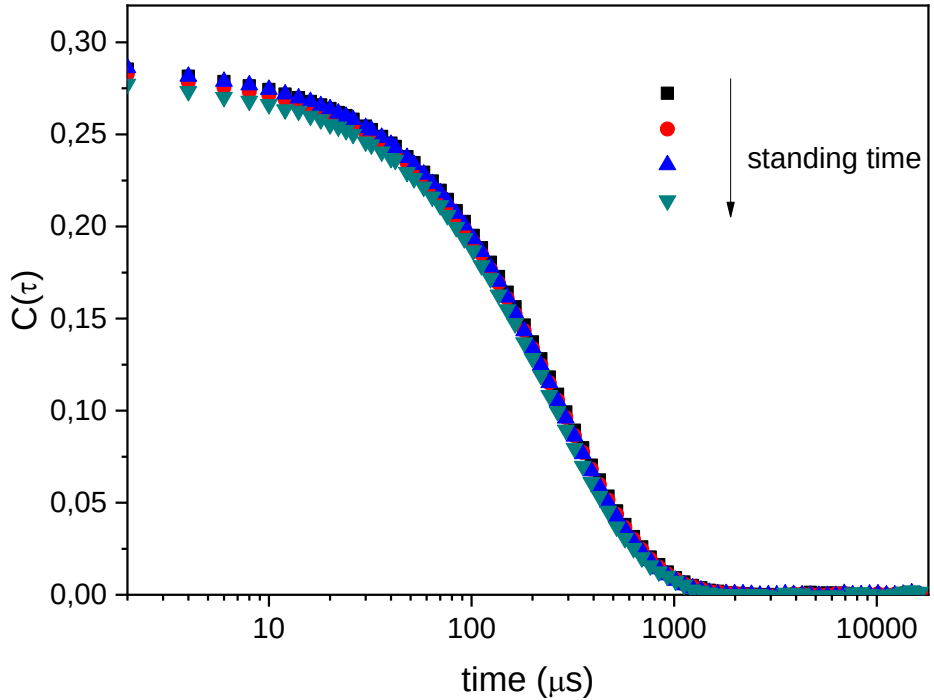
Preparation of the emulsion: apparatus

- Recovery and reuse of the organic solvent
- 260 g of emulsion

Properties of the emulsion

- All component allowed for food contact applications
- Bio-based content ≥ **86%**
- Dry matter: **14-20 %**
- Particle diameter: **180 nm**
- Dispersity: **0,14**
- Stable over several months

DLS analysis: emulsion stability over time



As prepared

Eff. Diam. (nm)	Polydispersity	Baseline Index
179,02	0,110	9,6
175,62	0,109	9,7
173,89	0,090	9,7
170,31	0,053	8,5

after 24 days

Eff. Diam. (nm)	Polydispersity	Baseline Index
174,80	0,150	9,3
174,43	0,128	8,8
172,83	0,160	9,7
170,96	0,128	9,2

Even **after** several **days** all the **emulsions** result **stable** and the dimension of the dispersed phase doesn't vary significantly

Rheological properties

Low viscosity *with values in the* ***1-10 mPa s range***

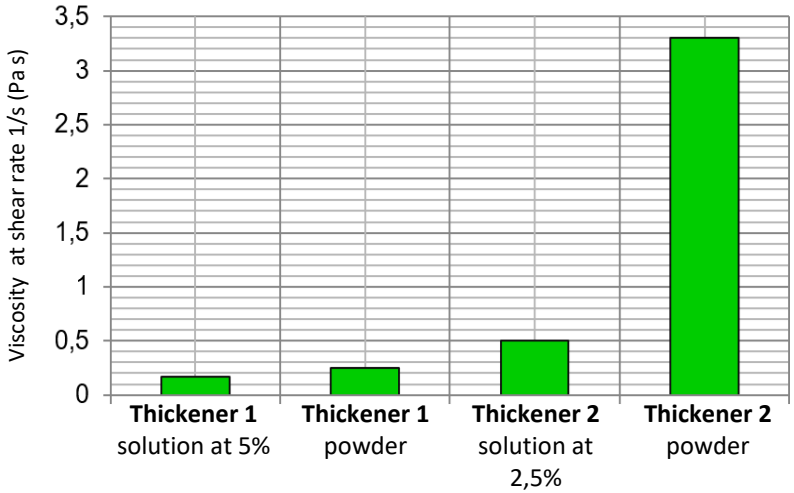
Water-like viscosity

thickening agent

Honey-like viscosity

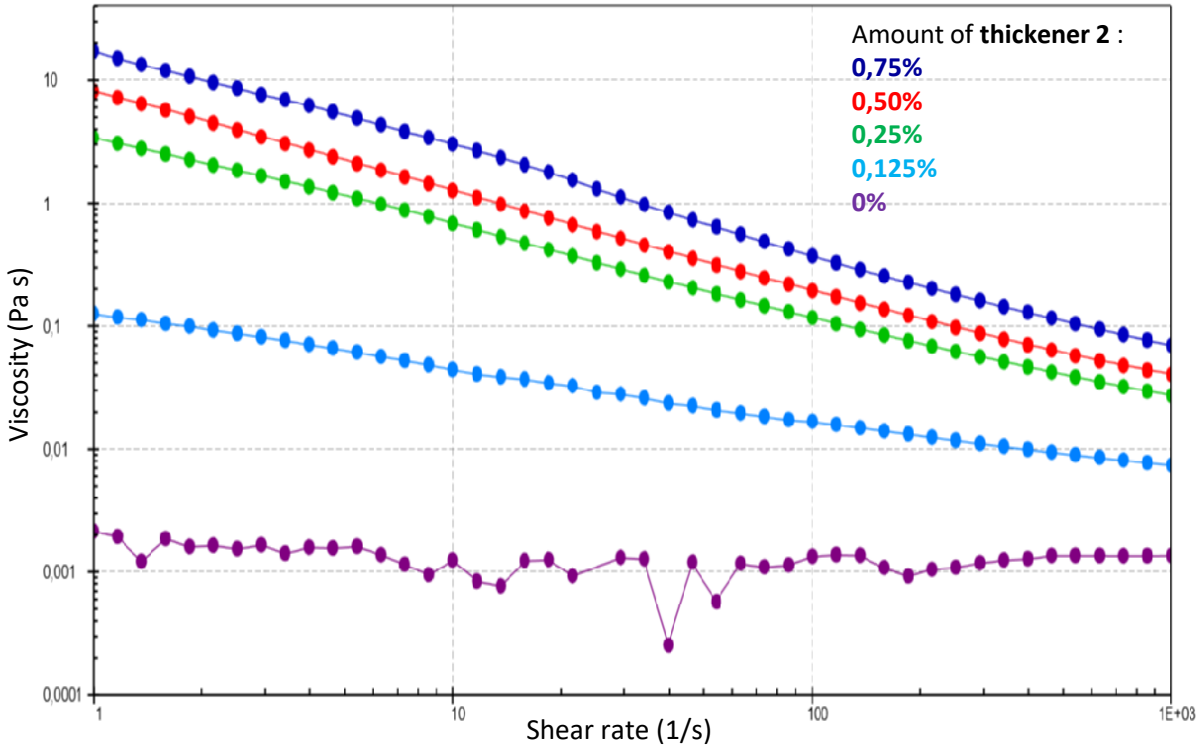
Viscosity values in the ***0,2-17 Pa s range***

Thickeners: food grade polysaccharides from Cargill



- The addition of a lower quantity of **thickener 2** allows to afford better results in terms of final viscosity than **thickener 1**

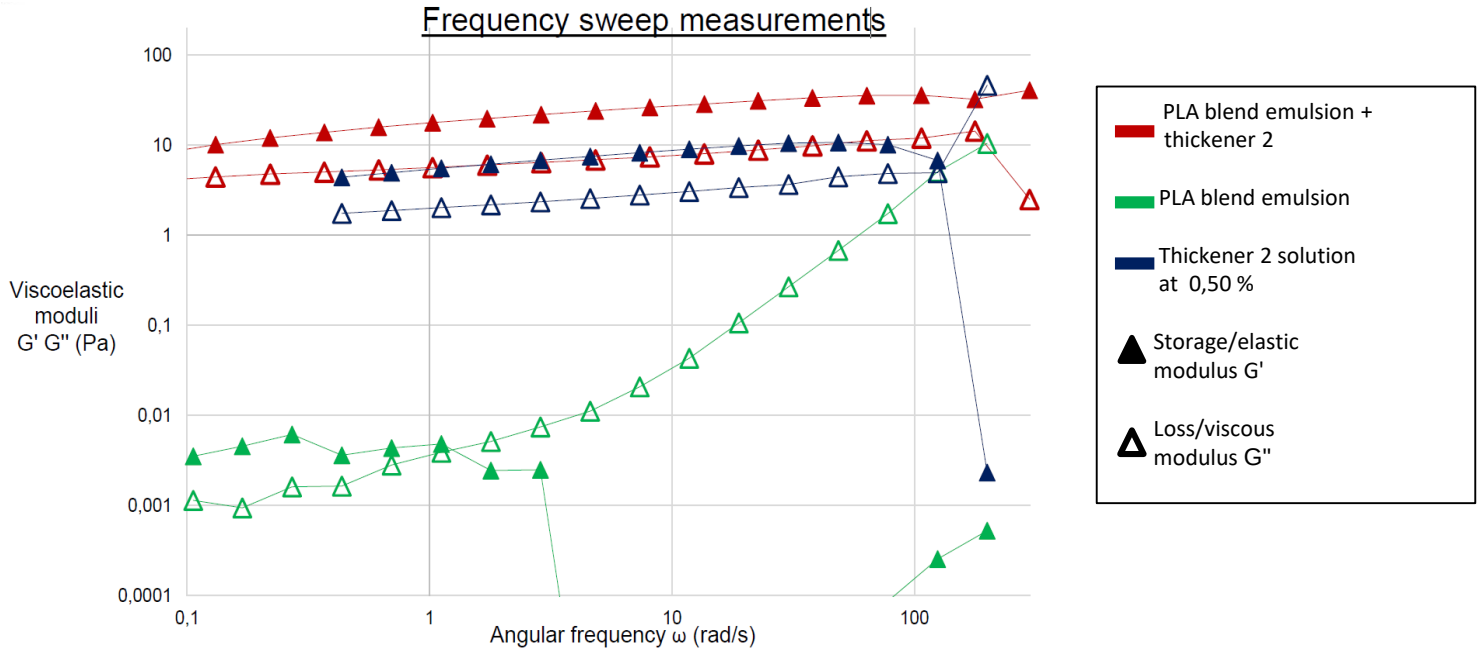
Rheological properties



Thickener 2:

- Stabilizes the emulsion
- Confers elastic character even at low frequencies

Rheological properties



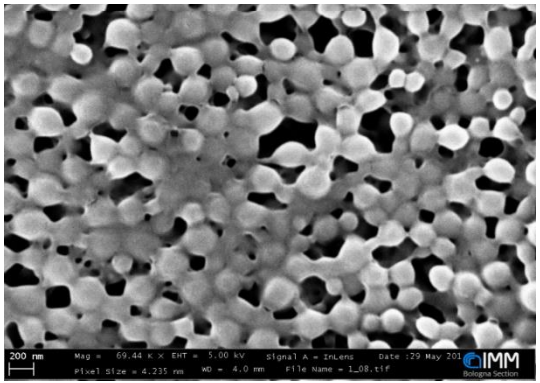
Viscoelastic properties enhanced

Morphology of the dry emulsion

PLA blend
dispersion in water

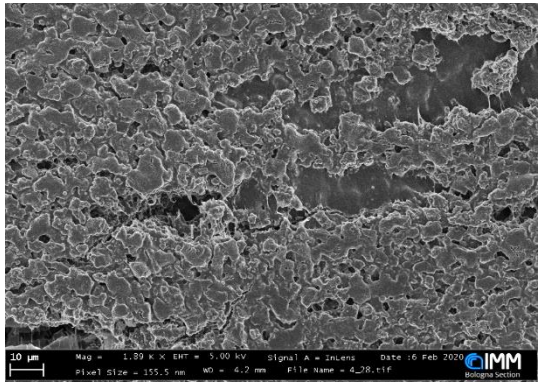
casting

room
temperature



PLA blend emulsion without thickener

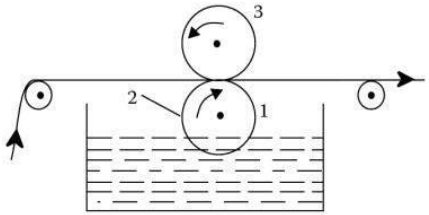
SEM
micrography



PLA blend emulsion with thickener

Emulsion coating on paper

PLA blend
dispersion in water with
honey-like viscosity

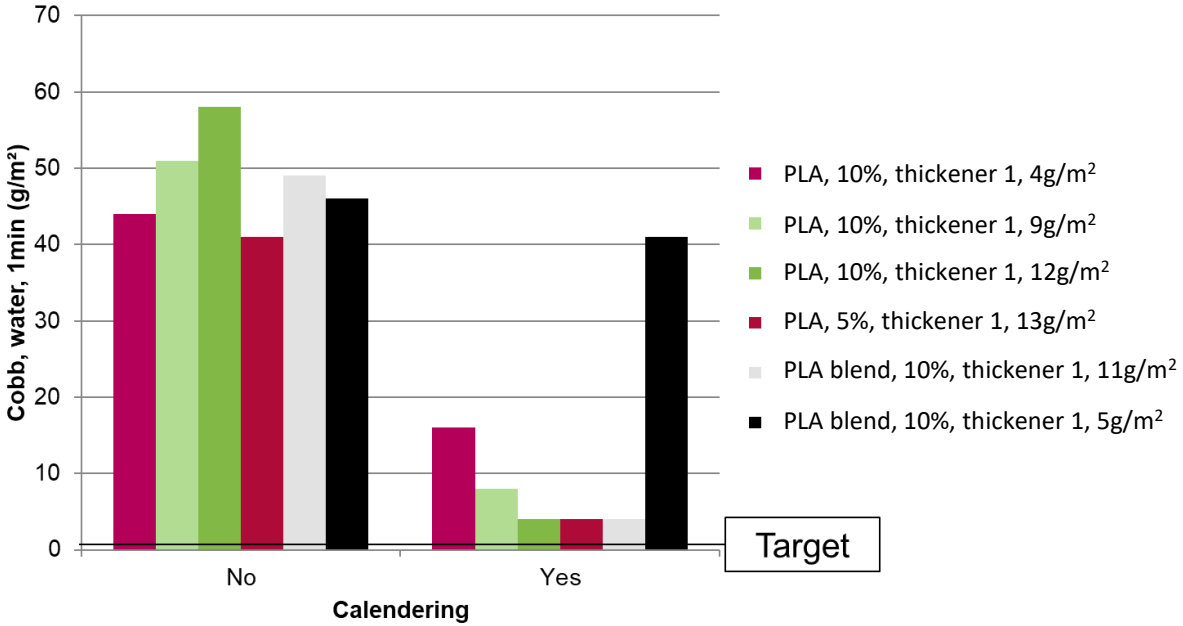


Coating process

- Mix with polysaccharide solutions
  - Honey-like viscosity
- Coating on a selected industrial paper grade for flexible packaging
  - CW 7g/m² → Cobb 5g/m² = good
  - CW 12g/m² → Cobb 2g/m² = very good

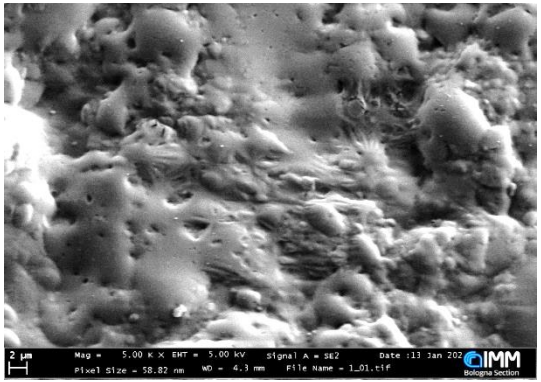
Emulsion coating on paper: calendering

→ calendering significantly improves the liquid water barrier of the coated paper

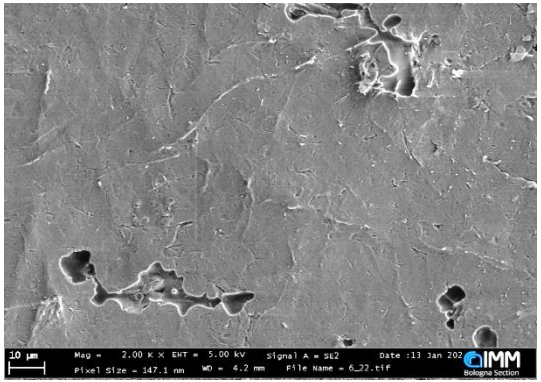


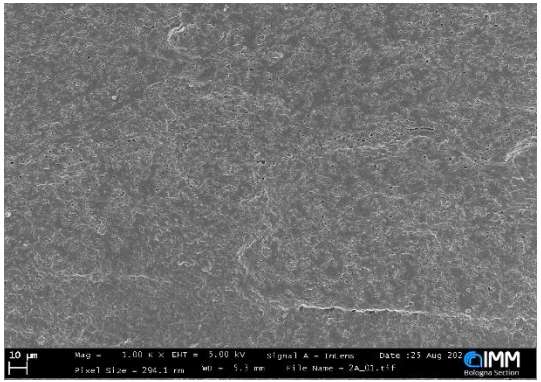
Morphology of the emulsion coating

MFC/PLA blend/thickener
1 not calendered
10 g/m^2



MFC/PLA blend/thickener 1
calendered 2 times (110 ° C)
10 g/m^2





PLA blend/thickener 2
not calendered
14 g/m^2

Conclusions

- An efficient method to obtain water emulsions of PLA and PLA based blends have been developed
- The obtained emulsions are made on all food grade approved substances
- PLA emulsions have been thickened with food grade polysaccharides and then successfully coated on paper
- Coated paper exhibits very good Cobb water index

Aknowledgement

- Sherpack project has received funding from the **Bio Based Industries Joint Undertaking** under the European Union's Horizon 2020 research and innovation programme under grant agreement No 745718.

Horizon 2020
European Union Funding
for Research & Innovation