# DEVELOPMENT OF POLYMERIZATION METHODS

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# OUTLINE

- **Presentation of our companies.**
- **Polymers and biopolymers.**
- **Polyester and copolymer synthesis:**
  - Synthetic approach
  - Characterization
  - Results (polyesters, extensions with lactide, PUDs)
- **Conclusions & future work**

# Ecopol Tech

- Technological company born in 2005, based on the R&D Experience in **Polymer Chemistry** of its promoter, Dr. Josep Rocas.

- It is located in the Technological Park EL FOIX, just between Barcelona and Tarragona. Close to chemical industrial hubs and plastic industries.

- The company is split into two different industrial units and is currently composed of 14 people.


# Ecopol Tech

BIOREFINE-2G

## DIRECTOR & TECHNICAL MANAGER

### External services

**Engineering**
**Informatics**
**Financial management**

### Commercial Department

1 commercial agent

### Lab scale

**R&D projects**

12 chemists in 3 laboratories




### Pilot plant

**10, 20, 50 liter jacketed reactors**

2 operators

### Fabrication plant

**1500, 4000 and 8000 liter reactors**

2 operators

# Ecopol Tech

BIOREFINE-2G

**Industrial Applications**

Adhesives, coatings, additives, reactive polymers, nanofoams…

**Cosmetic Science**

Encapsulated actives: fragrances, antioxidants, anti-aging agents; reactive polymers for hair care…

**Pharma Science**

Encapsulation of anticancer, antimicrobial, antifungal drugs for selective delivery systems

- **More eco-friendly**
- **Solvent-free or water based**
- **Biocompatible**
- **Biodegradable**
- **Recycled materials**

# What is AIMPLAS?

AIMPLAS is a **Technology Centre** with more than 25 years of experience helping companies in the plastic sector

# AIMPLAS STAFF

We are a team of more than 110 highly qualified professionals

# AIMPLAS RESOURCES


Over 8,500 m$^2$ facilities with state-of-the-art equipment and instrumentation

# AIMPLAS FIGURES

**€ 8.6M**
revenues

**+1,500**
customers

**+530**
members

2014 DATA

70% of incomes from R+D projects.
32 EU ongoing projects

# OUR CONTRIBUTION IN BIOREFINE-2G PROJECT

-Market overview
-New polymers/process
-New characterization tools

# European Plastics Industry

- In 2013 the European Plastics Industry employed more than **1,400,000 people.**
- Turnover of plastic industry is **300 billion Euros.**


Plastics, the Facts 2013

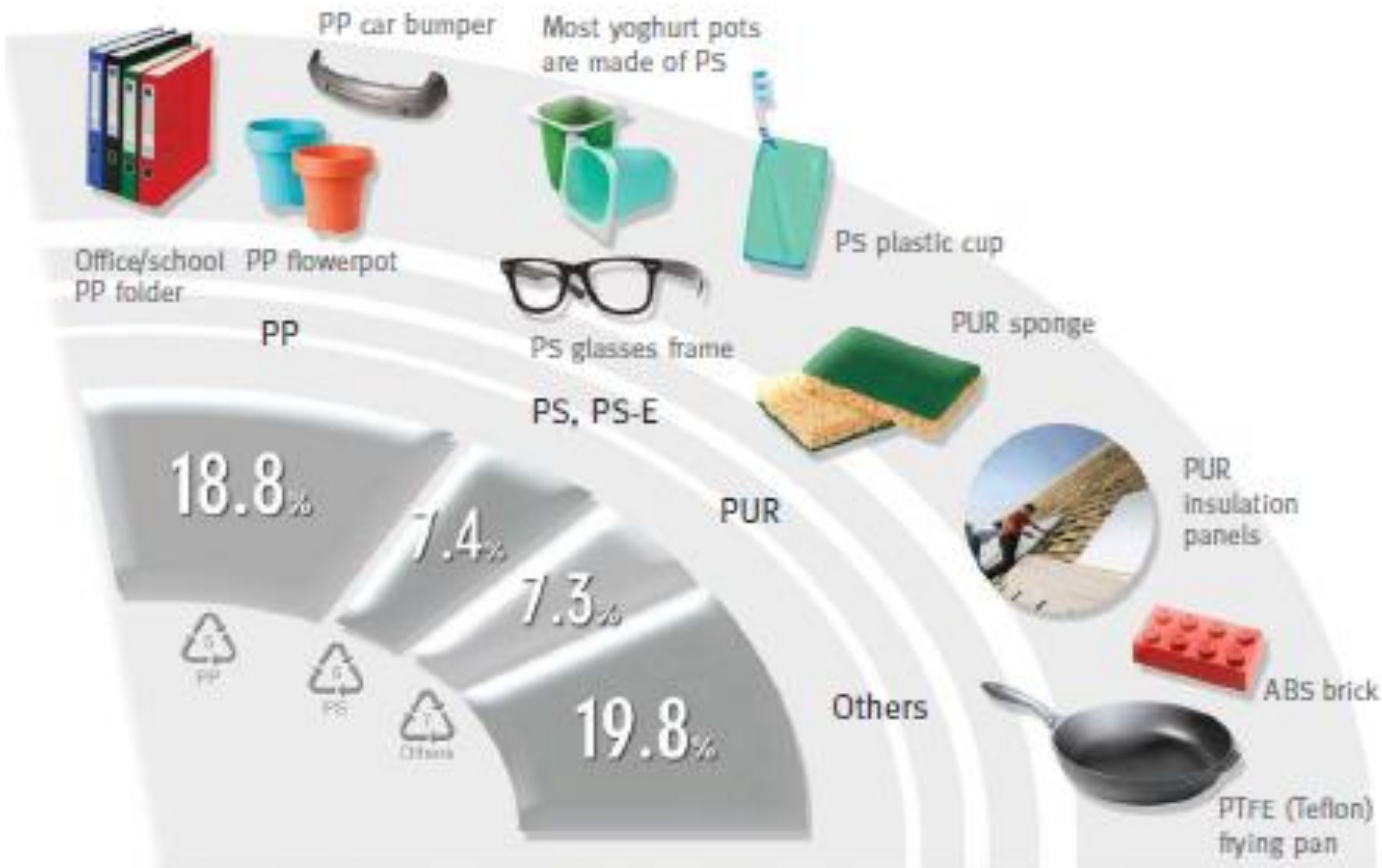
# European Plastic Demand

- Polyolefin markets represents 50% of polymer demand**.**
- Polyesters represent 10% (7% PET)of demand.
- Polyurethane represent 8% of demand.
- PVC represent 11% of demand.

# European Plastic Demand I


Plastics, the Facts 2013

# European Plastic Demand




Plastics, the Facts 2013

# European bioplastics

## Bioplastic concept:

*Whole **family of materials** which differ from conventional plastics insofar as that they are **biobased, biodegradable**, or both.*

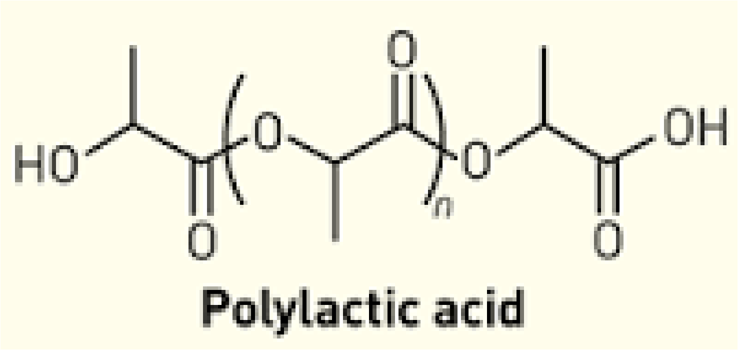
*Biobased means that the material or product is (partly) derived from biomass (plants).*

*European Bioplastics Org.*

# European bioplastics

## Why Bioplastics?

- **Save fossil resources by using biomass**
- **Biodegradability is an add-on**
- **PLA market 2-3000 $ mln.**

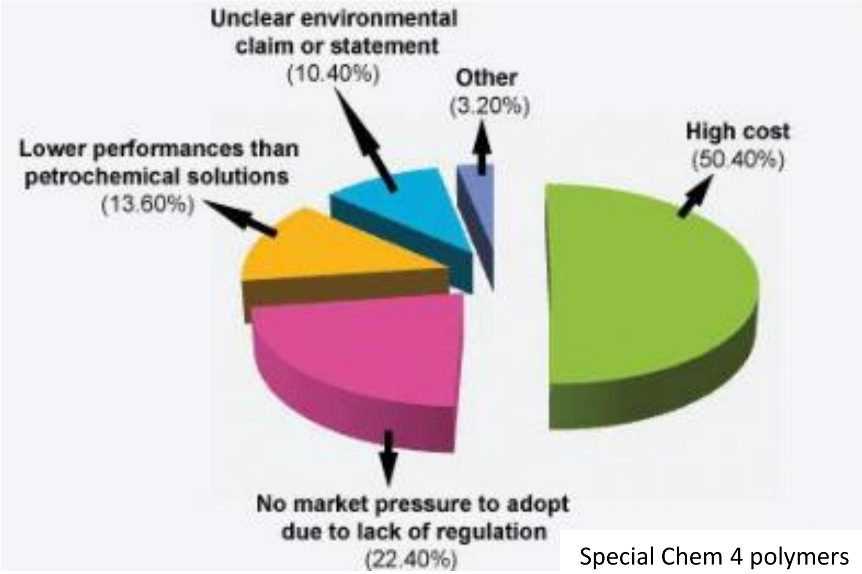




(2014 marketsandmarkets).

# European bioplastics

**Why not Bioplastics (according customers)**

- Mechanical properties
- Price
- Lack of regulation




Special Chem 4 polymers

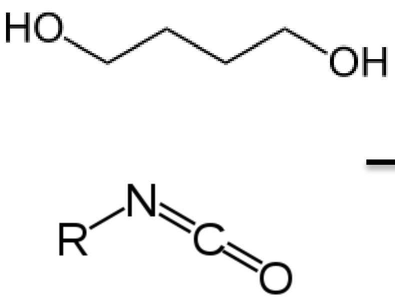
# European bioplastics

## Bioplastics industrial barriers?

- **Improve mechanical properties.**
  - Chemical design and use of additives.
- **Develop high efficient processes as in oil plastic industry.**
  - New processes as REX.

# Polymerization methods

## Polymer synthesis (Classical approach)




Synthesis


Post-Processing

-Solvent process.

-Management of high viscose products.

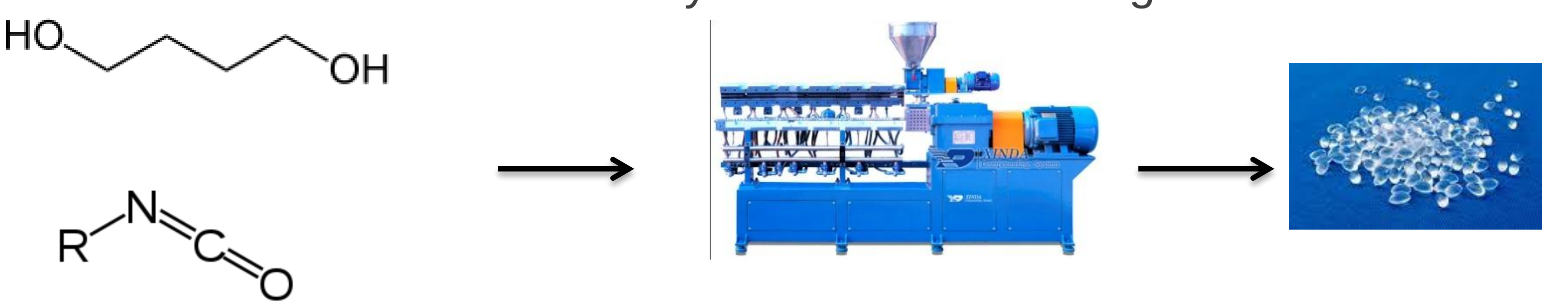
-Long reaction times as viscosity increase.

# Polymerization methods

## Reactive extrusion.

REX is a manufacturing method that combines the traditionally separated chemical process (polymer synthesis and/or modification) and extrusion (melting, blending, structuring, de-volatilization and shaping)

Synthesis & Processing




Lambla, M.; Macromolecular Symposia **1994**, *83,* 37-48

# Polymerization methods

## Reactive extrusion.


-Free solvent process.

-Fast process (3-10 minutes synthesis is carried out)

-Better management of high viscose products.

-Water can be removed due high temperature and devolatilization.

-Requires previous knowledge of polymerization reaction in solution.

# Goal and Starting materials choice

MAIN GOALS:

- Synthesis of **polyester with dicarboxilic acid from yeast**
- Very **low acid number** (max 0.2 mg KOH/g)
- Polyester with a molecular weight of **2500-3000 g/mol**
- **Synthesis of PLA copolymers**

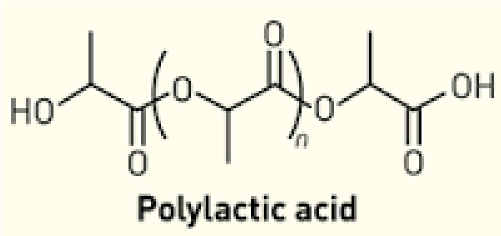
**DIACIDS obtained from renewable sources for polyester synthesis**

diol → **Polyester-Polyurethane**

diol → **Polyolefin analogues PLA-cop**

1 International Journal of Nanomedicine 2011:6 321-3032

# Other opportunities: PLA cop


-Development of PLA copolymers from diacids with enhanced properties lead us to get access to a market **2-3000 $ mln. (2014 marketsandmarkets).**

**-PLA MARKET is expected to reach 5000-6000 $ mln in 2019 (European Bioplastics estimation).**

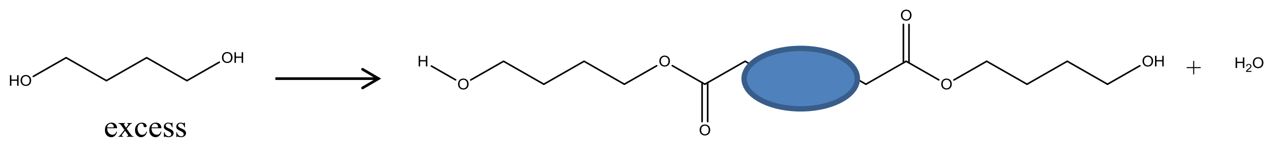
-Development of efficient process to obtain **monomers and polymers derived from PLA with "enhanced" properties.**

**MAIN OPORTUNITY, fut**

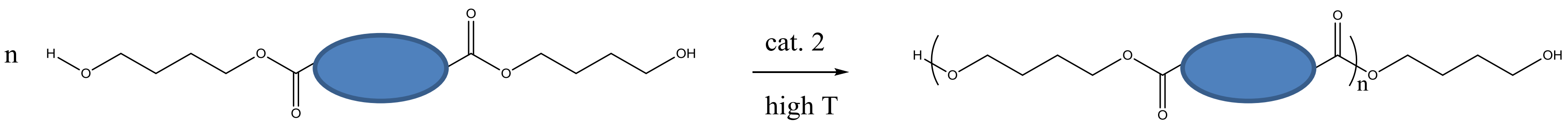
# Synthesis of polyesters at lab-scale

**OUR APPROACH is divided the process into two steps:**

1st STEP: **condensation reaction** (esterification) between diacid and diol with loss of water → obtain the **minimum acid number**:




2nd STEP: '**transesterification**' between different polyol-polyester chains to increase the **molecular weight** of the final polyester. Use of a catalyst.



# Synthesis of polyesters at lab-scale

## Characterization

### During and after reaction

• Correct ester bond formation by FT-IR:

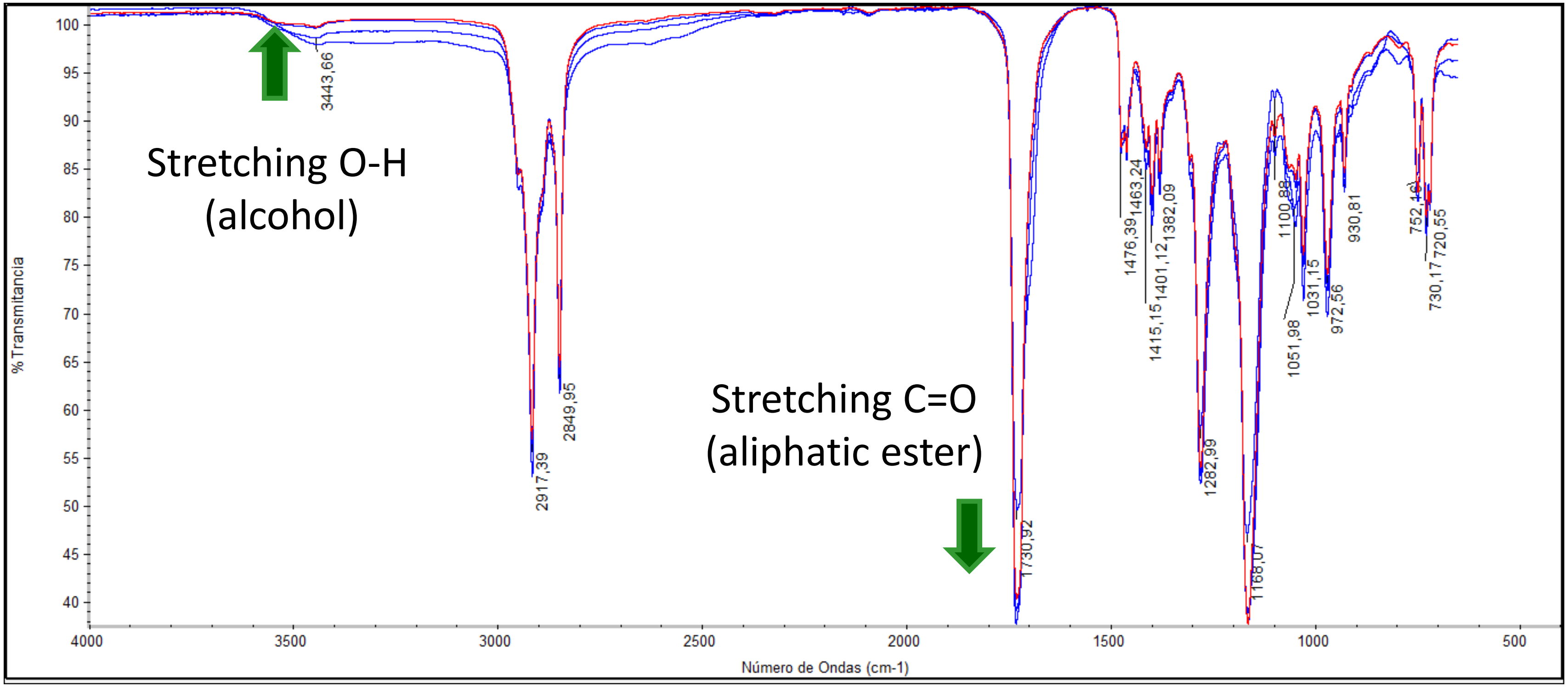



**Fig. 1**: FT-IR spectra of polyester synthesis over time

## Characterization

- Following the reaction by **acid number determination**:
(acid-base titration)

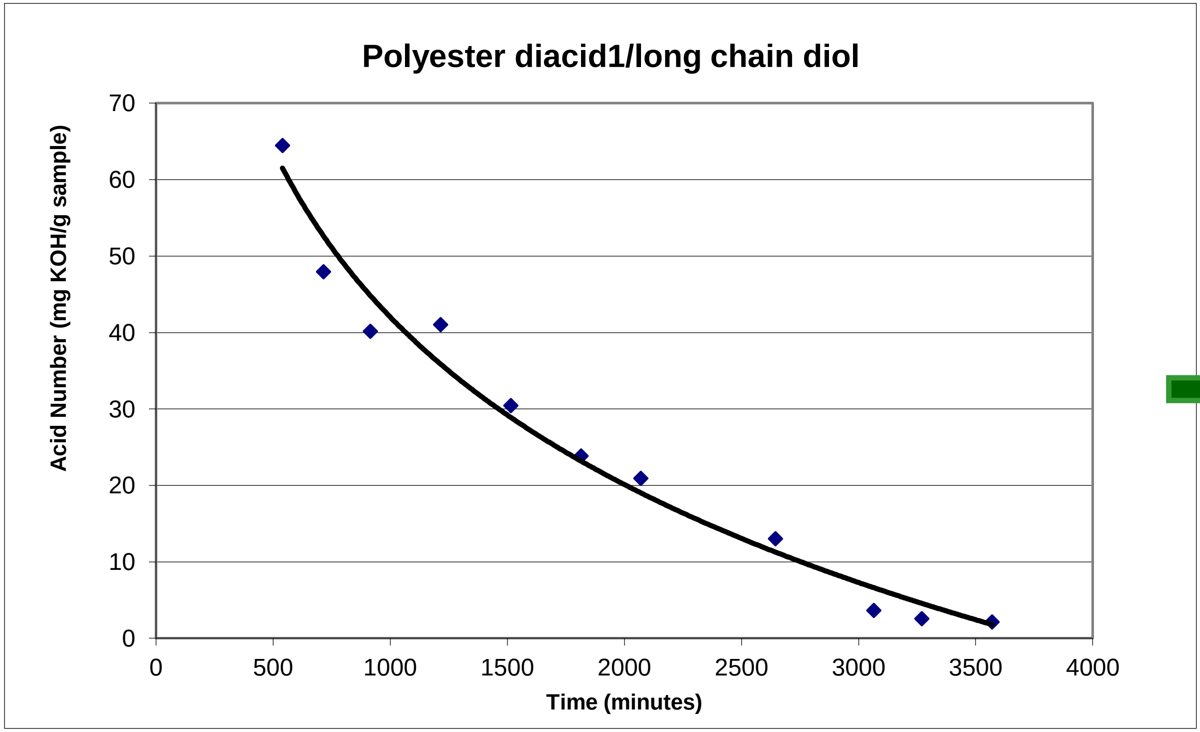



**Fig. 2**: acid number of the polyester sample over time

Decrease of acidity of the sample over time

# Results (I)

**Most representative polyesters and characterization values:**

| POLYESTER | OH:COOH ratio | MELTING POINT (º C) | ACID NUMBER (mg KOH/g) | HYDROXYL NUMBER (M2) (mg KOH/g) | CALCULATED MW (g/mol) |
|---|---|---|---|---|---|
| **EURO16** (diacid1) | 1.51:1 | 35-40 | 0.91 | 46.69 | 2357.14 |
| **EURO17** (diacid1) | 1.50:1 | 52-56 | 1.25 | 12.54 | 8139.28 |
| **EURO18** (diacid1) | 1.49:1 | 60-65 | 0.40 | 132.18 | 846.25 |
| **EURO19** (diacid1) | 2.24:1 | 35-40 | 1.60 | 84.34 | 1305.5 |
| **EURO21 (diacid1)** | **1.29:1** | **35-40** | **0.37** | **18.07** | **6089.92** |

**Very low acid number close to commercial (0.2 mg KOH/g)**

# Results (I)

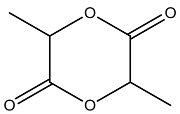
**Most representative polyesters and characterization values:**

| POLYESTER | OH:COOH ratio | MELTING POINT (º C) | ACID NUMBER (mg KOH/g) | HYDROXYL NUMBER (M2) (mg KOH/g) | CALCULATED MW (g/mol) |
|---|---|---|---|---|---|
| **EURO22** (diacid2) | **1.20:1** | **>125** | **-** | **-** | **-** |
| **EURO23** (diacid1) | **1.15:1** | **60-65** | **0.39** | **41.64** | **2669.52** |
| **EURO24** (diacid2) | **1.10:1** | **>125** | **-** | **-** | **-** |
| **EURO25** (diacid1) | **1.12:1** | **35-40** | **0.426** | **To be determined** | **To be determined** |

* Due to premature crosslinking problems, we have not been able to fully characterize some diacid-based polyesters. Some changes of synthetic approach are currently being considered.

# Results (II)

**EXPLORING OTHER POSSIBILITIES WITH BIOPOLYESTERS FOR REX SYNTHESIS.**



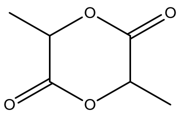
lactide

+ BIOPOLYESTER ⟶ PLA-BIOPOLYESTER-PLA

| AIMPLAS REF | MW of sm | Ratio lactide/SM | MW theor | MW nmr |
|---|---|---|---|---|
| PRO12-0319-10-01 | 2111,4 | 10,2 | 28475 | 26802 |
| PRO12-0319-10-02 | 2111,4 | 8,7 | 29588 | 28050 |
| PRO12-0319-10-03 | 2111,4 | 6,5 | 18146 | 17205 |
| PRO12-0319-10-04 | 2111,4 | 15,0 | 41875 | 39870 |
| PRO12-0319-10-05 | 2111,4 | 20,0 | 55883 | 50502 |

# Results (II)

## EXPLORING OTHER POSSIBILITIES WITH BIOPOLYESTERS:



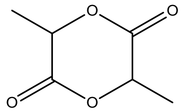
lactide + BIOPOLYESTER → PLA-BIOPOLYESTER-PLA

| AIMPLAS REF | Ecopol Tech SM | MW of sm | MW theor |
|---|---|---|---|
| PRO12-0319-09-01 | **Europeu18** | 846,25 | **20950** |
| PRO12-0319-09-02 | **Europeu18** | 846,25 | **41042** |
| PRO12-0319-09-03 | **Europeu18** | 846,25 | **63155** |
| PRO12-0319-08-01 | **-** | 8139,28 | **39962** |
| PRO12-0319-08-02 | **-** | 8139,28 | **70483** |

**RATIO in MW of both polymer is the key factor**

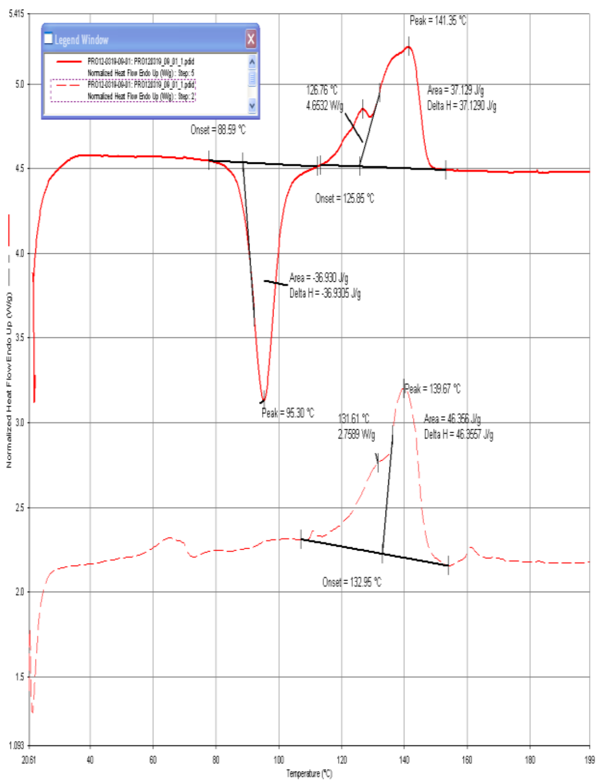
# Results (II)

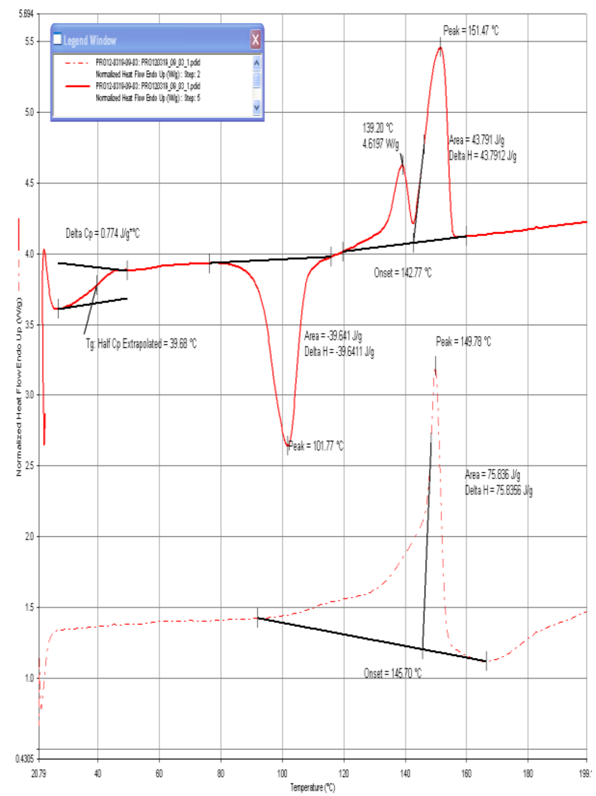
## EXPLORING OTHER POSSIBILITIES WITH BIOPOLYESTERS:



lactide

\+ BIOPOLYESTER ⟶ PLA-BIOPOLYESTER-PLA



# COMERCIAL OPORTUNITIES IN BIOREFINE-2G PROJECT

# Polyurethane polymers

**Application of the bio-based polyesters to prepare commercially interesting products: POLYURETHANE POLYMERS**

- **Waterborne Polyurethane Dispersion (PUDs)[5,6]**

- Coatings and adhesives that use water as the primary solvent.
- Ecological material.
- High solids content with low viscosity.
- Wide adhesion range and excellent stability values.
- Preparation of crystalline PUDs that adhere by melting.
- Application in flooring, fabric, leather, metal, plastics, wood, automotive…

Fig. 2: PUD film [2]

2 http://purpatents.com/2014/07/29/polyurethane-dispersions-with-reversible-drying/

# PLA copolymers

**Application of the bio-based polyesters to prepare commercially interesting products: PLA CO-POLYMERS**

- **Flexible PLA-Copolymers**

- Films with high flexibility
- Ecological material.
- High transparency
- Low processing temperature
- Packaging sector.
-Chemical companies are interested

# Ongoing & future work

- Improve the results in terms of acidity and molecular weight. Possible changes:

    -Changing the **catalyst**. Try with metallic oxides like Zr(OBu)4, and $GeO_2$ and special additives. Rare earth metals derivatives. Bismuth based compounds.

- Consider the use of **lipases** instead of organometallic catalysts. In this case, lower reaction temperatures should also be used.

- Develop **reactive extrusion for polyesters and PLA-polyesters.**

# Conclusions

• A wide range of polyesters have been prepared under different conditions. Diol:diacid ratio, temperature ramp, type and dose of catalyst, vacum/$N_2$ cycles have been tested in order to obtain **LOW ACID NUMBER POLYESTERS** (the lowest is around 0.35 mg KOH/g) **COMERCIAL GRADE POLYESTERS.**

•**AIMPLAS** has developed new copolymers of the polyester with **lactide.** New products have been prepared with improved properties compared to the initial polyester and poly-lactic acid. **PLA COPOLYMERS WITH ENHANCED PROPERTIES.**

• A new method has been developed to prepare polyurethane dispersions out of these bio-based polyesters (diacid1). Interesting properties have been found → **LOW MELTING POINT ADHESIVES** (around 40 ºC).

# Thank you for your attention !!

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