BIOECONOMÍA ARGENTINA 2015
EL POTENCIAL DE LAS REGIONES

New Developments on Polymers from Renewable Resources

by Marisa Spontón

UNL CONICET INTEC 40 Años

OUTLINE

- **INTEC (UNL – CONICET) – Polymer Group**

- **Introduction to Bio-Based Polymers, Bio-BasedTechnology and Trends**

- **Developments on Polymer from Renewable Resources**

  - ✓ **An Industrial Application of Lignin-Based Resol Decorative Laminates: from the Lab to the Industry**

  - ✓ **Polyurethanes from Vegetal Oil**

INTEC
Instituto de Desarrollo Tecnológico para la Industria Química

INTEC (UNL – CONICET)

Personnel

69 Researchers /Professors

45 Doctoral Fellows

23 Postdoctoral Fellows

43 Technicians and Assistants

3 Art. 9 SINEP

~24 Students

Main Activities

- ✓ **Scientific Research**
- ✓ **Teaching / HR Training**
- ✓ **Technological Transfer**

Main Groups

- ✓ Photoreactor Engineering and Pollution
- ✓ **POLYMER AND POLYMERIZATION REACTOR**
- ✓ Food Engineering and Biotechnology
- ✓ Fine Chemistry and Sustentability – Organic Synthesis and Organometalic
- ✓ Engineering and Environmental
- ✓ Process Control and Nonlinear Systems
- ✓ Fluid Mechanics, and Rheology

POLYMER AND POLYMERIZATION REACTOR GROUP

✓Characterization

✓Mathematical Modeling, Simulation and Control of Polymerization Processes

✓Polymer Synthesis

- Hybrid polymeric nanoparticles by miniemulsion polymerization
- Hybrid nanoparticles based on materials from renewable sources
- Formaldehyde resins (phenolic, urea and melamine resins): both traditional and modified with renewable resources
- Flame retardant phenolic and epoxy resins
- Bio-inspired and recyclable polymers
- Nanostructured membranes for water treatment
- Mono- and multilayer membranes for controlled delivery systems
- Polyurethanes based on vegetable oils
- Styrene polymers: polystyrene, high impact polystyrene, ABS and MBS with controlled molecular structure
- Functionalized monodisperse latex for the development of immunodiagnostic reagents
- Water soluble acrylic resins
- Hydrogels and nanogels for biomedical applications

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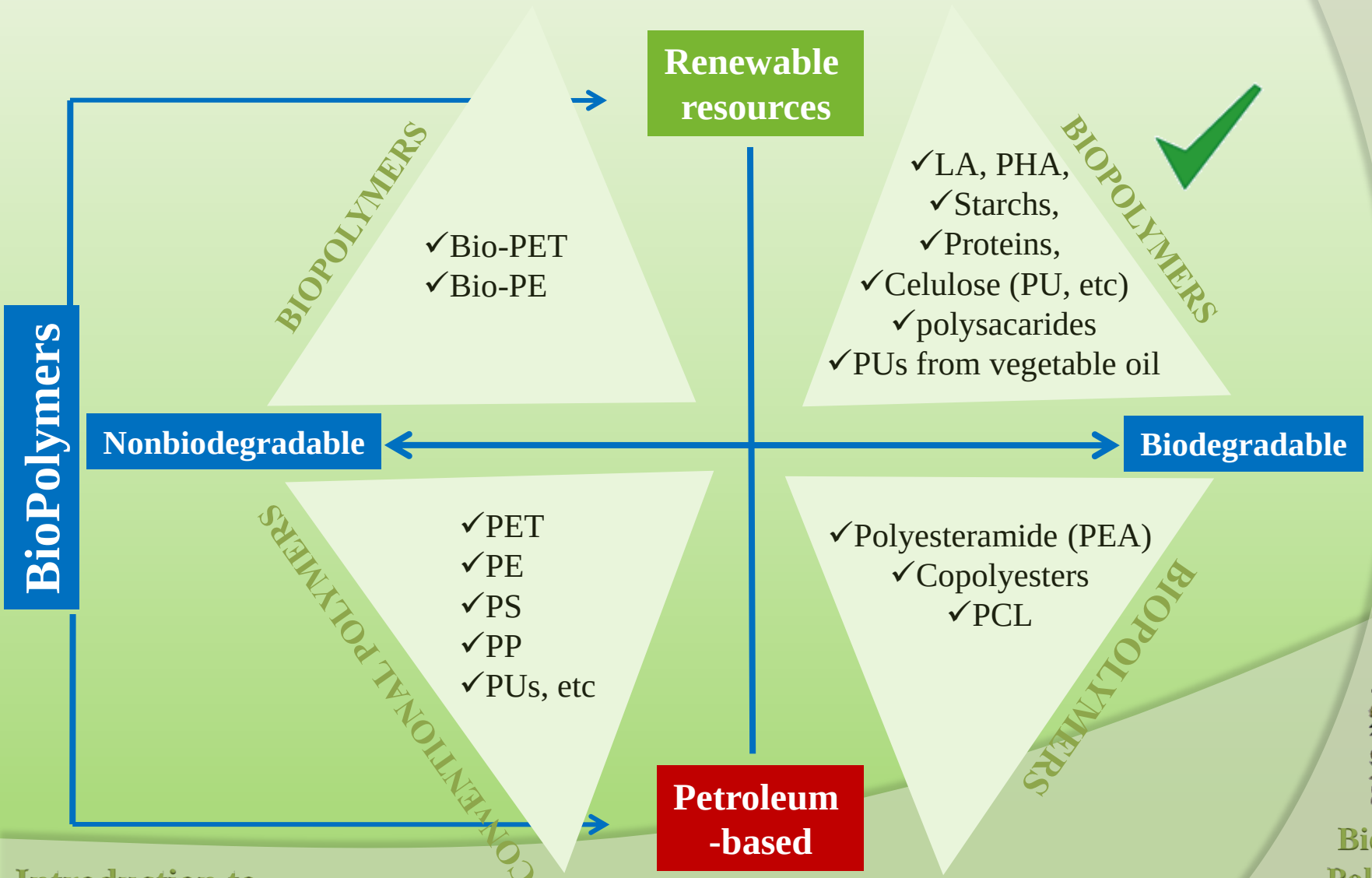
  - ✓ Polyurethanes from Vegetal Oil

✓ Higher oil prices
✓Huge amounts of waste plastics
✓Environmental regulations…

Development of new materials from raw materials more compatible with the environment



Polymers Based on Renewable Resources

from biomass

- **Polysaccharides**
  starch, cellulose, quitosane
- **Proteins**
  casein
  gluten
- **Lipids**
  Fatty acids
- **Lignins**

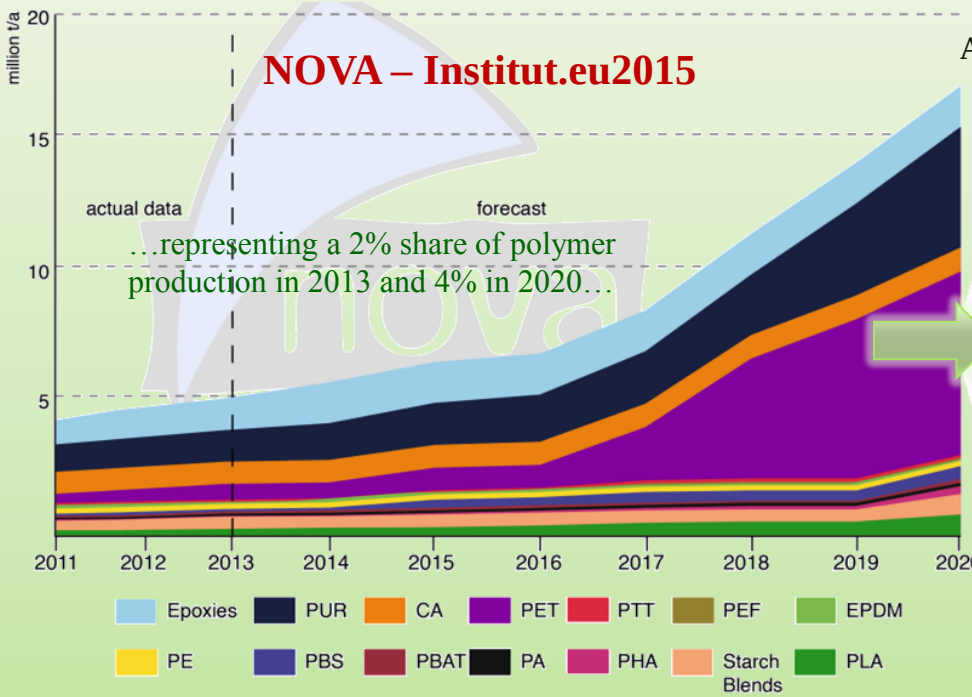
From monomers based in renewable resources

- **Lactic acid,**
- **Vegetable oils**
- **Derived from lignins**

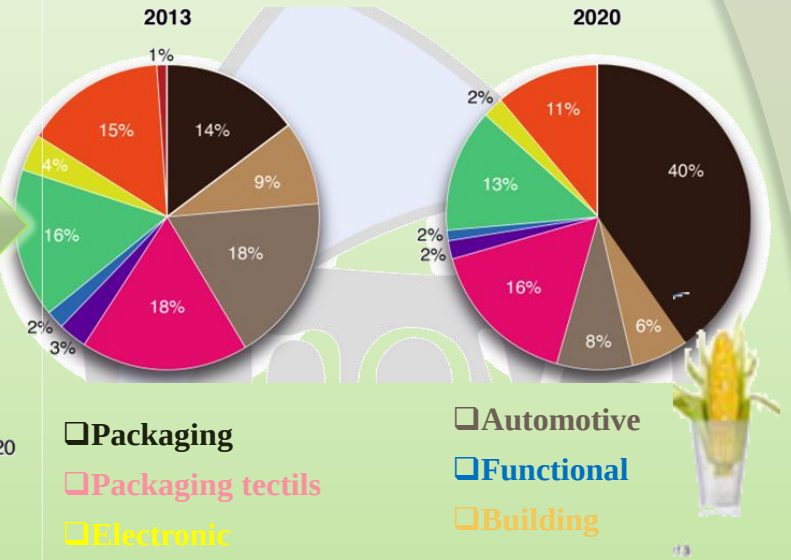
From microorganisms

- **Polyhydroxyalkanoates (PHA)**
- **Celullose**

Bio-based Polymers: Evolution of Worldwide Production Capacities from 2011 to 2020



A wide range of polymers derived from renewable resources are available for various applications



Argentina presents competitive advantages in the use of renewable raw materials:

- ❑ Leader in the production of sugarcane and soybeans.
- ❑Capacity of production of vegetable oils.
- ❑Tropical climates, suitable for productivity.
- ❑Land available for crops.
- ❑Human resources.

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DECORATIVE LAMINATE

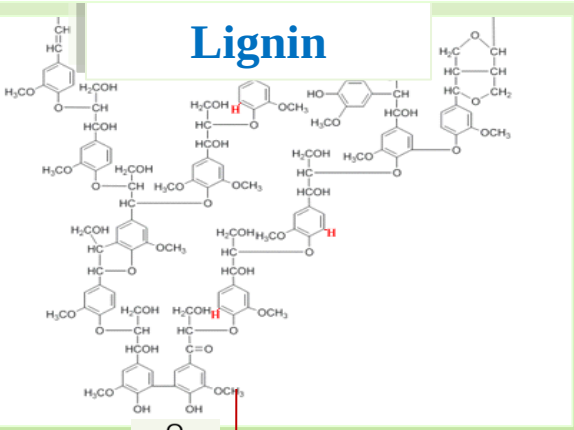
HIGH PRESSURE

LOW PRESSURE

Decorative Paper impregnated with formaldehyde resin

Objectives: partial substitution of phenol in resol by a modified lignin for decorative laminates

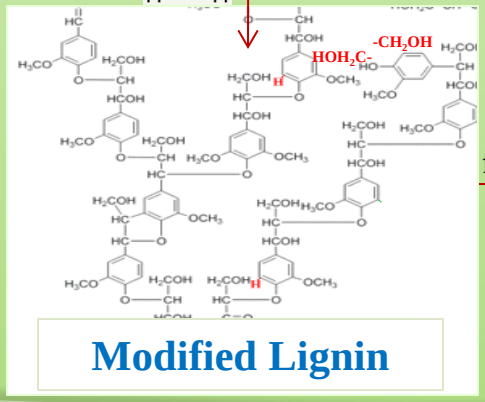
Lignin



- ❑ **Advantages**
- ❑ Natural Polymer
- ❑ Abundant
- ❑ Economical
- ❑ Similar structure to resol

- ❑ **Disadvantages**
- ❑ Structure depends on the *wood*
- ❑ Low reactivity

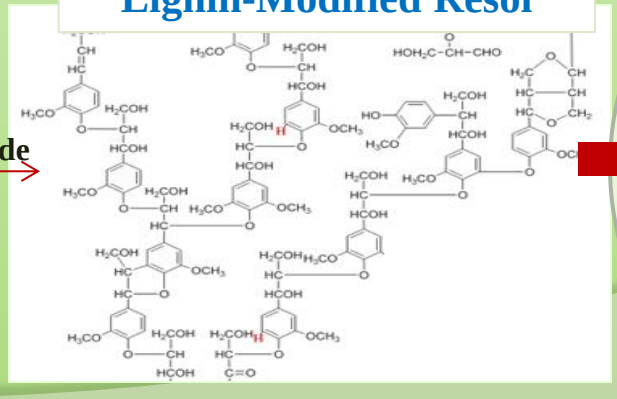
Pre-Hydroxymethylation



Modified Lignin

+ Phenol, formaldehyde

Lignin-Modified Resol



Characterization and modification of 3 Lignins:

- ✓ lignosulfonate,
- ✓ kraft and
- ✓ organolv

Obtention of Laminates: Curing of Impregnated Papers

1) Synthesis of Base Resin ⇨ 2) Drying and Impregnation ⇨ 3) Pressing

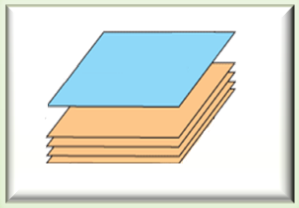
Impregnation of Papers

T = 135 °C

KARIKAL

Industrial Pressing

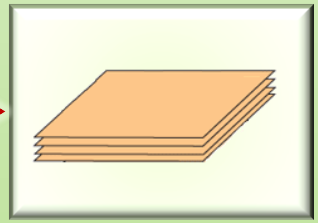
T = 150 °C; P = Kg/cm^2; t = 51 min.



- ✓ Water Boiling Resitance
- ✓ Ball Impact Resistance

Pilot Plant Pressing

T = 150 °C; P = 35 Kg/cm^2; t = 30 min.



- ✓ Tensile Strength
- ✓ Flexural Strength
- ✓ Dart Impact Resistance
- ✓ Delamination

Bio-based laminates exhibited mechanical properties similar to those of traditional laminates

INVESTIGATION STEPS

1. **Lignins characterization (lignosulfonate, kraft and organolv)**
2. **Lignins hydroxymethylation (Laboratory)**
3. **Optimization of lignosulfonate hydroxymethylation**
4. **Synthesis of traditional resols, and modified resols (obtained by replacing up to 10, 20 %w/w of phenol by sodium lignosulfonate**
5. **Obtention of laminates: curing of impregnated papers**
6. **Physical and mechanical characterization of laminates**

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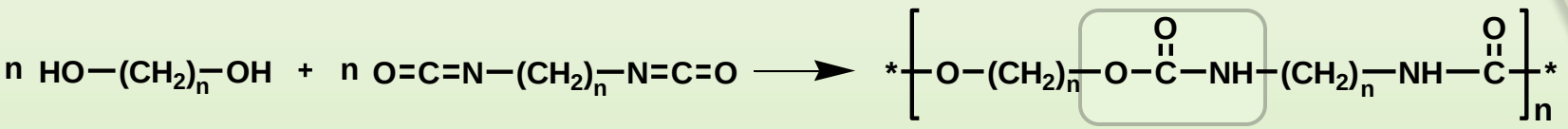
POLYURETHANES

Wide range of applications, properties and versatility



Synthesis of different materials such as:

- **Thermosetting:** foams rigid semi-rigid flexible
- **Thermoplastic:** elastomers

Objectives: Synthesis and characterization of new bio-based polyols from vegetable oils (castor oil) for obtaining biobased - PUs.

✓ **Polyurethane (PUs) foams from castor oil modified with maleic Anhydride.**

✓ **Segmented thermoplastic polyurethane (TPUs) from castor oil.**

Foams PUs from Vegetable Oils

Producers Worldwide

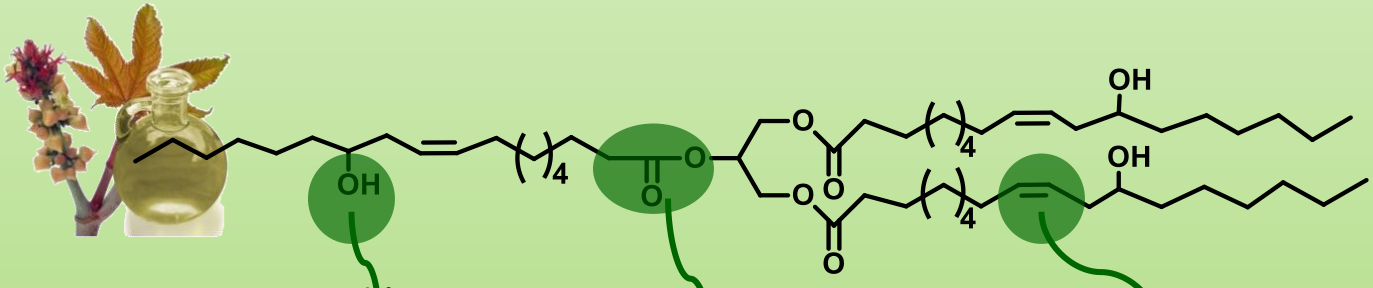
company	Production	Commercial name
Cargill-Dow	PUs from Soybeand	Renuva(BiOH)
Bayer	PUs	Baytherm
Urethane Soy System	PUs Soybeans	SoyMatrix(Soyol)
BASF	PUs from castor	Lupranol Balance
Metzeler Schaum	PUs from sunflower	Rubex Nawaro

Polyols from vegetable oils reduces:

✓emissions of CO_2 by 36% , and

✓non-renewable energy consumption by 61%

Castor Oil



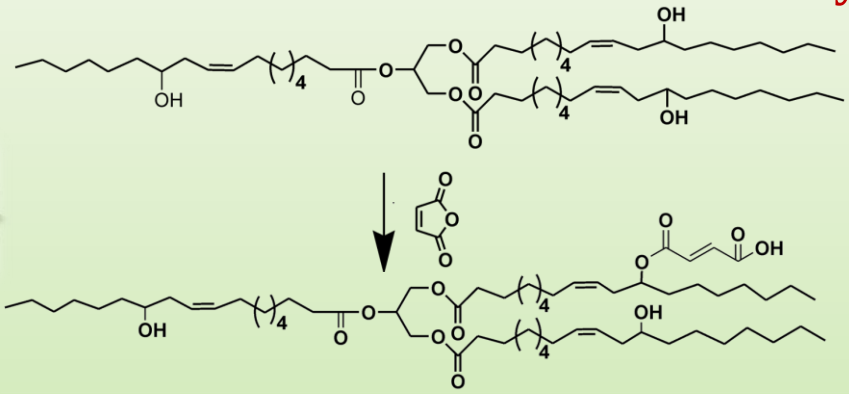
Hydroxyl Group Reactions:
Alkoxylation
Esterification
Urethane Formation, etc

Ester reactions:
Hydrolisis
Esterification, etc

Double Bond Reactions:
Oxidation, Polymerization,
Epoxidation, etc

A) Polyurethane (PUs) foams from castor oil

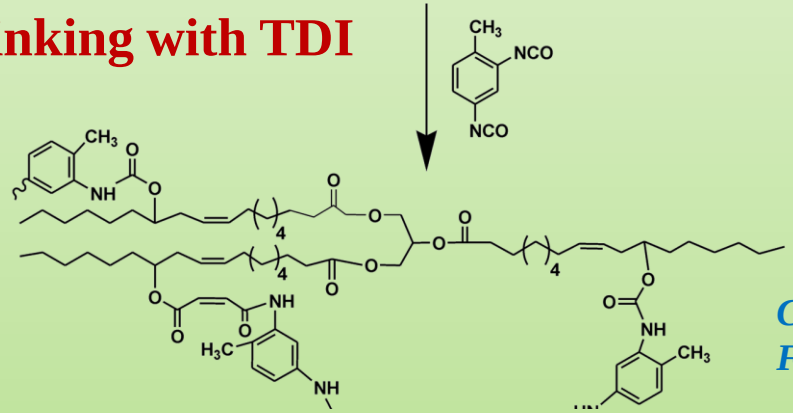
1) Modification of Castor Oil with Maleic Anhydride



Characterization

- ✓RMN
- ✓ GPC
- ✓ IR
- ✓ H I

2) Crosslinking with TDI



Characterization - Final Materials

- ✓ Mechanical properties
- ✓FTIR
- ✓ SEM
- ✓ Biodegradability

Synthesis of Polyurethane Foams. Reaction

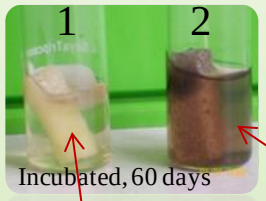
Sample	%w/w	Composition
MACO	100	1:1 TDI/OH molar ratio. Water: 1.5g; TEA: 0.25g; Silicone: 0.5g; stannum octoate : 0.2g.
MACO/CO (PU-C)	75:25	
MACO/CO (PU-B)	25:75	
POLYETHER (PU-A)	100	

Bio-based PUs exhibited mechanical properties similar to those of traditional PUs

Biodegradation by Enzymatic Attack of Different Microorganisms

- *Pseudomonas* sp
- *Aspergillus niger*
- *Aspergillus clavatus*

Incubated at 30°C for 60 days

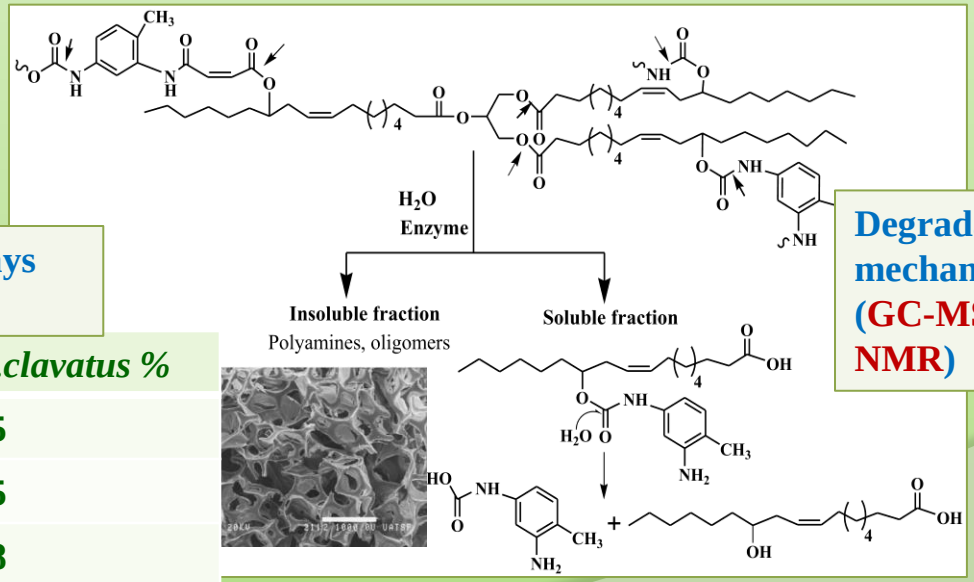


Absence of Microorganisms

Measurements before and after biodegradation

Polymers:
- Mass loss ….
- FT-IR and SEM
- Traction tests

Fraction soluble:
- Toxicity tests
- GC/MS and NMR



Degradation mechanism (GC-MS and NMR)

% Mass loss of PU foams 60 days biodegradation

	Bacterium	*A.niger (%)*	*A.clavatus %*
PU-0	-	60	55
PU-1	30	47	45
PU-2	15	38	48
PU-3	10	10	10

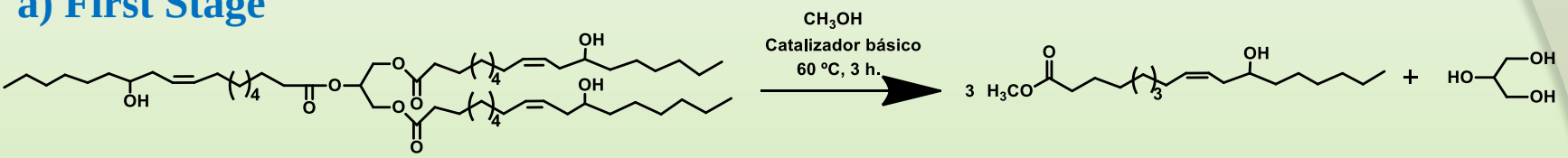
INVESTIGATION STEPS

1. **Castor oil characterization**
2. **Modification and characterization of vegetable oil**
3. **Synthesis and characterization of PUs from castor oil**
4. **Biodegradation of PU foams by enzymatic attack of different microorganisms under aerobic conditions**
5. **Degradation mechanism**

B) Segmented thermoplastic polyurethane (TPUs) from castor oil

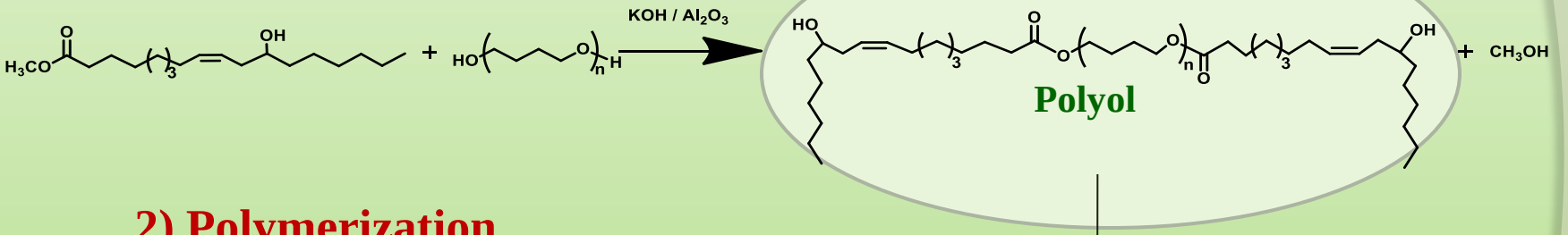
1) Polyol

a) First Stage

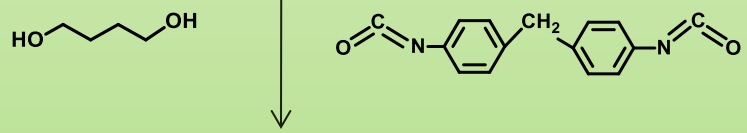


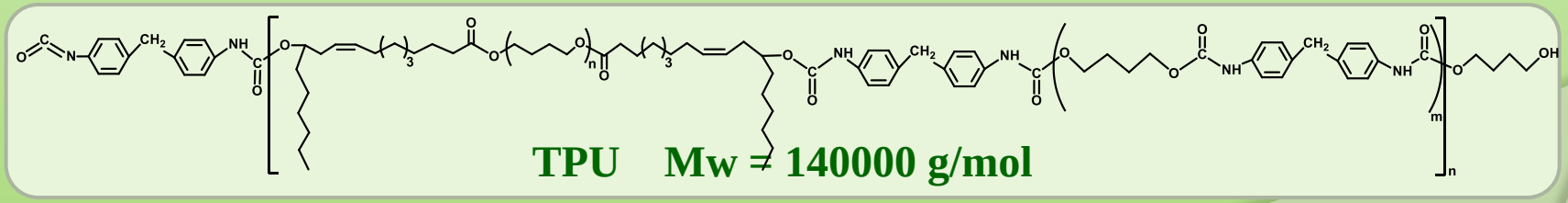
Oil castor

b) Second Stage



2) Polymerization





TPU Mw = 140000 g/mol

Conclusions

A wide range of polymers derived from renewable resources are available for various applications. It's expected that bio-based polymers replace more and more petroleum-based polymers.

The selected examples include resols modified by lignins and polyurethanes from vegetal oils.

Bio-based resols containing lignins as replacement of phenol were used for the fabrication of decorative laminates. Bio-based laminates exhibited mechanical properties similar to those of traditional laminates.

The synthesis and characterization of new bio-based polyols for the production of PUs foams and TPUs are being investigated. PUs exhibited biodegradability and susceptibility to hydrolytic degradation. Also, the mechanical performances were comparable to those of traditional polyurethanes

Thank you for your Attention!