Universidad Nacional del Litoral (UNL)

UNL
FACULTAD DE INGENIERÍA QUÍMICA
UNIVERSIDAD NACIONAL DEL LITORAL
SANTA FE, ARGENTINA

University, created in 1919.

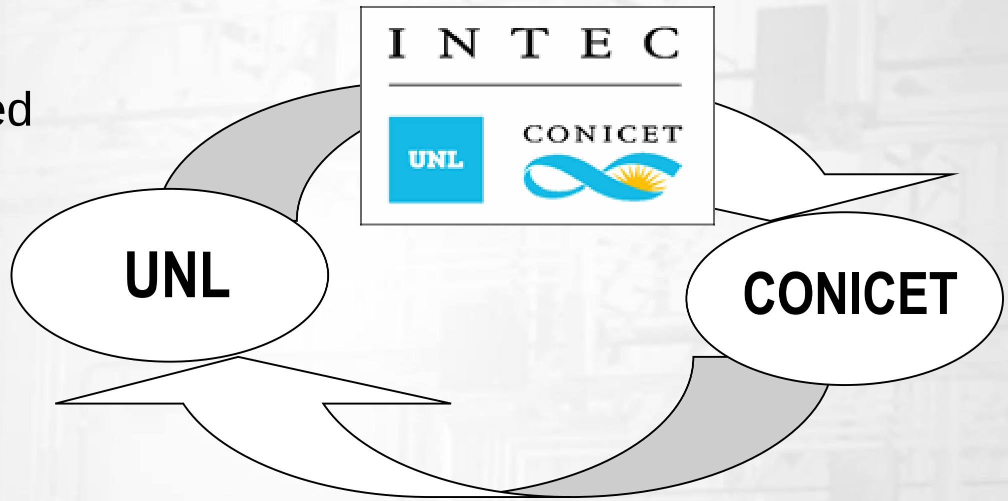
The quality of the graduated students, significant advances in research, the permanent transfer of science, technology and culture and its integration into the world, have generated a high social recognition and a position as an educational and cultural leader in the region and the country.

Instituto de Desarrollo Tecnológico para la Industria Química
INTEC (UNL – CONICET)

CONICET
UNL
I N T E C
40 Años

Multidisciplinary Institute focus on Engineering and Technology

Universidad Nacional del Litoral is a public higher education institution founded in 1919.



Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICET) is the main organization in charge of the promotion of Science and Technology in Argentina. The main objective of this agency is to boost and implement scientific and technical activities in the country and in all different fields of knowledge.

Where are we?

La República Argentina se encuentra dividida políticamente en 23 provincias. **Santa Fe** es una de las Provincias Argentinas, ubicada en la región Centro-Este del país.

Santa Fe

Capital: Santa Fe.

Límites geográficos:
Este: Entre Ríos (6) y Corrientes (7).
Norte: Chaco (8).
Oeste: Santiago del Estero (9) y Códoba (10).
Sur: Buenos Aires (11).

Polymer and Polymerization Reactors Group

Main Activities

1. Research and development on:

✓**Polymer Characterization**

✓ **Mathematical Modeling, Simulation and Control of Polymerization Processes**

✓ **Polymer Synthesis**

2. Teaching at undergraduate and graduate programs

3. Analytical services and technology transfer to industry

Polymer and Polymerization Reactors Group

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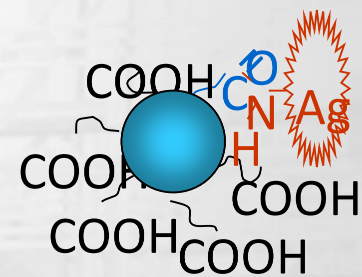
Current Research Topics

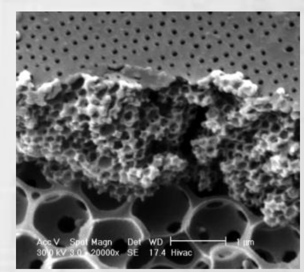
Polymer Synthesis

- Hybrid polymeric nanoparticles from renewable sources
- Hydrogels and nanogels for biomedical applications



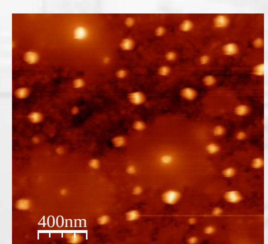
- Functionalized monodisperse latex for the development of immunodiagnostic reagents

- Nanostrutured membranes for water treatment



- Mono- and multilayer membranes for controlled delivery systems

- Bio-inspired and recyclable polymers



Polymer and Polymerization Reactors Group

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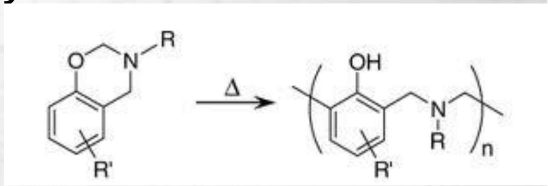
Current ResearchTopics

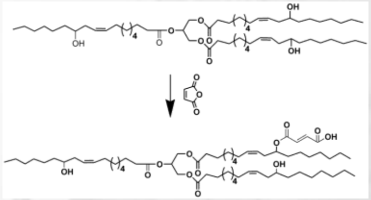
Polymer Synthesis

- Formaldehyde resins (phenolic, urea and melamine resins): both traditional and modified with renewable resources

- Flame retardant phenolic (polybenzoxazines) and epoxy resins

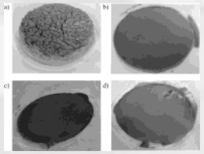


- Styrene polymers: polystyrene, high impact polystyrene, ABS and MBS with controlled molecular structure



- Polyurethanes based on vegetal oils

- Polymer for drilling fluids



Facilities

The total area of laboratories is approximately 150 m^2 (6 labs).

Polymerization Reaction Systems

- Totally equipped reactors, with computerized dosification, monitoring and control systems
- Tumbled polymerization reactor
- Ultrasonic equipment (Sonics VC 750)
- Dispersing rotor-stator Homogenizer (Kinematica AG PT 2500 E)

Characterization of Molecular Weights

- 2 Gel Permeation chromatographs (Waters), fitted with the following detectors: differential refractometer (Waters), UV spectrophotometer (Waters), specific viscosity (Viscotek 200), and multi-angle light scattering (DSP, Wyatt)
- Capillary viscometer (Schott Geräte)
- Membrane and vapor pressure osmometers (Knauer)

Characterization of Colloids

- Multiangle laser light scattering equipment (Brookhaven BI 200 y SM BI 9000).
- Capillary hydrodynamic chromatograph – CHDF 2000 (Matec)
- Turbiscan (TMA2000)

Facilities

Characterization of Thermal and Mechanical Properties

- Differential Scanning Calorimeter and Thermogravimetric Balance (Mettler).
- Discovery Mass Spectrometer and DMA Q800.
- Tensile test equipment (INSTRON)
- Thermal press

General Instrumentation and Equipment

- Gas chromatograph fit with FID and MS detectors (Perkin Elmer)
- Spectrometer UV/Vis (Perkin Elmer)
- Automatic Potentiometric Titrator with pHmeter (KEM AT-510)
- Brookfield Viscometer (Brookfield)
- High-speed Centrifuge (Heal Force, R18)
- Ultrasonic Baths (Cleanson)
- Drying ovens with vacuum and natural and forced convection

Other facilities

- Electronic Microscopy of polymeric particles and materials (TEM, SEM, AFM)
- Nuclear Magnetic Resonance (NMR)
- Fourier Transform Infrared Spectroscopy (FTiR)

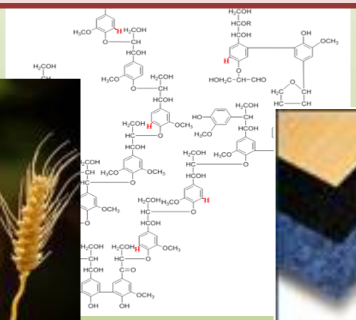
FAPESP WEEK MONTEVIDEO

COOPERACIÓN CIENTÍFICA EN AMÉRICA DEL SUR

17 y 18 de noviembre - 2016

New Developments on Polymeric Materials and Sustainable Technologies based on the Use of Renewable Resources

Diana A. Estenoz



OUTLINE

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- BIOPOLYMERS AND BIO-BASED POLYMERS
- ONGOING RESEARCH
- POLYMERS FROM RENEWABLE RESOURCES:
  - ✓ POLYURETHANES BASED ON VEGETABLE OILS
  - ✓ AN INDUSTRIAL APPLICATION OF LIGNIN BASED RESOL
- CONCLUSIONS

BIOPOLYMERS AND BIO-BASED POLYMERS

Environmental impact associated with commercial materials and to high energy inputs

environmentally-benign alternatives?

BIOPOLYMERS AND BIO-BASED POLYMERS

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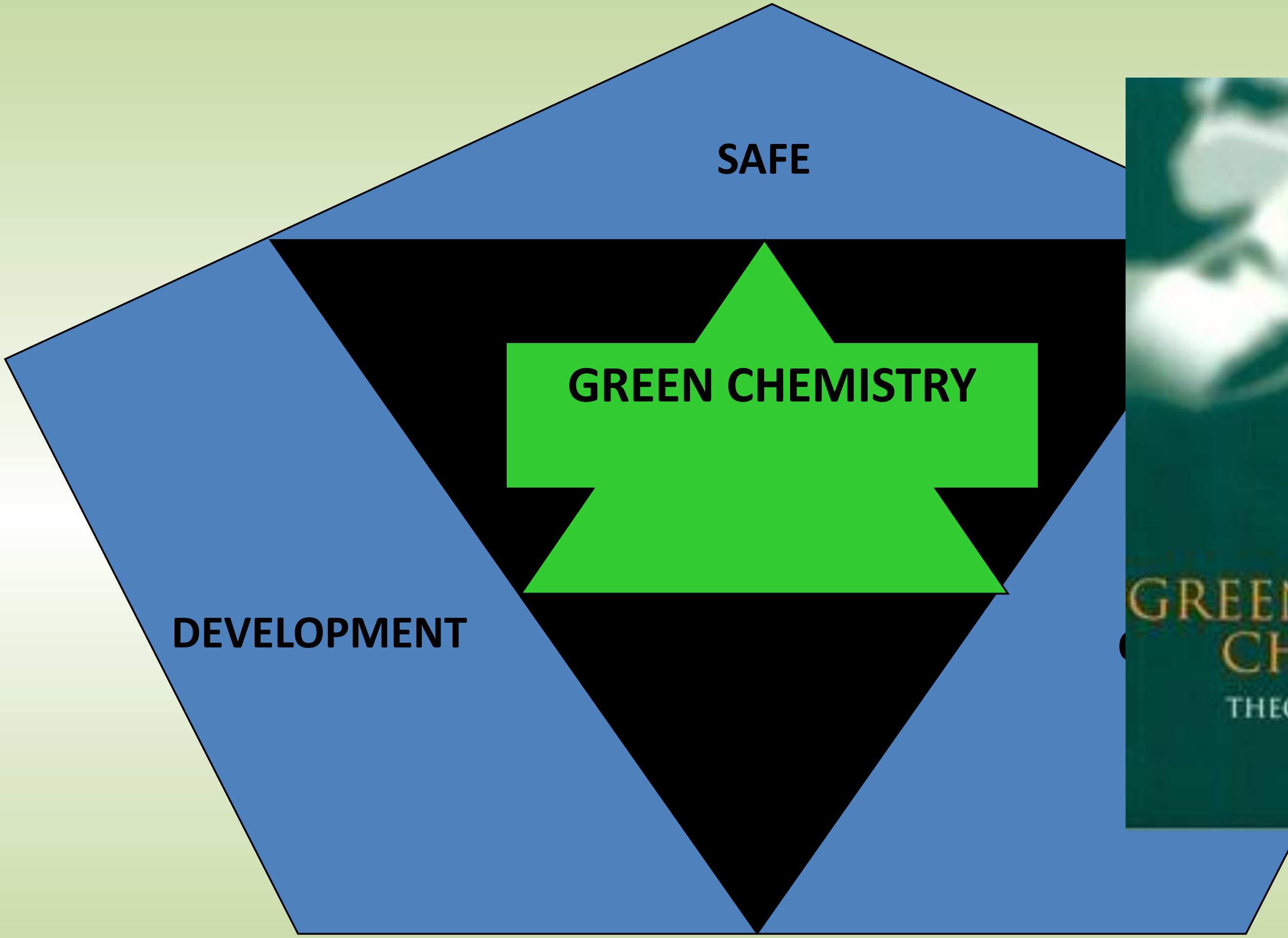

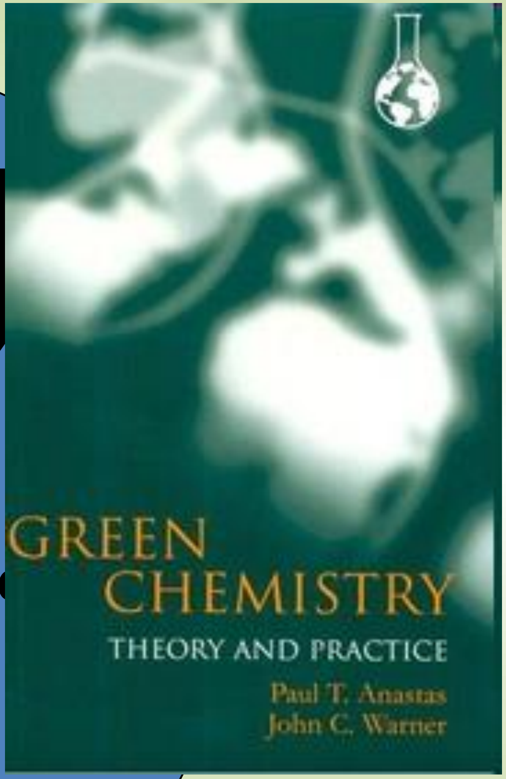

BIOPOLYMERS AND BIO-BASED POLYMERS

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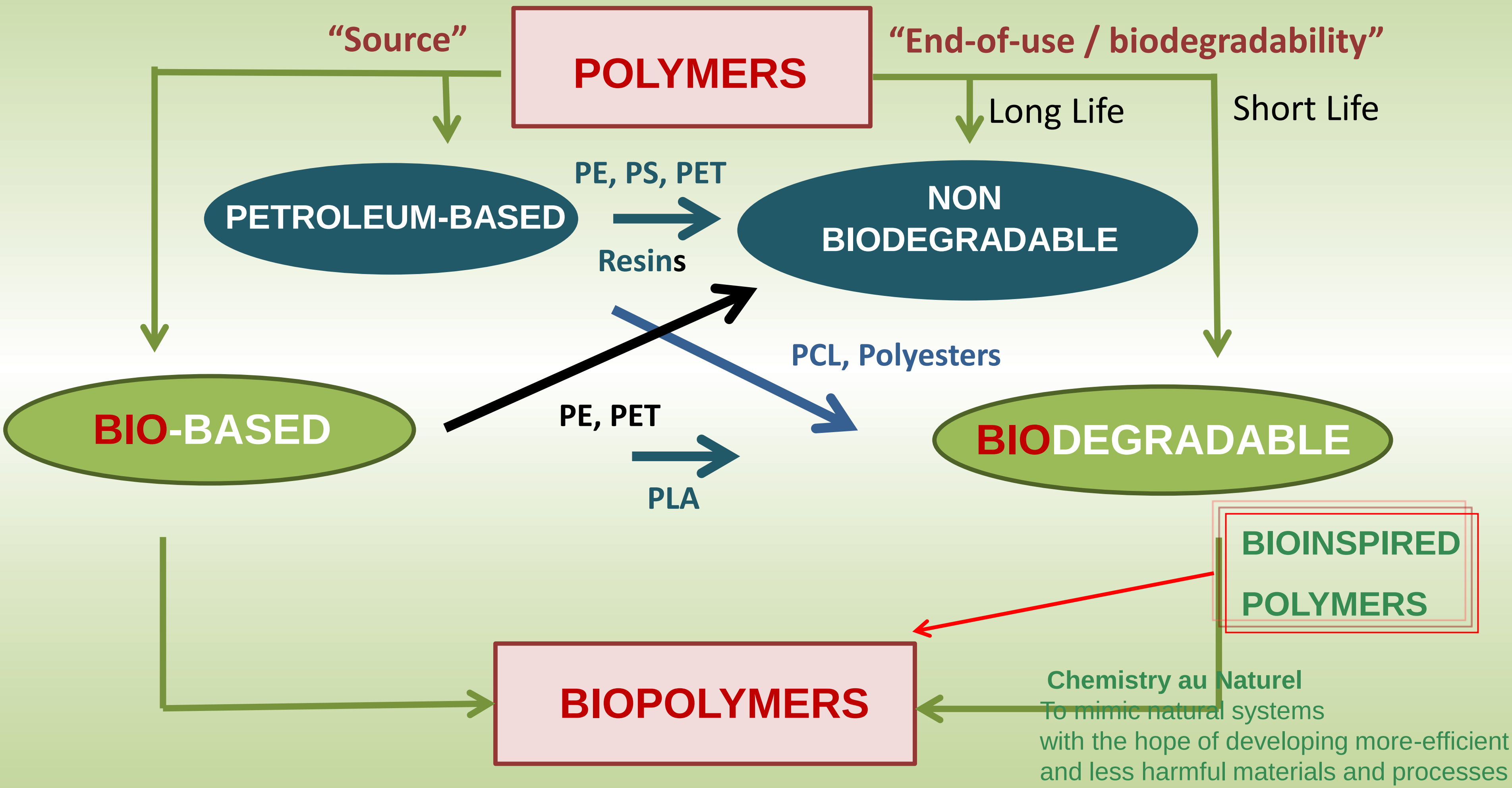

BIOPOLYMERS AND BIO-BASED POLYMERS

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PROTEINS
Casein… → **Protein-Based Polymers**

VEGETABLE OILS
Palm, castor, … → **Polyurethanes**
Polyesthers

CELLULOSE & LIGNIN
Corn, wood, … → **Cellulose-Based Polymers**
Adhesives

STARCH
Corn, wheat, potatoes, … → **Starch-Based Polymers**

SUGAR
Cane, …

Bacteria
Fermentation
Bacteria

→ **Polyhydroxyalcanoates (PHA)**
Polylactic Acid (PLA)

Biopolymers:

- ✓ Natural
- ✓ From bio-monomers
- ✓ From microorganisms

To be Bio or not to be, is not the question but Is the material sustainable ?

Industrial Wastes

- Agro-industrial by-products
- Milk whey

ONGOING RESEARCH

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Developments of new polymeric materials based on renewable resources. The use of raw materials, by-products and residues of industries or primary activities for their application to a second value chain is investigated.

a) Acrylic-protein hybrid latex for coatings and adhesives based on proteins from dairy industry and by-product of oil and bioethanol industry;
b) Thermoplastic, elastomeric and thermosetting polyurethanes based on vegetable oils and glicerol (by-product of biodiesel industry) for coatings, membranes and foams;
c) Formaldehyde resins modified with lignin (residue of paper industry) and furfural (residue of agroindustry) for adhesives and laminates;
d) Polybenzoxazines and epoxi resins modified with lignin for high-performance applications;
e) Polylactic acid from whey (dairy industry residue) for replacement of traditional thermoplastics

ONGOING RESEARCH

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Main objectives:

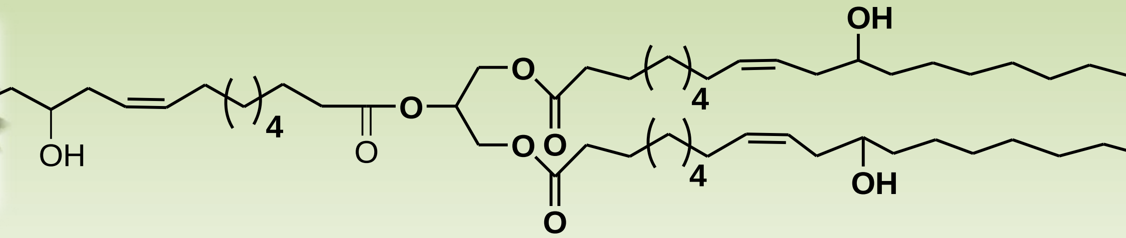
Development of sustainable technologies for the production of materials with a reduction of energy requirements and costs, and minimizing the use of toxic compounds, and waste disposal.

An integral study of processes…..

i) the chemical modification and characterization of renewal resources;
ii) the synthesis of materials;
iii) the structural characterization of prepolymers and polymers;
iv) the physico-chemical characterization of materials in a function of their application and end-use;
v) the biodegradation and environmental impact of synthesized materials; and
vi) the modelling, simulation and optimization of processes.

POLYURETHANES BASED ON VEGETABLE OILS

Castor Oil



- Renewability
- Availability
- Low cost
- Unusual chemical composition

Ester reactions:
Hydrolisis
Esterification
Alcoholysis
Saponification
Reduction

Double Bond Reactions:
Oxidation,
Polymerization
Hydrogenation
Epoxidation
Halogenation
Addition

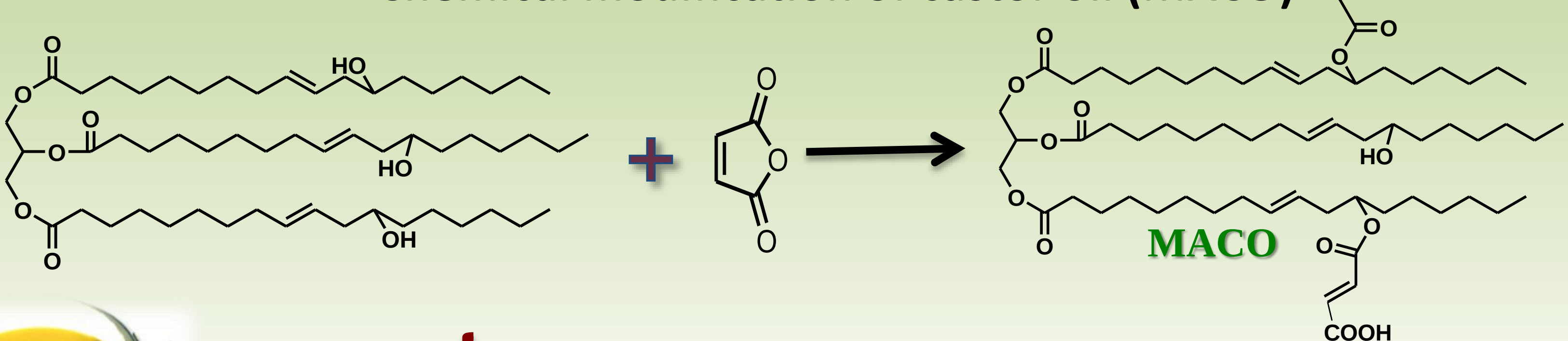
Hydroxyl Group Reactions:
Dehydration
Hydrolysis
Pyrolysis
Alkoxylation
Esterification
Urethane Formation

Aim: Synthesis of PUs based on castor oil with good mechanical properties and biodegradable

POLYURETHANES BASED ON VEGETABLE OILS

Experimental work

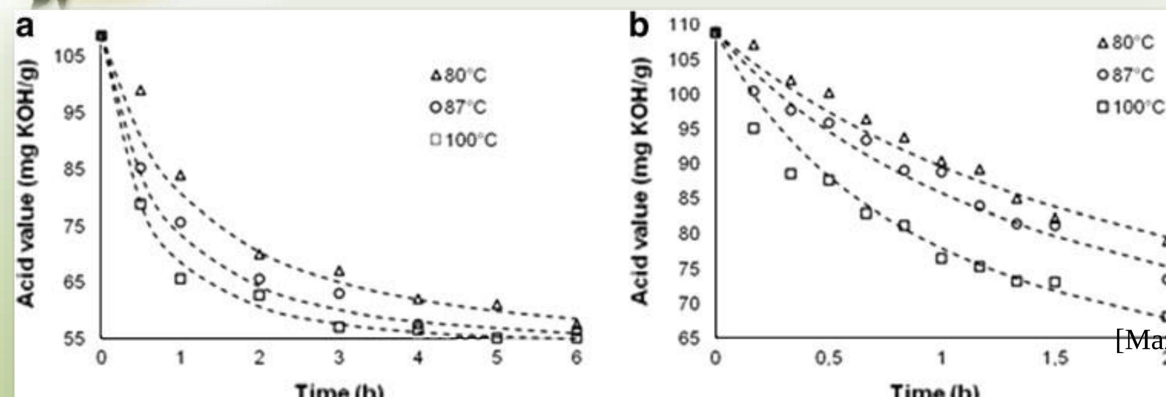
Chemical modification of castor oil (MACO)



- 100 ºC
- 3 h.

Castor oil
Maleic Anhydride

The scheme is a simplification; since statistically there could be triglyceride molecules reacted with zero, one, two or three maleic anhydride molecules.



[Mazo et al, *Chem. Eng. J.*, 185- 186, 347- 351 (2012)]

[Mazo et al, *Lat. Am. Ap.Res.*, **4**, 11-15 (2011)]

[Mazo et al, *J. Am. Oil Chem. Soc.*, **89**(7), 1355-1361 (2012)]

[Mazo et al, *Polímeros Ciencia y Tecnología*, **19** (2), 1-6 (2009)]

POLYURETHANES BASED ON VEGETABLE OILS

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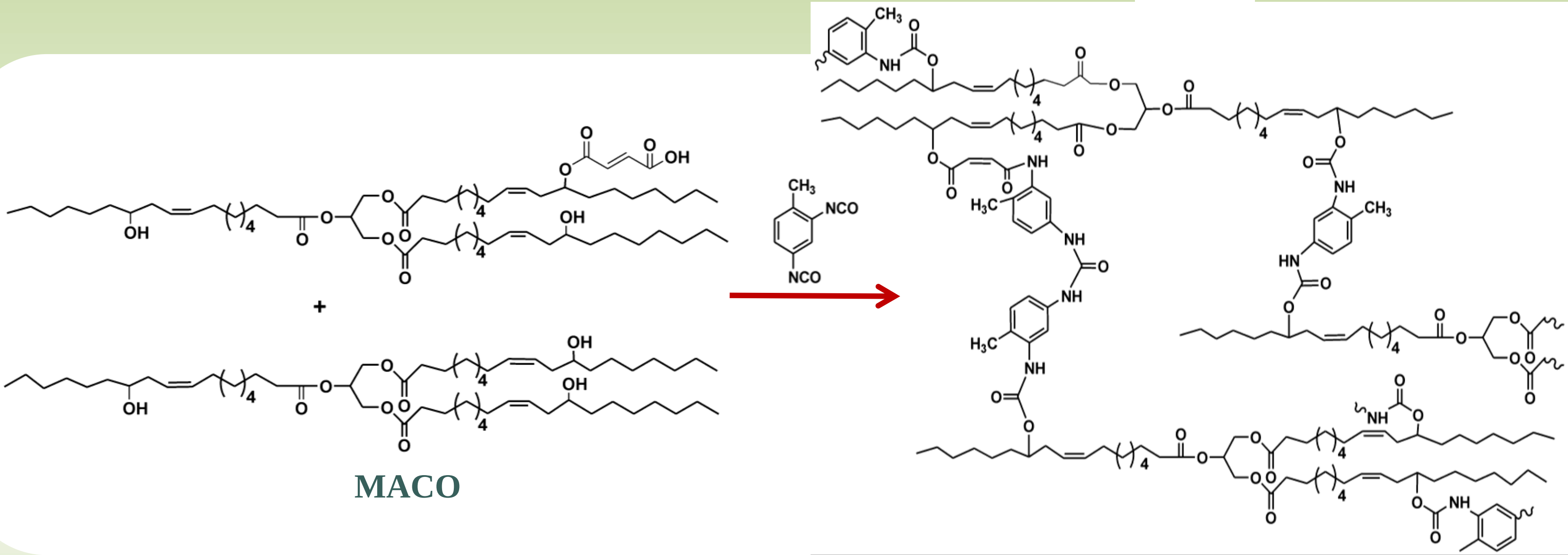
Preparation of polyurethane foams from Toluene Diisocyanate (TDI) and Castor Oil / MACO



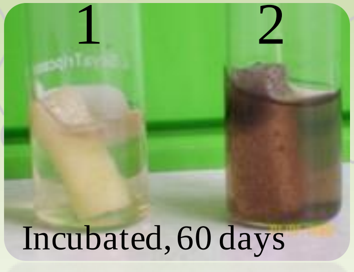
TDI:OH molar ratio. Water: 1.5g; TEA: 0.25g; Silicon: 0.5g; stannum octoate : 0.2g.

Main Properties

Sample	Weight Ratio (%)	Density (Kg/m^3)	Tensil Resistance (KPa)	Elongation (%)	Water Absorption (%)
MACO	100	40.93	190.65	100.74	-
MACO/CO	75:25	50.61	187.50	96.80	100
MACO/CO	25:75	130.40	169.30	90.00	80.26
POLIETER	100	43.64	137.84	89.54	39.59

Biodegradation study in liquid culture medium.

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



Incubated at 30ºC for 60 days

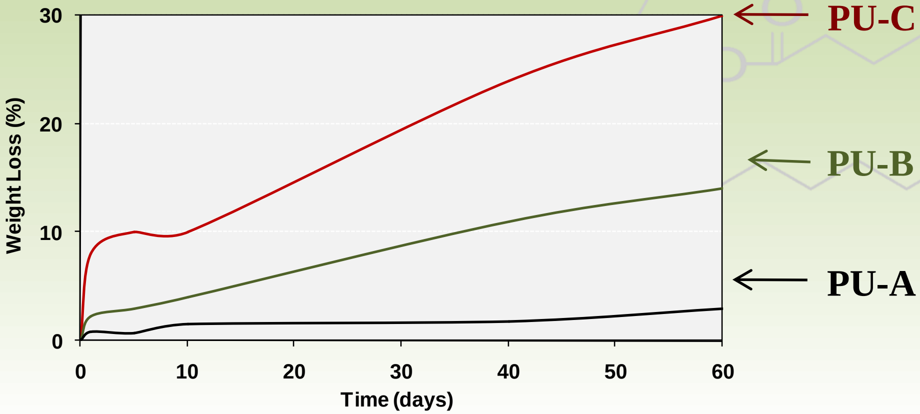
Measurements:

- **Mass loss along the process (by gravimetry)**
- **Bacterial growth (by viable cell)**
- **Chemical and morphological structures before and after degradation (by FT-IR and SEM)**
- **Mechanical properties (by traction tests)**
- **Toxicity (by bacterial Microtox bio-assay)**
- **Chemical characteristics of low molar-mass biodegradation products (by GC/MS in combination with NMR)**

[Sponton et al.,l *Int. Biodet. Biodeg.*, **85**, 85-94 (2013)]

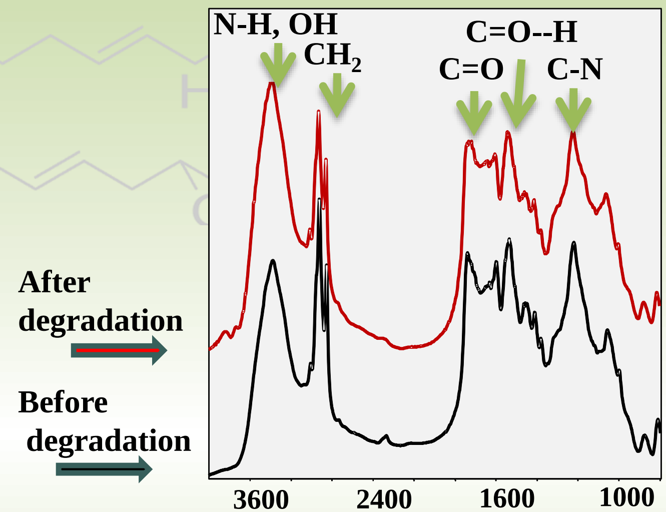
POLYURETHANES BASED ON VEGETABLE OILS

Pseudomonas sp.



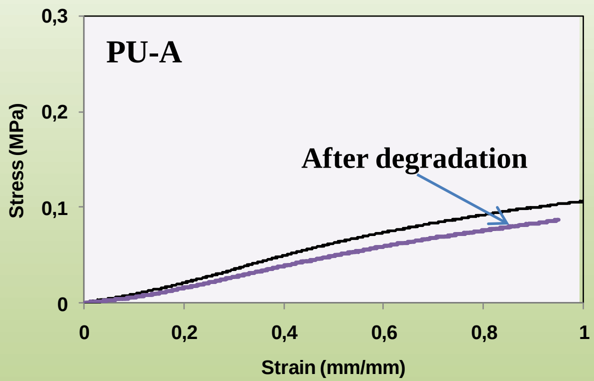
Hydrolysis in presence of *Pseudomonas sp.*

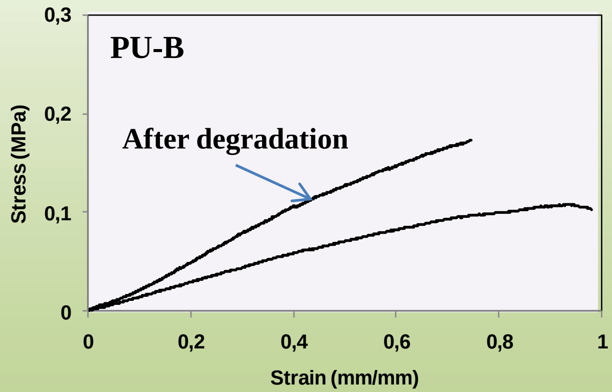
Chemical structures by IR

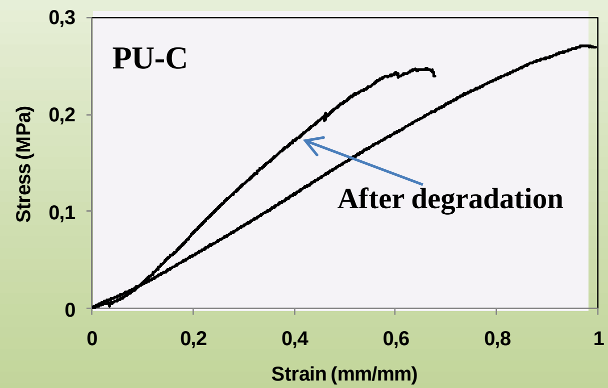


PU-B (CO/MACO 75/25)

Mechanical properties







POLYURETHANES BASED ON VEGETABLE OILS

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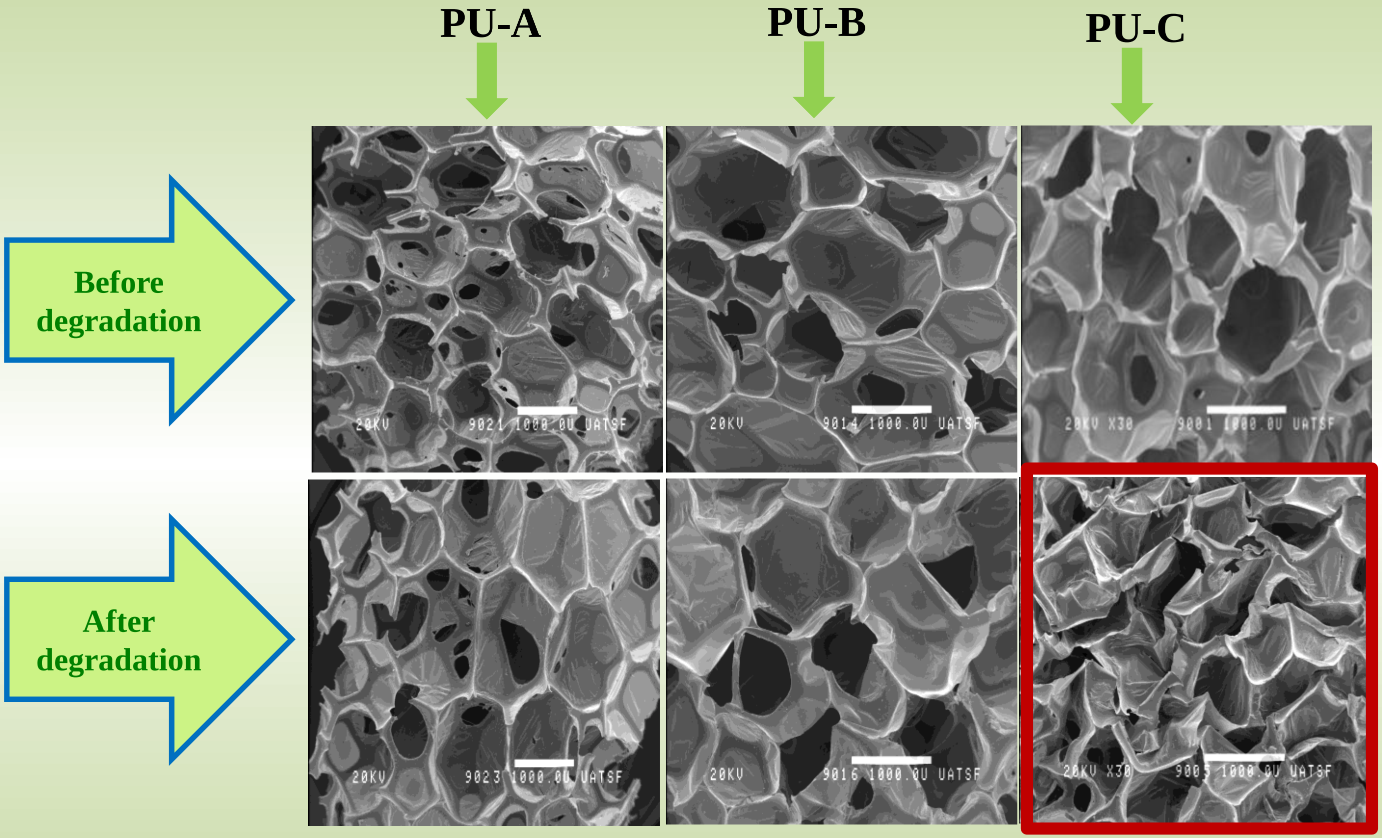
Morphological structures before and after degradation by SEM



PU foams from MACO exhibit mechanical properties comparable to commercial foams with considerable increase in degradation rates.

[Sponton et al.,l *Int. Biodet. Biodeg.*, **85**, 85-94 (2013)]

AN INDUSTRIAL APPLICATION OF LIGNIN BASED RESOL

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DECORATIVE LAMINATES

HIGH PRESSURE (HP)

LOW PRESSURE (LP)

Decorative Paper impregnated with melamine-formaldehyde resin

Kraft Papers impregnated with resol-type phenol-formaldehyde resin

- Temperature = 152°C
- Pressure = 70 Kg/cm^2

Decorative Paper impregnated with melamine-formaldehyde resin

Conglomerated Wood

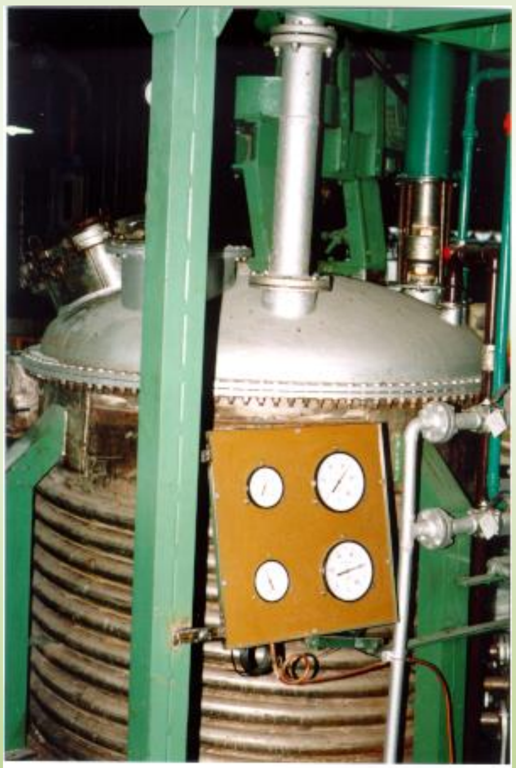
- Temperature = 170°C
- Pressure = 24 Kg/cm^2

Aim: Partial Substitution of Phenol in Resol by a Modified Lignin

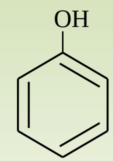
AN INDUSTRIAL APPLICATION OF LIGNIN BASED RESOL

THE INDUSTRIAL PROCESS

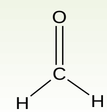
1- PHENOL-FORMALDEHYDE BASE RESIN SYNTHESIS



- Aqueous solution of phenol 91% w/w



- Aqueous solution of formaldehyde 37% w/w

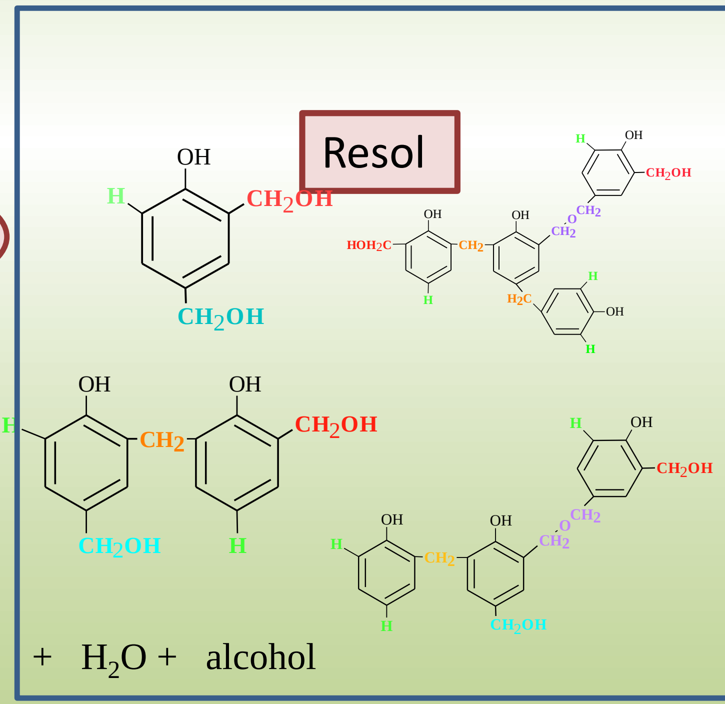


[Formaldehyde]/ [Phenol] > 1

Conditions:

Temperature: 95 °C

pH: 9.0



[Nicolau et al, in presss, *Ind. Eng. Chem. Res.*(2013)]

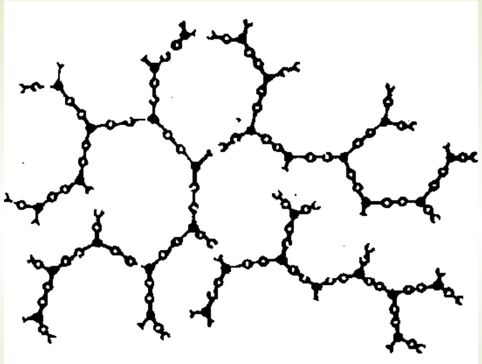
AN INDUSTRIAL APPLICATION OF LIGNIN BASED RESOL

2- DRYING AND IMPREGNATION

Impregnation machine

Metering Rolls

Knife



Oven Temperature: 135 °C

AN INDUSTRIAL APPLICATION OF LIGNIN BASED RESOL

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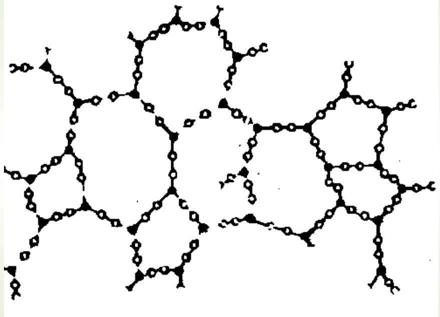
3- PRESSING

Cold-Hot Multi-Opening Press

Laminates/pressing : 160 (HP)
Temperature : 142 - 152 °C during 35 min.
Pressure: 70 kg/cm^2
Total time: 65 min.



Hot Single-Opening Press

Laminates/pressing : 2 (HP)
1 (LP)
Temperature : 160 - 170 °C
Pressure: 24 kg/cm^2 (HP)
70 kg/cm^2 (LP)
Total Time: 1 min.

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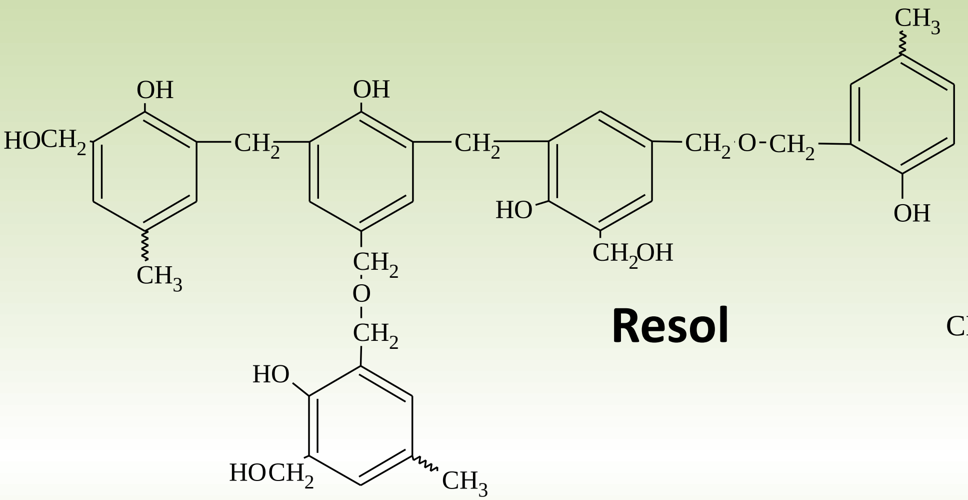
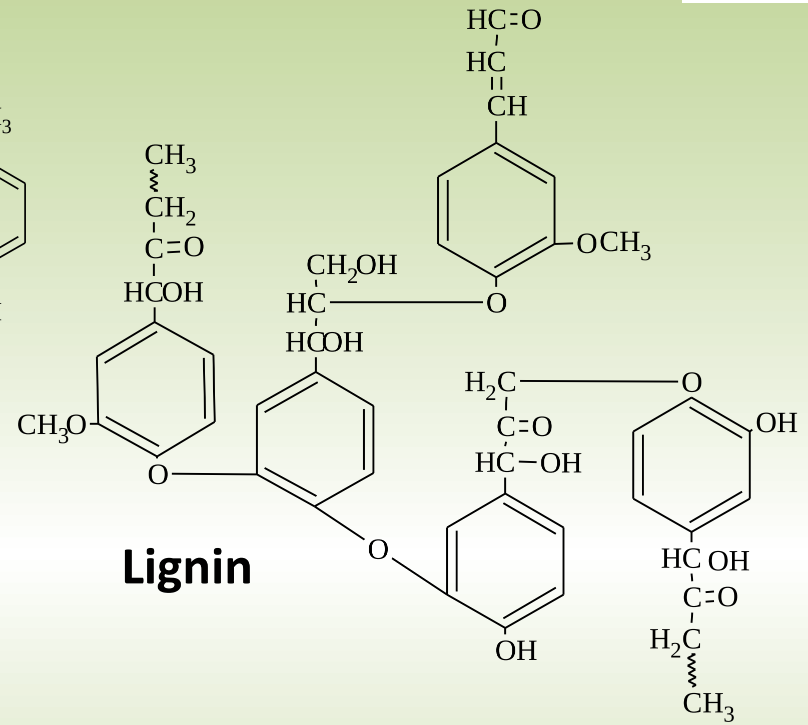
RESOL VS LIGNINS



Resol



Lignin

Advantages

- Natural Polymer
- Abundant
- Economical
- Similar structure to resol

Disadvantages

- Chemical structure depends on the *wood type* and the *isolation method*
- Low reactivity

AN INDUSTRIAL APPLICATION OF LIGNIN BASED RESOL

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FROM LABORATORY TO INDUSTRY …

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%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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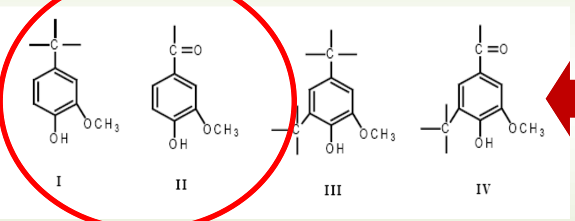
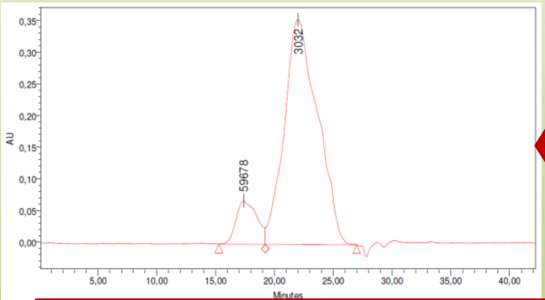
LIGNINS CHARACTERIZATION



Reactive OH



		LK	LO	LS
% Dry Matter		4.48	3.66	8.89
% Ash (dry basis)		21.67	0.05	23.45
% Sugar, acids and polysacharides content (dry basis)		5.16	4.30	13.63
% Phenolic OH	Struct. I	2.39	0.61	1.37
	Struct. II	0.37	0.87	0.1
	Struct. III	0.9	2.79	0.03
	Struct. IV	0.03	0.18	0.33
% Lignosulfonate		---	---	62.28
MWD (Fraction 1)	Mn (g/mol)	40655	---	---
	Mw (g/mol)	57314		
MWD (Fraction 2)	Mn (g/mol)	2080	---	---
	Mw (g/mol)	3253		

2.76 1.48 1.47

AN INDUSTRIAL APPLICATION OF LIGNIN BASED RESOL

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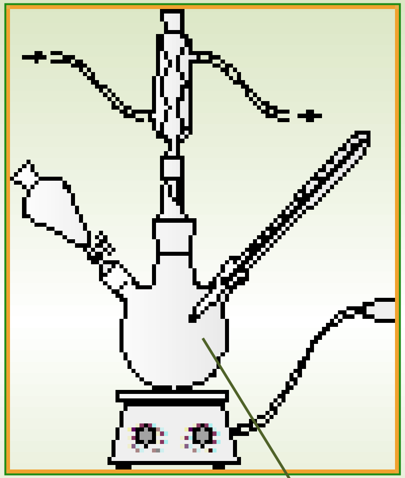
LIGNINS HYDROXYMETHYLATION (LABORATORY)



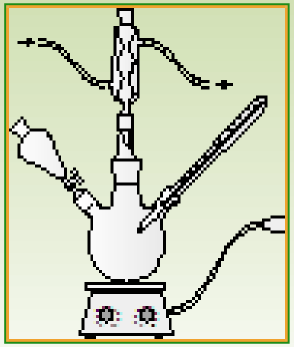
	LK	LO	LS	
Recipe:				
% F p/p	9.02	9.01	9.00	9.14
% NaOH p/p	1.38	1.35	1.41	0
% L p/p	6.11	6.12	6.13	6.03
F°/OH_r°	30.62	56.32	56.86	56.86
Reaction Conditions:				
T (°C)	50	50	50	50
pH	12.17	11.69	12.09	8.46
t (min)	240	240	240	240

Free Formaldehyde Determination (ISO 11402:2004)

AN INDUSTRIAL APPLICATION OF LIGNIN BASED RESOL

Universidad Nacional del Litoral

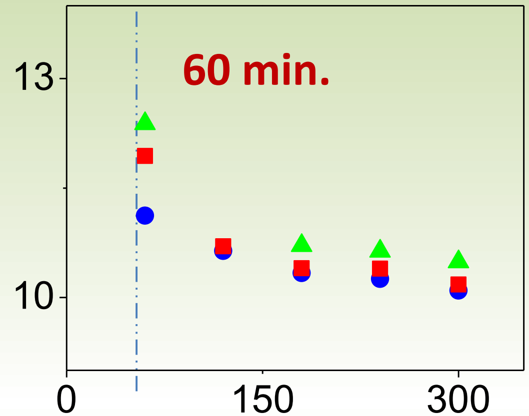
OPTIMIZATION OF LIGNOSULFONATE HYDROXYMETHYLATION



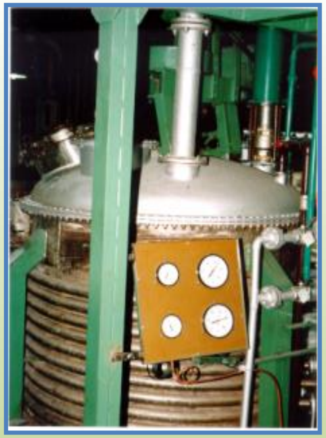
Laboratory

F/Lignin = 1.5 w/w
[F]°= 14 mol/L

%w/w F



40 ºC
70 ºC
50 ºC

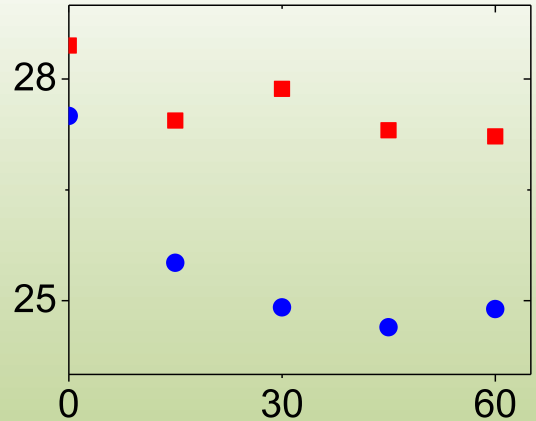


Industry

F/Lignin = 1.5 w/w
[F]°= 29 mol/L

%w/w F

KARIKAL



50 ºC

t (min.) [Nicolau et al, in presss, *Ind. Eng. Chem. Res.*(2013)]

AN INDUSTRIAL APPLICATION OF LIGNIN BASED RESOL

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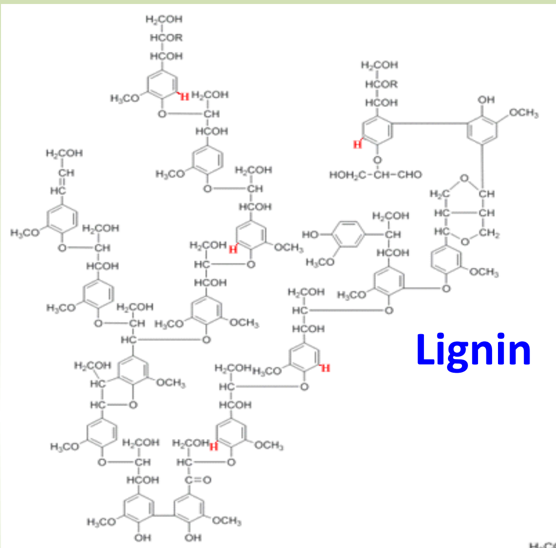
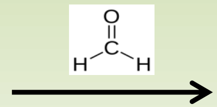
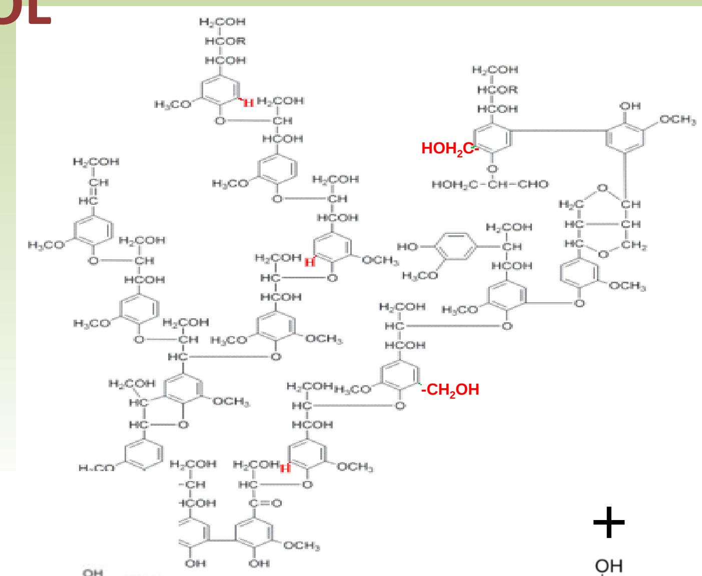
INDUSTRIAL SYNTHESIS OF BASE RESOL

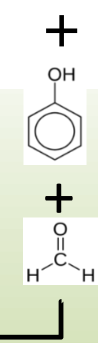


Lignin

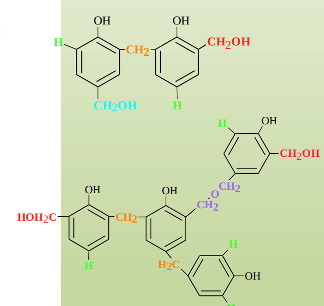


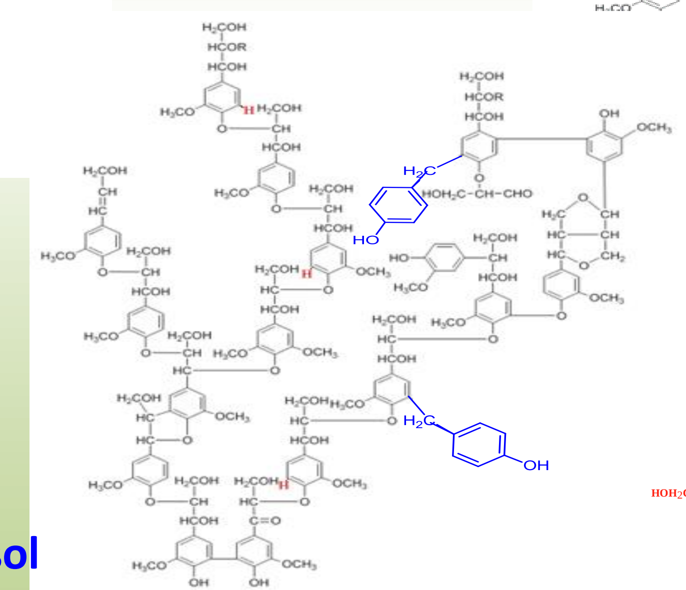
Pre-Hydroxymethylation





Trad. Resol
+
Ph-Mod. Lig.
Co-condensation





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Lignin-Modified Resol

AN INDUSTRIAL APPLICATION OF LIGNIN BASED RESOL

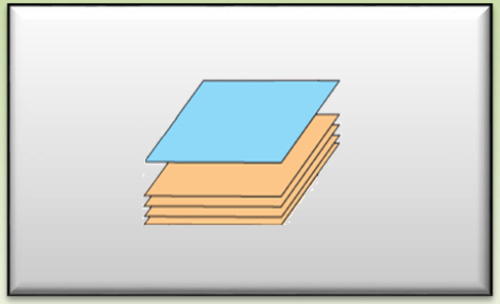
OBTENTION OF LAMINATES: CURING OF IMPREGNATED PAPERS

Impregnation of Papers

T = 135 °C

Industrial Pressing

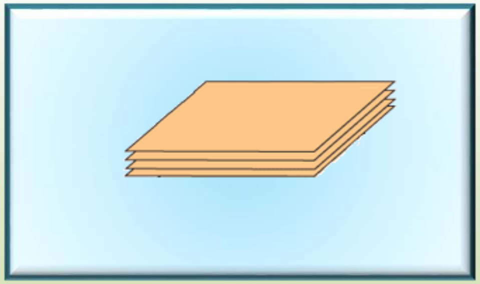
T = 150 °C; P = Kg/cm^2; t = 51 min.



- ✓ 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

AN INDUSTRIAL APPLICATION OF LIGNIN BASED RESOL

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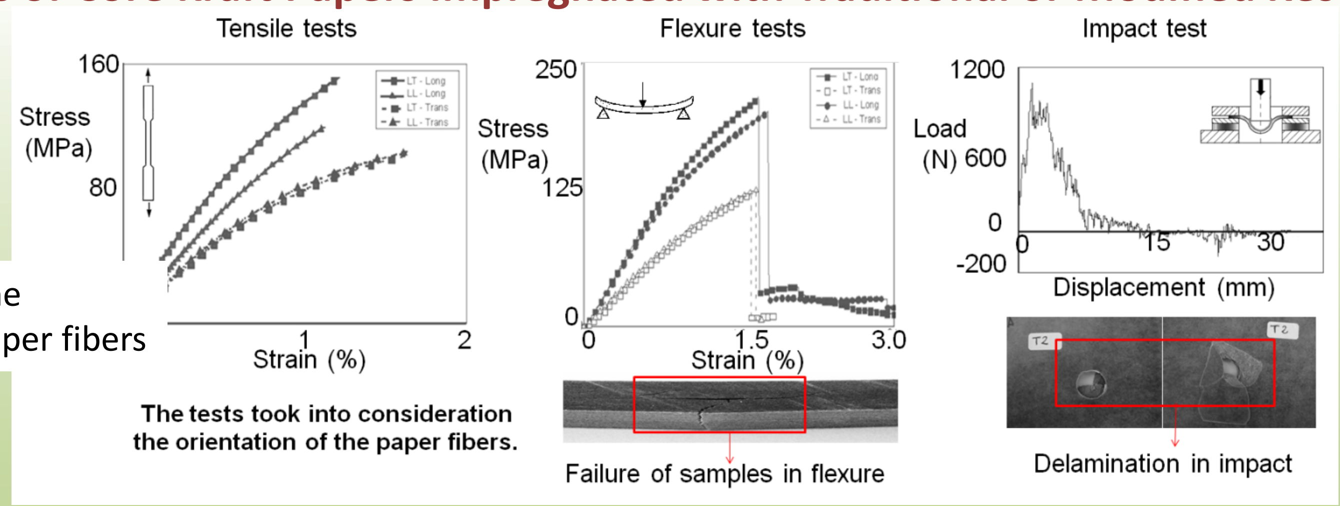
FINAL PROPERTIES OF LAMINATES

	Increment	Traditional Laminate	Modified Laminate
Water Boiling Resistance (IRAM 13367)	Mass, %	8.43	**10.8**
	Thickness, %	11.7	**14.4**
Ball Impact Resistance (IRAM 13370)	––	**Not affected**	

Mechanical Properties of Core Kraft Papers Impregnated with Traditional or Modified Resols



The tests consider the orientation of the paper fibers

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CORE OF KRAFT PAPERS IMPREGNATED WITH TRADITIONAL OR MODIFIED RESOLS. MECHANICAL PROPERTIES

Test	Property	Orientation	Laminate type		*p**	
			Traditional	Modified	Type of laminate	Orient.
Tensile (ASTM D3039/D 3039M-00	Resistance (MPa)	Longitudinal	132 ±14	122 ±20	0,226	$1,20\times10^{-2}$
		Transversal	109±8	105±2		
	Elastic modulus (GPa)	Longitudinal	14,2 ±2,2	12,9 ±1,5	0,168	$4,00\times10^{-4}$
		Transversal	10,5±0,5	10,2±0,3		
3 Point- Flexure (ASTM D790-03)	Resistance (MPa)	Longitudinal	209±13	199±12	0,573	$<2,00\times10^{-16}$
		Transversal	124±4	129±1		
	Elastic modulus (GPa)	Longitudinal	16,9±0,5	16,1±0,3	0,200	$<2,00\times10^{-16}$
		Transversal	9,64±0,29	9,96±0,09		
Dart impact (ASTM D5628-96)	Absorbed energy (J/mm)	––	1,25 ±0,11	1,42 ±0,16	0,125	––
	Maximun impact load (kN/mm)	––	0,330 ±0,010	0,360 ±0,030	0,111	––

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

[Taverna et al, *LAAR*, in press (2015)]

CONCLUSIONS

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

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

Polyurethanes from castor oil have exhibited biodegradability and susceptibility to hydrolytic degradation. Also, the mechanical performances were comparable to those of traditional polyurethanes.

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.

Phenol is a commodity, tracks oil price. Current prices of lignin and phenol indicate that lignin provides 20% saving.


Thank you for your
Attention!