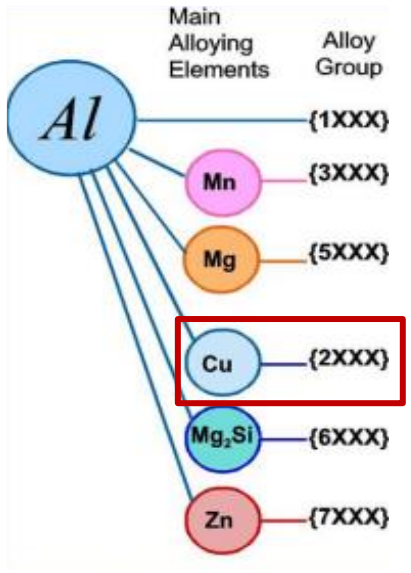
Design and elaboration of anti-corrosion hybrid bio-sourced coatings for aircraft industries via EISA methodology

Gabriel **CARDOSO GONÇALVES**

PhD supervisors: J.C. **DUPIN** & F. **CHARRIER-EL BOUHTOURY**

Collaboration: J. **ALLOUCHE**

Aluminum alloys



Al 2024

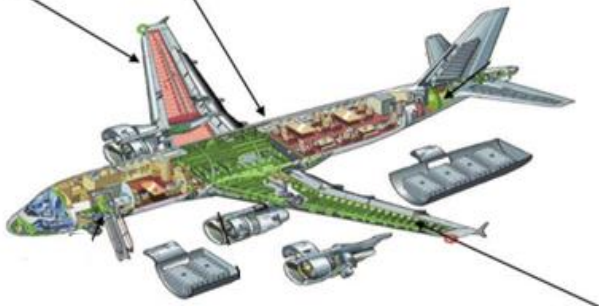
(1.2 - 1.8% Mg /3.8 - 4.9% Cu)

Corrosion Susceptibility

Mechanical properties

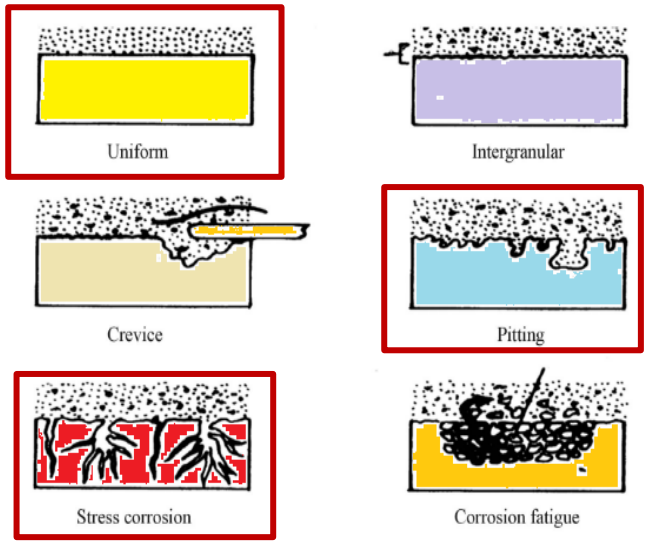
Light alloy – Weight reduction

Weight reduction → **Fuel save**



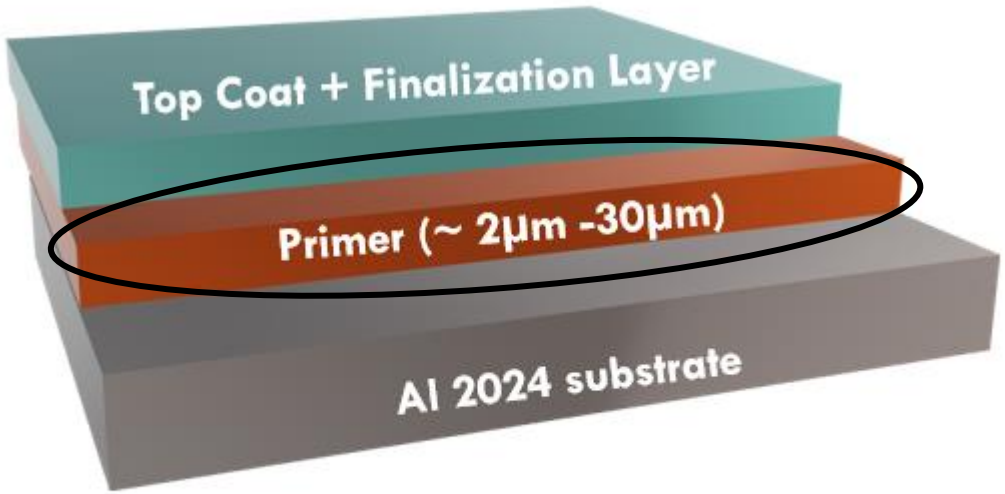
2.2 Billion USD/year

Corrosion



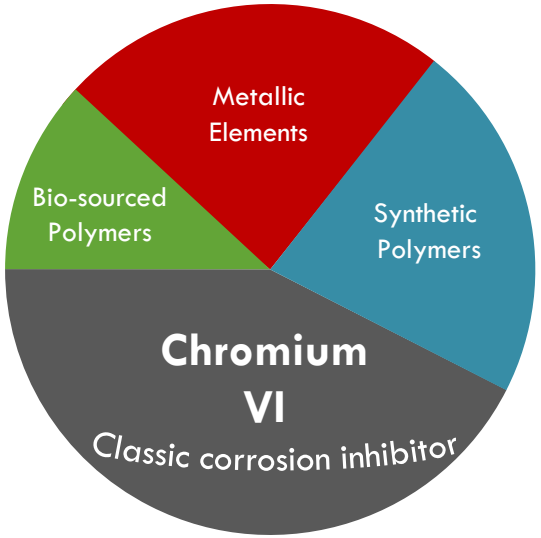
Mochène. T.. Mochène. M.. Thao. M.. Linga iso. L.. Tchékiste. O.. Songea. S.. Saguero. J.. Del Sol. I.. Gómez-Parra. Á.. & Batista Ponce. M. (2020). Machining of Al-Cu and Al-Zn Alloys for Aeronautical Components. In Intech (pp. 225–240).
Agence Nationale de Recherche (ANR) - COrrosion Quantification Through Extended use of Lamb waves – COQTEL – Project Report
Market Report. Aerospace Coatings Market by Resin Type. Technology User Type. End Use Industry. Application - Global Opportunity Analysis and Industry Forecast. 2022 – 2030. 2022

Context & Objective



Classic aircraft coating

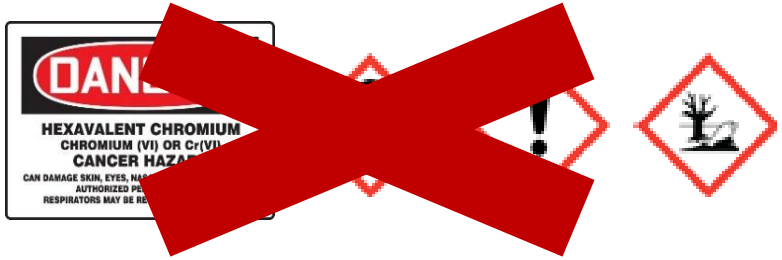
Primer Materials



REACH COMPLIANCE

2006-2030

New alternatives
Polymeric and composite materials



European Commission
Circular Economy Action Plan
The European Green Deal

Primer objectives

- Adhesion to both substrate and subsequent layers
- **Corrosion-inhibition**

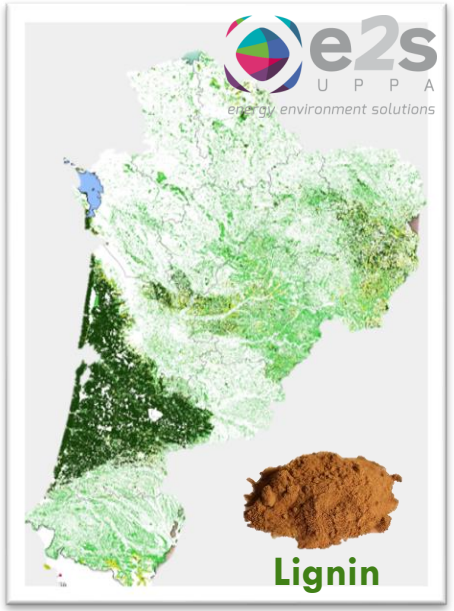
Bio-sourced Polymers

European Chemicals Agency. Understanding REACH [Online]. Available: https://echa.europa.eu/regulations/reach/understanding-reach. 2016
Bierwagen. G.. Brown. R.. Battocchi. D.. & Hayes. S. (2010). Active metal-based corrosion protective coating systems for aircraft requiring no-chromate pretreatment. Progress in Organic Coatings. 68(1–2). 48–61.

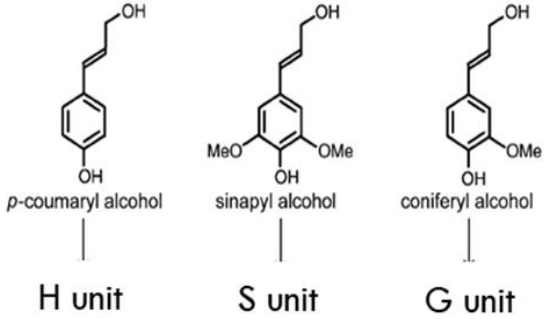
Bio-sourced polyme

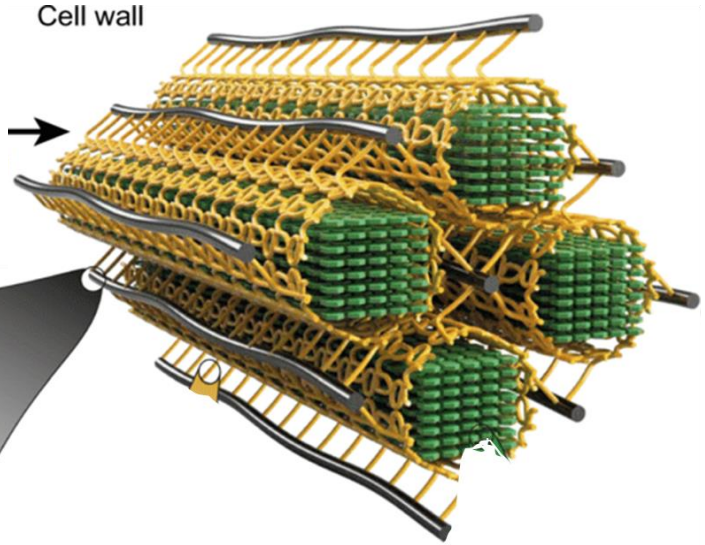
Circular Economy

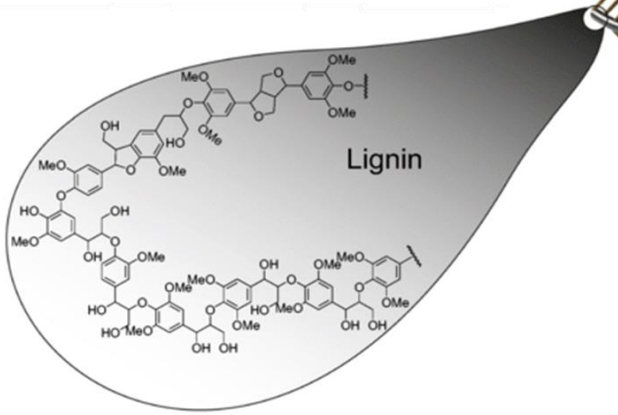
Forests at Nouvelle-Aquitaine



Valorization of local maritime pine and other tree species





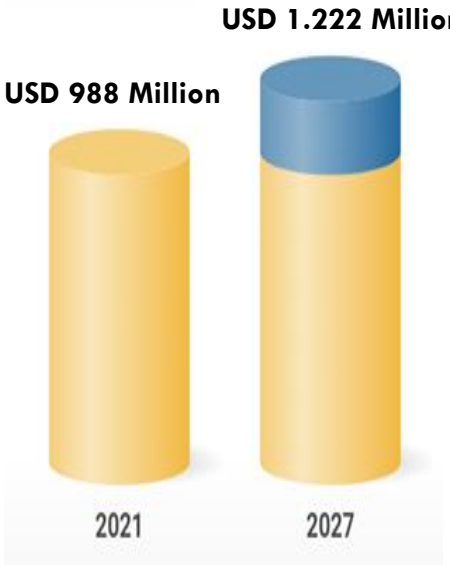


- Mechanical rigidity
- Water transport
- Abundance – **2nd most abundant polymer on Earth**
- Physico-Chemical properties (e.g. Hydrophobicity)

Kraft

Organosolv
Lignosulphonate

Lignin Market

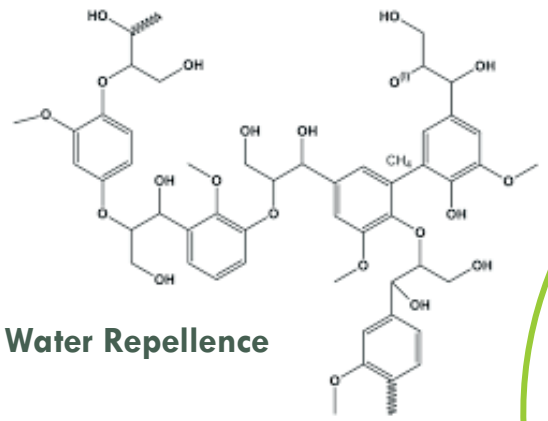


Kraft lignin represents **80%** of the total production

Low-cost material

Brethauer. S.. Shahab. R.. & Studer. M. (2020). Impacts of biofilms on the conversion of cellulose. *Applied Microbiology and Biotechnology. 104.*

LIGNIN

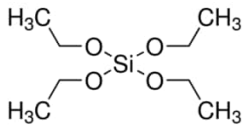


Water Repellence

Organic

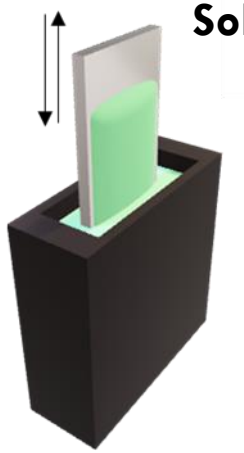
Inorganic

TEOS



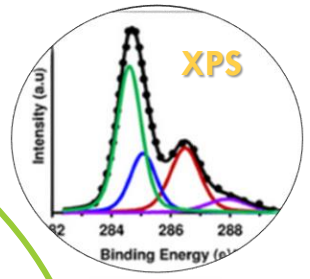
Mechanical behaviour robustness and stability

Elaboration of coatings

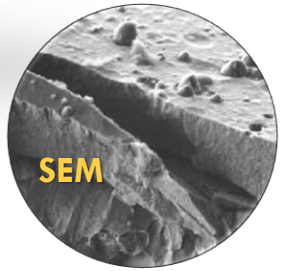


Sol-Gel/Dip-Coating/EISA combination

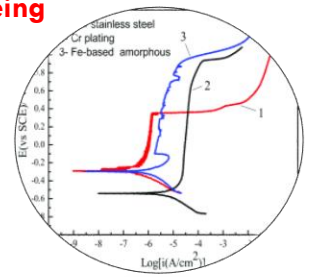
Chemical analysis
(chemical environment, oxidation state, …)



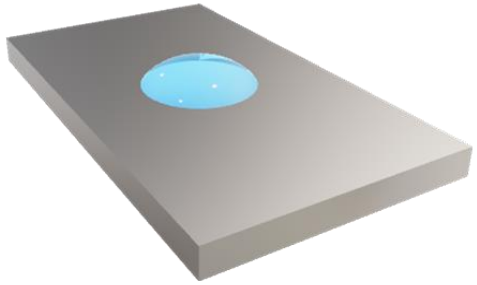
Physical surface state
(morphology, defects, apparent roughness, …)



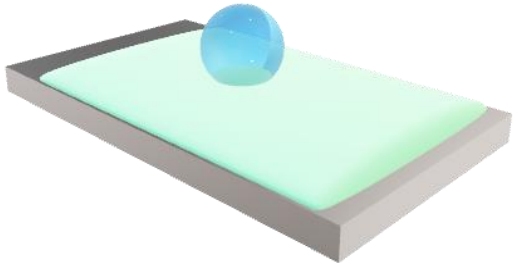
Coatings Corrosion & Ageing



Coatings Characterization



Hydrophilic surface

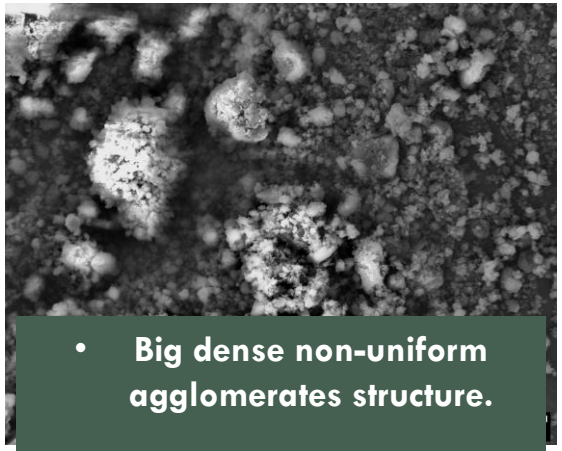


Hydrophobic surface

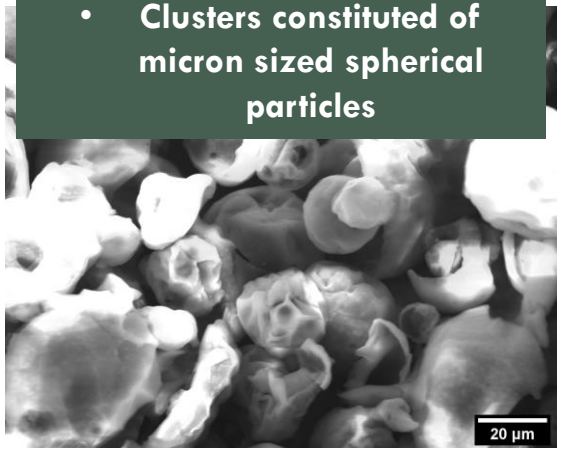
Hydrophobicity enhancement

Kraft lignin characterization

Maritime Pine softwood lignin
(mainly formed by **G units** – Mw: 5000g/mol)

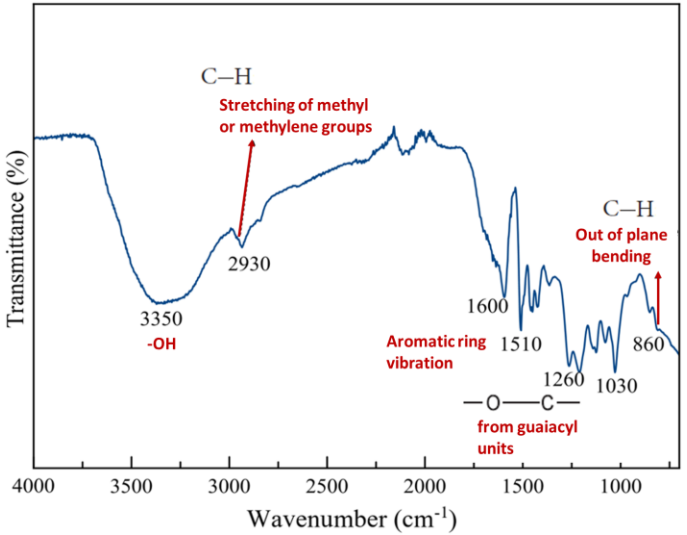


- **Big dense non-uniform agglomerates structure.**
- **Clusters constituted of micron sized spherical particles**



SEM of Kraft lignin morphology. Big agglomerates constituted of smaller particles (x600) and higher magnification of these particles. showing the globular morphology (x750).

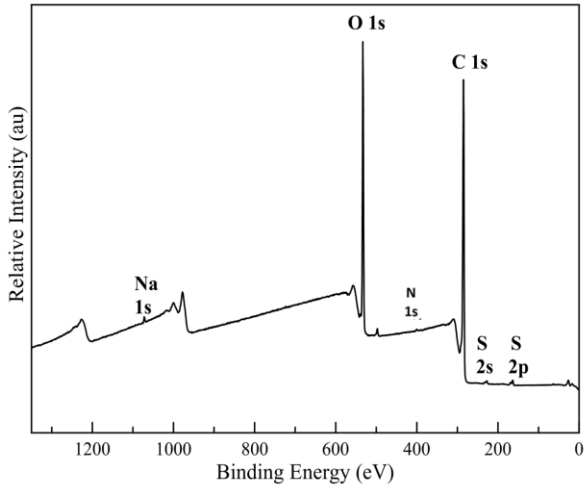
FTIR Analysis



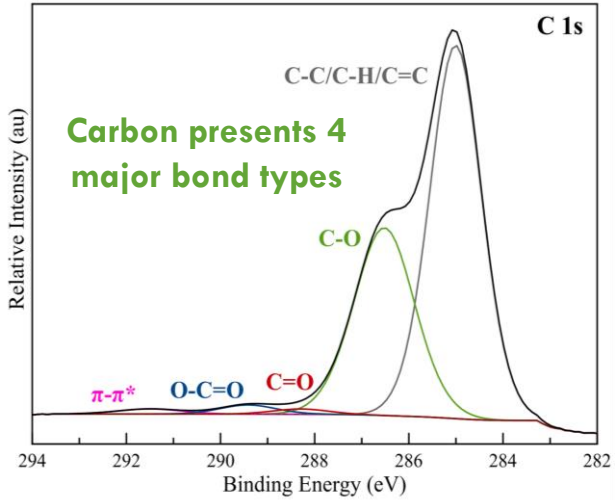
FTIR spectrum from Kraft © lignin

- **Strong signal from –OH groups and aromatic structures**
- **Identification of the G unit**

XPS Analysis



Kraft © lignin XPS general spectrum



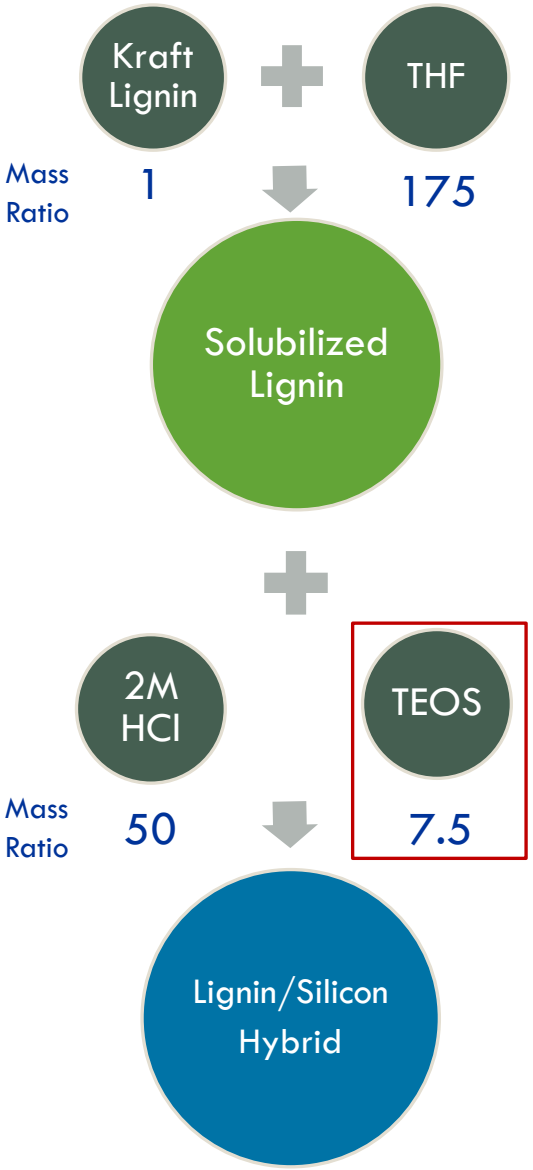
Kraft © lignin C 1s XPS core level spectrum

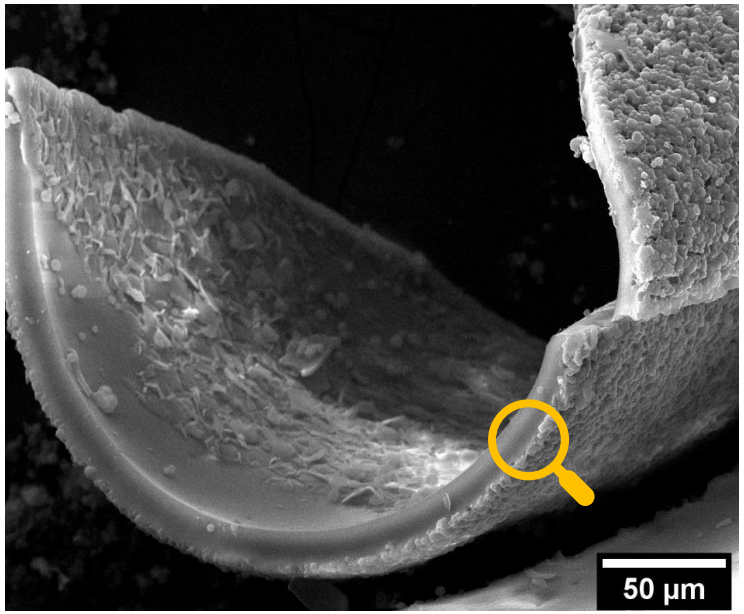
Core Peak	Total At. Conc (%)
C 1s	77.9
O 1s	20.8
N 1s	0.1
Na 1s	0.3
S 2p	0.9

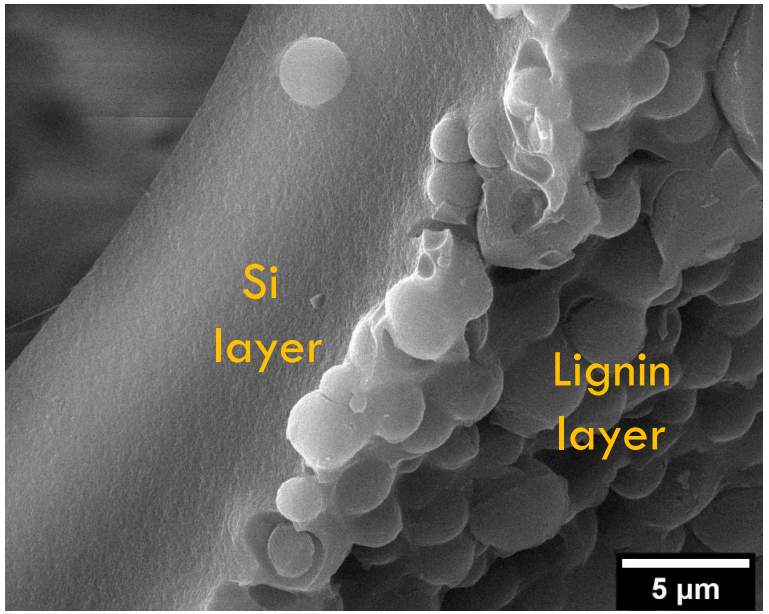
Impurities from Kraft lignin extraction process

Hararak, B., Winotapun, C., Inyai, J., Wannid, P., & Prahsarn, C. (2021). Production of UV-shielded spherical lignin particles as multifunctional bio-additives for polyvinyl alcohol composite films. Journal of Nanoparticle Research, 23

Lignin/Silicon hybrid solution



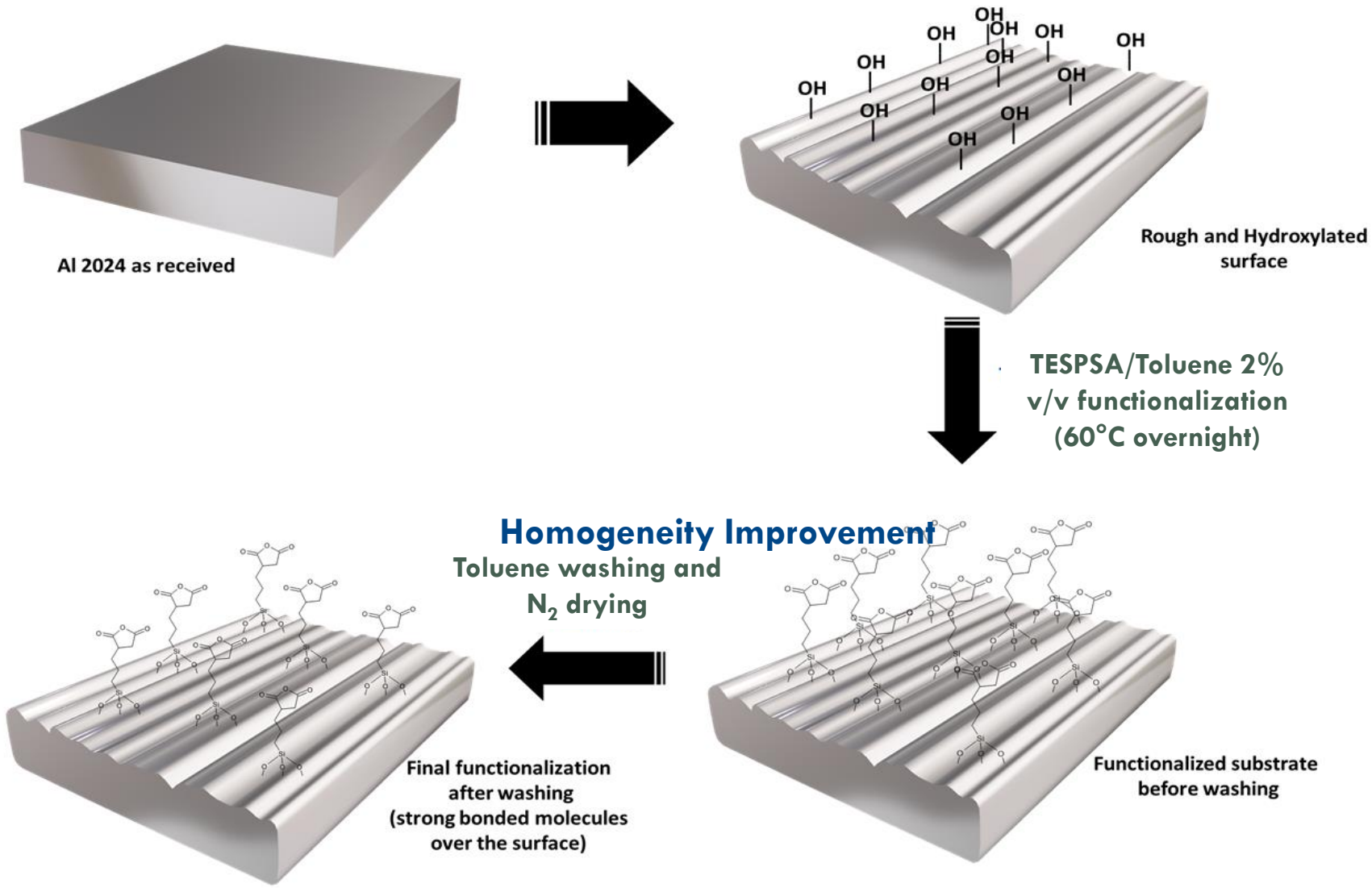




SEM images of Lignin/Silicon hybrid (1/7.5): general overview x400 magnification and dense smooth matrix/nodules interface x4000 magnification

Organic/inorganic phases interaction

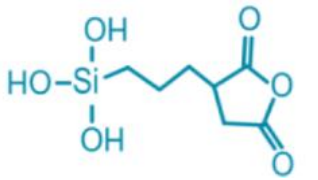
New synthesis route…substrate functionalization



Surface Functionalization

Organo-alkoxide linker coupling molecule

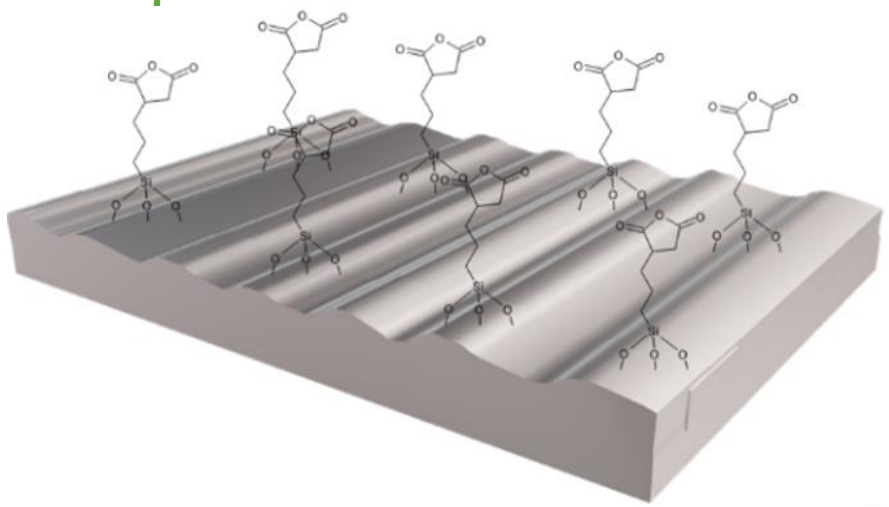
Promote a better distribution of the hybrid solution with the Al 2024 substrate



Triethoxysilylpropyl succinic anhydride

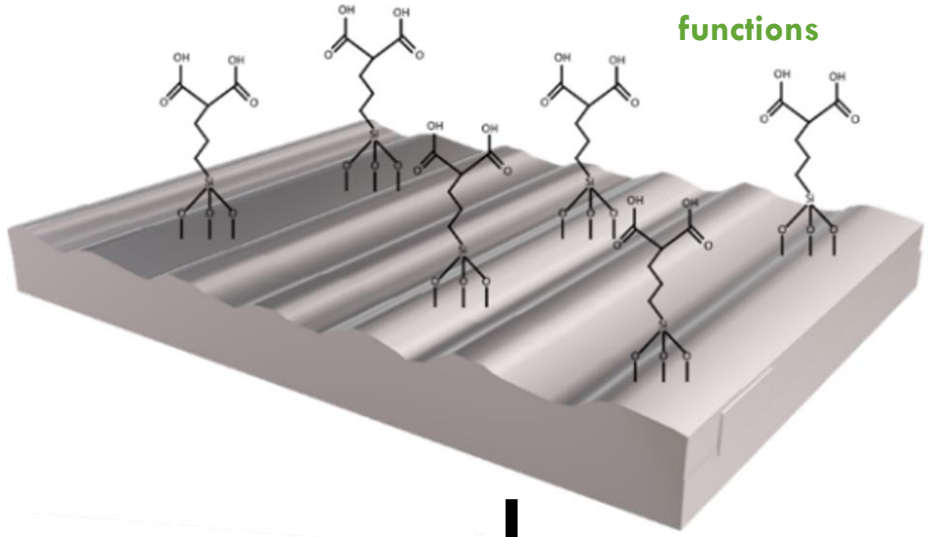
NDR Lignin/Silicon Hybrid_Chemical Mechanism

Esterification process



H^+

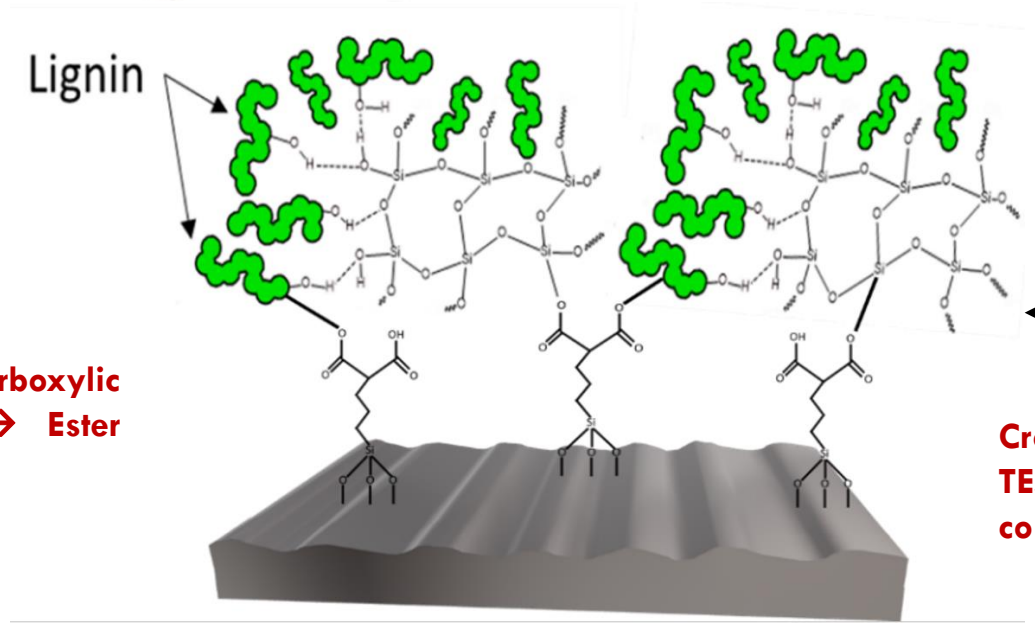
Formation of carboxylic acid functions

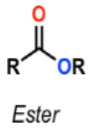


+ TEOS

+ Lignin

DIP-COATING

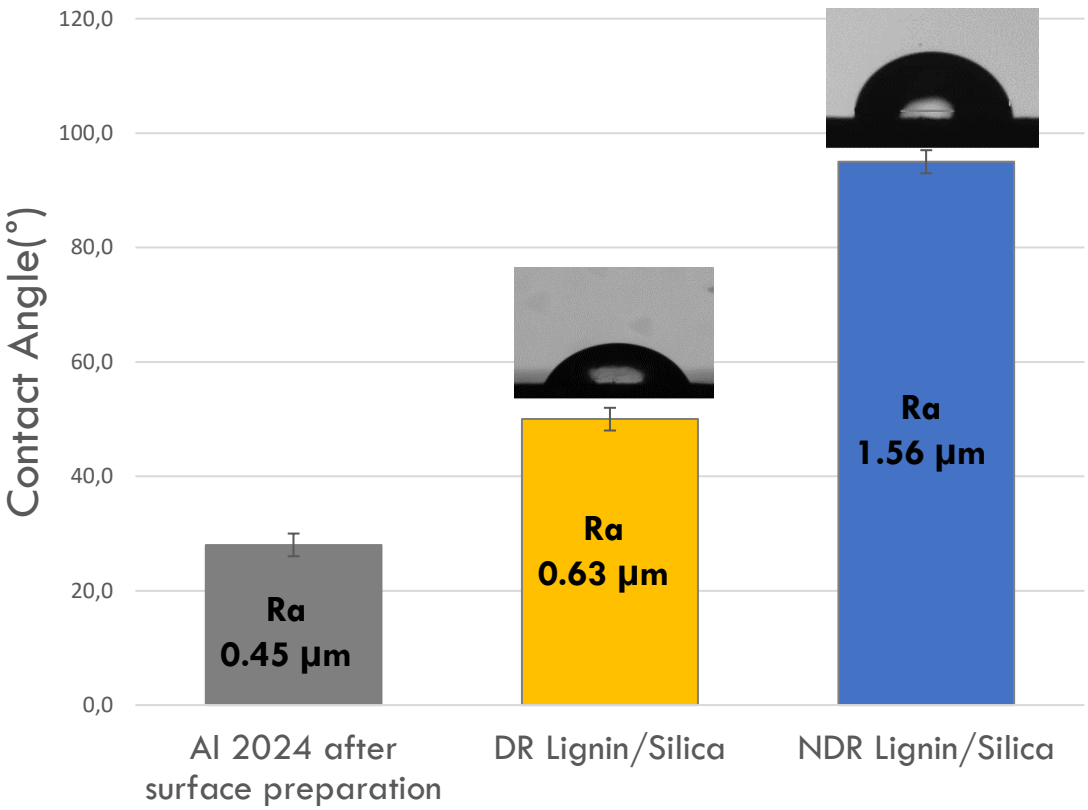




Reaction between Carboxylic Acid and Lignin OH → Ester Function Formation

Cross-linking between TEOS and TESPSA → Co-hydrolysis and co-condensation processes

Water Contact Angle analysis (WCA)



Hydrophobic behavior achieved – WCA 95°

Esterification increases the surficial presence of lignin (and simultaneously **reduces the amount of OH groups**) → Hydrophobization improvement

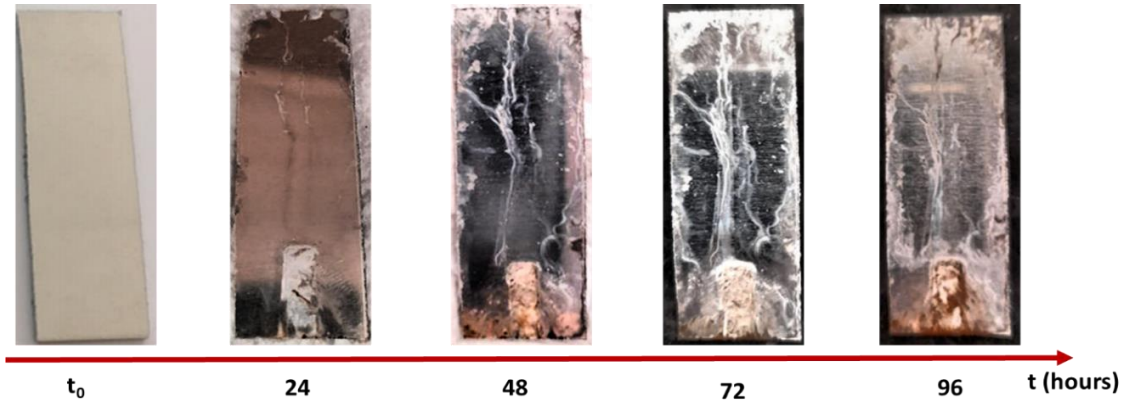
NDR Adhesion test

Grade 2 → same grade obtained for the DR hybrid coating

New morphological arrangement → **homogeneous coating & more lignin on the surface**

Salt Spray Test – Aggressive corrosion

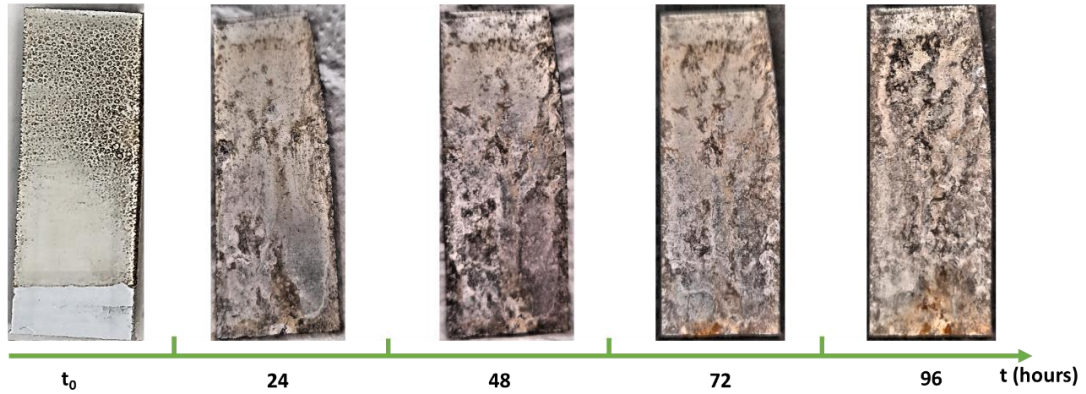
Raw Al 2024 alloy



- **24h** → New colors appearance…different corrosion states
- **48h** → Beginning of a general corrosion
- **96h** → General corrosion in both extremities

Commercially non-chromate AC-131 coating applied on Al 2024 substrate failed before 24h

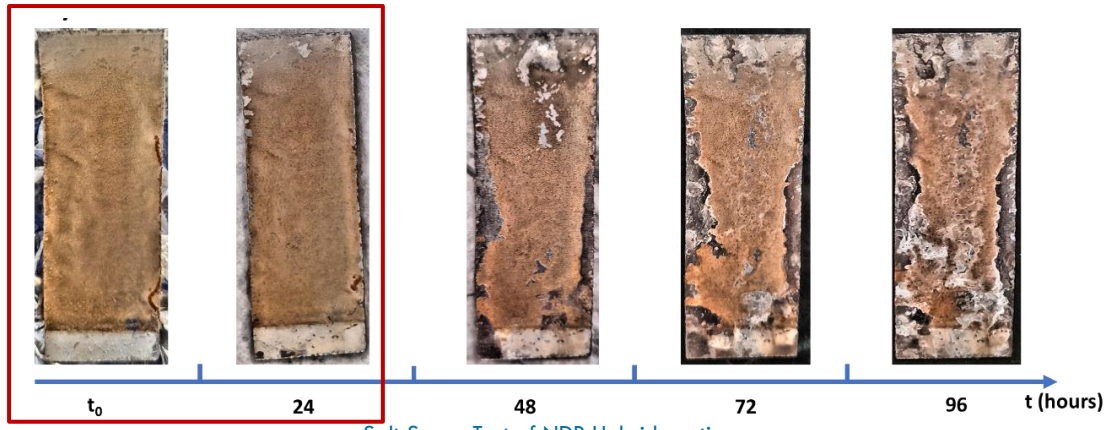
Direct Route (DR)



Salt Spray Test of DR Hybrid coating

More than 20 pitting corrosion spots from the first 24h

Non-Direct Route (NDR)



Salt Spray Test of NDR Hybrid coating

Slightly more than 20 possible pitting points after 48h.

Kakde, V., & Mannari, V. (2009). Advanced chrome-free organic–inorganic hybrid pretreatments for aerospace aluminum alloy 2024-T3—application of novel bis-ureasil sol–gel precursors. Journal of Coatings Technology and Research, 6(2), 201–211

Conclusion

- **Hybrid Lignin/Silicon biosourced coatings**

  EISA/Dip-Coating: RH=10% withdrawal speed = 0.05mm.s^{-1}

Direct Route

Raw ← **Al2024** → TESPSA

Non Direct Route

- Bad covering
- Agglomeration of Lignin
- XPS: C/Si = 7.5
- WCA around 50°
- Adhesion: Grade 2

- Homogeneous covering
- Dilution of Lignin within the coating
- XPS: C/Si = 24
- WCA of 95°
- Adhesion: Grade 2

- **1st attempts of Corrosion tests**

  Both DR & NDR coatings showed a promising protective effect

  E_{corr}: -0.75V (substrate) -0.52V (coatings)

- **New Focus: SF_6 Plasma surface modification**

  Various fluorine environments: clear difference between DR & NDR coatings

  Enhancement of hydrophobicity:

  +90% (DR) +15% (NDR)

THANK YOU FOR THE ATTENTION !

SPECIAL THANKS : POLYMERS AND ANALYTICAL CHEMISTRY DEPARTMENTS FROM UPPA, SURFACES AND THIN FILMS LABORATORY FROM UFRJ, IUT FROM MONT DE MARSAN