Development of an innovative range of bio-based structural adhesives

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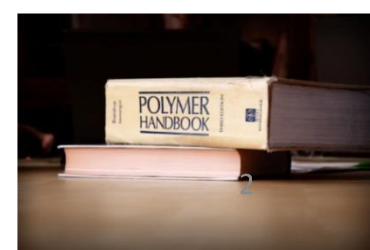
Rescoll

- **Independent technological company** located in Pessac (33) specialized in technologic innovation since 2001
- Rescoll's main expertise: formulation & characterization
- Innovation studies in industrial applications of polymer materials (adhesives and adhesive bonding, composite materials, special varnishes and paints, technical plastics, cosmetics, etc.) and related areas (materials fire behavior, surface treatments, ecodesign & LCA)
- Staff: 60 people
- **National & European labels**
  - CRT: *Centre de ressources technologiques.* Quality agreement for SMEs (by industry ministry)
  - SRC: *Société de recherche sous contrat.* Rescoll is approved as an Industrial Research Center (by research ministry)
  - Court-appointed expert by first instance and commerce court of Bordeaux
  - REACH national auditor
  - EWF trainer (European diploma for bonding specialists and operators)



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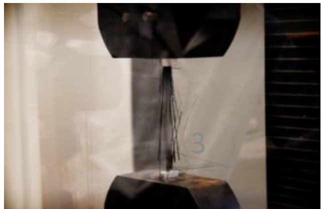
Rescoll

- **Analyses**

  - Composition analyses, raw materials and finished products controls, thermomechanical behavior (chromatography, FTIR, DSC, TMA, etc.)
  - Mechanical tests (tension, compression, bending, fatigue, etc.)
  - Ageing (climatic, UV, saline mist, etc.)
  - Quality certification: **ISO 9001: 2008**
  - Accreditations: **COFRAC** and **NADCAP** “Non Metallic Materials Testing”

- **R&D department (ISO 9001)**

  - Experience in the management of innovation studies in **B2B**
  - Experience in the management of **collaborative innovation projects** (European projects, Clusters, etc.)
  - Hundreds of studies in partnership with industrialists in a **wide variety of fields** (automotive, aeronautics, space, cosmetics, construction)
  - Development of **internal processes** (disassembling adhesives, conductive polymers)
  - More than 40 patents
  - More than 500 customers in Europe



General Context

- **Bio-based Industry Objectives[1]:**
  - Develop **innovative products** & accelerate **market introduction** → ETV
  - **Increase** the overall percentage of **biobased** chemical production

water

energy

waste

Fossil-based products substitution

Less resource intensive production

Importance of bio-based products

Renewable carbon

High bio-degradability

oil price increasing

[1]*Biobased for Growth – A Public-private partnership on biobased industries*

General Context: Challenges

- Studies concerning the use of bio-based resins for structural bonding applications are very limited
- Very little literature up to now regarding structural bonding applications
- Example: No "green solution" found up to now to answer all aeronautical specifications (mainly in terms of tensile lap shear strength, hardness, glass transition temperature, conditions of processability, etc.)
- **Epoxy resins** are mostly used in structural bonding applications due to their good mechanical and adhesion properties, durability, as well as thermal and chemical resistances

Our research : replacement of traditional mineral oil based epoxy resins with bio-based epoxy resin systems for structural bonding applications

General Context : Main “green” requirements

- Resins should be produced from natural and renewable resources
- Biobased developed resins should reach at least the **same level of quality** as **fossil based resins**
- The production of “green epoxy resins” should be energy extensive and result in lower CO_2 emissions than those of comparable epoxy resins

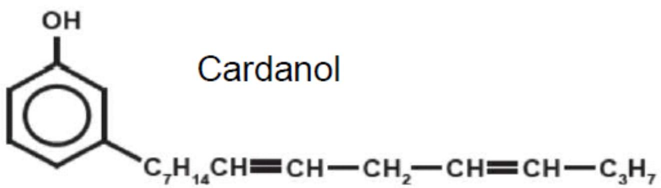
R&D Methodology

- Screening on **commercially available products** → to meet former requirements
- Implementation of **bio-based resin/hardener formulations** & **characterization tests** (lap shear, hardness, glass transition temperature, exothermic peak, rheological behavior…)
- **Comparison** with petrochemical epoxy resins **"already used"** as adhesives for **structural bonding applications**
- **Optimization study** conducted, both on the curing process and on the composition of the matrix
    - Another path consisting in blending petrochemical epoxy resins with bio based epoxy resins is also being explored → to adjust final properties of resins

Characteristics of formulations

Biobased Hardener characteristics

- Based on monomer Cardanol, distilled from Cashew Nut Shell Liquid, CNSL
- CNSL is a natural, non-food chain, and annually renewable biomaterial
- Renewable content > 60%



Cardanol

Biobased Epoxy resin characteristics

- Liquid epoxy resin produced from epichlorhydrin based on glycerine
- Renewable content : 28%

Technical Main Requirements

- The aim is to develop **new biobased adhesives** with levels of performance equal or superior to fossil based existing adhesives:
  - **Bonding properties**
  - **Mechanical properties**
  - **Reactivity**
  - **Bio renewable content**

- “Commercial adhesives”:
  - DP490
  - EA9396

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New biobased adhesive/fossil based adhesives comparison

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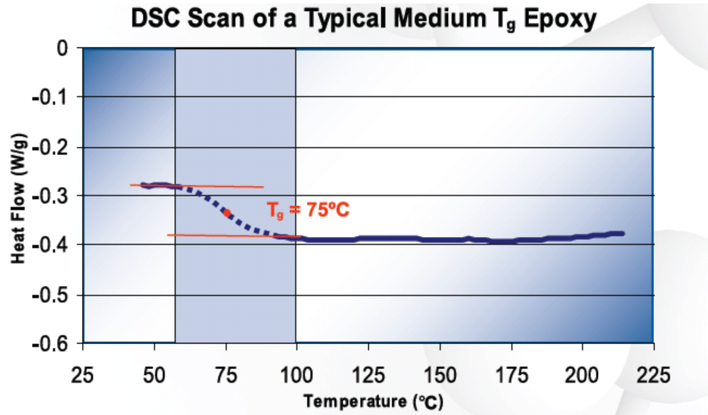
Glass Transition Temperature



Epoxy technology

- Glass transition temperature Tg: temperature region where a thermosetting polymer changes from a hard, rigid or “glassy” state to a more pliable, compliant or “rubbery” state
- Tg is strongly dependent on the cure schedule
- Typically, adhesives with highest Tg have the best heat resistance
- The higher the Tg, the higher the cross-linked density and the higher the modulus

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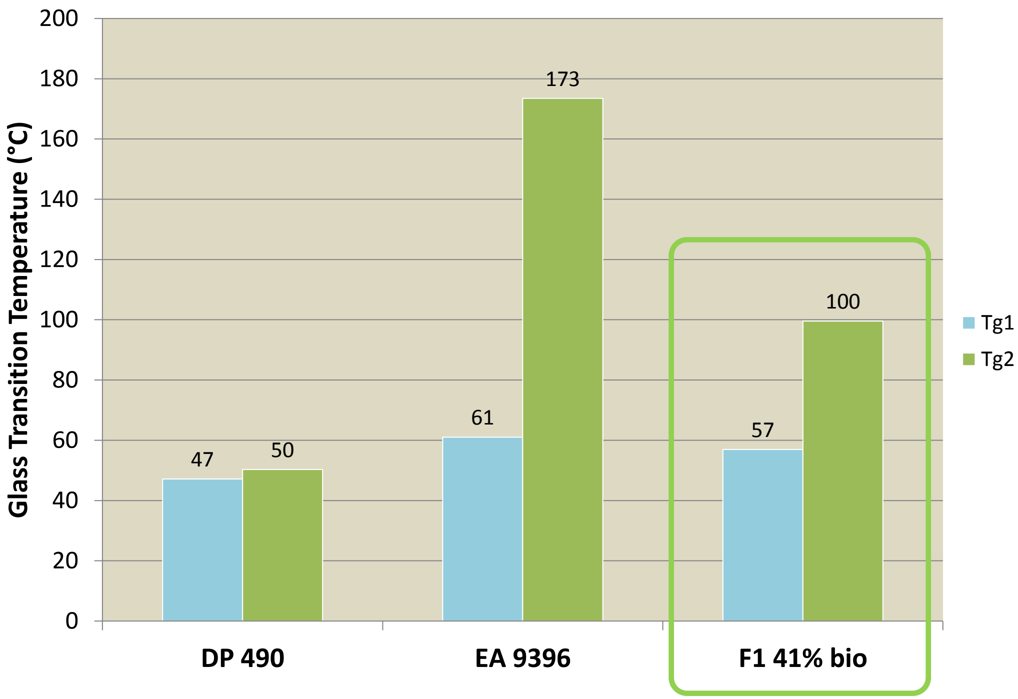
Glass Transition Temperature

Curing conditions of the sample: 7 days at 23°C

DSC – 2 thermal cycles ➔ Tg_1 & Tg_2



- Glass transition temperature value of bio based formulation is between that of commercial adhesives

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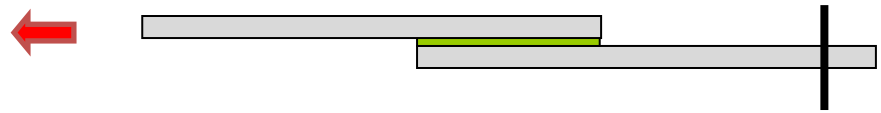
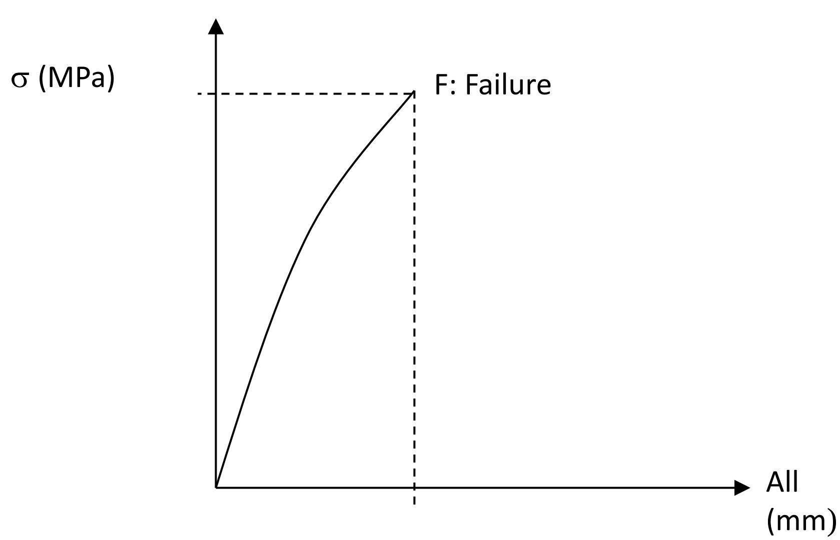
New biobased adhesive/fossil based adhesives comparison

Lap shear mechanical tests

Curing conditions of the sample: 7 days at 23°C
NF EN 1465
Surface preparation: Aluminum 2024 + chemical etching

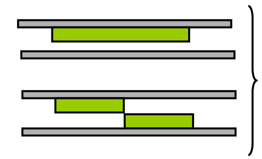




σ_F : Tensile lap shear strength = F/S_0

S_0 : surface of the adhesive joint

Fracture surfaces:



Adhesive failure

Cohesive failure

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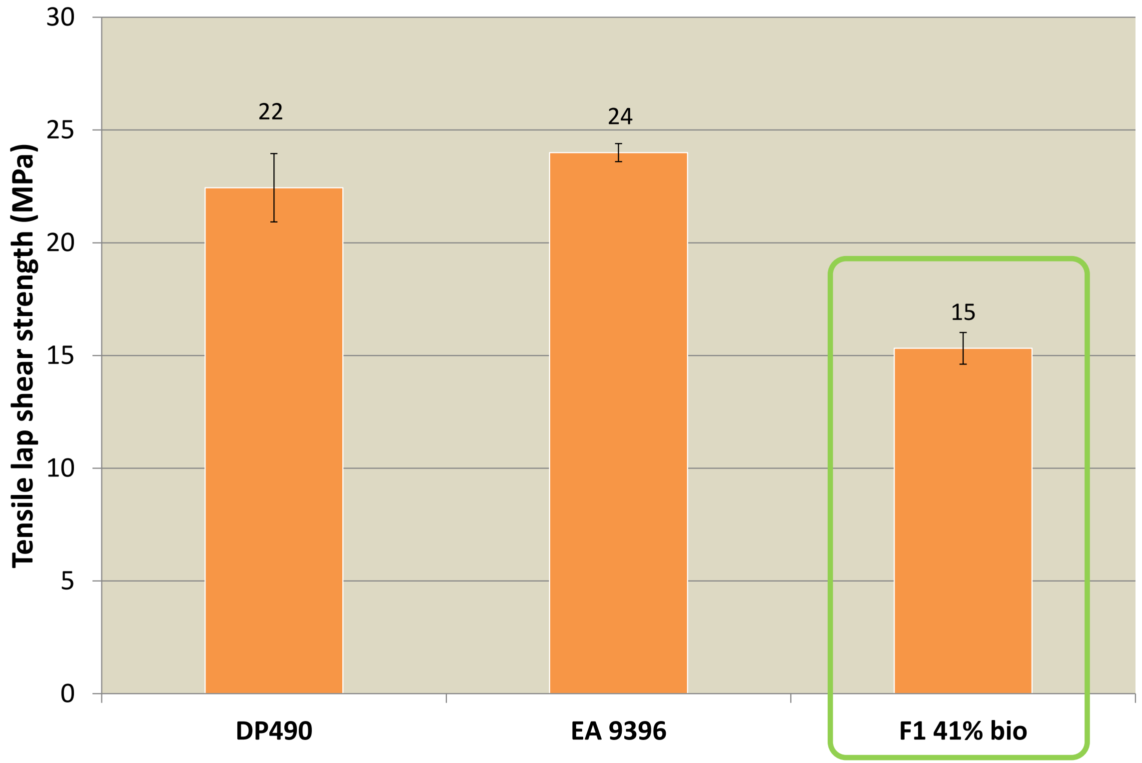
Lap shear mechanical tests



- Bonding properties of biobased formulation should be improved

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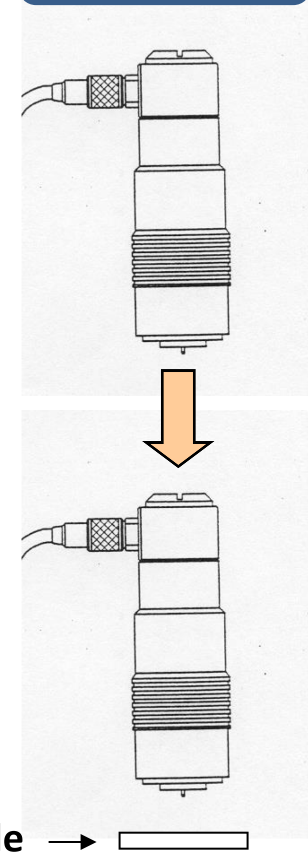
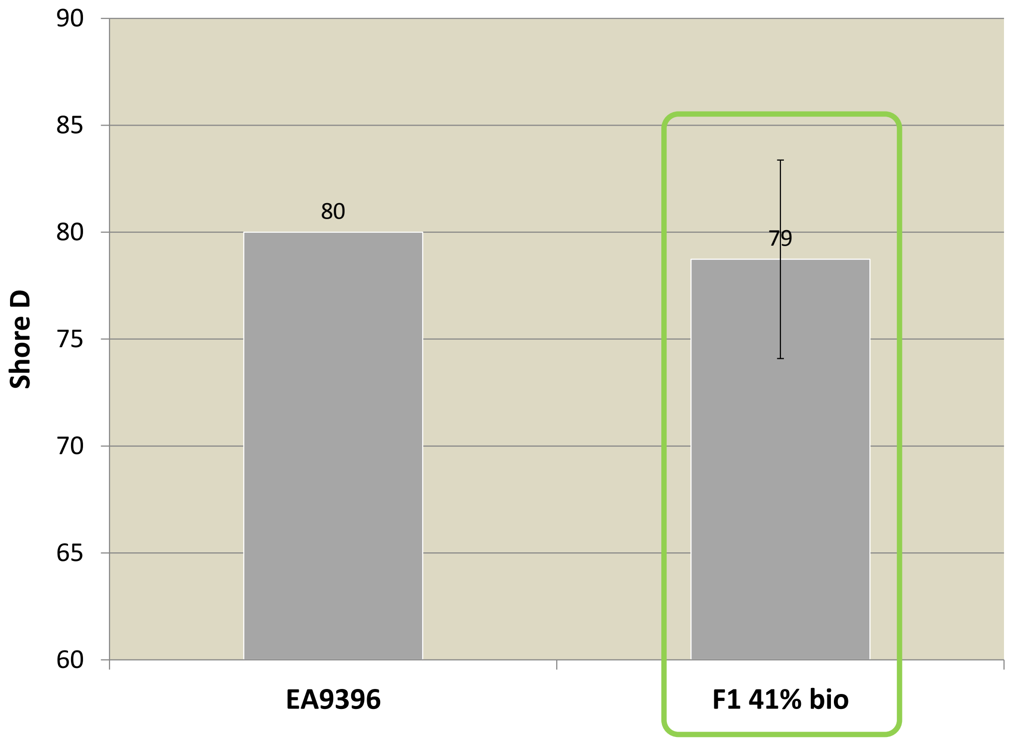
Hardness



Sample →

Curing conditions of the sample: : 7 days at 23°C
Shore D



- Same degree of performance as fossil formulations

New biobased adhesive optimization

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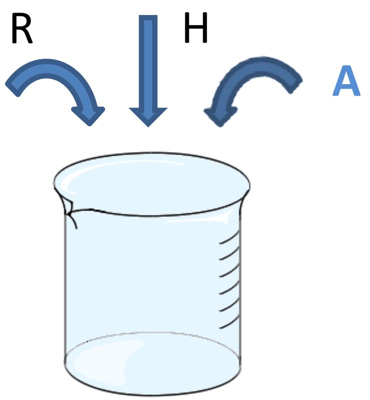
Biobased epoxy resin / biobased hardener



+ A:
- fossil toughener (**0% bio**)
- **or**
- biobased dilutant 1(**86% bio**)
- **or**
- biobased dilutant 2(**86% bio**)

Formulation	A	Renewable content (%)
F1 (baseline)	-	41
F2	Fossil toughener	39
F3	Biobased dilutant 1	43
F4	Biobased dilutant 2	43

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New biobased adhesive optimization

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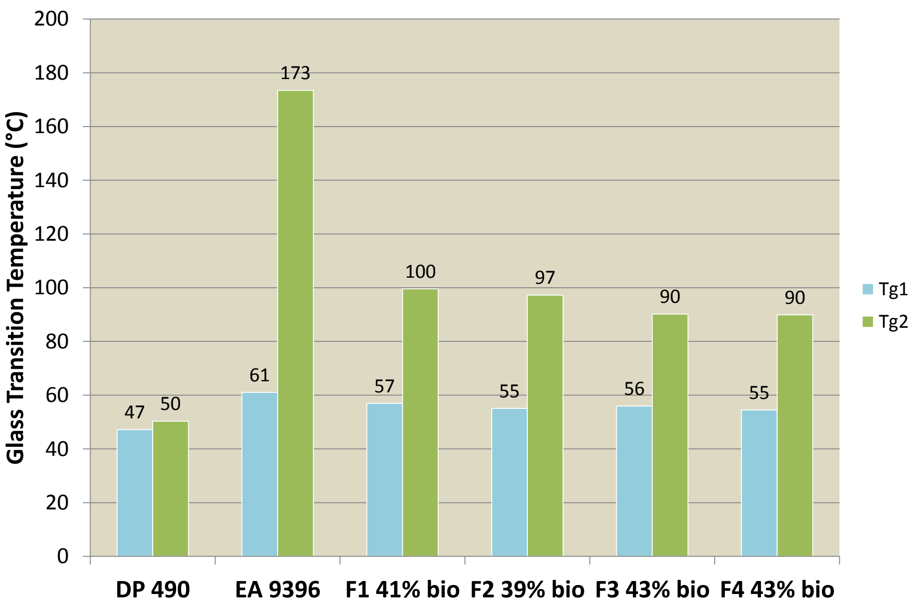

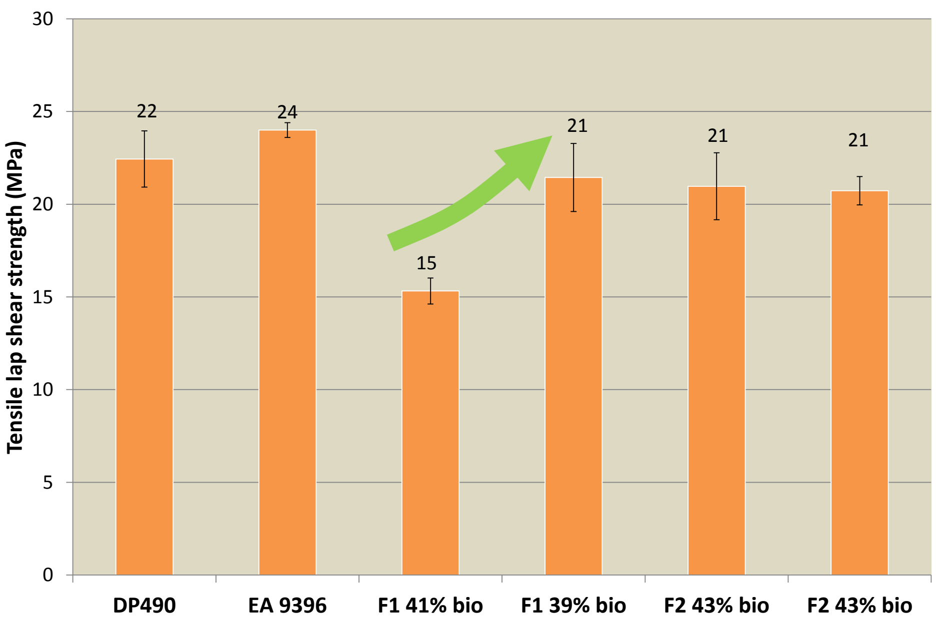

New biobased adhesive optimization

Formulation	Renewable content (%)	ΔT_{g2} (%)	$\Delta \sigma_F$ (%)
F1 (baseline)	41	-	-
F2	39	-3	40
F3	43	-10	40
F4	43	-10	40

- Whatever the compounds added to the formulation, the tensile strength increases by 40% for all three formulations.
- No obvious differences at the first Tg. The second Tg was reduced by 3% with fossil-based additives and by 10% with biobased dilutants.

Conclusions & Perspectives

✓ Cardanol based products seem worthy of interest for biobased structural adhesive applications

☒ Biobased epoxy resins just mimic the molecular structure of fossil based resins → use of less toxic biobased intermediates

- For aeronautic applications → Fire behavior, resistance to thermal cycling, ageing, aeronautic fluids
- Life cycle assessment (LCA) of innovative developed formulations → verification of environmental profile improvement

Thanks for your attention

www.institut-collage.fr

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