Development of innovative bio-based structural resins

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NEW BIO-BASED STRUCTURAL RESINS from RESCOLL

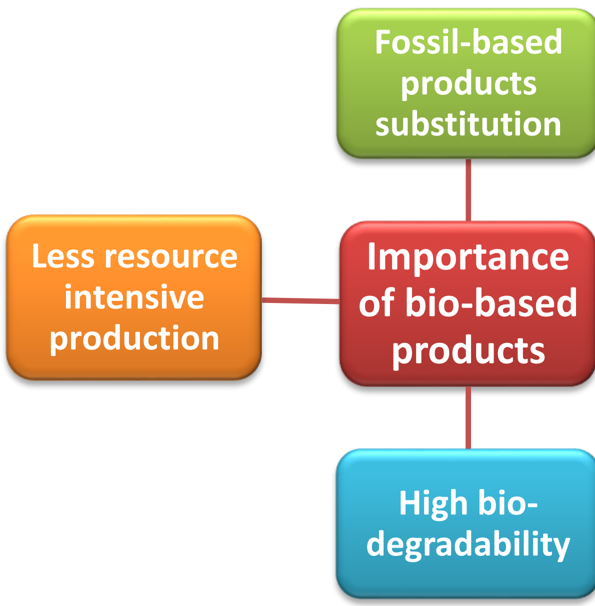
General Context

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

water

energy

waste



oil price increasing

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

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General Context: Challenges

- **Studies concerning the use of bio-based resins for structural applications are very limited**
- **Very little literature up to now regarding structural 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 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 applications

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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

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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 resins for **structural 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

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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%

Biobased Epoxy resin characteristics

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

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Technical Main Requirements

- The aim is to develop **new biobased resins** with levels of performance equal or superior to fossil based existing resins:

  - **Thermomechanical properties**
  - **Mechanical properties**
  - **Reactivity**
  - **Bio renewable content**
  - **Bonding properties for adhesives uses**

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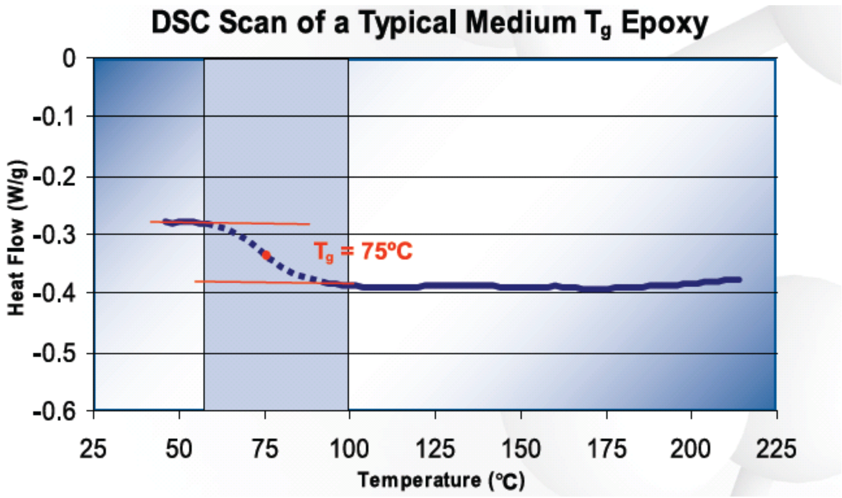
New biobased resin/fossil based resins comparison

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, resins 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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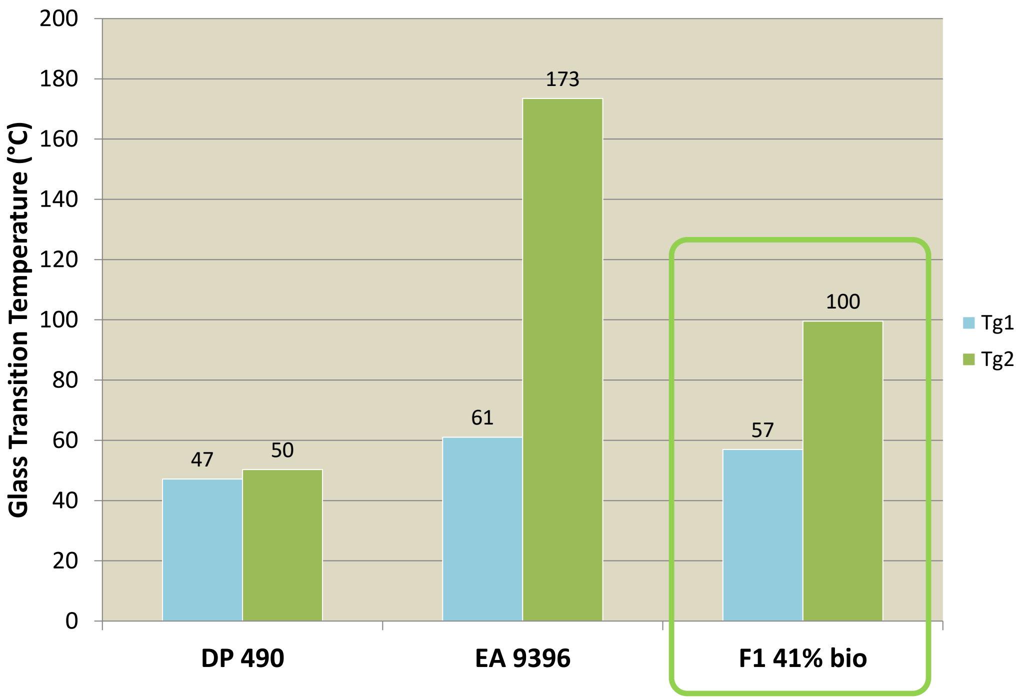
New biobased resins/fossil based resins comparison

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 resins

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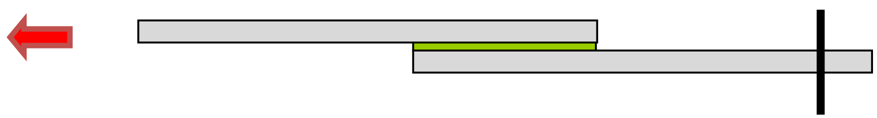
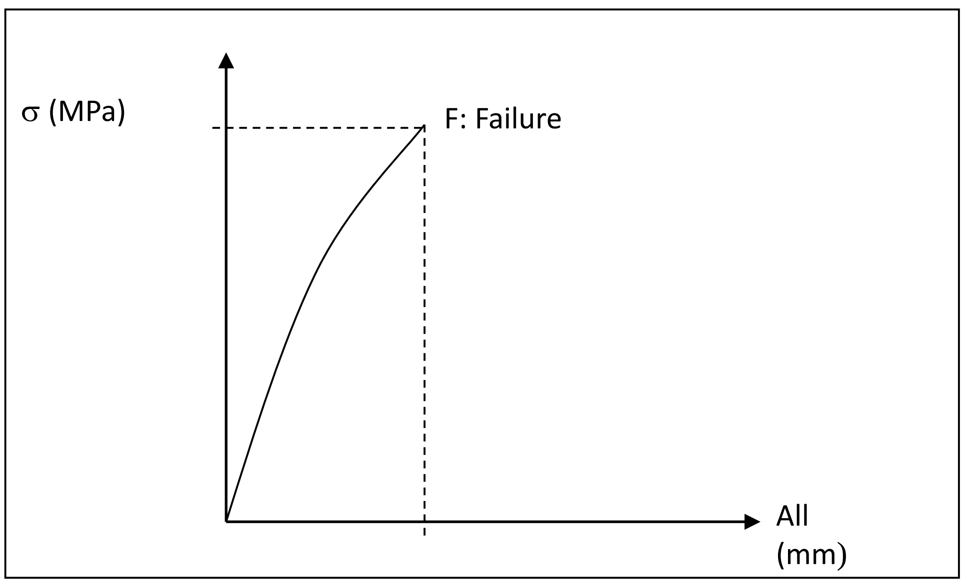
New biobased resins/fossil based resins comparison

Lap shear mechanical tests

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

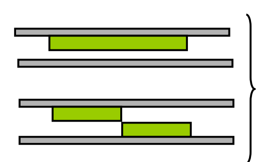




σ_F : Tensile lap shear strength = F/S_0

S_0 : surface of the adhesive joint

Fracture surfaces:



Adhesive failure

Cohesive failure

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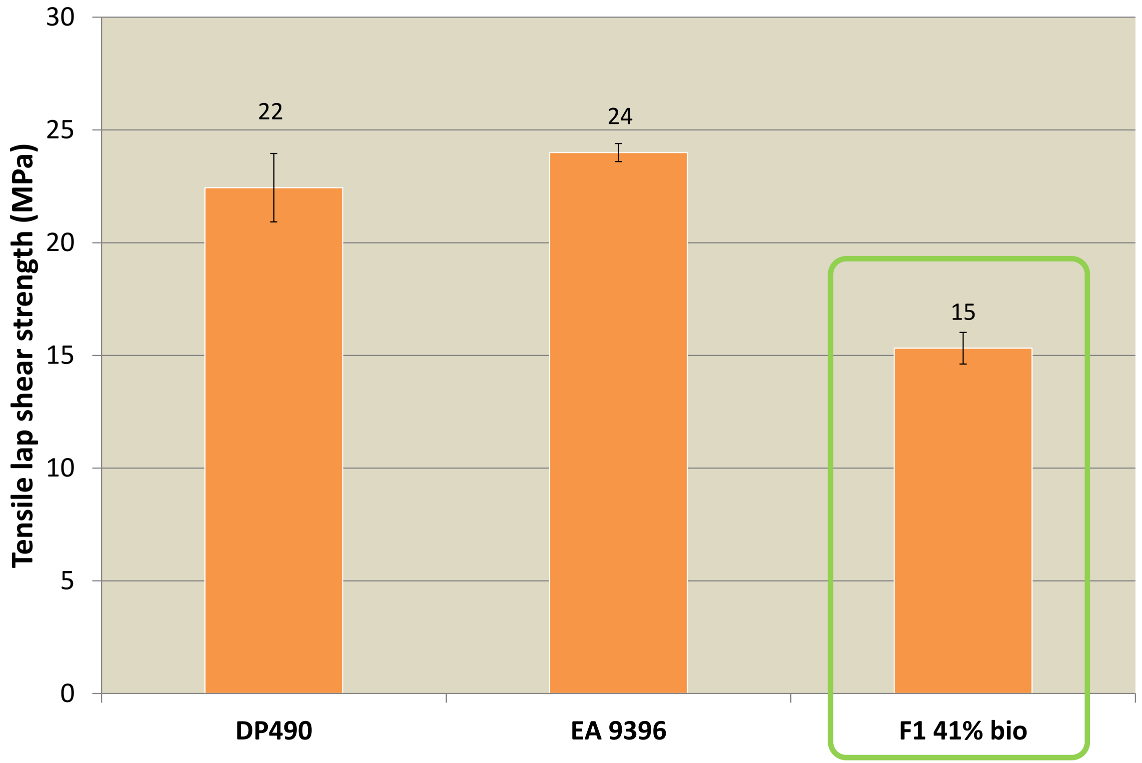
Lap shear mechanical tests



- Bonding properties of biobased formulation should be improved

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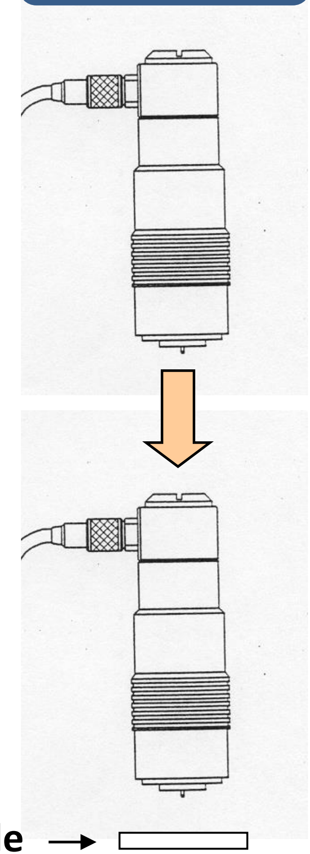
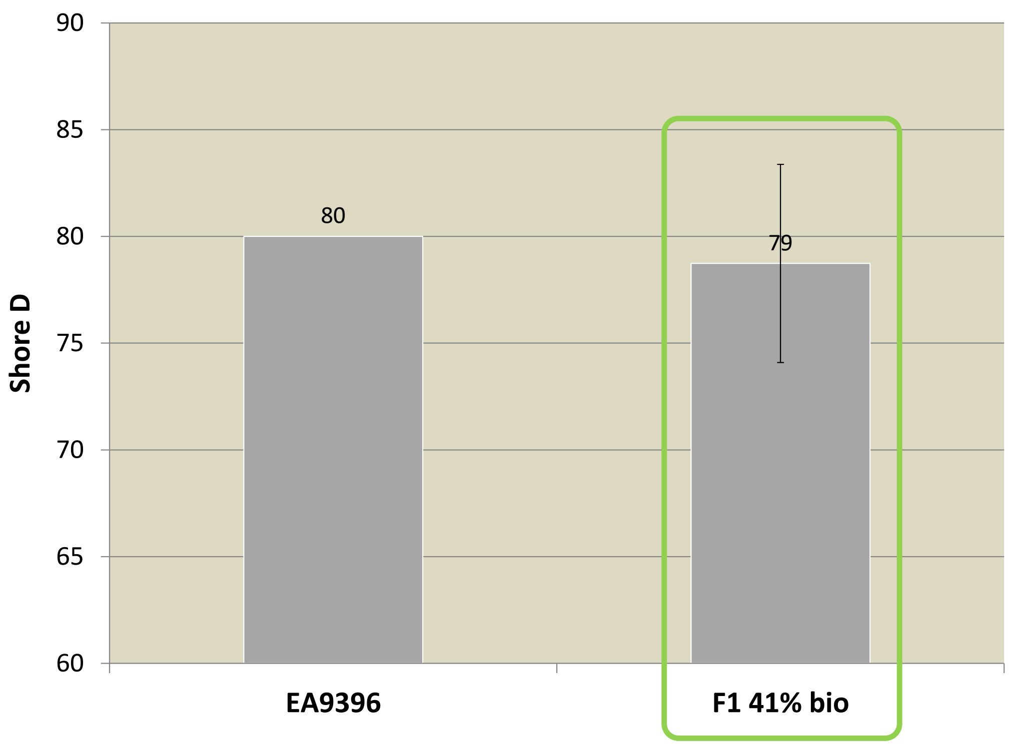
Hardness



Sample

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

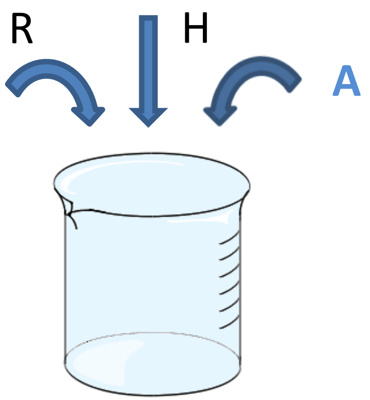


- Same degree of performance as fossil formulations

New biobased resin optimization

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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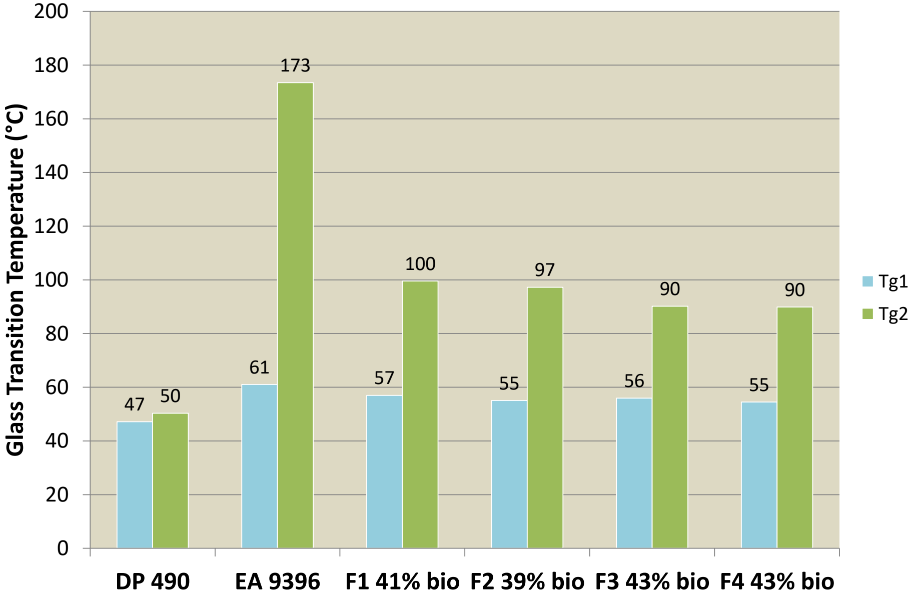
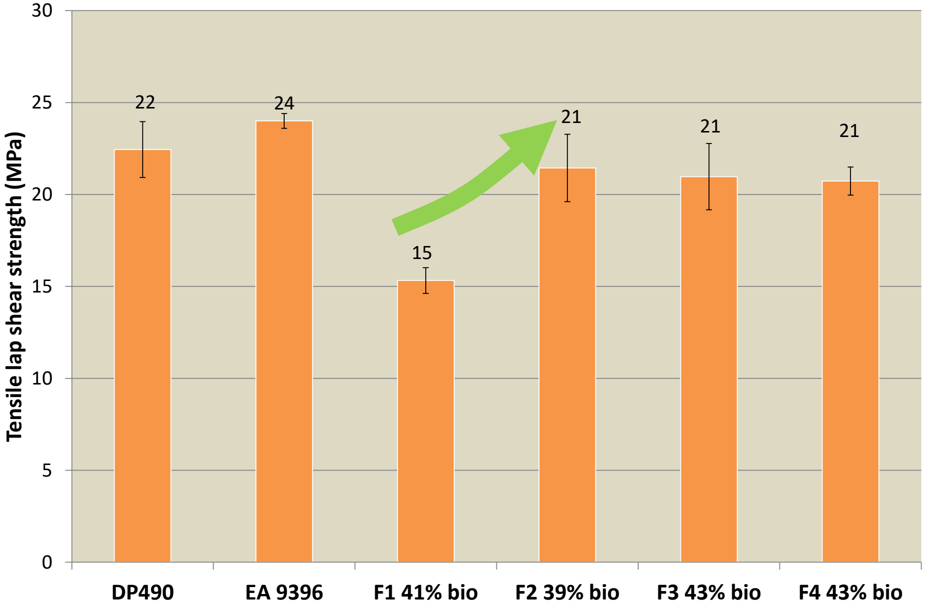
New biobased resin optimization





New biobased resin 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.**

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Conclusions & Perspectives

- ✓ Cardanol based products seem worthy of interest for biobased structural resin 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

For more information :

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