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Sustainable matrices for structural composites: processing and mechanical performance

Aromatic disulfide containing vitrimers: Promising materials towards fast commercialization (enduring prepreg (EPP) concept)

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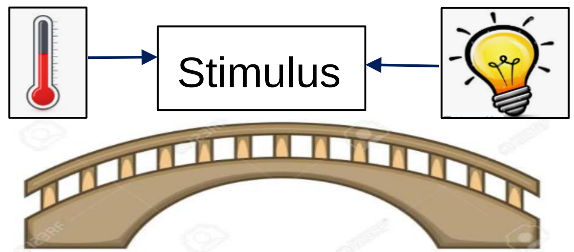
Outline

- Introduction & concepts
- 3R concept
- Enduring prepreg concept
- Conclusions

Thermoplastic *vs*. Thermoset polymers



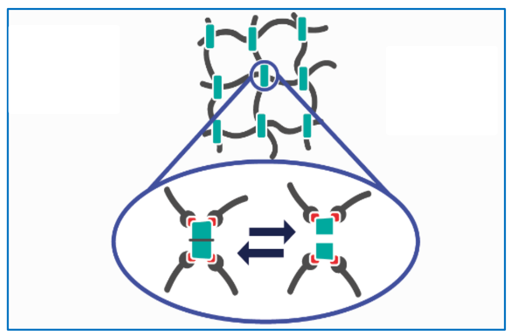
Thermosets

Covalent Adaptable Networks (CANs)

Thermoplastics

THERMOSET

- Covalently crosslinked
- Remains hard when heated
- Insoluble
- Chemical resistance
- Good mechanical properties
- Non-processable
- Non-recyclable



When T < Tg the network is static → thermoset behaviour

When T > Tg the network becomes dynamic → thermoplastic behaviour

THERMOPLASTIC

- Entangled linear polymer chains
- Reprocessable
- Recyclable
- Soluble
- Bad chemical resistance
- Softens when heated

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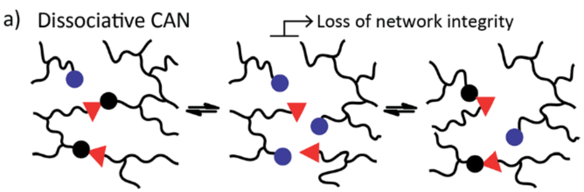
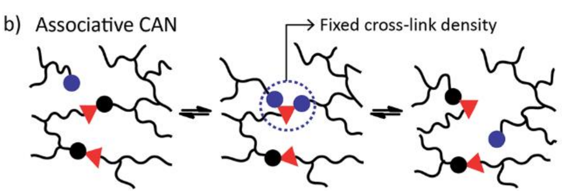
• Dissociative CANs

- Very fast topology rearrangement (stress relaxation and flow)
- Temporary loss of crosslinks results into sudden viscosity drop (similar to thermoplastics).
- Upon cooling the crosslinks are formed again recovering thermoset properties (stiffness and insolubility)
- Reprocessable when heating



• Associative CANs

- Do not depolymerize upon heating.
- They maintain fixed crosslinking density.
- Covalent bonds are only broken when new ones are formed, making these networks **permanent** as well as **dynamic**.
- Gradual viscosity decrease upon heating (similar to silica)
- Also known as **vitrimers**
- **Vitrimers (novel concept introduced for polymers by Ludwick Leibler)**



Main consequences: distinct viscoelastic behaviour during the thermal reprocessing step

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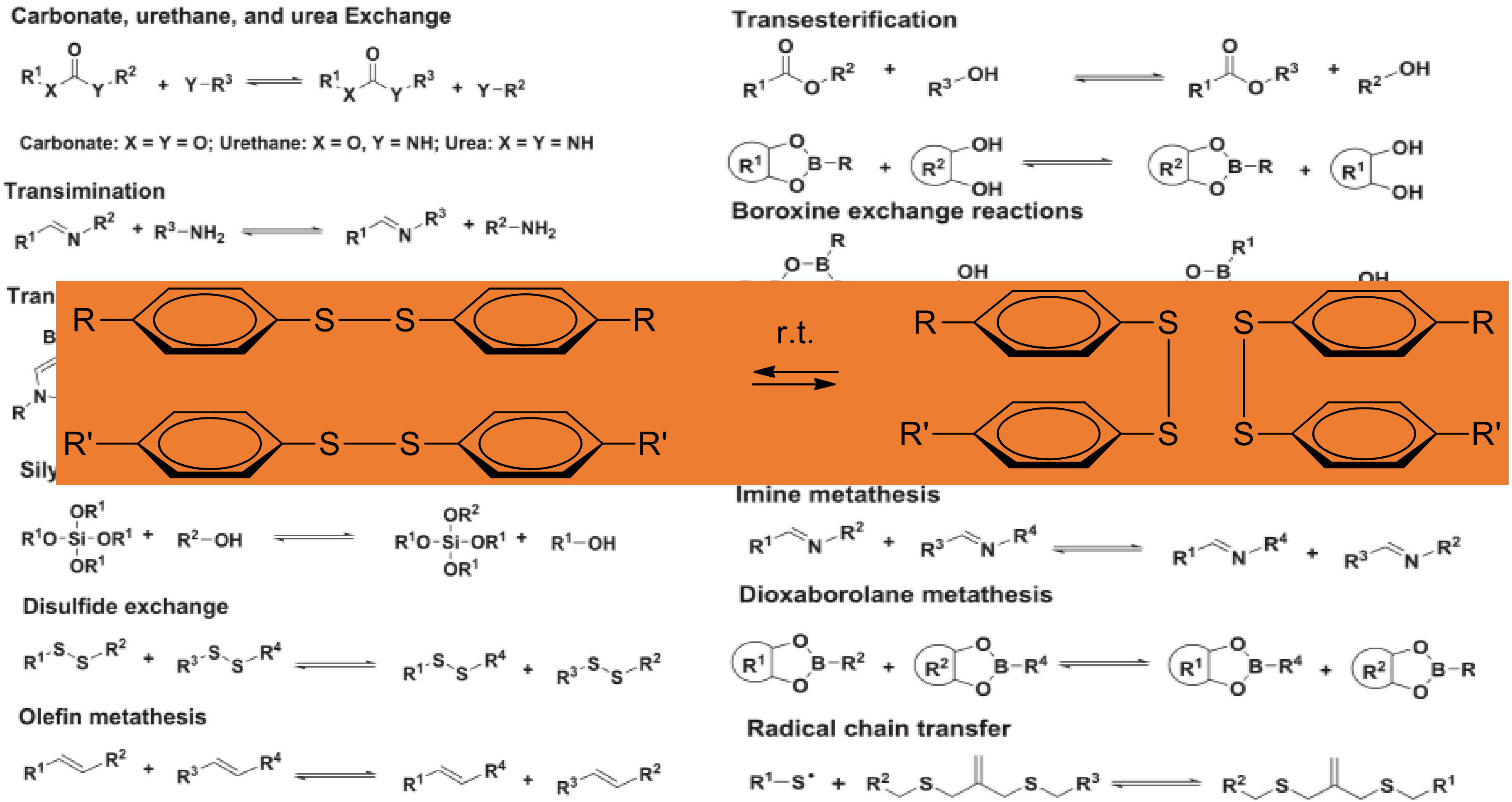
Exchangeable chemical bonds



Patent application:

EP 3 149 065 B1 – *"Thermomechanically reprocessable epoxy composites and processes for their manufacturing".*

A. Rekondo, R. Martin, A. Ruiz de Luzuriaga, G. Cabañero, H. J. Grande and I. Odriozola, *Mater. Horiz.*, **2014**, *1*, 237–240

A. Ruiz de Luzuriaga et al., Material Horizon, 2016, 3, 241.

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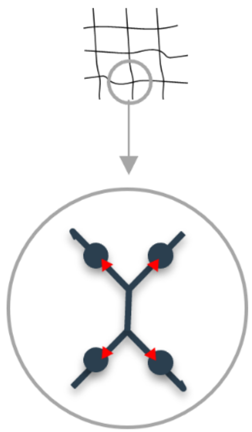
3R technology is based on the reversibility of aromatic disulfide bond:

Schematic representation of conventional epoxy vs **3R dynamic resin**.

Conventional polymer network

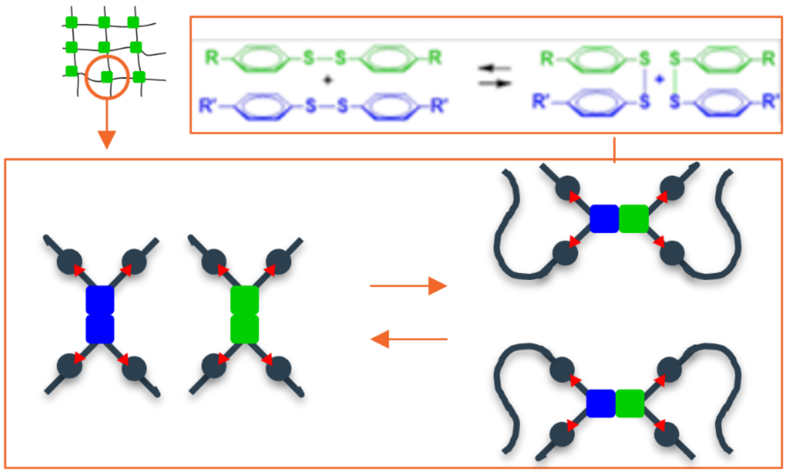


Permanent Crosslinks

Conventional epoxy resin

Non-Reprocesable
Non-Reparable
Non-Recyclable

Dynamic polymer network



Dynamic Crosslinks based on aromatic disulfide exchange

3R Dynamic epoxy resin

Reprocesable
Reparable
Recyclable

Patent application:
EP 3 149 065 B1 – *“Thermomechanically reprocessable epoxy composites and processes for their manufacturing”.*

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3R concept: Epoxy vitrimers based on aromatic disulfide

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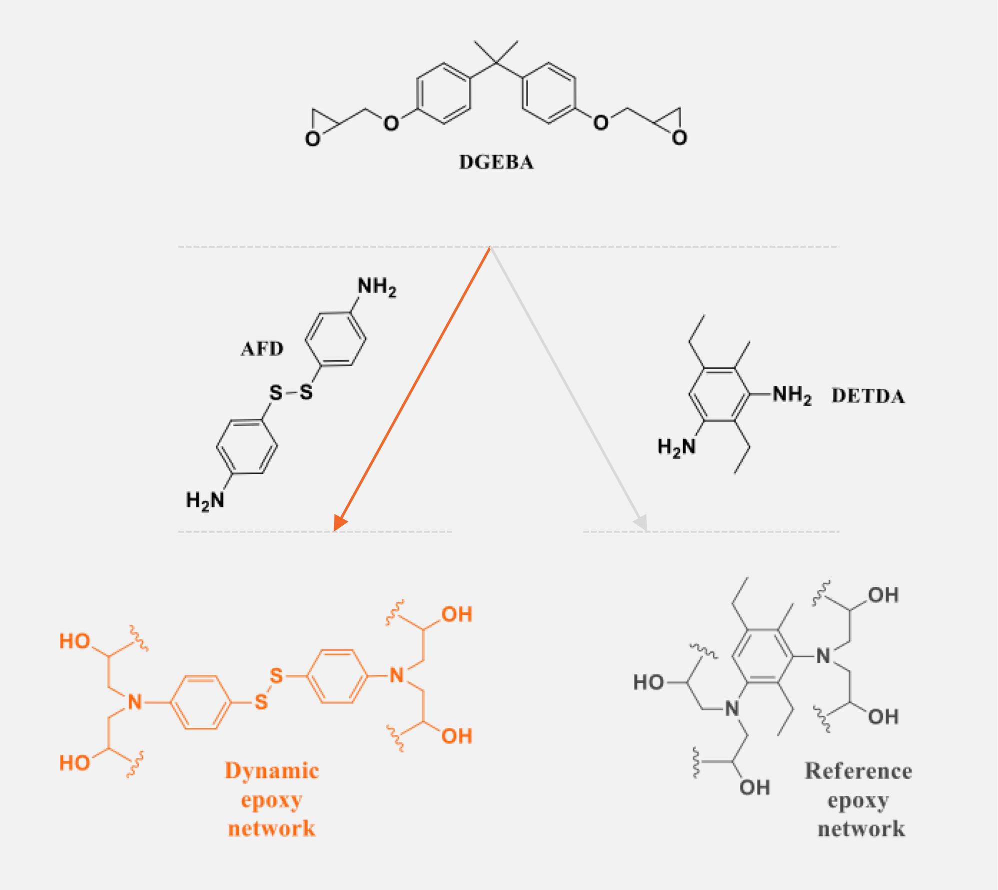

	Reference network	Dynamic network
Tg (DSC) [ºC]	127	**130**
Tg (DMA) [ºC]	130	**130**
Td [ºC]	350	**300**
E´(25ºC) [GPa]	2,5	**2,6**
E´(150ºC) [MPa]	20	**20**
Stress [MPa]	81	**88**
Strain [%]	7,3	**7,1**

Comparable thermal and mechanical properties using our dynamic hardener instead of a conventional hardener.

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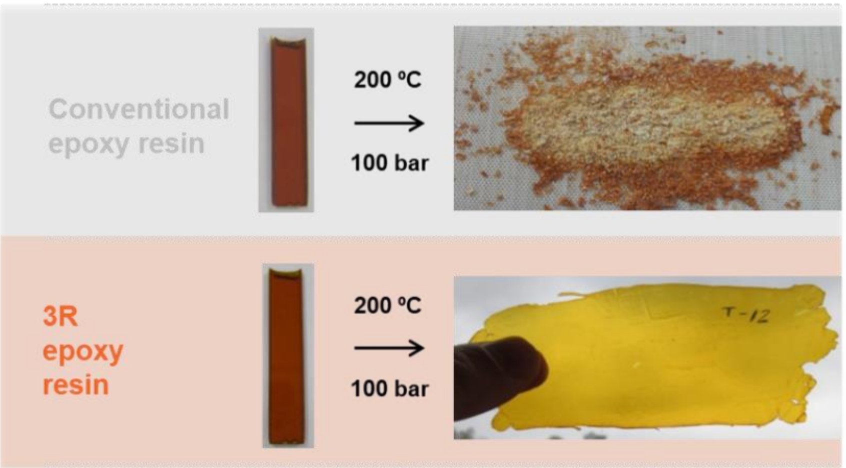
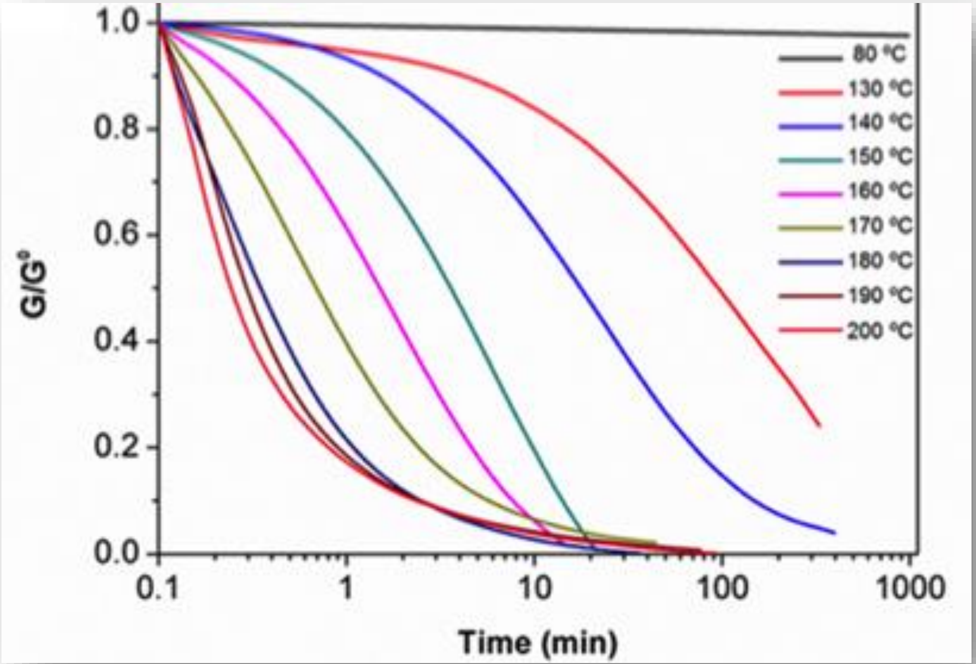


Characterization of the stress relaxation by DMA



- At temperatures above Tg, **the dynamic epoxy network** is able to completely relax stress and flow.
- The obtained relaxation times ranged **from 3 hours at 130 ºC to 20 seconds at 200 ºC.**

A. Ruiz de Luzuriaga *et al.*, *Material Horizon*, **2016**, *3*, 241.

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Dynamic fibre reinforced composites based on aromatic disulfide

3R Composites

- A new generation of **Reprocessable, Repairable and Recyclable high-performance fibre-reinforced thermoset composites.**
- They can be manufactured following traditional methods but the resulting material can be reprocessed, repaired and recycled.

Enduring PrePreg concept (EPP)

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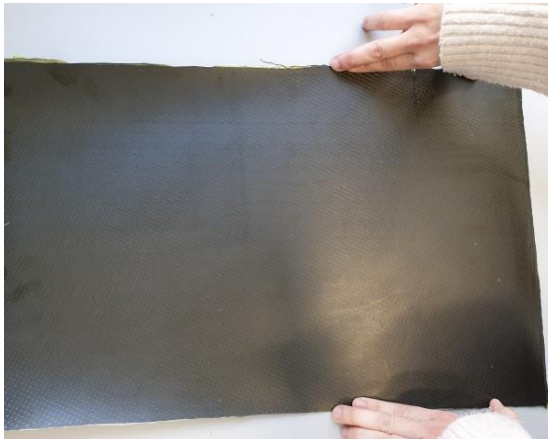
ENDURING PREPREG CONCEPT

- Traditional prepregs need to be stored in the freezer to stop the curing reaction
- Traditional prepregs have an out time of a few weeks at RT and a shelf life of 1 year at – 20 ºC.
- EPP can be stored at RT for years without loosing its reprocessability.
- EPP storage is much cheaper than conventional thermoset prepregs.
- EPP shipment has not any extra shipping cost
- The storage at RT offers clear logistical advantages
- Compression forming of pre-cured materials can take minutes to obtain high performance well consolidated parts.
- They can be like thermoplastic organosheets.

3R enduring prepreg (EPP)



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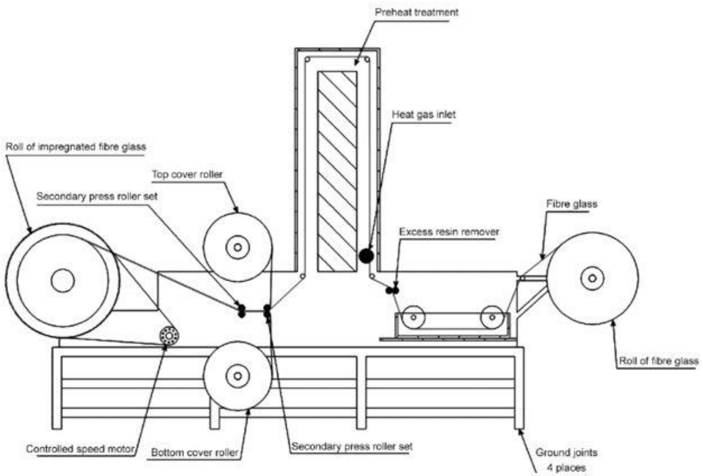
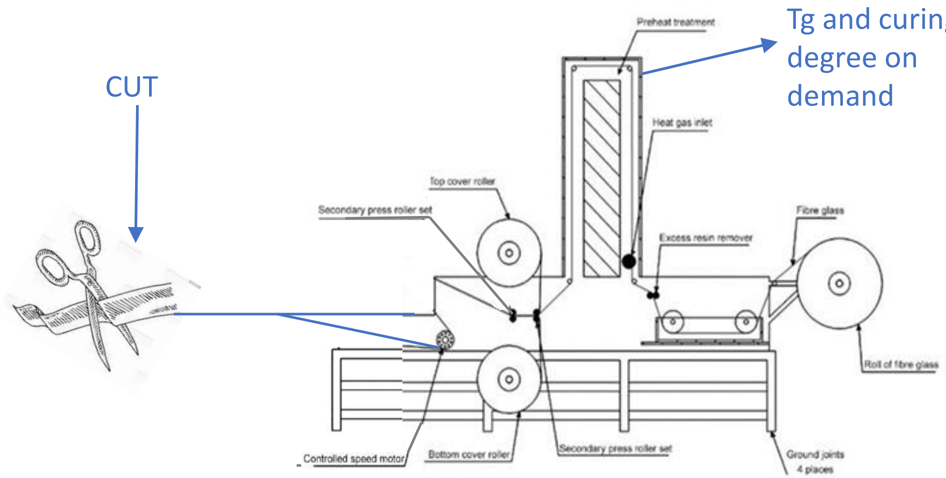
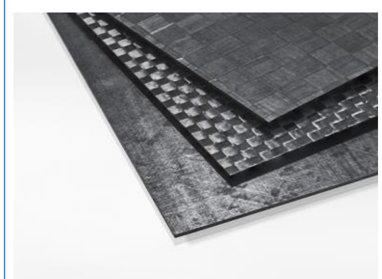
CONVENTIONAL PREPREG



Conventional prepregs are stored in the form of rolls and need to be stored in a freezer (-20 °C).

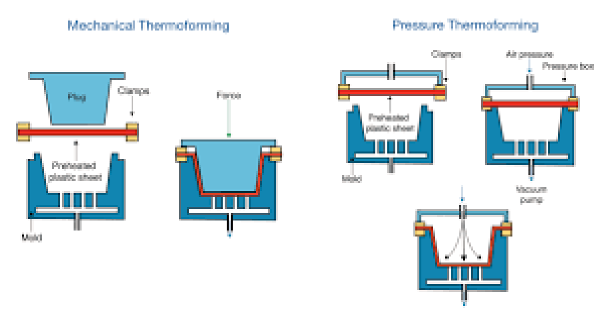
ENDURING PREPREG PROCESS





Enduring prepregs can be stored in the form of rolls, but also as flat laminates, at RT (similar to thermoplastic organosheets). The Tg and curing degree of the input material can be adjusted on request.

EPPs can be thermoformed to obtain the desired parts using high production rate processes.



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AIRPOXY

ThermoformAble, Bondable, Repalrable smart ePOXY resin for Aero structures

Input material: EPPs with different curing degress and initial Tg were tested

Final material: Tg = 180 ºC

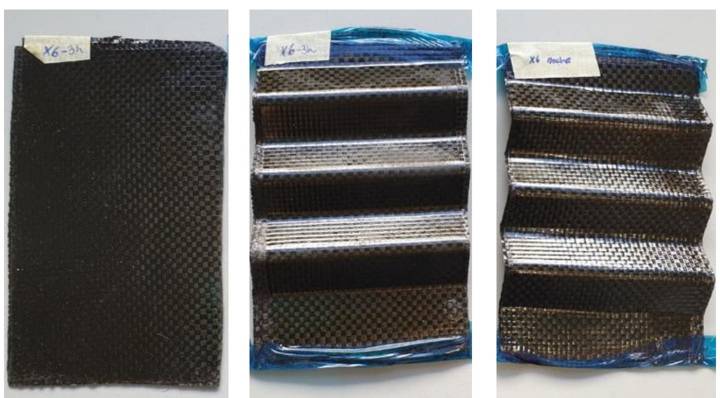
- **T = 210 ºC** for **3 min** and after switch off the heating and put the set point at 25 ºC ; **P = 50 bar**

Prepreg reference: **AIR-C-PP-F32-2 (V7)**

- Sample dimensions = 13 cm x 8 cm
- % resin = 36,67 %
- layers = 6
- Doctor Blade Gap = 0,3 mm initial
- Teflon above and below prepreg

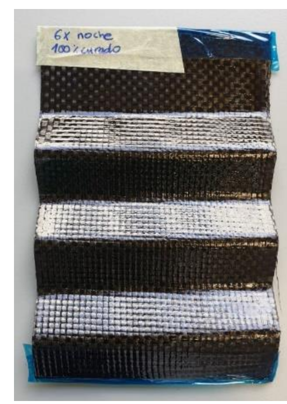
Sample	Tg (ºC)	Curing degre (%)	Result
1	55,36	58,98	Good
2	174	98,19	Good (some voids are present)

58,98 % of curing rate before pressing



Results: prepegs sheets show **good adhesion**, therefore it has a good rigidity and mechanical properties.

98,19 % of curing rate before pressing



Results: Good aspect but some delaminations appear when bending, higher press time and pressure are required

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AIRPOXY

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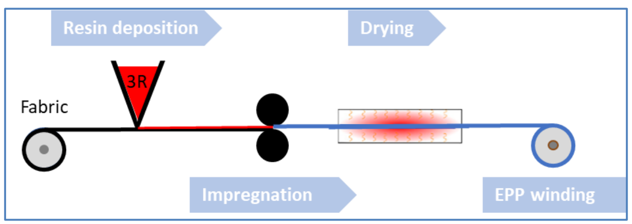
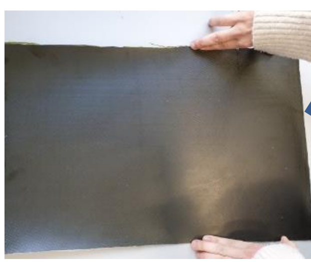
Two thermofoming processes studied with EPP input material:

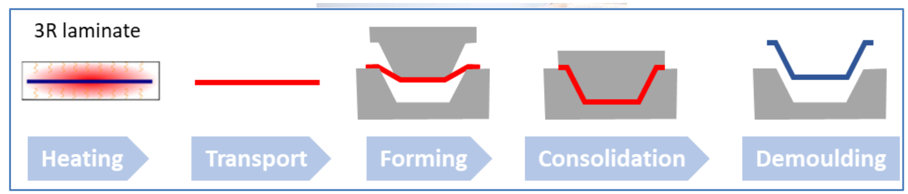
1. Discontinuous compression moulding (DCM)
2. Continuos compressiong moulding (CCM)

3R enduring prepreg (EPP)



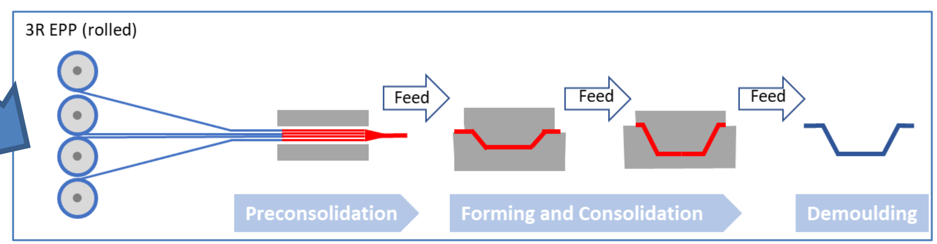


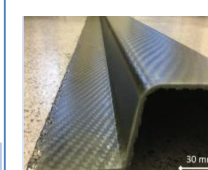
Discontinuous Compression Molding of laminate (DCM)



Omega-profile thermoformed with 3R-laminate at IVW

Continuous Compression Molding of EPP (CCM)





Omega-profile thermoformed with 3R-EPP in continuous process at IVW

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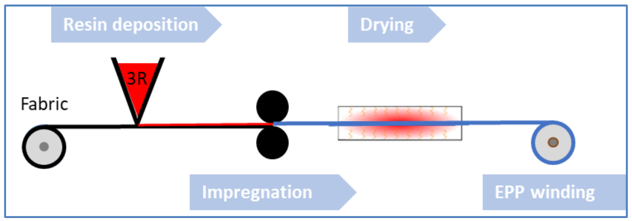
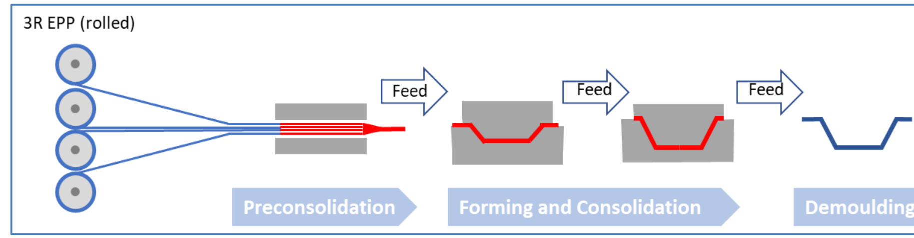
AIRPOXY

ThermoformAble, Bondable, RepaIrable smart ePOXY resin for Aero structures

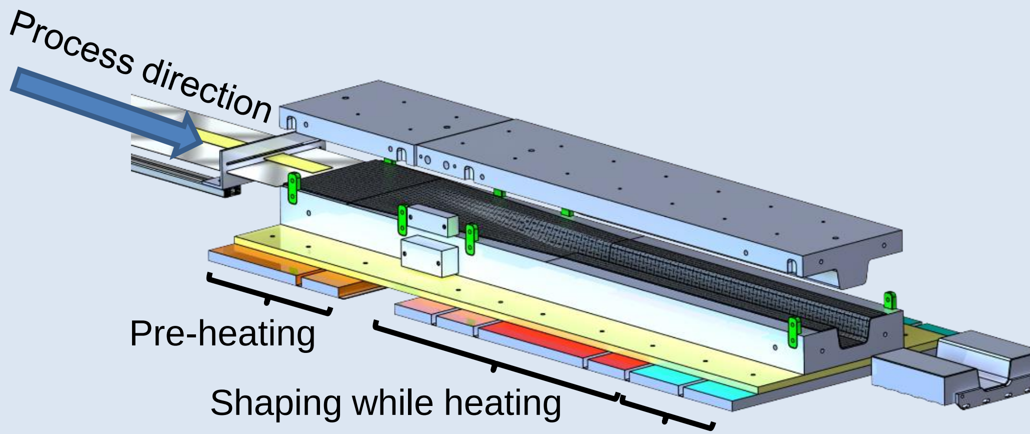
3R enduring prepreg (EPP)



Continuous Compression Molding of EPP (CCM)



CCM machine



CCM tooling

- Transport of the material between metal plates through the CCM process
- Additional silicone layer for good consolidation and good surfaces on one side

Longitudinal stiffener

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ThermoformAble, Bondable, RepaIrable smart ePOXY resin for Aero structures

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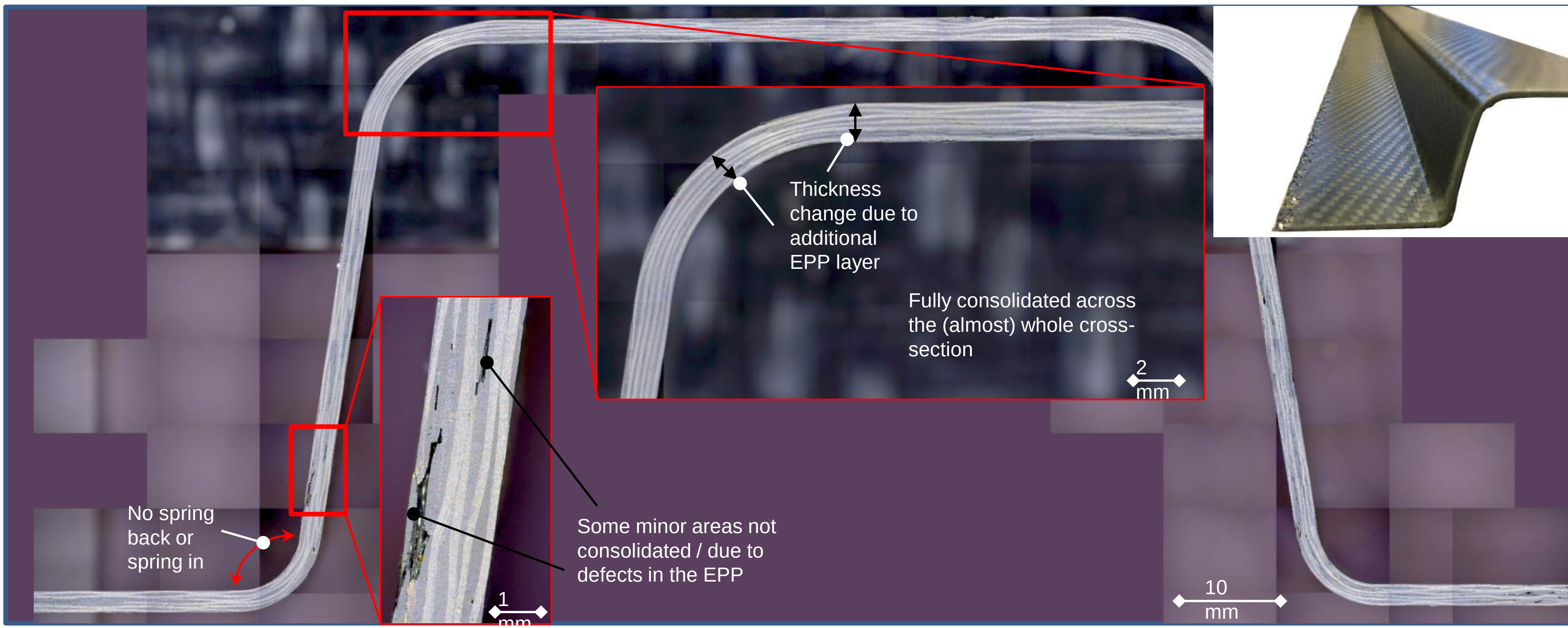
AIRPOXY

➢ Continuous Compression Moulding of Longitudinal stiffener



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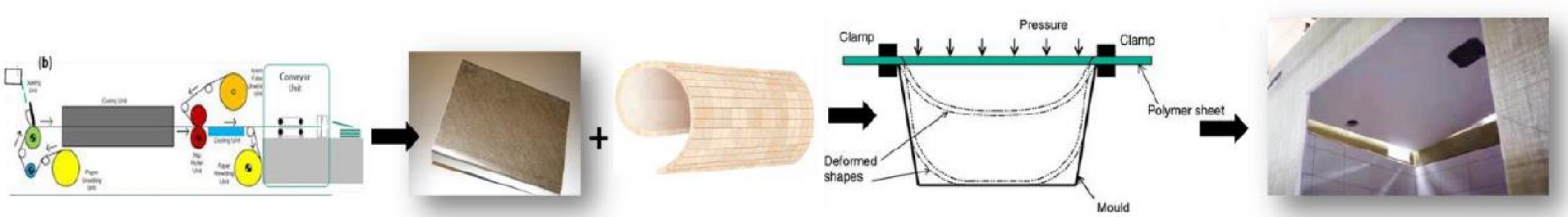
BIO-UPTAKE

BIOcomposites in smart plastic transformation processes to pave the way for the large-scale **UPTAKE** of sustainable bio-based products

EPP FOR THE MANUFACTURING OF MODULAR BATH CEILINGS



Balsa core + flax pre-impregnated with CAN-3R-bioepoxy
Layer/Sandwich configuration

Thermoforming of the pre-impregnated organosheet into final product structure (flat panel) for pre-fabricated bathroom pods (ceiling)

CURRENT MANUFACTURING PROCESS

- Handmade and slow process.
- Non-recyclable materials.
- Generates a lot of waste.
- Refrigeration/freezer to store the resin..

BIO-UPTAKE PROCESS

- Semi-automated process, 30% faster.
- Recyclable and reprocessable materials
- Minimisation of waste.
- No need for refrigeration/freezer.

Funded by the European Union

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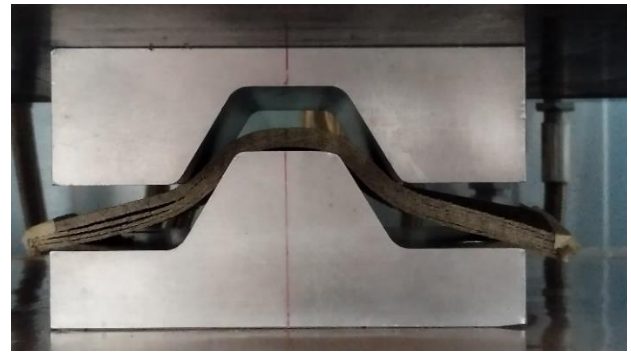
Enduring prepreg concept (EPP)

BIO-UPTAKE

BIOcomposites in smart plastic transformation processes to pave the way for the large-scale **UPTAKE** of sustainable bio-based products

T= 150 ºC
P = 50 bar



Input material Tg: 100 ºC
Curing degree: 100 %

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NEW GENERATION OF OFFSHORE TURBINE BLADES WITH INTELLIGENT ARCHITECTURES OF HYBRID, NANO-ENABLED MULTI-MATERIALS VIA ADVANCED MANUFACTURING

Input material Tg: 55 ºC
Curing degree: 58 %

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 953192".

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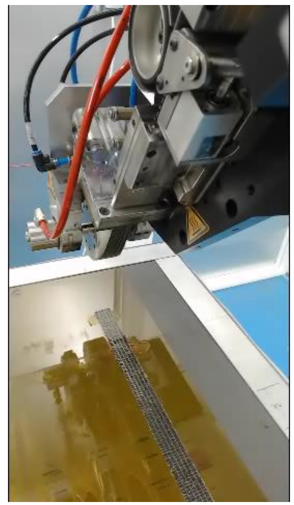
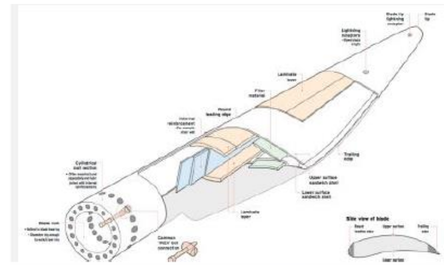
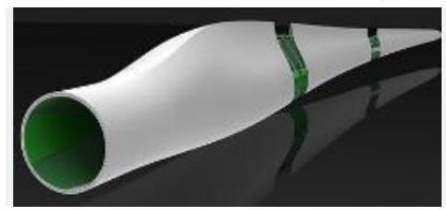
Enduring prepreg concept (EPP)

NEW GENERATION OF OFFSHORE TURBINE BLADES WITH INTELLIGENT ARCHITECTURES OF HYBRID, NANO-ENABLED MULTI-MATERIALS VIA ADVANCED MANUFACTURING

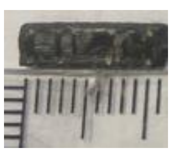
➢ Automatic tape layering (ATL)

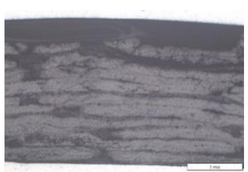


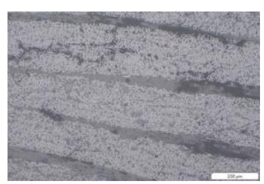




Parameters	
Heating Source	Laser
Power (W)	900
Speed (mm/seg)	150
Pressure (N)	360
Tª (°C)	160
Nº Layer	10
Thickness (mm)	2







ILSS Test
(D2344)
20 MPa
200 N
Failure: IS

	Tg (°C)	α (%)	Tª ONSET (ºC)	Tª Descomp. (ºC)	Resin (%)	Fibre (%)
Post-Processing AFP	99.5	100	260.6	347.3	33.6	71.76

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 9531

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Conclusions

-EPP allows storage at RT lowering storage price.

-EPP can be process like thermoplastic organosheets.

- Compression forming of pre-cured materials can take minutes to obtain high performance well consolidated parts.

- EPPs for ATL process have been developed.

- High energy savings related to part production.

- New 3R composites can be: **reprocessed, repaired and recycled**.

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a greater future today